2008
Hydrogen Storage
Summary of Annual Merit Review Hydrogen Storage Subprogram

Summary of Reviewer Comments on Hydrogen Storage Subprogram:

Reviewers stated that the Hydrogen Storage subprogram was well managed with a robust and diverse R&D portfolio. The storage program is sharply focused on technical targets and milestones. DOE acknowledged that progress towards volumetric capacity targets has lagged progress towards gravimetric capacity. The portfolio has benefitted from the down-selection of different storage technologies. It is recognized that on-board vehicular storage is a technically difficult application and that future strategic revisions and additional down-select points will be required. The reviewers stressed that DOE should continue to direct the researchers to emphasize all material performance attributes and cost and not solely gravimetric capacity. Reviewers recommended that DOE continue to periodically assess the funding allocation of the portfolio based upon the potential to meet on-board vehicle requirements.

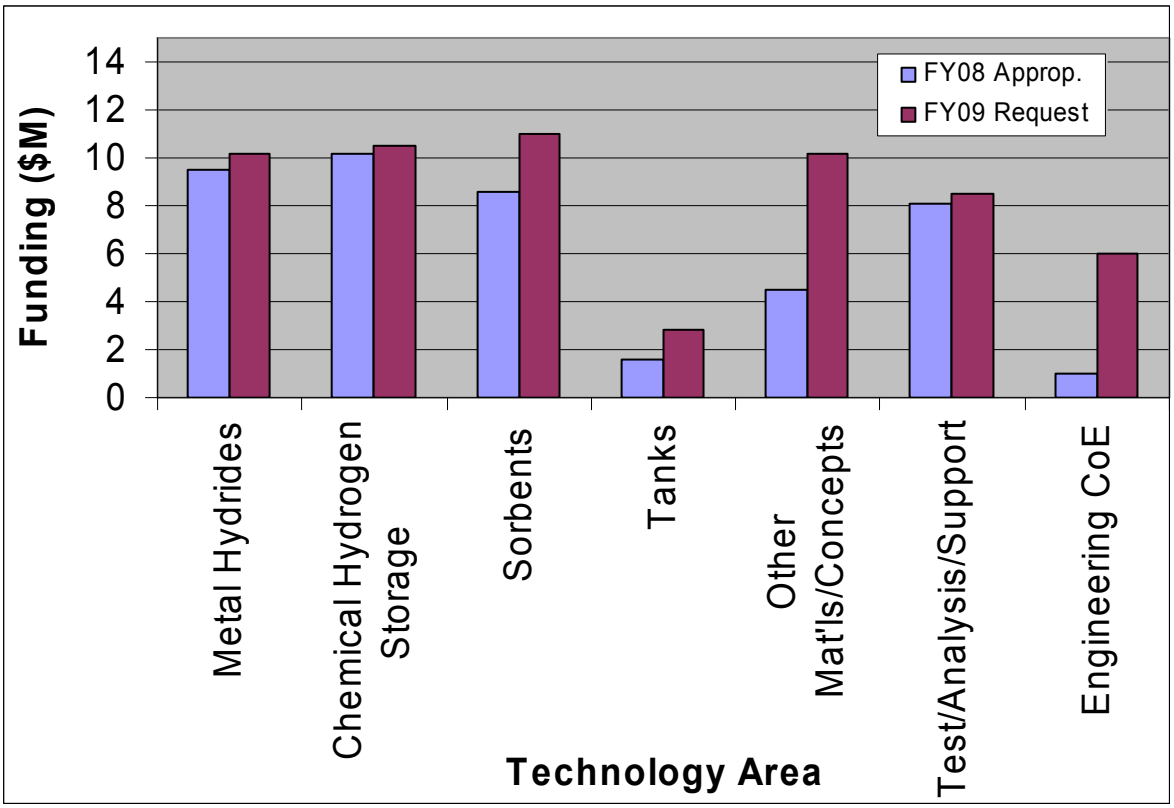
Some reviewers rated the DOE storage subprogram as "outstanding." The materials-based centers of excellence (CoEs) were assessed to be well-managed and organized. For the CoEs, it is important to continue to ensure transparency in the methods of operation and management (e.g. structure, decision process, communication flow and synergy among the sub-program areas, and intellectual property management). It is critical that the CoEs have mechanisms to share experiences and lessons learned particularly on cross-cutting issues across the DOE portfolio. The reviewers encouraged strong interactions among the CoEs and closer collaborations to stress commonalities, avoid duplication of efforts and optimize use of resources. These collaborations among the materials CoEs will also need to be extended to the new Hydrogen Storage Engineering Center of Excellence, which will start in FY 2009.

Finally, the reviewers identified hydrogen storage as "part of a long-term national research portfolio." The program was encouraged to continue its "lessons-learned" efforts, both technical and strategic, to contribute towards a "self-critical analysis of the effectiveness, progress, and the methodology for future program portfolio design." The reviewers recommended that DOE include in its portfolio strategy, consideration of the impact of scenarios where material(s) solutions are not found to meet the application's requirements. The reviewers suggested that DOE consider future funding scenarios that increase emphasis of approaches using high-pressure cold hydrogen or cryogenic hydrogen. Changes in the portfolio may be required to close the gaps of performance and cost requirements of using these physical approaches.

Hydrogen Storage Funding by Technology:

The funding portfolio for hydrogen storage addresses primarily long-term materials based R&D for on-board transportation applications. The EERE applied hydrogen storage program's goal continues to be developing and demonstrating commercially-viable hydrogen storage technology that enables greater than 300-mile vehicle driving range, while meeting safety, vehicular packaging, cost and performance requirements. The requested EERE FY2009 funding profile, which includes the materials-focused CoEs, the new Hydrogen Storage Engineering CoE and independent projects, continues to address the National Academies' and FreedomCAR and Fuel Partnership's recommendations. As mentioned above, plans for FY 2009 (subject to congressional appropriations and direction) include initiating the new Hydrogen Storage Engineering CoE to address on-board engineering R&D needs and system issues, as recommended by reviewers and stakeholders. The storage subprogram also plans to continue its annual solicitation process to allow flexibility in eliciting new concepts and approaches that may not be in the

current portfolio. A key milestone for FY2009 will be to conduct a down-select decision on sorbent materials under study in the portfolio. The chart below illustrates the appropriated funding in FY2008 for each major activity along with planned funding in FY2009 based on the Program's budget request.



Majority of Reviewer Comments and Recommendations:

Chemical Hydrogen Storage:
The chemical hydrogen storage R&D is conducted with a well-balanced approach, considering both material aspects and engineering issues, with good coupling between theoretical modeling and experimental activities. The reviewers suggested that the theory work be refined and validated with input from experimentalists. The chemical hydride R&D has made good progress toward addressing issues related to ammonia borane (AB) by reducing foaming and release temperature, as well as significantly increasing the kinetics for the release of the second equivalent of hydrogen from AB. Continued R&D is required to further improve these AB release parameters as well as addressing heterogeneous catalysis, liquid fuel formulation, and cost effective first fill. Reviewers noted heavy focus on ammonia borane. R&D has diversified to metal-boron-nitrogen materials. Significant progress was made in regenerating ammonia borane from spent fuel. It is recommended that future work incorporate cost analysis to assess AB regeneration schemes. The Chemical Hydrogen Storage Center of Excellence's (CHSCoE) down-select process and criteria were well received and 50% of the materials were discontinued as a result of the down-select process. It was recognized that the CHSCoE is a well coordinated group of quality researchers who understand the challenges related to chemical hydrogen storage materials and are focused on relevant research to the Hydrogen Storage Program.

Sorbent-based Materials:
The overall goal of sorbent materials applied research is to develop materials that will store hydrogen at close to ambient temperature and at moderate pressure. Very promising results in near room temperature hydrogen storage were presented that build upon R. Yang's work at the University of Michigan on materials that use a hydrogen spillover mechanism. This technique has expanded within the DOE portfolio and internationally. Issues remain to be explored include synthesis reproducibility, net available capacity, and hydrogen uptake and discharge kinetics. The reviewers recommended that this area of research be expanded to address these issues. The majority of reviewers emphasized the need to understand the system implications of the use of cryogenic (e.g. 77K) sorbents, and to continue to emphasize estimation of "net available" volumetric and gravimetric capacity, hydrogen uptake/discharge kinetics and durability. The reviewers suggested that theory work be refined and validated with input from the experimentalists to establish simulation models that best represent the experimental systems under study. It was recognized that the Hydrogen Sorption Center of Excellence is leveraging its partners' capabilities to expand its focus beyond carbon-only materials. The reviewers recommended that the portfolio be periodically reviewed to ensure that the projects emphasize vehicle application performance issues.

Advanced Metal Hydrides:
The overall goal of metal hydride materials applied research is to develop materials that can be charged with hydrogen on-board the vehicle at conditions amenable to the vehicle environment. Key barriers to this goal are the hydrogen charge and discharge kinetics at acceptable temperatures and pressures and the thermodynamics of the reactions which directly impact the net available capacity of the material. Since most of these materials may be embodied in a system as a packed powder, volumetric capacity of the material is also an issue. The Metal Hydride Center of Excellence (MHCoE) was considered by the reviewers to be a well coordinated group of quality researchers focused on relevant research to the Hydrogen Storage Program. The reviewers were in favor of the materials down-selection performed by the MHCoE and the flexibility demonstrated by the MHCoE in rescoping the engineering effort with the upcoming establishment of the Hydrogen Storage Engineering Center of Excellence. The computational modeling effort was also praised for the improvements and advances in methodology made over the past year, however it was recognized that more potential products, such as hydrocarbons, need to be included in the modeling database. It was recommended that the MHCoE and DOE continue to assess the viability of materials being investigated and minimize efforts on those that are not reversible under practical conditions.

Tanks:
Tank projects were not reviewed in FY2008. Reviewer comments on the validation of the cryo-compressed hydrogen storage tank project (Lawrence Livermore National Laboratory) are presented in the Technology Validation subprogram of this report.

Testing, Material Reactivity, Analysis:
These topics were considered critical to the overall subprogram and will be continued as planned. The new project to document best practices in the measurement of hydrogen storage materials was commended by the majority of reviewers. The area of materials' chemical and environmental reactivity R&D (a project under the International Partnership for the Hydrogen Economy) was also commended and will be strengthened, with increased coordination among the materials CoEs, engineering CoE and independent projects. The two storage systems analysis projects by TIAX and Argonne National Lab were rated highly. Further refinement of assumptions, continued coordination among stakeholders and developers, and validation of models were considered essential.

Note on Storage Report Structure:

Chemical Hydrogen Storage
ST-4 to 11 are partners of the Chemical Hydrogen CoE.
STP-5 is an independent project

Sorbent-based Materials
ST-15 to 25 and STP-6, STP-8 and STP-11 are partners of the Hydrogen Sorption CoE.
ST-13, STP-28 and STP-29 are independent projects

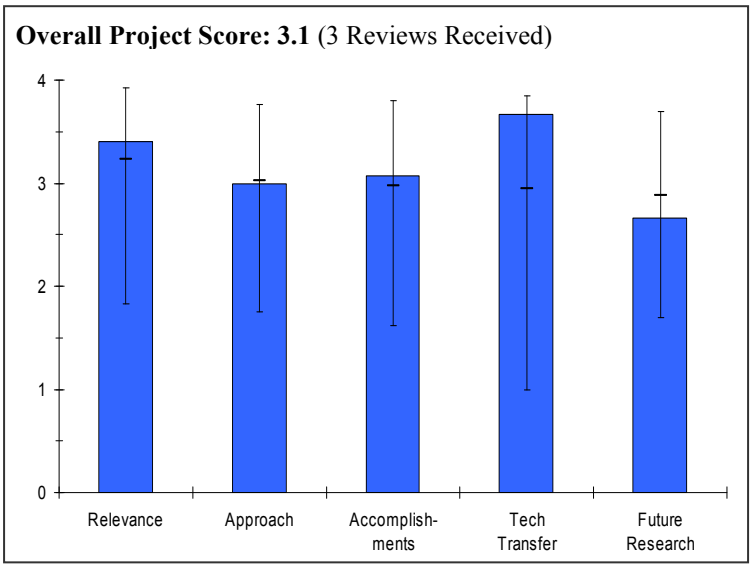
Advanced Metal Hydrides
ST-29 to 39 and STP-16, STP-18 to 21 are partners of the Metal Hydride CoE.
ST-14 and STP-24 are independent projects

Other New Materials and Concepts
ST-12, ST-26, ST-27, STP-26 and STP-27

Testing, Safety and Analysis
ST-1 to 3 and ST-40 to 42

Cross-Cutting
STP-4 and STP 32 to 34

Project # ST-01: Analyses of Hydrogen Storage Materials and On-Board Systems
Stephen Lasher; TIAX LLC



[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

TIAX is evaluating the projected manufactured cost and performance of several on-board hydrogen storage options: baseline (compressed hydrogen), liquid and cryo-compressed hydrogen, reversible on-board (e.g., metal hydrides, high surface area sorbents/carbon-based materials), and regenerable off-board (e.g., chemical hydrogen storage). System-level conceptual designs, process models, activities-based cost models, and lifecycle performance/cost predictions are being developed for each system based on developers' on-going research, input from DOE and key stakeholders, in-house experience, and input from material and component experts. This is an on-going and iterative process so that DOE and its contractors can increasingly focus their efforts on the most promising technology options.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- The project is expected to provide DOE and developers guidance by evaluating the status of various on-board storage options, and is therefore highly relevant to overall DOE RD&D objectives.
- On-board storage technology is well known to be one of the challenging areas that must have breakthrough technology to meet its targets. This project is supplying important cost and performance analyses of the various storage technology approaches being researched. It is imperative to have these analyses to help guide the overall storage program.
- The project is highly relevant to the DOE Hydrogen Program objectives. It is providing an early indication of the cost and efficiency of various hydrogen storage technologies.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- The approach used appears to be adequate.
- The overall approach to this analysis effort is excellent. Careful and state-of-the-art in-depth analysis of the systems is being done resulting in excellent cost and performance information.
- The overall objective of the project includes both on-board and upstream systems. This is very important. Unfortunately only recent on-board results were presented. This can be misguiding without discussing the upstream system costs and performance as well.
- The project includes analyzing all the critical cost and performance measures for on-board systems as well as the upstream system needs. It is very important to have complete well-to-tank cost, energy efficiencies, and greenhouse gas emissions for good decision making concerning on-board storage system research directions.
- There appears to be good collaboration between this project and the other relevant projects in the storage and hydrogen delivery program. It is important that this is maintained and possibly further strengthened.
- It is important that all the performance issues of the on-board systems are included in the overall analysis comparisons. For example, standard liquid hydrogen tanks will have boil-off issues and the full hydrogen

charge will not be available for use by the fuel cell. Comparing ~10 kg cryo-compressed and liquid hydrogen systems with ~5 kg high pressure gas or other storage technologies is not really an "apples-to-apples" comparison. Issues such as these were mentioned but only appear as footnotes in the presentation.
- The approach is based on established methods for estimating high rate manufacturing costs. It appears to have been generally accepted by the developers who also have provided input to the assumptions and manufacturing processes assumed in the analysis.
- The methods have been validated for some commercial type products but applying the methods for high rate manufacturing of storage materials and systems that have not been developed into viable systems are more speculative.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- None of the on-board storage systems evaluated in this project meet the 2010 volume target based on their assumptions. However, the project identifies the dominant contributions to the overall costs, which will help developers to concentrate their efforts in these key areas in the initial developing stage.
- Considering the funding that has been made available by DOE, the project has made considerable progress this past year.
- With somewhat better collaboration between this project and some of the other storage and delivery projects, there could have been more accomplished relative to analysis of the other on-board storage systems being researched.
- Progress appears to be reasonable; refining compressed H_2 designs and cost estimates is worthwhile as is the first formalized look at cryo-compressed systems. Not sure what benefit was derived from the sodium borohydride update.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.7** for technology transfer and collaboration.

- The research team attempted to incorporate the latest developments in hydrogen research from various centers.
- This project has made a considerable effort to collaborate with other storage and delivery projects and to present the results of its efforts for the benefit of these other projects. Even more effort to disseminate the results to the broader hydrogen community of stakeholders and to have even more in depth discussions with key projects in the storage and delivery program would be very helpful.
- Collaboration with other organizations is very good. The developers of a particular material/system have provided input to TIAX to enable a model system to be defined and costed. ANL provides a model system analysis and design that accounts for reaction kinetics, thermodynamics, and heat transfer.
- Several other organizations have reviewed the results of the analysis and assumptions.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.7** for proposed future work.

- The planned research is on-course. However, how realistic these analyses are will strongly depend on the overall economy.
- In addition to the liquid hydrocarbon and ammonia borane systems, it is very important to begin the analysis of the promising adsorption based systems such as metal organic frameworks.
- This effort should continue full well-to-tank analyses and include not only cost and performance issues but also energy efficiency and greenhouse gas emissions.
- The presentation materials did not indicate what analyses will be conducted next year.

Strengths and weaknesses

Strengths

- On-board storage technology is well known to be one of the challenging areas that must have breakthrough technology to meet its targets. This project is supplying important cost and performance analyses of the various storage technology approaches being researched. It is imperative to have these analyses to help guide the overall storage program.
- The overall approach to this analysis effort is excellent. Careful and state-of-the-art in-depth analysis of the systems is being done resulting in excellent cost and performance information.
- The methods used for cost estimating have been validated with reference to established commercial products.

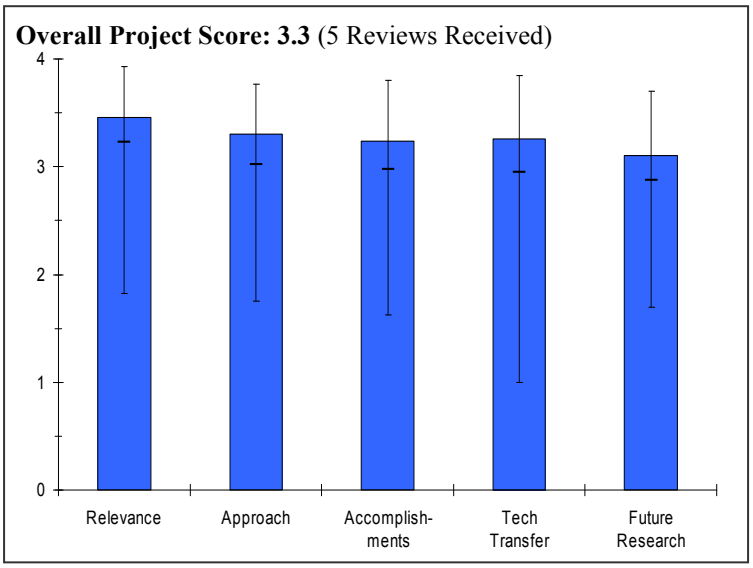
Weaknesses

- Only recent on-board results were presented. This can be misguiding without the upstream system costs and performance as well.
- It is important to do these analyses on a well-to-tank basis which is being done. However only system cost and performance is being analyzed. Energy efficiency and greenhouse gas emissions also need to be included. [DOE clarification: The analyses to estimate energy efficiency and greenhouse gas emissions are conducted by ANL. See project ST-02.]
- Because materials-based storage systems are not currently manufactured at high rates, the systems configuration and manufacturing processes are not well defined. Thus the analyses are preliminary.

Specific recommendations and additions or deletions to the work scope

- A preliminary analysis of a generic or most promising adsorption system would be very enlightening.
- Well-to-tank costs, energy efficiencies and greenhouse gas emissions all need to be included as well as recognizing any other particular performance issues (i.e. a standard liquid hydrogen system has severe boil-off issues).
- It is important to recognize that these cost estimates are based on assumptions regarding the physical and chemical characteristics of the systems that may not be completely validated. It is probably not worth the effort to refine the estimates much further until a prototype of a viable system that meets DOE targets is demonstrated.

Project # ST-02: System Level Analysis of Hydrogen Storage Options
Rajesh Ahluwalia; Argonne National Laboratory



[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project
The objective of this project is to perform independent systems analysis for DOE on all approaches for on-board vehicular hydrogen storage technologies. Specific goals include the following:

• Model and analyze various developmental hydrogen storage systems to determine system performance (e.g. gravimetric and volumetric capacity, operability, etc.).
• Analyze hybrid systems that combine features of more than one concept.
• Develop models that can be used to "reverse-engineer" particular technologies to determine material requirements to meet DOE system targets
• Provide guidance on properties required to meet targets.
• Provide input for go/no-go decisions; and
• Identify interface issues and opportunities and data needs for technology development.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- It appears some of these technologies could have been down-selected earlier without a full analysis.
- Provides important system-level analysis of all hydrogen storage approaches.
- The system level analyses covered in this project are extremely important to assess the feasibility of various hydrogen storage options in a future hydrogen economy and set targets for various R&D efforts.
- PI is providing information that should accelerate the process of hydrogen storage technology prioritization.
- Excellent work, which allows a direct comparison of the different storage technologies on a system level.
- Emphasizes "the credo the DOE Hydrogen Storage Team", that for hydrogen storage materials and systems, gravimetric and volumetric densities are not the only parameters.
- Shows in an educational way the complexity of the overall systems.
- Translates basic material research data into real-world automotive demands.
- Overview gives directions to the different storage technologies, in which fields they can improve their materials and efforts.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- The storage performance results of AlH_3 hydride appear to be biased by the artificially high hydrogen on-board demand assumptions.
- Approach seems to be thorough and comprehensive.
- The approach appears to be adequate.
- Well done!

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- For an analysis project it is hard to tell what the technical accomplishment was.
- Completed analysis of metal hydride storage approach this year.
- Provided important input to and support for go/no-go decision for sodium borohydride storage concept.
- The team analyzed metal hydrides, sodium borohydride and hydrogen storage in liquid carriers, and is on-course to complete analysis of hydrogen storage in amine borane.
- Project seems to be ahead of project ST-01 [TIAX LLC project].
- Inclusion not only of efficiencies, but also start-up energy, time and hydrogen-buffering is highly appreciated.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- Many, many interactions and collaborations.
- The team worked closely with other stakeholders.
- Good inter-DOE-contractor collaboration. It may be time to get some input from the automotive OEMs regarding packaging, interface and other requirements and limits.
- Input from other partners seems to be well-organized and considered in the work.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- It is not clear that the proposed future work, if successful, would yield better candidate storage systems that address the barriers.
- Future plans will extend analysis techniques to the remaining storage approaches and will continue to support scheduled go/no-go decisions.
- The proposed research attempted to refine their analyses for a number of systems to reflect the latest experimental results as well as emerging new systems.
- Future research seems to be very well planned and structured.

Strengths and weaknesses

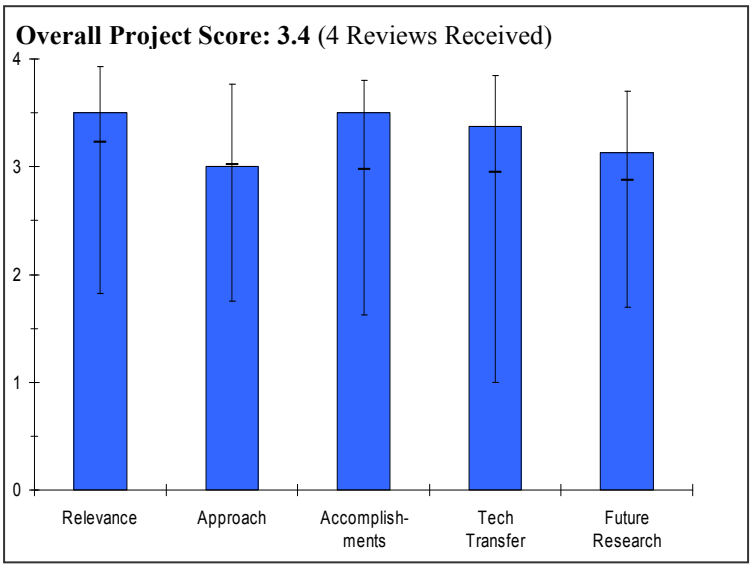
Strengths
- A lot of effort put into individual projects.
- Very quantitative, especially on kinetics.
- Good analysis methodology and strong interactions with the centers of excellence.
- Good modeling with the alane slurry.
- Excellent work, which allows a direct comparison of the different storage technologies on a system level.
- Shows in an educational way the complexity of the overall systems.
- Translates basic material research data into real-world automotive demands.
- Overview gives directions to the different storage technologies, in which fields they can improve their materials and efforts.
- Important project to compare different storage technologies amongst each other.
- Calibration and validation of modeling explicitly mentioned and integrated as part of the project's approach.
- Includes and addresses parameters like heat-up energy, time and hydrogen buffering.

Weaknesses
- There is a bias towards being comprehensive when this may not be necessary for down selecting technologies.
- It is unknown whether the shown processes and overall systems are the best and most representative ones.

Specific recommendations and additions or deletions to the work scope

- Should be more strategic rather than comprehensive. The PI should focus on the critical weaknesses.
- Include single solid phase alane study, at least to learn the kind of innovation needed for material handling for on-board and off-board. Potential in higher weight percent.
- With the collaboration with TIAX, include a multi-parametric model for technical performance and cost.
- Addition of metal organic frameworks and other sorbent materials is recommended.
- Disclosure of values (mass and volume) for the additional system components like burners or hydrogen ballast tanks is recommended.
- Harmonizing and synchronizing of presented results of project ST-01 [TIAX] and ST-02 recommended.

Project # ST-03: Best Practices for Characterizing Hydrogen Storage Properties of Materials
Karl Gross; H_2 Technology Consulting LLC (formerly of HyEnergy)



[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objective of this project is to develop and publish a reference document on best practices and limitations in measuring hydrogen storage properties of materials, including kinetics, capacity, thermodynamics and cycle life. The benefits include:
• Transferring the knowledge and experience in making critical performance measurements from experts in this field to the entire hydrogen storage research community.
• Aiding in the establishment of uniform measurement practices and presentation of uniform performance data.
• Providing a published resource to aid those just entering to this rapidly expanding field.
• Improving international communications on these issues among government, university, and industry entities and enabling the reporting of data using standardized measurement techniques.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Due to the number of investigators in the program with little or no previous experience in the study of hydrogen storage properties, a compendium of this type has value, provided that this work is made required reading by those who are new to the field. For those in the field and amongst reviewers, it will still make-up valuable reading so that data can be judged in a critical fashion.
- A project of this type probably should have been initiated earlier in the life of the program.
- The project is important to the overall subprogram and clearly of value for its advancement. It will be making a contribution to the development of uniform practices for making measurements and presenting performance data for hydrogen storage candidate materials.
- This program is highly relevant to meeting the program goals.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- Web dissemination is probably the most effective way of getting this information out.
- Most aspects of the work being done by investigators who will need this seem to be addressed.
- There are no actual technical barriers so this weighting for the work should not be used.
- It has a straightforward approach, with go/no-go decision points based on the delivery and quality of produced documents. It addresses important issues for assessing the performance of hydrogen storage materials. Quite useful is the latest restructuring of the project into sections including a background introductory section.
- Its main output will be best practices documents on measurements covering definitions and procedures, which will be made publicly available. Such guideline documents will be useful particularly to newcomers for improving the quality of data obtained and published. The PI gets input and feedback to his drafts from experts in the field ensuring that the end result is accurate and useable.

- The approach is well constructed. However, care should be taken to ensure broad applicability rather than too much focus on one technical field (e.g. metal hydrides).

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.5** based on accomplishments.

- Most of the areas covered appear to cover the more relevant areas of technological interest.
- It is definitely useful to have this data in one source rather than having to interpret information that otherwise needs to be gleaned from textbooks or papers.
- During questioning, the subject of the hydrogen equation of state was brought up and the author was able to address this.
- Seems to be on time with its first deliverable – the kinetics section – posted on the web for feedback and a second document on capacity already drafted. The kinetics deliverable released is actually the latest version following edits and recommendations by a number of experts in the field.
- The progress towards the stated objectives appears to be on track.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- There appears to be good collaboration with those who are involved with subtleties of measurements.
- Exploring strong links established at international level - a number of experts in the field are kindly contributing with their edits, suggestions and improvements to the draft best practices documents.
- The PI has obtained guidance from a broad group of knowledgeable scientists in the field. The program calls for open input from any interested parties.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Unfortunately, it may be necessary to address spillover effects in some way. The kinetics of these systems are extremely poor and looking specifically into issues related to acquiring data over long periods of time would be handy. While this runs counter to the on-board refueling model, there may be some value in addressing measurement instrument stability against pressure or high pressure and temperature.
- Use of excess density: it should be noted that the excess density is not the engineering system's energy density target of the DOE. Although on a materials science basis it makes sense to use it (because of the lesser ambiguity of the definition), it does not represent the end goal of the DOE hydrogen storage program. It should be pointed out that comparing excess densities between, say, physisorption materials and metal hydrides could be construed as questionable when discussing their relative merit, as the weight, volume and nature of the required containment unit and subsystems may differ qualitatively.
- The proposed future work is well defined and it is targeting the deliverables for the various sections.
- It appears that, at the moment, the whole project is focused on experiences from the metal hydrides work and does not accommodate the specificities of the different hydrogen storage materials currently handled by the researchers. No apparent planning has been made to demonstrate how these best practices could translate to other material types.
- The forward plan appears to be appropriate for meeting the project goals.

Strengths and weaknesses

Strengths
- The issue of a common and proper definition of the storage capacity, in view of the DOE storage objectives and in the context of a new center of excellence on storage systems, will be an important contribution.
- Valuable contribution. Excellent progress overall and good response to input from reviewers.
- Important attempt at standardizing the terminology and definitions.

- Lots of useful information in one tome.
- Excellent and important contribution to provide a common framework for the materials storage community.
- A solid contribution to the development of testing protocols, harmonization of data acquisition and reporting. Also a valuable step in the right direction for enabling accurate, reliable, critical performance assessment and benchmarking of potential hydrogen stores.
- This project brings relevant learnings from the conventional metal hydride work of the past forward to the present where they can help educate new hydrogen storage researchers.
- This project attempts to define a common terminology and standardize measurements methodology, the write-up of this document constitutes a very valuable contribution.

Weaknesses

- The work is a bit metal hydride-centric, efforts should be done in integrating terminology and concepts from physisorption.
- The deliverables are limited to metal hydrides at the moment. No future plans are made for addressing the same issues for non-hydride materials, for instance metal organic frameworks, carbon, chemical hydrides.
- It may be prove to be difficult to get wide acceptance and approval of the proposed guidelines, particularly from scientists in whose laboratories such measurements are routinely performed for a number of years.
- This project may be too focused on metal hydrides at the moment. Hopefully the final document will be more balanced and include significant content related to sorption materials and chemical hydrides.

Specific recommendations and additions or deletions to the work scope

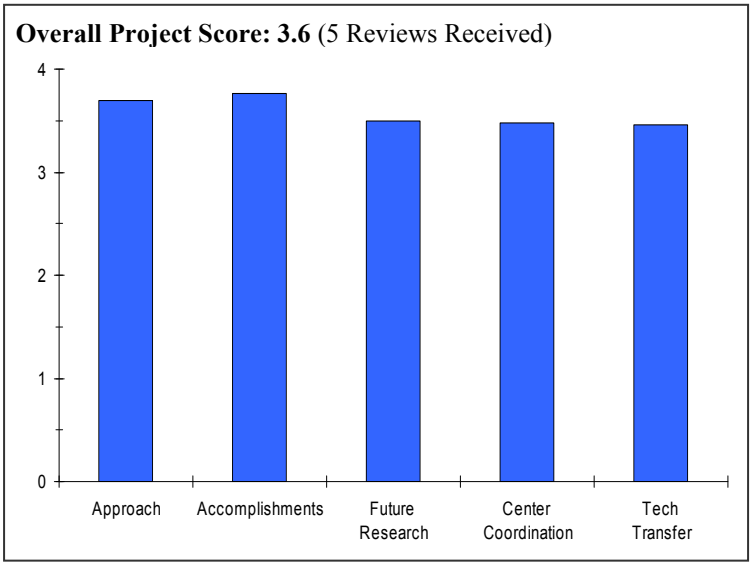
- This project may be too focused on metal hydrides. The final document should be more balanced and include content related to sorption materials and chemical hydrides.
- In the presentation, a detailed discussion of the feedback (to date) from the community would be valuable to gauge the degree to which this document constitutes a consensus (how many responded of the 50+ participants of IEA HIA Task 22, what were the highlights of the comments etc).
- Gathering feedback from IEA HIA Task 22 and other experts in the field is extremely valuable to bring about a consensus document.
- An explicit recommendation as it pertains to the grade requirements of hydrogen for uptake measurements (particularly adsorptive measurements) would be interesting as part of section 2.6.1.1. Suggestions on which electro-optical system for hydrogen should be minimally acceptable (say in volumetric approaches) would be a valuable contribution for a best practice document.
- At the project's end, some means of project maintenance or updating may be of value as engineering related issues may arise that the present work does not cover.
- A relative discussion on the thermodynamics (and on the proper thermodynamic definitions of response functions and observables) specifically for physisorption would help clarify several concepts which surprisingly remain ill-defined or misused in the literature.
- Consider expanding the scope of the best practices documents to accommodate all forms of hydrogen storage materials, and also account for future, as required, refinements.
- Address also sample handling and preparation conditions - not clear at the moment whether this is accounted for in the introduction or the other sections.
- Any help from the PI on teaching the correct methods for volumetric adsorption measurements is very welcome. This will hopefully assist researchers in the field in making correct measurements and avoiding either "false positives" or "false negatives".

Project # ST-04: DOE Chemical Hydrogen Storage Center of Excellence Overview
Kevin Ott; Los Alamos National Laboratory

[NOTE: This presentation was to evaluate the entire Chemical Hydrogen Storage Center of Excellence as a whole. A separate review form was used and can be found in Appendix C. LANL's technical contribution to the center is evaluated in ST-6.]

Brief Summary of Project

The overall objective of this project is to identify, research, develop and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet 2010 DOE system goals with the potential to meet 2015 goals. The specific goals are to 1) develop chemistries, materials, catalysts and new concepts to control thermochemistry and reaction pathways for hydrogen release; 2) develop and demonstrate chemical steps leading to efficient off-board regeneration of fuel from spent fuel; 3) assess concepts and systems using engineering analysis and studies using DOE targets as guidance; 4) down select the most promising chemical systems for more detailed work and engineering development; and 5) develop life cycle analysis.



Question 1: Approach to performing the R&D including Center Management

This project earned a score of **3.7**.

- The director, coordinating council and DOE are doing a very good job of leading and directing the group.
- The ideal value of well-managed and coordinated center of excellence approach is nicely shown here.
- Outstanding relevance clearly demonstrated. Management is keeping the Chemical Hydrogen Storage Center of Excellence (CHSCoE) focused on virtually all aspects of DOE goals and objectives for hydrogen storage in relation to the Hydrogen Fuel Initiative and Multi-Year RD&D plan.
- Approach is engineering oriented; modeling is an important component.
- The center uses a well-balanced approach, considering fundamental aspects as well as engineering considerations in their materials development. There is good coupling between theoretical modeling and experimental activities. It is very focused on the targets and is effective in keeping individual center projects aimed at overcoming obstacles toward achieving the targets.
- Facing the key challenges, mostly well-designed – only a few weaker programs, uses skills well. Planned downselects are needed and process is pretty good, too.
- Chemical hydride materials have the potential for high hydrogen storage capacities and rapid release rates.
- The center has very effectively reconfigured itself after the no-go decision on sodium borohydride.
- The approach avenues of hydrogen capacity, hydrogen release rate, and spent fuel regeneration are the correct ones.
- The engineering assessment approach to guide downselection is the right one.
- Approach to improving kinetics is not clear.
- Does the superacid regeneration approach have any chance of meeting the 60% efficiency target?

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **3.8**.

- Recent results have been many and impressive. DOE 2010 system weight and volume targets seem close to achievement in this CoE.
- There is a good balance among materials, operational materials properties and spent fuel regeneration work.
- Important progress has been achieved on a number of fronts and significant improvements have been demonstrated in ammonia borane materials in terms of capacity, temperature and kinetics. Regeneration process steps for spent ammonia borane materials have been developed and currently have multiple pathways toward effective reprocessing. Downselection process on materials was completed this fiscal year.
- The downselection criteria are very good and a 50% downselection has recently taken place.
- The go/no-go decision and downselection processes have been finely tuned here. The sodium borohydride no-go decision process was done as a valuable experiment for the future, using expert outside inputs.
- Good catalytic accomplishments on ammonia borane, and antifoaming
- The 2008 heterogeneous catalyst shows good hydrogen capacity, but the release rate still needs to be improved.
- Results for the non-precious metal copper catalyst for ammonia borane look good.
- Good flow rates demonstrated.
- 0.02 g/sec hydrogen release is not easy for these materials since we cannot heat up and shut all the material at once.
- Keeping the fuel liquid is a key, though also good to be sure they also have good regeneration still.
- Given the bottom line for commercial vehicle storage is spent fuel regeneration cost, not strictly energy efficiency, cost calculations seem to be underutilized at this stage. That is the ultimate potential show-stopper.

Question 3: Proposed future research approach and relevance

This project was rated **3.5**.

- The future work proposed is broadly and qualitatively fine.
- Regeneration is correctly listed as the most important task of the future.
- A quantitative go/no-go target on ammonia borane regeneration (efficiency and cost) would have been useful for FY2009.
- Hope for developing on-board regenerable materials is welcome.
- The description of the planned future work was done at a high level, but could have been a little more detailed. There was not much discussion of potential new materials (this may have been done to allow the individual PIs more freedom to present their future plans).
- Continue to concentrate on regeneration for ammonia borane.
- Kinetic improvement must also be promoted.
- Engineering concerns are the key in this area, good choice of future work.
- New materials are important.
- When will the complete recycle of the one gram of actual spent fuel be completed?
- Is a downselect of solid ammonia borane versus liquid ammonia borane planned before the end of the center?
- In the final analysis, the success of chemical hydride materials hinges on the success of regeneration. The overview indicates that 60-70% of the center's activities are on regeneration. This emphasis should be maintained.

Question 4: Coordination, collaborations and effectiveness of communications within the CoE

This project was rated **3.5**.

- The center seems to be working very well. There is a very good synergism and communication among the partners.
- The center has effective methods of communication. Regularly scheduled phone conferences fill in the time gaps between face-to-face meetings. Additional meetings are held on specific topics (e.g., the downselect process).
- Seem well coordinated in general. Some degree of running largely separately, but very little.
- Some of the new materials activities may have relevance to and may benefit from the Metal Hydride Center of Excellence work.
- The level and extent of interactions between the various participants in the center is very good.

Question 5: Collaborations/Technology Transfer Outside the CoE

This project was rated **3.5**.

- Collaborations and technology transfer seem outstanding, both within the center and between the center and outside organizations.
- International connections (International Partnership for the Hydrogen Economy (IPHE), Japan & others) are unusually good.
- Good collaborations with the other two centers. IPHE project gives the PIs an opportunity to collaborate with international research organizations.
- International collaboration good to very good.
- The IPHE work has yielded excellent results.
- Not clear how theoretical work couples to other centers. But to be fair there is less need for interaction than between the Sorption Center of Excellence and the Metal Hydride Center of Excellence.
- Alane is the logical place and it is not clear that there is as much communication between the Chemical Hydrogen Storage Center of Excellence and the Metal Hydride Center of Excellence on this topic.

Strengths and weaknesses

Strengths
- Excellent, well-working example of a center.
- Many knowledgeable researcher involvements.
- Various methods of approach to generate and regenerate the materials.
- Excellent technical team.
- Proper emphasis on the key issues.
- Excellent integration of the various activities and participants.
- Good organization; recognizes and faces major shortcomings of the chemical area, good team by and large, theory and experiment and engineering.
- Has moved gracefully from $NaBH_4$ focus to other chemistry.

Weaknesses
- Could be a little more effort on economics.
- Theory does get some calibration from experiments but to at least some extent, not incorporating feedback to improve the calculations fundamentally, and that would benefit the center.
- Probably vulnerably dedicated to ammonia borane at this point; deliberate effort to diversify somewhat (not a huge amount) is indicated.
- None.

Specific recommendations and additions or deletions to the work scope

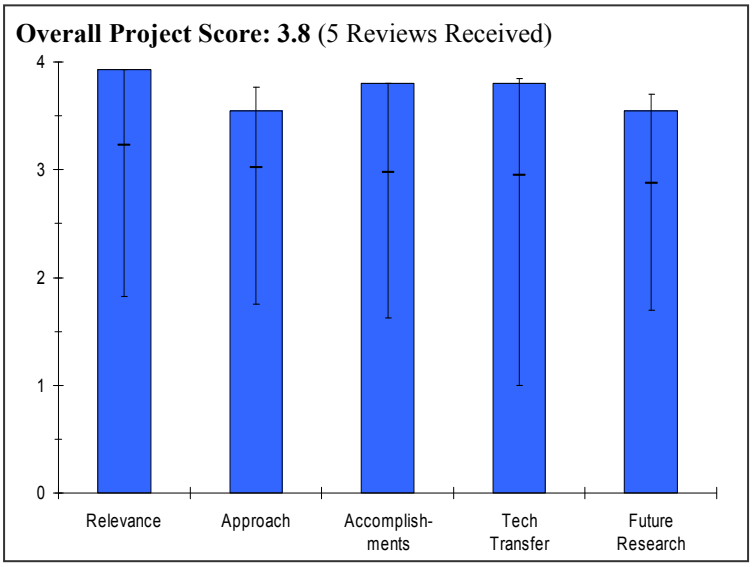
- Increase effort at getting some regeneration cost estimates. In terms of $/kg hydrogen stored ($/gge), how will this compare to DOE hydrogen production targets (or ever-changing gasoline price).
- Add some more view of how the material will be used.
- Material characteristics such as thermal conductivities and density will be very important for the real reactor design.

Project # ST-05: Chemical Hydrogen Storage R&D at Pacific Northwest National Laboratory
Chris Aardahl; Pacific Northwest National Laboratory

[Member of the Chemical Hydrogen Storage Center of Excellence]

Brief Summary of Project

The Center of Excellence's (COE's) objectives for this project are to 1) develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve the Department of Energy targets; and 2) develop high efficiency off-board methods for chemical hydride spent fuel regeneration. Pacific Northwest National Laboratory's goal is to meet the COE objectives through studies and development of high capacity chemical hydrides that increase kinetics while maintaining high capacity.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.9** for its relevance to DOE objectives.

- The project is critical to the Hydrogen Fuel Initiative.
- Project has outstanding, virtually complete relevance to DOE objectives.
- Project fully supports DOE objectives.
- The object to increase kinetics while maintaining high capacity in chemical hydrides is good.
- Regeneration of NH_3BH_3 is an important objective.
- Focused on major problems and the methods are appropriate to actually generate relevant results.
- Engineering, science and theory are good mix that is consistent with mandate.
- The materials being investigated are very high hydrogen capacity ones with the potential for high release rates at relatively low temperatures.

Question 2: Approach to performing the research and development

This project was rated **3.6** on its approach.

- Logical engineering problems chosen and approached with a good combination of science and engineering approaches - both in house and out of house.
- The project is focused on high hydrogen capacity materials, fast hydrogen release kinetics, and regeneration of the spent product.
- Consideration of engineering issues in materials development is an important attribute of the work.
- Project focuses very largely on ammonia borane (NH_3BH_3) and its many possible derivatives. This family of compounds has the greatest near-term potential to meet DOE weight, volume and rate goals for vehicle applications.
- The project is a good combination of ammonia borane release and regeneration technology.
- It is obvious that the project activities fit well into the Chemical Hydrogen Storage Center of Excellence and does not significantly overlap other technical approaches to use and regenerate ammonia borane.
- Fully focused on overcoming limitations of ammonia borane material systems for hydrogen storage applications.

- Effective use of analytical techniques available at PNNL to help understand material properties. The nuclear magnetic resonance (NMR) work has been shown to be a valuable technique, both for material behavior and for regeneration.
- The approach is focused on technical barriers such as to achieve rate target.
- Would prefer to see feedback to theory which generated the experimental approaches.
- The focus on solid ammonia borane materials, while of high capacities, may not ultimately prove viable for vehicular applications due to the problems with solids handling. To be successful for vehicles, excellent hydrogen capacity and release rate/temperature characteristics must overwhelm the handling issue.
- What is the evidence that "activated hydrogen" actually occurs?
- Using cobalt may not be good to regenerate the hydride. It may be of help to use oxidizing material such as titanium.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.8** based on accomplishments.

- Results obtained during the past year were numerous and progress very well in the direction of the DOE system goals.
- Good progress toward overcoming issues with ammonia borane, e.g., foaming, diborane release, release temperature, kinetics.
- Impressive publication.
- Lithium ammonia borane material studied this year has excellent potential as a storage material.
- Lithium ammonia borane is a VERY promising improvement.
- The lithium ammonia borane results look excellent. Release temperatures are lowered and release rates are increased.
- Very promising results on lithium ammonia borane. Weight, volume and kinetic results suggest the chances are very good, a workable prototype system can soon be built.
- Improved kinetics is valuable in this ammonia borane system. But reduced temperature is probably more valuable.
- Significant progress towards achieving morphology control during hydrogen release in NH_3BH_3.
- Excellent progress on the issue of foaming; identification and synthesis of hydride transfer reagents; and digesting solvent system.
- The anti-foaming results for the ammonia borane look good.
- The idea and implementation of a binder seems to be viable and surely will be valuable if proven out long term.
- The key to the NH_4BH_4 materials is improving their stability.
- Excellent progress has been developed on regeneration. Theory and experiment are working in concert. The ultimate answer on regeneration will make or break ammonia borane as a potential vehicular storage medium.
- Good progress toward regeneration process for spent ammonia borane.
- Using "failures" to find success in regeneration.
- Progress on regeneration appears to be slower than progress on new materials and hydrogen release rates.
- On the negative side, worrisome levels of impurities (e.g., 170 ppm NH_3) were shown to be contained in the exit hydrogen from decomposed ammonia boranes. Can they really be trapped in a practical vehicle environment?

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.8** for technology transfer and collaboration.

- Very impressive collaboration with center and other organizations.
- Well-connected via the center and seem to be using those connections.
- Also well connected outside.
- The excellent lithium ammonia borane results were obtained in association with the International Partnership for the Hydrogen Economy (IPHE).
- Interactions with other members of the center are very good.
- Excellent collaborations and coordination within the Chemical Hydrogen Storage Center of Excellence.

- Excellent international collaborations with the IPHE.
- Collaboration with center partners in a number of areas.
- Good coordination with partners on regeneration processes.
- The IPHE project is a good approach to international collaboration.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.6** for proposed future work.

- Plans build on past progress.
- Theory to guide in regeneration schemes will be helpful.
- Suitable.
- Again would prefer to see feedback to theory so that the theory is improved.
- The NH_4BH_4 approach is high pay-off, but also high risk because of the instability issue.
- The reduction aspect of the regeneration process is being aggressively addressed.
- The lithium ammonia borane approach looks very promising, provided that regeneration does not become too difficult.
- In general, good and logical list of future work.
- There are many irons in the fire; more downselection may be necessary.
- New work on ammonium borohydride should be very interesting, both on fundamental and practical bases. Many questions remain to be answered.
- Focus on downselected materials good.
- Focus on regeneration of spent ammonia borane materials and important element in achieving storage goals.

Strengths and weaknesses

Strengths
- Impressive group of researchers.
- Good interaction between theory, science, and engineering to keep focused on meritorious approaches, rather than systems with some highlights but also huge weaknesses.
- Team quality.
- Excellent team.
- Excellent international collaborations.
- Excellent technical approaches.
- Pioneering efforts on ammonia borane with excellent thoughts on the paths forward.
- Very close to the DOE targets, perhaps the closest of all activities in the program.
- Very productive in a practical sense.
- Effective use of advanced diagnostic capabilities available at PNNL.

Weaknesses
- Fuel cost & fuel cycle energy efficiency were not addressed.
- Cost of work at national labs - might benefit by using lower cost labor where possible and use higher cost lab personnel for analysis and expertise to a greater extent.
- None.

Specific recommendations and additions or deletions to the work scope

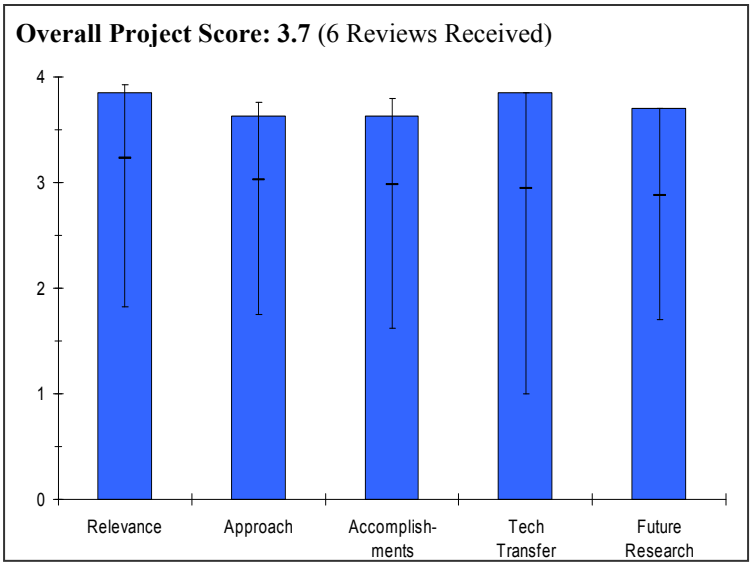
- Strongly suggest regeneration of lithium ammonia borane be looked at directly as it seems your lead candidate from a purity and kinetics of hydrogen point of view, and with good capacity to boot.
- Work on single pot regeneration is laudable but not highly likely, so some effort on minimizing unit operations and then developing those steps is a good practice to consider.
- In view of the fact the regeneration scheme(s) is (are) getting filled out well, the next year should be ripe for some hard cost estimates.
- Consider a slightly increased effort on safety studies.

Project # ST-06: Chemical Hydrogen Storage R&D at Los Alamos National Laboratory
Anthony Burrell; Los Alamos National Laboratory

[NOTE: This review is for LANL's technical contribution to the CHSCoE. Member of the Chemical Hydrogen Storage Center of Excellence]

Brief Summary of Project

The objectives for this project are to: 1) develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release; 2) identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release; 3) demonstrate all chemical steps and conduct engineering assessment for energy efficient AB regeneration process (high yields, rates and energy efficiency, integrate steps when possible); and 4) develop materials and processes to minimize gas phase impurities and demonstrate adequate purity of hydrogen stream.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.9** for its relevance to DOE objectives.

- High hydrogen capacity chemical hydrides in a liquid form and with suitable hydrogen release rates and efficient, cost-effective regeneration would have a very major impact on vehicular hydrogen storage.
- Outstanding relevance to the DOE objectives.
- Project is directly focused on storage system targets and fully supports DOE RD&D objectives.
- Project is directly relevant to DOE objectives for chemical hydrogen storage.
- Identification and synthesis of new ammonia borane-related systems.
- Developing a detailed mechanistic understanding and proof of hydrogen release catalysis.
- Develop and optimize a spent fuel regeneration system.
- Initiate testing of impurity impact on a PEM fuel cell.
- Initiate evaluation of a heterogeneous catalyst system for hydrogen release.
- Ammonia borane has the potential of meeting DOE 2010 targets.
- Catalysis is a problem of merit.
- Liquid would be a useful state for off-board regeneration.
- Energy is a major concern in spent fuel recycling - but it is not clear this is well-designed.
- Demonstration is critical.

Question 2: Approach to performing the research and development

This project was rated **3.6** on its approach.

- Theory, experiment and engineering work are very well integrated.
- Good mix of theory, synthesis and characterization.
- Good feedback strategy between above activities.
- Good balance between ammonia borane liquid forms, regeneration and exploration for new materials.
- Good effort on catalyst development that should fill the gap.
- Good coupling between materials development and engineering properties (e.g., gas purity).
- Engineering-guided research is an excellent approach to guide downselection of materials and processes.

- Seems good overall.
- Downselects are key.
- Important emphasis on mechanism and kinetic studies.
- New ammonia borane liquid fuels can avoid many engineering issues associated with solid fuel.
- Well-planned approach to maximize storage capacity and hydrogen release rate.
- The search for thermoneutrality is important.
- Interesting new ammonia borane derivative materials are being investigated.
- Catalyst work is excellent. Improved release rates and non-precious metal catalysts.
- Looking at catalyzed ammonia borane for increasing rates and liquid ammonia boranes for handling convenience.
- The liquid ammonia borane-based route has engineering advantages over the solid ammonia borane-based route.
- Looking at purity is a key item that is not really looked at to date in as definitive of a way.
- The use of a fuel cell element as an ultimate test for impurities (borazine) in the output hydrogen is a very nice, practical twist.
- Initiation of PEM fuel cell testing is excellent, but the data presented does not address key poisoning issues.
- The regeneration issue is being aggressively addressed.
- Approach generally complementary to PNNL activities.
- I compliment LANL for their very timely action to investigate alternative ammonia borane regeneration pathways that do not require formic acid.
- Organometallic, transition metal hydride digestion and reduction is different approach for regeneration.
- The regeneration flow diagrams look rather complex. Will costs of regeneration be as low as the relatively high estimated efficiencies suggest?
- A good case is not made for the interest and emphasis on a neat liquid system. This should be a very low priority.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.6** based on accomplishments.

- Very good progress has been made, both for understanding the catalyzed and liquid ammonia borane variants studied and the necessary engineering integration of same.
- Accomplishments this year move the project forward in a major manner.
- Project is moving close to the DOE system goals.
- Demonstrated new heterogeneous catalysts that increase hydrogen release rate at lower temperature than previously achieved.
- New experimental capabilities developed.
- Good progress in experimental work for new heterogeneous catalyst screening.
- Catalyst work is promising.
- Identified effective heterogeneous catalysts.
- Non-precious metal catalysts are being identified.
- Promising results have been shown with a copper-based catalyst.
- New hydrogen storage materials are being discovered.
- Low melting point liquids are being studied.
- New liquid fuels developed.
- Liquid fuels that are liquid down to -30°C have many advantages over solid fuel.
- Maintaining liquid is great at -30°C – please be sure they are also ones that can be recycled efficiently while maintaining capacity.
- The successful demonstration of an in-line borazine removal cartridge was very interesting. It would have been nice to see more details on this presented, e.g., what an actual on-board purification device would look like.
- Low-level impurities are being evaluated via a fuel cell system.
- Test of hydrogen is not exotic, but is valuable, glad they are doing that because it is another key concern. What is missing is how they will deal with the problem.
- Impressive progress that demonstrates the necessary steps in ammonia borane regeneration.
- Regeneration with only 25% overhead energy is impressive if it actually works and actually is that low in a real system.

- Progress toward completing this particular regeneration scheme is good. Reviewer looks forward to a complete lab-scale demonstration and cost estimate.
- A carbon dioxide-free regeneration process is being developed.
- The possibility for an onboard regeneration (direct rehydrogenation) scheme is exciting.
- I would have liked to hear some preliminary concepts for an on-board storage system.
- Good progress though also high cost.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.9** for technology transfer and collaboration.

- Extensive interaction with collaborators.
- Excellent interaction between labs on the identification and synthesis of hydride donors.
- Excellent interaction on interface with a PEM fuel cell.
- Good interplay of science and engineering concerns.
- Extensive collaboration across the board with center partners.
- Good relations with center partners and using them well.
- The International Partnership for the Hydrogen Economy (IPHE) collaboration is producing very valuable results.
- Excellent collaboration and integration of the activities of the other participants.
- Good collaborations within and integration with the Chemical Hydrogen Storage Center of Excellence. Obviously there is good coordination.
- Good international activities via IPHE.
- Industry involved.
- Good coupling with partners on ammonia borane regeneration routes and processes.
- IPHE project affords an opportunity for international collaborations.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.7** for proposed future work.

- The continued emphasis on new materials, high release rates via non-precious metal catalysts, and liquid ammonia borane-type systems is very good.
- Good plans based on this year's findings.
- Excellent strategic approach.
- New engineering-guided research in ammonia borane regeneration will help to improve overall energy efficiency.
- Further work to identify non-precious metal heterogeneous catalysts is on track.
- Appropriate and suitable work planned.
- Attack the problem on several fronts.
- Seems to learn from current work.
- Going to look at regenerated fuel to see how well it works. This is very good.
- Regeneration appears to be the only potential show-stopper for the chemical hydrogen route. Thus, the laboratory-scale demonstration of the entire regeneration process is crucial. Major emphasis should be placed on this.
- Activities are planned.
- This is an extensive and diverse effort, perhaps a little too ambitious. Increased focus may be desirable.
- Continued work on non-PM catalysts is of course encouraged, but the success of the recent work may be close enough to the targets for now.
- The flow reactor will help speed up catalyst screening.
- Proposed future work builds on progress achieved to date as well as continuing to search for new materials and catalysts.
- "Engineering-guided research" is an excellent approach at this stage of the project.

Strengths and weaknesses

Strengths
- Collaborative.
- Strong synthesis component and skills.
- Excellent mechanism/kinetic studies.
- Good understanding of chemistry and engineering issues.
- Work is well focused.
- Very solid theoretical and experimental work.
- Liquid ammonia borane fuels may be more practical for on-board storage systems.
- Downselect process is robust in concept and seems to be used effectively.
- Use of theory to accelerate progress is good.
- Excellent team and approach.
- Different versions of ammonia borane, very complementary to the PNNL materials.
- Practical engineering integration work.
- The prospect of direct onboard rehydrogenation ties very nicely into the Chemical Hydrogen Storage Center of Excellence.
- Good balance between materials research and engineering considerations.

Weaknesses
- PEM fuel cell studies are important, but the work to date does not address the issue of poisoning, and should not be presented as such. 100 ppm of CO, the prototypical PEM fuel cell poison, requires ~10 hours of exposure to kill the catalyst. Thus, the 2-3 hour data collected to date does not address catalyst poisoning from a real world point of view. Also, cell impact is better addressed using voltage/current (V x i) curves rather than current/time (i x time) curves.
- Work on a liquid system seems misplaced at this time. A workable solid-state system should be the focus and activities that detract from this goal should be deferred.
- Need to address methods to treat volatile by-products following hydrogen release.
- One of the barriers with liquid fuel is the formation of solid spent fuel that requires proper engineering treatment.
- Higher hydrogen release rate is desirable.
- Cost basis as noted above, max use of lower cost labor would be good.
- Might be trying to do too much at once.

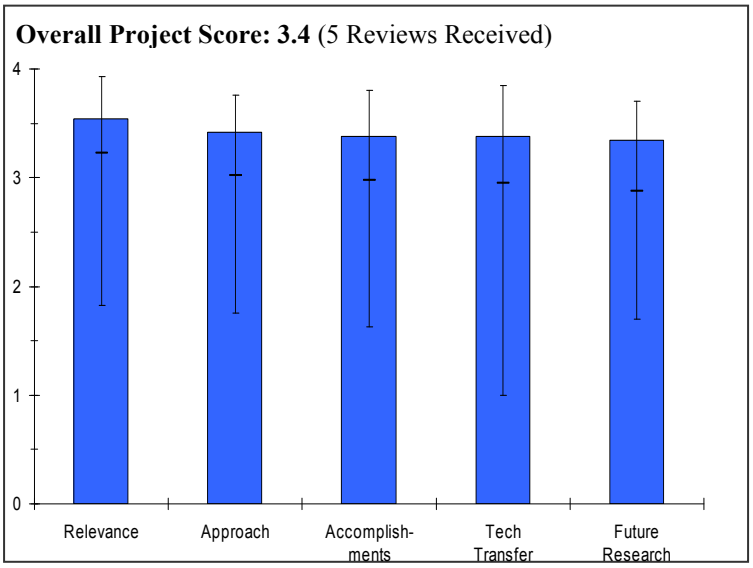
Specific recommendations and additions or deletions to the work scope

- Continue work with emphasis on mechanism, digestion, hydride reagents, PEM fuel cell poisoning. Defer other issues.
- A question: Could the hydrogenation be carried out electrochemically at a non-noble electrode (cobalt for example, which would produce a surface metal hydride)? This might provide a very clean system.
- Formulate methods to treat volatile by-products following hydrogen release.
- For the liquid fuel option, develop methods to address issues due to formation of solids in spent fuel.
- Effort on the on-board regeneration should be minimal in that, inherently that is going to be very hard in these sorts of systems due to the delta G being against you.
- Need to demonstrate some of these processes, in theory this looks good but need to demonstrate.
- Be careful of the amount of effort on fuel cell poisoning - this is valuable work but if it is to be done in depth, it needs a fuel cell expert's input. Also, I would suggest not.
- Heterogeneous catalyst work seems to be successful in nearly meeting targets. Maybe it is time to reduce that effort and focus more effort on the regeneration scheme - efficiency, cost and practicality.
- Given the clear impurity problem with ammonia borane, this reviewer suggests adding an engineering analysis of the in-line hydrogen purification process. What will an onboard purification process and associated apparatus look like on a vehicle? How often will it have to be regenerated? Initial cost?
- The fuel cell impact is better addressed using voltage/current (V x i) curves rather than current/time (i x time) curves.

Project # ST-07: Amineborane-Based Chemical Hydrogen Storage
Larry Sneddon; University of Pennsylvania
[Member of the Chemical Hydrogen Storage Center of Excellence]

Brief Summary of Project

The overall objectives for this project are to 1) develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve Department of Energy targets; and 2) develop high conversion off-board methods for chemical hydride regeneration. In collaboration with Center partners, the goal of this project is to develop new methods for hydrogen release and spent fuel regeneration that will enable the use of amineboranes for chemical hydrogen storage. Penn will use the activating effects of ionic liquids, chemical promoters and/or metal-catalysts to enhance the rate and extent of hydrogen release from amineboranes.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Objectives in enhancing hydrogen release rate from NH_3BH_3 and the mitigation of borazine formation is relevant to the DOE objectives due to the high weight percent of hydrogen in NH_3BH_3.
- This project is highly relevant to the Hydrogen Fuel Initiative because of its potential for high hydrogen capacities, high release rates at temperatures close to 80°C, and liquid forms of the storage medium.
- Project shows excellent orientation and relevance to DOE goals: weight, volume, rates, spent fuel regeneration efficiency, etc.
- The materials under investigation are important for reaching storage system targets and DOE program goals.

Question 2: Approach to performing the research and development

This project was rated **3.4** on its approach.

- Approach correctly looks at both increasing the hydrogen release properties of ammonia borane, followed by a practical, efficient and economic spent fuel regeneration process, similar in objectives to the Pacific Northwest National Laboratory and Los Alamos National Laboratory projects.
- Utilization of the proton sponge to avoid NH_3BH_3 foaming shows very good approach in indentifying and solving problems.
- The approach of using ammonia borane in ionic liquids, with chemical promoters and/or catalysts to enhance hydrogen release kinetics is a very good one.
- The approach in reducing the ionic liquid content is good as it enhances the weight percent of hydrogen.
- The regeneration approach of converting BNH_x dehydrogenation products to boron trihalides that are then converted to ammonia borane is a very good one because it avoids B-O or diborane intermediates.
- The release work is complimentary to Pacific Northwest National Laboratory and Los Alamos National Laboratory. It looks at accelerating release of hydrogen by ammonia borane through the use of ionic liquids, M-catalyzed ionic liquids and chemical promoters.
- The spent fuel regeneration process is also different and seems to be conceptually simpler than the Pacific Northwest National Laboratory and Los Alamos National Laboratory regeneration processes: acid-halide

digestion followed by 3-step, "one-pot" reduction and conversion. Importantly, the Penn process avoids the formation/use of troublesome B_2H_6.
- There is nice, innovative chemistry in this project.
- The PI is very qualified to conduct this project. However, the approach may be too reliant on homogeneous catalysts that have limited commercial prospects.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.4** based on accomplishments.

- Good progress has been made over the last year.
- A significant improvement in hydrogen release kinetics has been achieved in a 10.2 weight percent ammonia borane - ionic liquid material at 120°C. However, this material appears to be semi-solid in morphology.
- Foaming of the material during hydrogen release has been significantly reduced with a proton sponge addition.
- The use of proton sponges was important to show the increased decomposition kinetics, as well as eliminate the foaming problem.
- Reduction of the ionic liquid amount added to NH_3BH_3 is good however potential formation of toxic gases such as NH3 and borazine needs to be checked.
- Solubility limitation of NH_3BH_3 as the ionic liquid amount is reduced needs to be addressed.
- Presenting new regeneration processes of NH_3BH_3 is good, however proof of concept needs to be illustrated, i.e., the reduction with silane step followed by reacting with NH_3.
- Progress has been made with the regeneration of dehydrogenation products via the boron trihalide approach.
- Decomposition kinetics of the enhanced ionic liquid ammonia boranes has been increased.
- The Penn regeneration approach has been largely demonstrated on a lab scale and seems to this Reviewer to be simpler and closer to practical than the Pacific Northwest National Laboratory and Los Alamos National Laboratory processes.
- The progress towards the objectives has been very good for addressing aminoborane dehydrogenation. The progress towards effective aminoborane regeneration has been limited.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- There is effective collaboration between the PI and other members of the Chemical Hydride CoE.
- Significant interactions occur with the other members of the Chemical Hydrogen Storage Center of Excellence.
- Good technology collaborations within the center, including important industry connections.
- Suggested to have more visible collaboration with other members.
- Unlike the National Lab projects, there seem to be no significant international collaborations.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.3** for proposed future work.

- Optimization of the ratio of ionic liquid: NH_3BH_3 is a good step; however many other factors such as solubility limitation and formation of toxic gases need to be addressed more.
- It is suggested to measure the effects of using different ionic liquids to down select the better ones
- Focus of the superacid/halide reduction for the regeneration of MNH_2BH_3 is good and needs to be illustrated
- Emphasis on improvements in the regeneration scheme, particularly the more effective conversion of dehydrogenation products to BX_3 species, is crucial.
- Future work is a logical extension of the past.
- The project should focus on aminoborane dehydrogenation and the use of heterogeneous catalysts to effect the dehydrogenation.

Strengths and weaknesses

Strengths
- Liquid form of the material is very strong when we design the reactor.
- Again, liquid phase has a potential of controlling speed of release.
- Synthetic approaches and considering reducing the penalties for solvating NH_3BH_3 in ionic liquids
- Excellent PI.
- Very good technical approach.
- Excellent, practical chemistry.
- A promising, hopefully practical, efficient and cheap regeneration process.
- Low vapor pressure of ionic liquids has significant advantage for hydrogen separation from liquid.
- Optimization of ionic liquid/aminoborane ratio to increase overall material capacity.
- Non-precious metal catalysts are highly desirable.

Weaknesses
- The spent fuel regeneration approach must be proven to be viable on a laboratory scale.
- It is not clear how the release efforts compare in practicality to those in Pacific Northwest National Laboratory and Los Alamos National Laboratory.
- Catalysts can lower the temperature of hydrogen release but are homogeneous rhodium catalysts too expensive and fragile?

Specific recommendations and additions or deletions to the work scope

- It is suggested to have more collaboration with other members working on catalyst design as the NH_3BH_3-ionic liquid systems are being optimized.
- The project showed good progress and enhancing the NH_3BH_3-solution weight percent should be pursued while improving the kinetics.
- Optionally consider reducing the decomposition efforts in favor of the regeneration efforts. Should there be some deference to the Pacific Northwest National Laboratory and Los Alamos National Laboratory approaches on release?
- Minor suggestion: Chemists may like equivalents and engineers may like weight percent. Suggest using dual scales to satisfy both.
- More emphasis on dehydrogenation work versus the aminoborane regeneration.

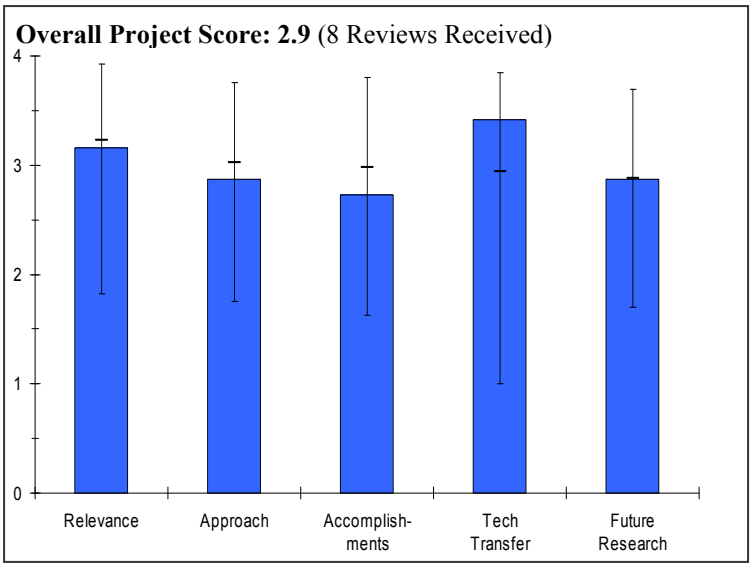
Project # ST-08: Chemical Hydrogen CoE - Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides

Suzanne Linehan; Rohm and Haas

[Member of the Chemical Hydrogen Storage Center of Excellence]

Brief Summary of Project

The overall objectives for this project are to 1) develop and advance novel hydrogen storage materials to meet the Department of Energy 2010 targets and with the potential to meet 2015 targets; 2) leverage expertise and experience across the Center; and 3) support the DOE Chemical H_2 Storage Systems Analysis Sub-Group. The Phase 1 goal is to define and evaluate novel chemistries and process for producing chemical hydrides. The emphasis will be on low-cost routes to regenerate sodium borohydride (SBH) from spent fuel leading to go/no-go review. The Phase 2 goal will be to identify cost and energy efficient pathways to "first fill" and regeneration for ammonia borane and other borane storage materials.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- The development of lower cost and scalable production methods for sodium borohydride ($NaBH_4$) is key to the implementation of ammonia borane (ammonia borane) and other boranes as viable chemical storage media.
- This project plays a critical role, providing industrial expertise and perspective, to the Chemical Hydrogen Storage CoE.
- Low cost $NaBH_4$ synthesis from $NaBO_2$ is needed for first fill ammonia borane.
- Work is relevant to DOE objectives.
- Activity supports the initial processing of raw borate to storage precursor borohydrides.
- Focus on process and cost.
- Development of new chemistry leading to $NaBH_4$.
- Work on $NaBH_4$ regeneration provided essential data for DOE Go/No GO decision in September 2007.
- After no-go decision for $NaNH_4$, the project is aligned with hydrogen vision & DOE R&D objectives.
- Objective to select single pathway for low-cost $NaBH_4$ is important in the development of ammonia borane.
- The most relevant aspect of this project is the exploratory work towards low-cost sodium borohydride production.

Question 2: Approach to performing the research and development

This project was rated **2.9** on its approach.

- Provided strong support for the sodium borohydride storage concept including potential regeneration pathways and played a key role in supplying important input to the sodium borohydride go/no-go decision process.
- Following the no-go decision this project has fully supported the redirection to study sodium borohydride preparation as a feedstock for other potential storage materials, e.g. amine borohydrides.

- Flow of approach looks good, identify possible processes, evaluate in the lab, and develop process models and costs.
- Process and cost models are being presented without key considerations or data (How do the three processes presented compare to each other, for example?)
- Open issues that may dramatically change the model includes: 1)What metal(s) and is metal recovery necessary (or could the metal oxide be left as a waste product); 2) What are product separation and work up costs; and 3) How large of a carbon footprint does carbo-reduction generate (syngas is a carbon burden as soon as it is burned).
- This project is focused on a single goal to identify more cost effective methods for large scale production of $NaBH_4$ via analyses of alternative synthesis routes with limited laboratory scale testing to assess feasibility and limitation of the two approaches being considered.
- Emphasis has changed from regeneration of products from the hydrolysis of $NaBH_4$ solutions to initial synthesis of lower cost feed stock material for making ammonia borane or other boranes.
- This project still emphasizes analytical evaluations of the general processes with relatively little assessments of more practical aspects such as efficient separation of reaction products to obtain pure $NaBH_4$ and experimentally identify the by-products that could seriously impact either synthesis route.
- Very good experimental technique to demonstrate metal reduction pathway toward $NaBH_4$ synthesis from $NaBO_2$.
- There are more uncertainties and practical barriers in the carbothermal reduction pathway than metal reduction pathway (proposed scheme is based on limited experimental data from Idaho National Labs).
- Comprehensive methodology established for costing.
- Rohm & Haas's contributions toward the development of low cost $NaBH_4$ are important for first fill ammonia borane.
- Focus to look for best pathway for low cost $NaBH_4$ is good.
- Focus on low-cost $NaBH_4$ helps to meet DOE cost target.
- More technical results from the laboratory-scale production of sodium borohydride are necessary to meet the objectives of a scalable production process. There is too much emphasis on process modeling of production methods that may not be technically feasible.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- Has showed good progress in meeting roles and technical responsibilities as a fully participating member of the Chemical Hydrogen Storage CoE.
- Identification of potential process chemistries is an important accomplishment.
- Produced useful and helpful results in both energy and cost analysis for sodium borohydride go/no-go decision in September 2007.
- In the absence of specifics (metals under consideration or at least the parameters that would idealize a metal system) it is impossible to evaluate the proposed system(s).
- The investigators have demonstrated the feasibility of the metal-based reduction process to produce $NaBH_4$ in good yields with at least one unidentified metal hydride. However, the cost of these hydrides does not seem to have been addressed nor has the methods necessary to separate $NaBH_4$ from resulting oxides or other by-products.
- From the team presentation information, the carbothermal reduction reaction will require very high reaction temperatures with formation of copious quantities of carbon monoxide to be recovered as well as using the greenhouse gas methane as a feedstock. The team has given inadequate attention on impact of these issues to total system cost as well as the associated environmental and safety concerns.
- Important progress has been made on this project for the use of ammonia borane.
- Progress appears to be quite slow after September 2007.
- Cost analysis for two pathways show significant progress.
- There seems to be little progress towards finding scalable synthesis methods for sodium borohydride. The PI did not present much technical progress.

- Much of the process analysis work presented here was carried out previously in support of a Millennium Cell process.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- Outstanding interactions and collaborations with members of the Chemical Hydrogen Storage CoE.
- The primary collaboration appears to be participation in the go/no-go decision on "hydrogen on demand" type systems. The input to the decision was highly collaborative.
- Most of the new work presented appears to be in-house work. However, that appears totally appropriate.
- The Rohm & Haas team has been interacting mostly with the two lead organizations of the Chemical Hydrogen Storage CoE but it has provided input regarding regeneration costs to the no-go decision for on-board hydrolysis of $NaBH_4$.
- Has very close interactions with Chemical Hydrogen Storage CoE partners.
- Needed collaborations exist.
- There appears to be effective collaboration with other partners in the Chemical Hydrogen Storage CoE.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- Good plan for continued support of CoE activities including taking the lead in low-cost, scalable process for SBH (sodium borohydride) as precursor to ammonia borane.
- Key open questions have been noted above. It is unclear that key issues have been identified and approaches put into place to address these issues.
- To the point: a limited set of specific chemistries must be selected before a reliable process/cost analysis can be obtained. How high a priority is limiting the chemistries that will be considered?
- The team intends to assess both metal-based and carbothermal reduction routes for producing less expensive $NaBH_4$ for first fill ammonia borane usage.
- The emphasis still seems to be more on thermochemical trades and modeling assessments rather than laboratory testing of the reactions themselves and identification of practical and efficient methods for separating $NaBH_4$ from residual reactants and other by-products.
- Future work to support first fill ammonia borane and ammonia borane regeneration is relevant and crucial to ammonia borane hydrogen storage option.
- Plans are effectively built based on past progress.
- The plans for next year were not clearly presented. There appears to be more emphasis on experimental progress which is necessary to meet the project goals.

Strengths and weaknesses

Strengths

- The team provided systematic chemical production schemes for two reactions that may decrease cost for manufacturing industrial quantities of $NaBH_4$ as the intermediate material for ammonia borane and perhaps other boranes for chemical hydrogen storage options.
- An important issue if boron species are ever to become an accessible storage system.
- Approach considers both chemistry and cost in an interactive manner.
- Investigators are willing to move far away from the existing process to achieve breakout energy and cost efficiencies.
- They presented laboratory-scale test results that show significant yields of $NaBH_4$ can be achieved with at least one or two metal hydrides using the metal reduction approach.
- The analysis methodology tool developed for $NaBH_4$ production should be useful to assess ammonia borane and other storage materials.
- Step by step approach toward the cost estimation and regeneration of important material.

- Team of experts with broad range expertise.
- Strong experimental capability.
- Well established methodology for costing.
- The initiation has a good track record in this area.
- The project team has the capacity to perform very sophisticated process modeling and economic evaluation.
- Relatively modest budget for the work being performed.
- Strong internal team with extensive industrial experience and expertise in necessary chemical areas.

Weaknesses

- Specific chemistries have not been elucidated.
- Much of the work presented appears not to involve new thinking, but is related to prior Millennium Cell related work.
- The cost analysis appears premature (and thus potentially not trustworthy), given the number of open questions related to chemistry and process.
- There was insufficient investigation into methods of separating $NaBH_4$ products for either reaction scheme.
- More laboratory testing and analyses of the reaction products should have been done to better establish practical yields and requirements for cost and energy effective synthesis.
- Inconsistent year over year progress.
- Impurity concern such as borazine has not been addressed.
- The stated experimental processes for sodium borohydride production (reactive milling and carbothermal) may not be suitable for large-scale production at levels that will enable the DOE program goals for hydrogen cost. From the equation for carbothermal production as shown in the presentation - delta G only goes negative at >1900 °C - can you really process large amounts of material at these temperatures?

Specific recommendations and additions or deletions to the work scope

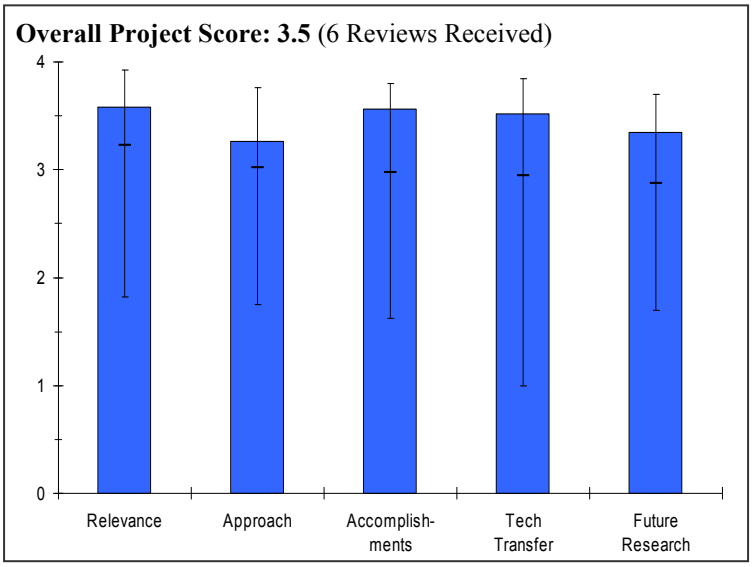
- Continue work by identifying specific chemical systems to evaluate.
- During the remainder of the project, the team should de-scope the system trade studies and cost estimating analyses until the actual chemical reactions and operating requirements are better established.
- The team should spend more time in the laboratory evaluating the reaction conditions and products generated by both synthesis schemes.
- If possible, consider lab-scale experiments to validate the carbothermal reduction pathway.
- The project should focus on validating the production processes before expending resources on process modeling.

Project # ST-09: Main Group Element and Organic Chemistry for Hydrogen Storage and Activation
David Dixon; University of Alabama

[Member of the Chemical Hydrogen Storage Center of Excellence]

Brief Summary of Project

The objectives of this project are to 1) develop promising approaches to chemical hydrogen storage for current and future Department of Energy (DOE) targets using computational chemistry and synthetic organic/inorganic chemistry; and 2) provide computational chemistry support (thermodynamics, kinetics, properties prediction) to the experiment efforts of the DOE Center of Excellence for Chemical hydrogen Storage to reduce the time to design and develop new materials that meet the DOE targets. Experimental focus is on organic and main group chemistries which may be able to perform better for release and regeneration by improving the energy balance. This will provide longer term alternatives.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- This project couples strongly with many activities in the Chemical Hydrogen Storage CoE, and is helpful in understanding experimental results, guiding experiments towards new materials and catalysts, and plays a significant role in the success of the center.
- Addresses the DOE goals for hydrogen storage and regeneration of spent fuel.
- The theoretical work complements some aspects of the experimental activities in the center and is relevant to the DOE objectives.
- The project supports processes for regeneration of amino-borane which has a potential of high hydrogen release over 10 weight percent.
- The computational aspects of the project are highly relevant to a number of aspects of the Chemical Hydrogen Storage Center of Excellence activities.
- Highly relevant.
- How are system costs addressed by the project?

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- The University of Alabama team used a combination of molecular orbital theory and density functional theory implemented on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of regeneration systems – release and addition of hydrogen.
- Their technique for accurate and validated first principles computational chemistry is effectively incorporated in Chemical Hydrogen Storage CoE.
- The computational approach and the issues being addressed are excellent.

- The strength of this project include: 1) theory can certainly efficiently guide experimental work reducing R&D costs and efforts, and 2) efficiency issues are seriously considered. The weakness is that validation data has not been discussed in much detail.
- The experimental focus on carbene/TCNE and amino (imidazolo)-boranes is good, but must soon start to yield some significant improvements in hydrogen storage capacities.
- This project has the potential to link theoretical and experimental efforts at the same institution.
- Theory effort seems to be making bulk of contribution -- how does Arduengo tie in?
- The approach uses accurate quantum chemistry methods to explore a wide variety of materials' energetics. More accurate molecular orbital (MO) methods are used, as opposed to things like density functional theory (DFT). However, all calculations are for molecular systems, and some of the materials being simulated are condensed solid-state (or liquids). It would be useful to the other researchers in the computational hydrogen storage community (e.g., metal hydrides, or sorbent materials where DFT approaches are much more commonly used) to provide accurate comparisons between the errors associated with using DFT for the solid-state systems versus using MO theory for the molecular systems. And, it would be useful to characterize this "tradeoff" of errors for various types of systems (molecular solids, sorbent systems, as well as more typical ionic solids such as complex hydrides), to really try and understand where DFT approaches suffice, and where they do not.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.6** based on accomplishments.

- Examples of significant accomplishments and impressive body of knowledge generated so far include: (1) exploration of regeneration schemes and of new chemical storage systems, (2) improvement of efficiencies, (3) examining pathways to improved kinetics and (4) contribution to fundamental knowledge about mechanisms (etc.)
- The accomplishments include predicted reliable thermodynamics for more than 500 reactions for regeneration schemes. Impressive productivity!
- Many processes for amino-borane regeneration have been precisely evaluated. This information is considered to be effective to choose appropriate reactions and to analyze reaction mechanism in Chemical Hydrogen Storage CoE.
- Valuable theoretical results associated with ammonia borane regeneration.
- Produced a huge amount of data; large number of reactions, thermodynamics, kinetic mechanisms, catalysts, etc., surveyed.
- Alane shown to be an effective catalyst for hydrogen release from NH_3BH_3, but this work has also produced useful information for alane regeneration. A very significant synergy.
- Nice results for the Carbene/Cyanocarbon (particularly as it pertains to volumetric density).
- Interesting results on possible CBNH materials.
- While the accomplishments of the theoretical work are obvious, the experimental contributions are less well defined.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.5** for technology transfer and collaboration.

- Very large number of external collaborations. Seems to be the "central hub" for theory within the Chemical Hydrogen Storage CoE.
- Excellent theory calculation interactions with other members of the center.
- Theory work is clearly closely coupled with experimental work being done by center partners.
- Good interactions with partners within the center.
- Good collaborations with other team members.
- Collaboration with Los Alamos National Laboratory is effectively conducted in experimental confirmation of their prediction and process design at Los Alamos National Laboratory.
- However, a discussion on how theory and experiments interact precisely within this project should be provided.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.4** for proposed future work.

- Use computational chemistry to support overall center efforts in hydrogen release, spent fuel regeneration, new concepts including alternative inorganic and organic compounds, and mechanisms for hydrogen release and spent fuel regeneration. Improve hydrogen storage by mass stored and kinetics for hydrogen release for main group substituted organic compounds.
- Future work appears ambitious; however the team has generated an impressive amount of results so far and very likely will be able to do the job.
- Their prediction is still very important to the center.
- Future work includes studies of solids using density functional theory, and will systematically study 25 different exchange correlations to find which one works best for the solids.
- Would be nice to see the computations take on more of a "predictive" aspect by leading experiments in new directions. At the moment it appears as though the role of computation is strictly to *follow* experiments by "putting out fires." This is OK, as clearly computation is making a large contribution by operating in this fashion, but I think even larger impact would be possible by having computation take the lead in some areas.
- Seems to largely prioritize the huge amount of potential computations based on what is most urgently required by experimental colleagues.
- Computational future work looks well-focused.
- Experimental future work looks vague.

Strengths and weaknesses

Strengths
- Appears to have a very strong and good connection with the experimental groups; maintains good contact, and gives very fast turnaround.
- Impressive body of knowledge obtained in direct support of DOE storage objectives.
- Efficiency and energetics are seriously considered by the team.
- Ability in highly accurate and validated first principles computational chemistry.
- Effective interaction with experimental groups.
- The theory and calculation portion of the project is very strong and useful to the center activities.
- Predicting spectroscopic properties for comparing with experiments.
- Good coupling with experiments.
- Strong communication with other center projects.

Weaknesses
- Validation of theory work has to be clearly established and discussed, interaction between theory team and experimental partners should be clarified.
- Although the accurate molecular properties are important, the overall accuracy of prediction will strongly depends on the model selected for simulation. The prediction from the model systems which better represent experimental systems may be more useful than the accurate molecular orbital calculations.
- The experimental portion of the project does not appear to be producing significant improvements in hydrogen storage capacity materials.
- Strength of contributions of Arduengo's project unclear.
- Very large budget for what appears to be largely a single PI project.

Specific recommendations and additions or deletions to the work scope

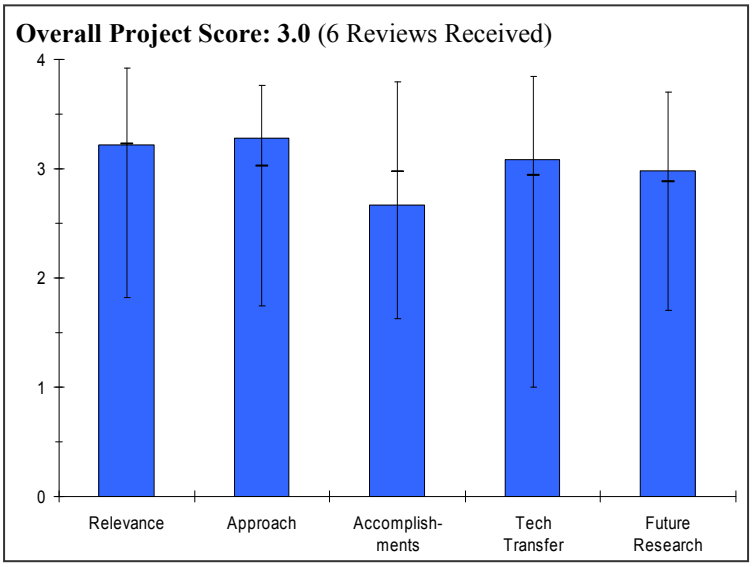
- Some validation of the simulations/calculations should be discussed in more details to show feedback between theory and experiments.
- Unless significant improvements are obtained soon, consideration should be given to a no-go decision on the continuation of the carbene/TCNE and amino (imidazolo)-borane work.
- Clarify role of Arduengo.

Project # ST-10: Solutions for Chemical Hydrogen Storage: Hydrogenation/Dehydrogenation of B-N Bonds
Karen Goldberg; University of Washington

[Member of the Chemical Hydrogen Storage Center of Excellence]

Brief Summary of Project

The Center-wide objective of this project is directed toward the use of amine borane (BN materials) as on-board vehicular hydrogen storage materials. The University of Washington objectives are to: 1) develop cost-effective metal catalysts for the dehydrogenation of BN hydrogen storage materials; 2) optimize catalysts to meet the Department of Energy target goals of hydrogen discharging rates from BN materials; and 3) identify and develop new BN materials to address challenges for automotive hydrogen storage materials.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- Designing catalysts for enhancing the performance of high capacity materials is related to the DOE objectives in increasing the dehydrogenation rates.
- Improved catalysts to increase the kinetics of ammonia borane-type hydrogen storage materials are important to meet storage targets.
- The exploration of combined exothermic and endothermic chemical approaches may lead to the possibility of on-board rehydrogenation.
- Amine-boranes are of no interest without good catalysts for both hydrogenation and dehydrogenation.
- The organometallic chemistry presented here is fundamental to generating a robust low cost catalyst for dehydrogenation.
- New CBN substrates may potentially dramatically improve the energy balance in the ammonia borane type of systems.
- Work is relevant to DOE objectives.
- Ammonia borane has high material capacity and the potential to meet DOE 2010 targets.
- New CBN materials have the potential for direct rehydrogenation on-board.
- Search for optimized catalysts is relevant.
- Finding solutions to ammonia borane regeneration, catalysis and liquefaction are key to the center objectives. These three subjects are the fundamental issues facing ammonia borane materials today. Perhaps the PI is stretched thin by working on three subjects at once.
- CBN materials work appears to be redundant with earlier work by Air Products.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- Original catalyst employed expensive iridium as the backbone - recent attempts have tried to replace iridium with cheaper metals such as cobalt with limited success.
- PI should incorporate some modeling guided theory to aid in catalyst design.
- The approach is focused on key issues.
- A good interplay of synthesis, calculation, and kinetic analysis is provided.

- Synthesizing low cost catalysts is important to the ammonia borane hydrogen storage option.
- What is the fall-back position of cobalt turns out not to work?
- What is the contingency plan if modifying ligand structure fails to yield a viable catalyst?
- Approach seems to have a significant trial-and-error component.
- The project indentified the barriers in the system studied and made decisions to downselect or modify approach.
- The idea to develop CBN materials that couple exothermic dehydrogenation BN bond to endothermic dehydrogenation CC bond is good. However, the benefit of such coupling may be reduced significantly if the dehydrogenation temperatures of these two bonds are too far apart. So, it is necessary to look at not only delta H but also reaction temperatures in the design of CBN materials.
- Is there a go-no/go decision point on the CBN materials?
- PI should reduce efforts on CBN regeneration and concentrate on catalysts.
- Liquid ammonia borane fuels have many advantages over solid fuels.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- PI made tremendous progress in synthesizing new catalysts and approaches - unfortunately they do not work as well as the original iridium systems.
- The previous and current catalysts still only work to remove the first equivalent of hydrogen- 2nd and 3rd equivalents are required if capacity targets are to be approached.
- Good progress on lowering the metals cost.
- Question: While the indicated tridentate ligands work, have you investigated the possibility that the first row systems many not require a tridentate system?
- It appears as though little progress has been made with catalyst development.
- Determined that cobalt catalyst is not stable at temperatures above 60°C.
- The technical approach in manipulating the ligands and moving from the iridium based catalyst is a good approach, however, as the catalysts are designed, the metals used need to be cheap and abundant.
- The attempts with development of the cobalt catalyst are very good, but the possibility exists that cobalt will not work, based on the present results.
- Determined that mixed ammonia borane/MeAB polymers are not suitable for direct rehydrogenation due to high exothermicity.
- Reasonable progress on synthesizing and investigating new BCN substrates.
- Developed concept and synthetic methods to obtain CBN materials.
- Considering the CBN compounds as new storage materials is good however, concerns on the potential formation of gases other than hydrogen, i.e. NH_3, CH_4, B_2H_6 which could occur.
- How do the bond energies of B-H, N-H, and C-H compare? Is it possible to lower the C-H bond energy?

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- PI working well with the key strong players in aminoborane research (Los Alamos National Laboratory and Pacific Northwest National Laboratory).
- Strong collaborative interactions with theory group.
- Good interaction with Chemical Hydrogen Storage CoE partners and university.
- Suggested to have more visible collaboration with other members, i.e. for the CBN compounds, collaboration with the theory group and Air Products.
- Is there any benefit in strengthening interactions with Los Alamos National Laboratory for catalyst screening?
- For the CBN materials there is clear overlap (and possible duplication) with prior work by Air Products (Note: Air Products work was on CN materials.) However there appears to be no communication or collaboration with Air Products in acknowledgement of this.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.0** for proposed future work.

- PI should defer CBN materials to Air Products or collaborate with them.
- PI should provide reviewers with some guidance as to the robustness of a ligand based material in such an ammonia borane environment.
- This is a strong program. It is pointed in the right direction with a promising trajectory.
- The researchers should include the determination of turnover numbers since the stability of the catalyst is an important unexplored parameter. It could turn out for example that the iridium catalyst is less expensive than the cobalt catalyst if they have widely different turnover numbers.
- Continue to develop and optimize inexpensive first-row transition metal catalysts.
- What is the plan to get more than one hydrogen equivalent from the cobalt-based catalysts?
- The development of CBN materials that meet the dehydrogenation and rehydrogenation criteria will be a significant breakthrough for the ammonia borane hydrogen storage option.
- PIs need to also consider cost of CBN materials in future work.
- The synthetic routes for the formation of CBN compounds need to be clarified. Also, the vapor pressures of the compounds prepared need to be tested.
- Given the pay-off if potentially on-board reversible CBN materials could be discovered, synthesized, and optimized, perhaps this should be a higher priority than the catalyst work.
- CBN work should be halted until a unique research plan (distinct from prior Air Products work) has been developed.

Strengths and weaknesses

Strengths
- Good synthetic capability.
- Clever ideas related to reaction mechanism and substrate design.
- Key understanding of the underlying coordination chemistry.
- Good understanding of chemistry and ammonia borane dehydrogenation/rehydrogenation issues.
- Close collaboration with center partners.
- Research is very well focused.
- Synthetic approaches and catalyst designs.
- Attempts to develop non-precious metal catalysts.
- Exploration of novel CBN hydrogen storage materials.

Weaknesses
- Ligand approach and complex nature of catalyst might decrease the overall robustness. PI does not seem to have a plan or modeling guided approach to determine if cheaper metals can be substituted for iridium.
- A wider view of ligand systems should be considered.
- It is suggested to have more collaboration with other members as mentioned above.

Specific recommendations and additions or deletions to the work scope

- Continue as is.
- The project showed good progress in designing catalysts and it's recommended to keep the project.
- Consider dehydrogenation/rehydrogenation temperatures of B-N and C-C bonds in search for the most favorable CBN materials.
- Provide some cost estimates of CBN materials.
- More emphasis on the CBN materials.
- CBN work should be halted until a unique research plan (distinct from prior Air Products work) has been developed. Note: Air Products work was on CN materials.
- Air Products is investigating similar CBN type materials. PI should coordinate activities with Air Products.

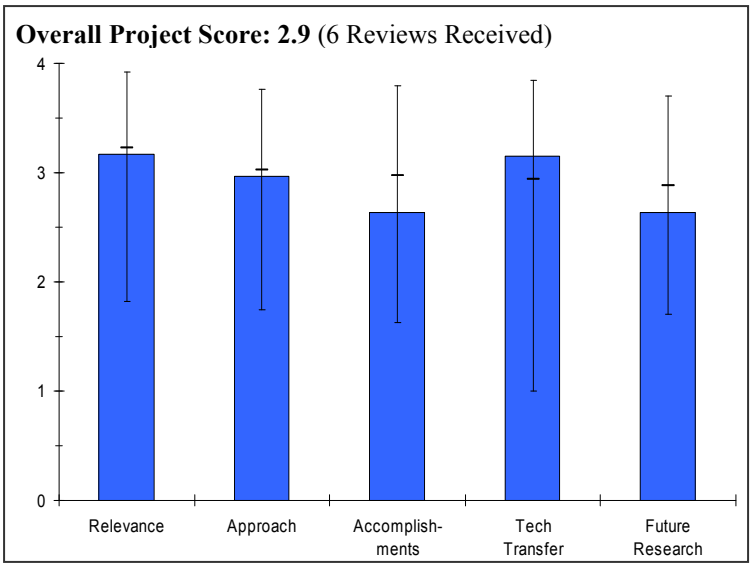
Project # ST-11: Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Materials & the Development of Efficient Amine-Borane Regeneration Cycles

Philip Powers; University of California - Davis

[Member of the Chemical Hydrogen Storage Center of Excellence]

Brief Summary of Project

The objectives of this project are to: 1) provide new materials, compounds and support for chemical regeneration of amine-boranes or boran amides from B-X (X = halide or oxide) compounds; 2) develop a method of regenerating amine-boranes from spent fuel with use of a metal formate/hydride cyclable system; 3) develop light element hydride nanomaterials for spent chemical hydride regeneration such as ammonia-borane "AB" regeneration; and 4) enhance the hydrogen release for chemical hydrides such as ammonia-borane "AB" with light element hydride nanoparticles.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- Strength: The project is relevant to regeneration cycles for chemical hydride materials and release mechanisms (and suppression of foaming) that could lead to a storage strategy that meets the DOE volume and weight targets.
- Strength issue: choice of cheap precursor materials.
- The work on light element nanoparticles for hydrogen evolution is strong science directly related to DOE objectives.
- The work of metal formates to hydrides is consistent with the original program goals, but has recently been jettisoned in revised goals based on thermochemical analysis of the proposed cycle.
- Though the metal formate work is not of current interest, the chemistry studied in these systems provides important basic science; so, there is a positive spin-off.
- The objectives of the project are to develop efficient methods to regenerate amine-boranes or boron amides, in support of the center's selection.
- This project appears to have been successfully re-directed after the no-go decision on the silicon-based hydrides.
- The PI is pursuing innovative chemical cycles for ammonia borane off-board regeneration consistent with much needed efforts in establishing the practicality of chemical hydride approaches.
- A key factor in the inherently complex regeneration of ammonia borane is to incorporate low-cost chemical precursors in order to meet or exceed DOE cost targets. The PI has given a significant amount of thought to this challenge.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- The light nanoparticle approach for hydrogen evolution is excellent, but not well understood.
- An understanding of the chemical mechanisms associated with the hydrogen release process is needed.

- The work that addresses enhanced hydrogen release from ammonia borane by incorporating nanoparticles of boron nitride (BN) appears to immediately solve the foaming problem while reducing the temperature for desorption.
- What will be the basis for hydride formation?
- The team used main group formate small molecules or hydride nanomaterials as low cost reagents to convert B–O or B–X in one step to B–H.
- The regeneration aspects are closely interfaced with theoretical predictions.
- In the area of regeneration, the exploration of metal formates as ammonia borane regeneration precursors is intriguing and potentially viable for select metals. There are, however, unexpected thermodynamic consequences which the PI has encountered relative to the conversion of metal formate intermediates to the starting material via benzene dithiol (vis-à-vis, tin diformate). Further complications have been discovered with the choice of substituent for the metal formate which inhibits decomposition of the metal formate. Overall, the approach is clever as it permits exploration of a variety of substituents and establishes priorities for parallel modeling efforts prior to experimentation.
- No information was provided as to whether or not other hydride generation mechanisms would be explored now that the formate system has been abandoned.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.6** based on accomplishments.

- The hydrogen evolution side of the project appears on track with several "initial hits".
- More information on the effects of nanoparticles on ammonia borane hydrogen release kinetics would have been useful, since this appears to be a positive result.
- Consideration: project has been substantially modified recently so performance in relative terms is good if this is factored in.
- The technical accomplishments of this project are impressive. However, greater diligence is needed in screening the potential barriers associated with 1) tin monoformate substituent-interactions and 2) decomposition of the substituted tin monoformate. In this context, computational calculations need to progress more rapidly.
- Initial program goals were reasonably on track for being met, but has not actually been met.
- No information on reorientation of the program was provided.
- The research confirmed the Pacific Northwest National Laboratory prediction that boron formates eject carbon monoxide rather than carbon dioxide.
- Regeneration work, although useful, does not appear to have produced interesting results yet.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- Good inter-partner communication.
- Premature to evaluate technology transfer.
- The teams work closely with the other center members, including University of Alabama and Pacific Northwest National Laboratory groups.
- Close interaction with the theoretical portion of the Chemical Hydrogen Storage CoE.
- The choice and number of technical partners is consistent with the level of effort and expected outcome of the project.
- As mentioned above, greater interaction and collaboration with University of Alabama is needed to progress further in the modeling efforts.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.6** for proposed future work.

- Nanoparticle effects on hydrogen release of ammonia borane are the most interesting aspect of the future work.
- Future work in the area of hydrogen release from ammonia borane is appropriate based on the accomplishments up to this point.
- Further work on light nanoparticles on the release rate and foam reduction seems worthwhile.
- Reasonable program goals on hydrogen evolution catalysts.
- Plans build on the previous progresses.
- No information provided on the hydride synthesis project.

Strengths and weaknesses

Strengths
- The project has adapted its task list to results and made go/no-go decisions when required and has proposed adequate modifications (to direct hydrogenation).
- Role of project partners is clear (e.g. nanoparticles input, energetics) and their input has been considered by the team.
- Preliminary results show positive effects of nanoparticles for release and foaming issues.
- Elimination of boron formates as hydride precursor (no carbon monoxide).
- Strategy for regeneration and release objectives seemed sound initially.
- Good science.
- Strong synthetic chemical component.
- Interesting initial observations with regard to light nanoparticle effects on hydrogen evolution.
- Nanoparticle effects on hydrogen storage.
- Innovative concepts for an ammonia borane regeneration cycle which take into consideration the cost targets (i.e., cheap starting materials), while simultaneously advancing new knowledge in an interesting field of chemistry.
- The project has demonstrated success in establishing low-cost routes to synthesis of target chemical precursors and in synthesizing a select number of such precursors.

Weaknesses
- In absolute terms, overall progress to meeting DOE objectives is modest considering the lifecycle of the project.
- Energetics of formate.
- Little understanding of nanoparticle effects.
- No revised goals given for hydride formation chemistry.
- The efficiency of the tin-formates route is questionable as the hydride formation requires hydrogen to migrate from carbon site to tin site via an O-bridge.
- Ammonia borane regeneration work may not lead to much that is useful for the regeneration process.
- The project plan does not take better advantage of computationally-based screening approaches for the selection of viable chemical precursors.

Specific recommendations and additions or deletions to the work scope

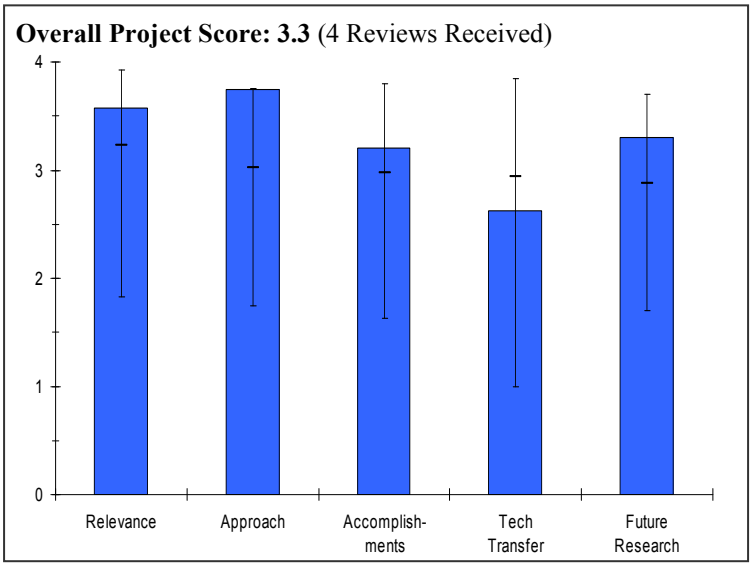
- In the area of regeneration, the PI should consider adopting computations as a means of screening the choice of metal and substituent in the metal-formate-based regeneration cycle.
- More emphasis on nanoparticle effects on release.
- Recommend augmenting computational efforts for screening and predicting energetics associated with metal formate decomposition.
- Formate portion of project should be defunded unless a revised project is submitted for new hydride formation chemistry.

Project # ST-12: Hydrogen Storage in Metal-Organic Frameworks
Omar Yaghi; University of California – Los Angeles

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objectives of this project are to 1) research the relationship between MOF structure and binding energy (low pressure measurements at various temperatures); 2) conduct high pressure hydrogen adsorption measurement at room temperature (impregnation of polymer and metal complex); 3) move toward the practical use of MOFs (cycling and kinetics of hydrogen charge/discharge) and 4) coordinate with theory (prediction of hydrogen uptake capacity).



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.6** for its relevance to DOE objectives.

- Critical to develop an adsorbent designed from the ground up.
- The target of the project to explore the metal organic framework working at room temperature is adequate.
- This is very important work on a promising class of materials critical to the hydrogen initiative.
- While relevant and aligned with the Program, the presented work looks like attempts to repeat earlier success and does not seem to be poised to address the major barriers that were identified in the investigator's earlier successes.

Question 2: Approach to performing the research and development

This project was rated **3.8** on its approach.

- Had a diverse comprehensive line of attack.
- The approach of "materials development" is proper.
- The approach is sound, and seeks to reach DOE system targets and is sharply focused on them (page 6-7 of the presentation).
- The group has tackled practical considerations concerning the actual use of sorbents (uptake, release, effects of impurities).
- It is clear that using metal organic frameworks for storage will require moving beyond incremental improvements, and pursuing substantially different/additional concepts. This project is working on such different/additional concepts.
- Intentionally developing interpenetrating networks that will increase the density of higher-energy unsaturated-metal binding sites could be one such different/additional concept, using polar atoms/bonds in the organic framework could be another, developing hydrogen-dissolving organics in polymer-filled metal organic frameworks and in carbon organic frameworks could be a third. Lithium incorporation could be a fourth.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Marries theory with experiment.
- Good improvement in ambient temperature performance.
- Obtained hydrogen capacity at room temperature with room to improve.
- Substantial progress has been achieved over the last 5 years (volumetric density having risen from 14 to 58 gH_2/L @50 bar and 77K).
- Preliminary work on potential chemisorbents initiated.
- Good cycling uptake/release, good reliability, fast charge rate.
- While providing materials of general interest, none of the different/additional concepts above has achieved, nor appears poised to achieve, the breakthrough needed to overcome the hydrogen binding energy / capacity barrier.
- The reported results for interpenetrating networks are both encouraging and discouraging. Encouraging in the sense that somewhat higher binding energies appear to result, discouraging in the sense that the improvement in binding energy and storage capacity appear to be incremental. Agreed, there is indeed an immense number of interpenetrating network systems that could be made and studied, but right now it appears that the concept is already close to "maxing out" its impact.
- Successful formation of materials that incorporate unencumbered lithium centers would be interesting, but so far the path is unclear.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.6** for technology transfer and collaboration.

- Collaboration with four professors and BASF.
- In the presentation, collaboration with industry and academia was mentioned little.
- Input from the theory group of Goddard et al. guides R&D experimental efforts.
- Coordination with other program participants should be explained more clearly.
- Not clear that this project is closely collaborating or cooperating with any other. But neither is it clear that such would lead to more rapid advances.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.3** for proposed future work.

- Good plan.
- The future work is well organized. Especially, collaboration with computational scientists is effective to explore materials.
- Lithium-enhanced compounds show promise (theory; comment on slide 26: please indicate pressure and temperature info when mentioning uptake).
- Including lithium or other "lithium-like" open centers in the framework appears to be the most ambitious new/different concept in the future plans for this project, other parts of its future plans look incremental. Based on other presentations from the Program, such "open metal" centers appear to the "final frontier" of sorption-based hydrogen storage, and this project appears better poised than some others to achieve materials that have such "open metal" centers.
- That said, a more systematic and determined approach to preparing "open metal" centers would be preferred. There is some old literature on preparing "coordinatively unsaturated" metal centers by first preparing ether-solvated compounds, using NEt3 to displace ether (because the ether could not be removed by vacuum alone), then using vacuum and gentle heating to remove N.

Strengths and weaknesses

Strengths
- Good, dedicated researchers.
- Much work delivered.
- The research on metal organic frameworks has been initiated by this group and they have successfully prepared various metal organic frameworks.

- The team has performed an impressive amount of very relevant and interesting work which has had a considerable impact on the field.
- These investigators opened the field of metal organic frameworks and should have greater appreciation for the types of materials that are possible, and what modifications they can tolerate.

Weaknesses

- Room temperature hydrogen capacity has not been improved.
- The field of sorptive hydrogen storage needs a fundamental breakthrough; the inclusion of additional open metal centers (whether by lithiation etc. or by interpenetration) seems the most likely way to achieve such a fundamental breakthrough; but do not see this receiving the emphasis it could warrant.

Specific recommendations and additions or deletions to the work scope

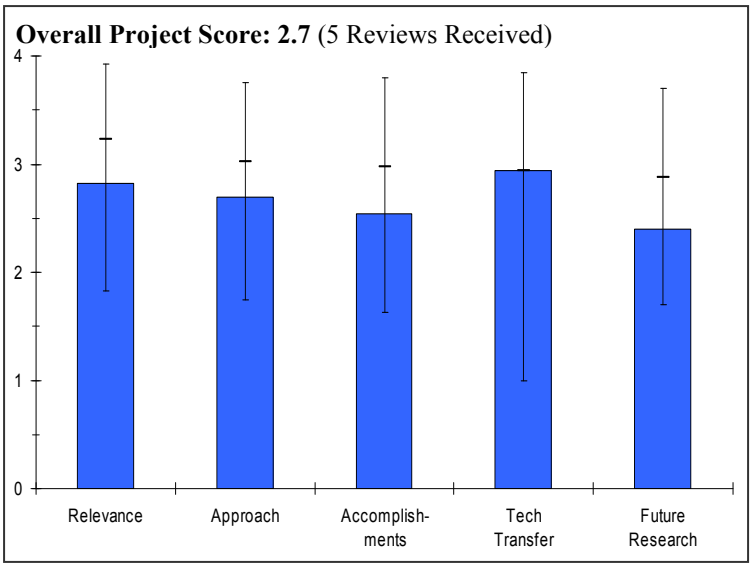
- Should indicate the effect of different materials and processes on hydrogen uptake. Do these have a major effect on engineering properties?
- Combination of theory and experiments is strongly recommended.
- Per above, put additional emphasis on increasing density of open metal centers.

Project # ST-13: Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage
Jack Fischer, presenting, University of Pennsylvania; Yury Gogotsi, Co-PI, Drexel University; Taner Yildirim, Co-PI, NIST

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objectives of this project are to:
- Develop and demonstrate efficient, durable and reversible hydrogen storage in carbide-derived carbons (CDC) with tunable nanoporosity (2004-2005).
- Determine the optimum pore size for hydrogen storage using experiment and theory (2005-2006).
- Identify post-processing strategies and catalytic additives which maximize the performance of CDC-based hydrogen storage materials, using experiment and theory (2006-2007).
- Finalize the design of a CDC-based H_2 storage material that meets 2010 DOE performance targets and commercialize it (2007-2008).



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.8** for its relevance to DOE objectives.

- This project seeks to develop carbide-derived carbon (CDC) powders as hydrogen storage materials with higher levels of performance compared to other types of adsorption materials such as activated carbons or metal organic framework compounds.
- While this is an independent project outside of the Hydrogen Sorption Center of Excellence (HSCoE), it shares common objectives and approaches particularly with respect to increasing both hydrogen storage capacity for the mass and volume targets as well as increase operating temperatures towards ambient conditions.
- The objectives are well aligned with DOE R&D objectives.
- It is great to see the PI address scale-up issues in the project scope.
- Concern: Investigators have identified importance of small pores, but have not shown that even optimal materials would have a volumetric capacity sufficient to meet DOE objectives.
- To their credit, investigators have one of the best-understood "amorphous carbon" systems known to date, which should enable more sophisticated study and better understanding of such materials than will be provided by competing projects.
- CDCs might not exceed the gravimetric densities of activated carbons.
- CDCs need high temperatures and aggressive leaching chemicals [for synthesis].
- Research on new high surface area carbon materials is important for reaching the program goals for hydrogen storage.

Question 2: Approach to performing the research and development

This project was rated **2.7** on its approach.

- The prior empirical synthesis approach is now being supplemented by more theoretical modeling and neutron scattering studies via the National Institute of Standards and Technology [NIST] partner as well as exploring metal doping and alternative "activation" processing to improve capacity and hydrogen binding.

- The idea of tuning pore shape by choosing different precursors is really good.
- The "designer" pore structure approach is good in theory. It needs to be experimentally validated.
- Post treatment can create more pore volume. However it is important to know the size of the pores created in this step.
- It is not clear how to achieve the optimum pore size.
- The binding energy and volumetric uptake are not addressed.
- Although they have identified small pores as necessary, their route to developing materials with more such pores isn't clear.
- Sodium doping doesn't seem to have accomplished much, nor have preliminary experiments in titanium loading; what do they plan if further experiments do not pan out?
- The project has taken a comprehensible approach to design and create new CDCs.
- Usage of energy intensive temperatures and aggressive leaching chemicals is a critical path.
- The approach of activating carbide-derived-carbons (CDC) with CO_2 or KOH does not generate materials with any added benefits for hydrogen storage vs. conventional activated carbons. The significant added expense of CDC over activated carbons calls into question the logic of the PI's approach.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.5** based on accomplishments.

- The investigators have shown that KOH activation increases the excess hydrogen gravimetric capacity up by ~40 percent for adsorption at 77K primarily due to greater surface area and pore volume. However, binding energies of hydrogen have about the same values as the capacity was not improved at room temperature during limited assessments.
- Researchers looked into possible improvements via metal dopants where serious issues remain with efficient doping and blocking of the porous structure within the CDC powders that severely limited storage capacity.
- The PI does not have enough data to show the pore size distribution which is critical to correlate the data.
- It is not clear how doped titanium is distributed on the CDC.
- When comparing Ti-doped TiC-CDC with activated carbon, it is necessary to plot both of them on the same chart at same temperature (Slide #14).
- Within the scope of this project, there have been some interesting technical accomplishments, although, continued work within this scope appears to offer only diminishing returns. Were this project to be continued, this reviewer would recommend radical changes in scope.
- The presentation did not show comparisons between "old" and "new" results.
- It stayed unclear, whether chemical surface modifications could be successfully applied to CDCs.
- Usage of alkali metal doping showed "slight" or even "significant" reduction of gravimetric densities.
- The PI demonstrated progress in surface modification that increased the heat of adsorption. This is important for realizing practical hydrogen storage materials.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.9** for technology transfer and collaboration.

- The three partners within the team complement each other in conducting theoretical analyses and experimental assessments of the CDC materials as improved hydrogen storage materials.
- The involvement of the Spanish group with KOH activation led to significantly enhanced sorption capacity at 77K.
- Some collaboration exists but need more collaboration to achieve a fundamental understanding of the materials produced.
- It was not clear what parts of this project were done at which of the partner institutions. This could be because the partnership is working very well, or because the partnership is not working at all - difficult to judge.
- There could be significant advances were this team to collaborate with the Sorption COE on using their materials in "spillover hydrogenation" studies.
- The project has very good collaborations with a remarkable fraction of international and industry partners.

- Project has found an industry partner, who tries to scale-up the material manufacturing.
- There is little evidence of significant collaborations for this project.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.4** for proposed future work.

- Planned future work is consistent with past study with appropriate characterization and hydrogen adsorption measurements on titanium-doped CDC and investigation to alternative surface treatments to increase surface areas and porosities without compromising other properties.
- Lack of general understanding on how activation protocol can impact the pore size distribution which is critical for improved hydrogen uptake.
- 100 mg sample size is too small to obtain some meaningful results.
- Other metals than titanium should be explored.
- Continued work within the project scope as outlined in this presentation is likely to face diminishing returns. Optimization is very unlikely to greatly increase volumetric capacity.
- The project tries to fine-tune their materials with the already existing tools and measures.
- It stayed unclear, which extra measures would be applied to promote the project towards the envisioned objectives.
- It stayed unclear, how results of the theoretical modeling can be successfully applied to the production and generation of improved materials.
- It is doubtful, whether the project will reach its key milestone of "getting excess material capacities at the level of the best metal organic frameworks" within the short remaining project time and the remaining budget.
- The PI did not clearly present how the materials development will address overcoming the barriers of low adsorption enthalpy.

Strengths and weaknesses

Strengths
- The team has adapted its preparation and activation processes to enhance 77K sorption capacities.
- There is currently greater inclusion of theoretical efforts and structural characterization to assist in interpretation of adsorption of the CDC powders and to search for additives to increase hydrogen binding energies.
- CDC approach provides a valuable path of producing sorbent material with well controlled pore size distribution.
- The CDC materials and activation procedures offer some of the best understood of the "amorphous carbons" under study.
- Results of the project are showing an alternative way of possible hydrogen storage materials through hydrogen absorption.
- The PI has a very good understanding of microporous carbons and adsorption.

Weaknesses
- The best 77K sorption capacities are still equivalent to most activated carbons and metal organic framework compounds for hydrogen desorption that is leading to enhance performance wanted by DOE.
- Lack of fundamental understanding of how post-treatment can affect the material property design.
- Metal doping and further optimization of pore size distributions do not appear to offer a path to significantly improved hydrogen storage performance. More radical experimentation with the activated CDC materials could however provide new leads.
- For the preparation of CDCs, usage of chlorine at high temperatures up to 1200°C is needed. For the chemical activation, e.g. KOH at 1000°C is needed.
- The necessity of using leaching materials at high temperatures as a crucial process step is energy demanding.
- The necessity of using leaching materials at high temperatures as a crucial process step is raising safety issues.
- As mentioned by the project's presenter, CDCs might one day match the gravimetric densities of activated carbons, but will not beat them significantly.

- CDC are likely to be expensive and do not demonstrate any significant advantage over activated carbons for hydrogen storage.

Specific recommendations and additions or deletions to the work scope

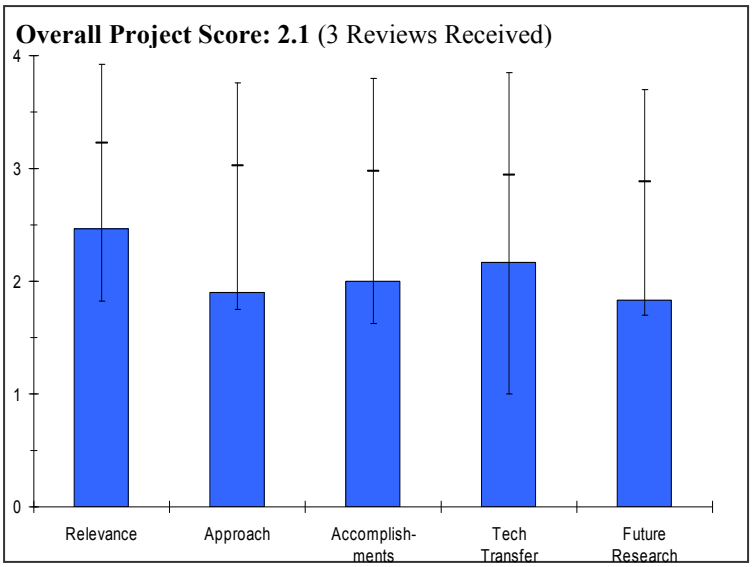
- Independent characterizations of pore size distribution and hydrogen occupancy is still needed.
- Additional external collaborations especially having in-situ nuclear magnetic resonance assessments of pore size with the University of North Carolina would benefit this effort.
- Team should measure adsorption isotherms at different temperatures to determine heat of reaction on the CDC materials especially to assess whether metal doping or surface processing can lead to stronger chemical bonding.
- Recommend that collaboration be started to characterize pore and slit dimensions via in-situ nuclear magnetic resonance.
- Try "spillover hydrogenation" with the activated CDC materials - what happens?
- Addition of an evaluation of needed process energies, ingredients and safety hazards during production of CDCs. Comparison of that evaluation with other sorption materials, especially metal organic frameworks and activated carbon.
- If CDCs might not exceed the gravimetric densities of activated carbons, the project should point out much clearer where the advantages of their CDCs are.
- The PI should focus on understanding the observed effects of surface activation on the heat of hydrogen adsorption. This may lead to materials with better adsorption properties.

Project # ST-14: Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

Leon Shaw; University of Connecticut

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project



Project objectives in FY 07 were to: 1) identify hydriding/dehydriding reaction mechanisms and rate-limiting steps of ($LiNH_2$+ LiH) systems; 2) enhance hydriding/dehydriding rates via nano-engineering and mechanical activation; and 3) improve hydriding/dehydriding properties via thermodynamic destabilization. Objectives in FY 08 have been to: 1) further improve hydriding/dehydriding properties of ($LiNH_2$+ LiH) systems via nano-engineering, mechanical activation, and thermodynamic destabilization; 2) establish the atomic level understanding of the reaction mechanism and kinetics of mechanically activated, nano-engineered ($LiNH_2$+ LiH) systems; 3) perform nano-engineering and mechanical activation of $LiBH_4$-based materials; and 4) demonstrate hydrogen uptake and release of ($LiBH_4$ + MgH_2) systems with a storage capacity of ~ 10 wt% H_2at 200°C.

Question 1: Relevance to overall DOE objectives

This project earned a score of **2.5** for its relevance to DOE objectives.

- The base material has a very high desorption temperature and a gravimetric capacity that will not achieve 2010/15 targets. Ball milling to decrease the thermodynamics has been thoroughly investigated with limited success and many drawbacks.
- $LiNH_2$/LiH system: The MHCoE has discontinued consideration of this system due to low plateau pressure and slow kinetics, therefore the studies are relevant only to the extent that understanding this system will lead to improving other, systems under consideration. The particular phenomenological observations are intriguing but not well enough understood to offer great improvements to other systems.
- $LiBH_4$/MgH_2 system: similar concern as with the $LiNH_2$/LiH system, although as long as this system is still under consideration in the Program as a system with potential, performing the phenomenological studies has some value.
- The project supports the goal of developing high-density hydrogen storage with materials that have adequate kinetics to meet the program goals for refueling time.

Question 2: Approach to performing the research and development

This project was rated **1.9** on its approach.

- Ball milling may not be a viable process for large scale automotive manufacturing and their associated volumes. Creating nano size particles of most metal hydrides is only useful if they can be immobilized and prevented from agglomeration, sintering and etc. The PI does not address these requirements at all.
- Attempts to overcome diffusion barriers by mechanical treatment alone seem very unlikely to succeed. The empirical observation of improved reaction rates begs more questions than it answers, which the PI should be driven to address, for instance: How can the system possibly "remember" the temperature at which it was ball-

milled after several cycles at >200°C? What kind of "defects" could be durable through these cycles (ex.: maybe different amounts of iron or chromium slough off the ball mill onto the hydride material and serve as catalysts?).

- As long as the investigators are looking at thermodynamic phase destabilization by mixing metals, it seems surprising that they didn't also look at kinetic effects of mixing metal hydrides, e.g. combine $LiNH_2$/LiH (slow dehydriding) with $Mg(NH_2)_2$/LiH (rapid dehydriding) to see if the mixture exhibits intermediate dehydriding rates.
- The approach relies on simple modifications of known hydrogen storage materials. These hydrogen storage materials do not have a high probability of meeting the DOE program goals. The material capacity is very small unless the pressure is reduced to a vacuum which is not feasible for onboard hydrogen storage.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.0** based on accomplishments.

- Thermodynamics were predictably reduced by ball milling however the desorption temp of ~200°C is still far too high for use in automotive systems. Little progress or direction has been demonstrated in improving the cycling performance of such materials.
- Progress appears to be limited to cataloging the effects of different milling conditions. The results do show that these are interesting to catalog, but the underlying understanding does not reach the level of sophistication to be broadly applicable.
- After some number of hydriding/dehydriding cycles, it would seem inevitable that the material will lose its "memory" of milling conditions. The investigators should establish how many cycles, and develop a more sophisticated understanding of the effects.
- The PI did not present any breakthrough results that indicate a high probability of reaching the project milestones. The project milestones are very aggressive.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.2** for technology transfer and collaboration.

- The PI appears to have strong collaborators however is perhaps not utilizing them to their full potential.
- Good use of nuclear magnetic resonance characterization in Pacific Northwest National Laboratory collaboration, but there is little evidence of other collaboration in this project. More detailed characterization of particle size and defect concentration would seem in order, are there collaborators who could provide this?
- The PI presented little evidence for collaboration or even understanding of the parallel efforts within the DOE hydrogen program.

Question 5: Approach to and relevance of proposed future research

This project was rated **1.8** for proposed future work.

- The PI is not clear about what approach will be used to stabilize the nanostructure materials. It is clear that these materials are not stable with cycling and will need to be immobilized. It is not clear that the PI has a solid understanding of this and what tradeoffs will be incurred in capacity with various immobilization techniques such as scaffolds. The work proposal is proprietary at this point – he should at least provide a direction as to what routes will be pursued.
- It is not at all clear what "nano-engineering" means or what experimental path is intended. While it is true that understanding, and even more important, intentionally controlling, the interphasic reactions in these "thermodynamically destabilized" systems would be very useful, it is not clear the project has a clear path to the necessary level of understanding and control.
- The future research plan that was presented by the PI has little potential of meeting the system weight percent target with the existing hydrogen storage materials. New materials development will be needed to meet the project goals.

Strengths and weaknesses

Strengths
- If the interphasic reactions can be fully controlled to give the necessary rates, these systems have some promise, although the heat of dehydriding needs to be lowered further.
- The PI showed characterization results that were of high quality.

Weaknesses
- Needs to move beyond observing and cataloging the effects of different milling conditions and particle sizes.
- The project approach of modification of metal amide systems is not likely to meet the project milestones.

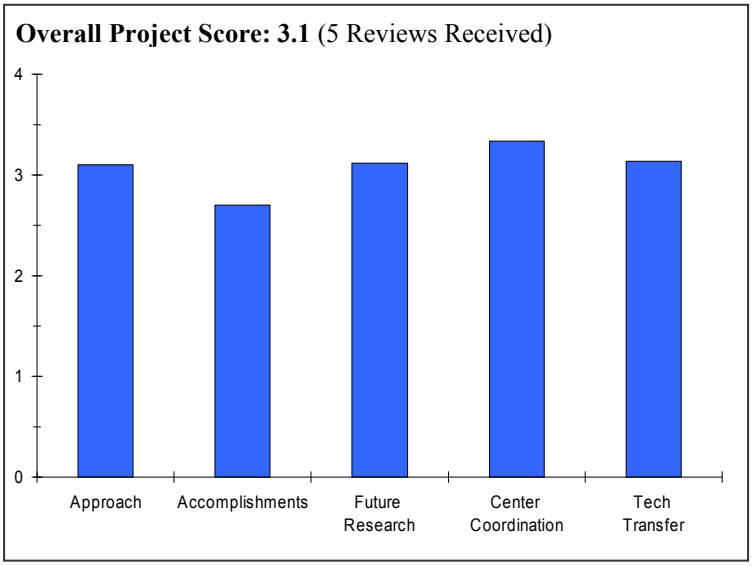
Specific recommendations and additions or deletions to the work scope

- Proprietary nature of the scaffolding approach - this is clearly where all the focus and novel discovery of the project should be and should be elucidated / described up front.
- The PI should coordinate with other projects that attempt to destabilize metal hydrides and provide some kind of scaffold or support, such as aerogels, in order to fully understand the challenges and tradeoffs with such techniques.
- Either develop scope for a detailed understanding of the inter/intraphasic reactions within this project, or transfer scope to other projects.
- Novel materials development will be necessary to reach the project milestones. The capacity should be measured under realistic system operating conditions (e.g. desorption at 2 bar, not vacuum).

Project # ST-15: DOE Hydrogen Sorption Center of Excellence (HSCoE) Overview
Mike Heben; National Renewable Energy Laboratory

[NOTE: This presentation was to evaluate the entire Hydrogen Sorption Center of Excellence as a whole. A separate review form was used and can be found in Appendix C. NREL's technical contribution to the center is evaluated in ST-19.]

Brief Summary of Project



The mission of the DOE Hydrogen Sorption Center of Excellence (HSCoE) is to develop materials that will enable close to room temperature storage of hydrogen on-board a vehicle at moderate pressure. The strategy used by the HSCoE is to design and synthesize materials which bind hydrogen as either (a) weakly and reversibly bound atoms or (b) as strongly bound molecules. Examples include nanoporous polymers, boron/carbon polymers, metal-organic frameworks (MOFs), carbon nanohorns, aerogels, carbon-metal hybrid nanomaterials, new materials "built from the ground up", and new multi-component sorbents. Additional objectives are to understand mechanisms and the interplay between structure, binding, and material stability and storage densities (per volume and per weight) and develop the experimental and computational tools to speed discovery, development and testing of materials that meet DOE system goals. The final objective is to overcome barriers to 2010 Department of Energy system goals and identify pathways to meet 2015 goals.

Question 1: Approach to performing the R&D including Center Management

This project earned a score of **3.1**.

- The overall CoE effort is very well designed and technically feasible.
- CoE has a good balance between universities, DOE, national labs and industry.
- The separation of research work in research clusters shows a way how to reasonably divide the tasks into "digestible" parts.
- Some challenges in finding new materials are clearly addressed, like weight percent, binding for higher temperature storage, less so for volume which is the most significant challenge. The CoE seems to use partner skills well and is coordinated with only rare exceptions. Down selection has been done. Audits are unclear.
- Formation of the clusters is a good idea.
- Research cluster organization has gelled into an effective approach to enhance development in the different thrust areas of research.
- Good coupling between theory and experiment.
- Broad spectrum of research areas looking at different hydrogen surface interaction mechanisms.
- Center remains in discovery mode. Center doesn't use hard metrics for go/no-go decisions.
- The center consists of four research clusters that are led by senior National Renewable Energy Laboratory staff with a roadmap. This makes targets and research of each cluster and individual very clear.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **2.7**.

- The significant amount of progress across the center is appreciated.
- Especially, the amount of publications, presentations and review work is outstanding.
- Yet, it was not clear enough, whether sorption materials will ever meet the DOE system targets, especially without using higher pressures and/or lower temperatures.
- Improvement in binding energy and volumetric densities is appreciated.
- Not clear about measurement to milestones but progress [observed] in several areas. Would prefer to see addressing the key remaining problems more quickly, for example kinetics in spillover.
- More emphasis on establishing the feasibility of materials synthesis estimated from theory by providing a plan and addressing key challenges at the beginning.
- Although spillover approach appears very promising, progress has been slow and many questions remain.
- Metal organic frameworks (MOF) – determined relation between binding energy and binding site on MOF-74.
- Have demonstrated a number of materials with binding energies higher than molecular physisorption.
- The major research topic of this CoE is "spillover" but the progress from last year [appears] little, especially in hydrogen capacity.

Question 3: Proposed future research approach and relevance

This project was rated **3.1**.

- The future work plan is well planned and addresses the key technical barriers.
- Actual plan details are less clear but the areas are appropriate. Would like to see theory plans and theory interaction with experiment plans, but glad that something is intended.
- Proposed future work is finally beginning to focus on less exotic species (such as metal doped fullerenes) and towards cheaper, more readily available materials.
- Consideration of non-carbon based materials is a good expansion of current work.
- Lithium intercalated graphite may hold promise as a storage material.
- Future plan does not clearly show the direction of the material development. There is no "Kubas" compound any more. Scale-up in preparation and high-pressure measurements of spillover material, which is a major focus of the center, are only shown.

Question 4: Coordination, collaborations and effectiveness of communications within the CoE

This project was rated **3.3**.

- There is no doubt that there is outstanding continuing cross-center communication and collaboration inside and also outside the CoE.
- The center coordinator seems to have the right means to leverage the right resources for the necessary research and has created a fruitful platform on which new ideas can be created.
- All partners seem to profit from the overall group effort.
- Generally good, mostly working together with maybe a single counter example, good structure to get communication between logical partners often and all partners on occasion.
- Collaboration with others is visible.
- Collaborations between center partners do exist, but there is some room for improvement.
- Individual PIs appear focused on their own research projects and there could be better interaction to facilitate developments in some areas.
- Practical and engineering inputs from the industrial partner, Air Products and Chemicals, Inc., are not apparent from the presentation.
- Coordination through research clusters works effectively. In addition, research of theory is coordinated across the clusters.

Question 5: Collaborations/Technology Transfer Outside the CoE

This project was rated **3.1**.

- Like the previous work with the hydride center, there is a good degree of interaction with the world community.
- More collaboration is suggested to ensure testing reproducibility and the utilization of the Southwest Research Institute facility is recommended.
- International Energy Agency (IEA) [Hydrogen Implementing Agreement, HIA] and International Partnership for the Hydrogen Economy (IPHE) involvements are good.
- Collaborations outside of the center [are] on a personal PI basis, rather than being focused on a thrust area, material or process.
- Collaborations with other CoEs and institutes outside are few.

Strengths and weaknesses

Strengths
- World-renowned researchers.
- Good mix of competencies and partners.
- Spillover methodology as one of the most promising storage material candidates.
- Powerful team.
- Visible collaboration between theory and experiments.
- Center leveraging others' work.
- The center explores novel materials in a large number including carbon nanotubes, "Kubas" compounds, spillover materials and so on for hydrogen storage.

Weaknesses
- It was not clear, whether sorption materials will ever meet the DOE system targets, especially without using higher pressures and/or lower temperatures.
- No significant effort in producing the desired material quantities for a 1 kg storage system. [NOTE From DOE: A 1-kg prototype is no longer part of the scope of work for this HSCoE effort.]
- Do not seem to be attacking the key problem in spillover – kinetics. However, it is not clear they have the power to tell partners to do certain things – they may not be able to push experimenters.
- Relying on modeling to down-select materials and not having a path forward and a plan towards materials synthesis while addressing key challenges.
- The materials predicted by theory are not synthesized in real experiments. "Kubas" compounds are one of the examples. One of the reasons is that the materials prepared have been too small in the amount for precise characterization.

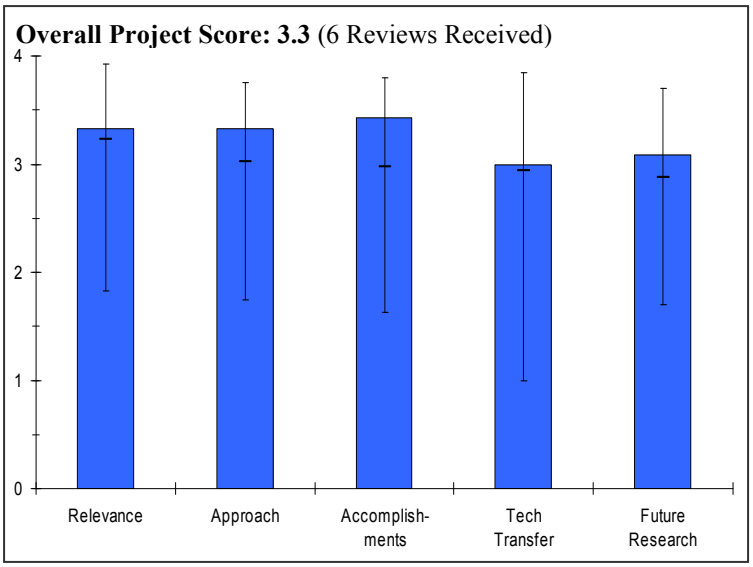
Specific recommendations and additions or deletions to the work scope
- While focusing resources on spillover, it is suggested to clarify/confirm this phenomenon and evaluate its potential for hydrogen storage experimentally with theory support.
- Center needs to ensure resolving testing discrepancies observed especially in the spillover topic.
- Attention should be paid to not confuse the difference between system and material densities especially at presentations.
- Presentations should contain an overview plot or list of the best achieved materials and measurements.
- Why is there "No significant effort in producing 1 kg system in agreement with new DOE goals"? [NOTE From DOE: A 1-kg prototype is no longer part of the scope of work for this HSCoE effort.]
- CoE Coordinator's answers in the "white paper" on low temperature focus at 77K should address the question, whether adsorption materials will ever be able to hit DOE targets at low pressures and room temperature.
- Is the storage density of the new materials independent of their surface areas?
- Somehow the raft of negative experimental results on the metal atoms needs desperately to be used to update the theory until the theory can predict reality and then turn the theorists loose again on predicting materials.
- Keep the center scope but suggest to devise plan towards targets while clearly addressing challenges.
- The materials that cannot be operated at ambient condition should be decided as "No-Go" like another CoE.

Project # ST-16: A Biomimetic Approach to New Adsorptive Carbonaceous Hydrogen Storage Materials
Joe Zhou; Miami University of Ohio

[NOTE: This project is part of the Hydrogen Sorption Center of Excellence; as of the Fall of 2008, Joe Zhou will be at Texas A&M University.]

Brief Summary of Project

The objective of this project is to design, synthesize and characterize MOFs with active (open site) metal centers aligned in porous channels and accessible by hydrogen molecules. Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity or binding energy to hydrogen. These MOFs can help to reach the Department of Energy 2010 and ultimately the 2015 hydrogen storage goals.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Project is aligned with DOE objectives and targets for hydrogen storage.
- The objectives are well aligned with DOE R&D objectives.
- Project is aligned with DOE objectives and targets for hydrogen storage.
- The work scope for this project aligns with the hydrogen vision and the DOE RD&D objectives in most respects.
- If relevance means that a project can either demonstrate achievement of the DOE targets for hydrogen storage or provide seminal new insights that assist in the identification of materials/concepts with the potential to meet one or more of the DOE targets for hydrogen storage, this project falls in the latter category.
- The project's objectives and strategy are sufficiently well aligned to the DOE program vision and aims. The idea of aligning coordinatively unsaturated metal centers (UMC) in order to obtain significantly stronger hydrogen-framework interaction is innovative and may provide fruitful insights and quite useful results.
- Though the work is nominally focused on the 2010 DOE storage targets, it's not completely clear how the PI hopes to achieve these targets. It does not seem as though increasing the binding energy alone will enable all the targets (e.g., they've already increased the binding energy to 12 kJ/mol, but only are able to get < 0.5 weight percent at room temperature). So, if the PI is able to achieve the targeted binding of 15 kJ/mol, will this really enable room-temperature storage?
- The volumetric densities of these materials are inherently low, and only some reference to future work on interpenetration seems to address this crucial issue.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- The approach to try to align metal bonding sites to increase interaction with hydrogen is sensible.
- The concept of aligning the metal center is good.
- It is not clear how theory can guide the experimental design.
- Is only aligning the metal center enough to achieve targets or do some other approaches need to be explored at the same time?

- This project applies biomimetic concepts and logics to extend the hydrogen storage capacity of metal-organic framework materials (MOFs), primarily by incorporating coordinatively unsaturated metal centers (UMCs) in the MOFs.
- The metal organic framework synthesis efforts are directed at compact, aligned, interpenetrating structures with hydrogen adsorption enthalpies in the desired range (ca. 15 kJ/mol) for DOE's hydrogen storage targets.
- The overall approach is indeed focused on the technical barriers addressed and leads already to tangible results. The project integrates well with other ongoing research on framework materials.
- Interesting, and unique approach to the design of novel MOFs for hydrogen storage. The connection between the approach of a close-packed array of metal sites, and the oxygen transport of hemoglobin (which seems to underlie the entire philosophy) is not completely clear.
- Would be valuable to see a more rational, directed approach to decide how the many variables in the synthesis will be optimized.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.4** based on accomplishments.

- Achieved relatively high storage density (5.5 weight percent, ~45g/L) at 77K and 50 bar pressure.
- Demonstrated increased heat of adsorption through alignment of open metal sites.
- The PI has shown some interesting results to prove the concept.
- The progress is reasonably good considering this is a new project.
- Metal organic framework structures with the desired aligned UMC deployments were successfully synthesized and hydrogen adsorption properties were measured.
- The hydrogen uptake properties of these new structures were marginally better than those of the best MOFs without UMCs; a heat of adsorption near 12 kJ/mol was obtained for one of the UMC-based MOFs.
- A limited amount of characterization (beyond hydrogen sorption measurements) was reported (i.e., inelastic neutron scattering (INS) results).
- Although the project is underway for a little under a year (started in July 2007), a number of promising results have been obtained. Several milestones have been reached in FY2007 and some significant technical accomplishments were presented (like the promising hydrogen uptake of PCN-12 following optimization attempts for the alignment of coordinatively UMCs). INS measurements have also shown strong hydrogen-metal organic framework interactions.
- Good progress in synthesis of proposed compounds and measurements of their storage capacities. Results are not entirely encouraging, but progress is strong.
- PI is to be commended for focusing on volumetric density, and reporting these numbers (even if they are somewhat "ideal" in the sense that they are based on the single crystal density). The volumetric density is at least as significant a challenge for sorbent materials as gravimetric density, though the latter gets much more attention.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- Some good collaborations exist.
- This project involves six partnering organizations.
- The nature of the collaboration with some (but not all) of these partners was spelled out in the presentation.
- The project seems to be well connected with the Hydrogen Sorption CoE.
- Collaborations through partnership with several research groups (including the industrial ones) are shown. They seem to complement nicely the work done by the PI's team. Of note are the collaborations with groups outside the United States (Korea Research Institute of Chemical Technology, Korea; University of Gottingen, Germany).

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Plans to increase metal center density and increasing metal organic framework stability are addressing proper barriers.
- Plans for interpenetrating metal organic framework networks have potential for significant increases in storage density.
- The general direction of the future plan is good.
- The absolute gravimetric and volumetric storage value should not be used as a single go or no-go decision point. The degree of improvement is more important to justify if the approach works.
- The proposed future research builds logically on the results of the past year's work.
- It must be said here that the hydrogen storage results presented at the review are not impressive in the context of DOE's storage targets for 2010 (and less so for 2015 targets) and it is hard to imagine what the research team could possibly accomplish in FY 2009 to change this.
- Future research plans for 2008 and 2009 build on the progress achieved so far. A milestone is rightly set for the 3rd quarter of 2009 (go/no-go decision) as to whether the project can substantially contribute towards the attainment of the DOE 2010 goals.
- For reasons stated above, it is not clear that the future research will result in materials that could enable the DOE 2010 goals (if 12 kJ/mol currently is only getting 0.5 weight percent at 300K, how will 15 kJ/mol really help?).

Strengths and weaknesses

Strengths
- The PI appears to have a good handle on designing metal organic frameworks (MOF) of desired geometries, and how synthetic variations affect structures.
- All the appropriate characterization tools are in place for characterizing new MOFs.
- Novel concept.
- A very competent synthesis team has designed and then proceeded to produce some very interesting metal organic framework structures.
- The resources and facilities needed to perform the required synthesis and characterization work are available to the team.
- The overall level of the science produced by this project is very high; several high profile peer reviewed publications have appeared or are in press.
- Innovative idea, strong research team and partners.
- Promising initial results.
- Novel approach to design new metal organic framework materials for storage.
- More focus on volumetric density than other sorbent programs.

Weaknesses
- Lack of a general strategy on how to achieve the desired orientation in order to meet DOE targets.
- Lack of theory prediction and an overall experimental approach strategy.
- There is very little hope that any type of metal organic framework structure will be able to meet DOE's 2010 hydrogen storage "system" targets for ambient temperature operation; simple back-of-the-envelope calculations would prove this; there's just too many other atoms in the UMC/metal organic framework structure along with the stored hydrogen; if the project team disagrees with this statement, they should be prepared to demonstrate otherwise at the next Merit Review.
- A rational design strategy for improving capacity is lacking. It is not clear that increasing binding energy will really enable capacities that they are targeting.
- Budget seems excessive for what appears to be largely a single PI project.

Specific recommendations and additions or deletions to the work scope
- There exist a large number of available options regarding different parameters to be considered (e.g. metal nature, geometry, etc.). An effort should be made to narrow down these options based on a sound approach.
- Future work should have a stronger focus on improving volumetric densities.
- The PI needs to work more closely with the theory group to guide the experimental direction.

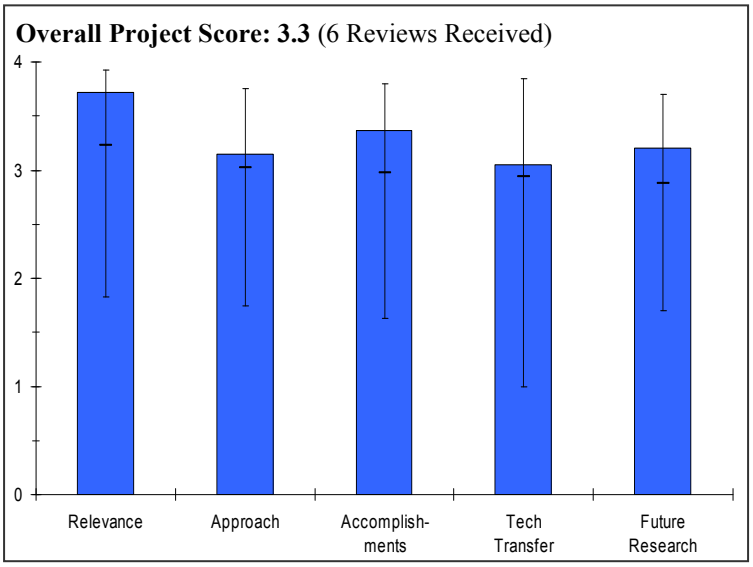
- At the next Merit Review, the PI should present an appropriately determined upper bound for the ambient temperature gravimetric and volumetric hydrogen storage capacities one could expect to achieve with the leading candidate unsaturated metal centers/metal organic framework structure for which the team has presentable test data.
- Alternatively, the presenter should make a compelling argument for why 77K results represent a useable condition for on-board hydrogen storage. It's time for the physisorption/chemisorption teams to show they are getting within range of the 2010 DOE system targets for gravimetric and volumetric hydrogen storage- December of 2010 is only 30 months away.
- The possible assessment of the porous coordination network (PCN) metal organic frameworks for spillover should be considered.
- The PI expressed concerns about the usable capacity (between e.g. 50 bar and 2 bar) of the materials. This may not be a real problem as temperature swing techniques may bypass the issue.

Project # ST-17: Hydrogen Storage by Spillover
Ralph Yang; University of Michigan

[NOTE: This project is part of the Hydrogen Sorption Center of Excellence.]

Brief Summary of Project

The objectives of this project are to 1) develop hydrogen storage materials with capacities in excess of 6 wt% (and 45 g/L) at ambient temperature by using the spillover mechanism; 2) develop and optimize the bridge-building techniques for spillover to enhance hydrogen storage in metal organic frameworks (MOFs); 3) develop direct doping techniques for spillover on carbons with ultra-high surface areas (higher than all MOFs); and 4) obtain a mechanistic understanding for hydrogen spillover in nanostructured materials for the purpose of hydrogen storage.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.7** for its relevance to DOE objectives.

- Addresses relevant DOE hydrogen storage targets and goals.
- This project is focusing on improving the room temperature adsorption hydrogen storage capacity towards the DOE mass and volumetric targets via a spillover process with metallic clusters/particles on the surfaces of adsorbent materials. The concept of building bridges between the metal species and carbon host materials was shown to significantly enhance these capacities although reaction rates are much too slow to meet DOE charging and discharging requirements. The observed 1-2 weight percent capacities are still too small but do point the direction for a viable adsorption storage system.
- This project is well aligned with the hydrogen vision and the DOE RD&D objectives; hydrogen spillover is one of, if not the key to meeting DOE hydrogen storage targets with sorption-type materials/processes.
- The insights that emanate from this work are having a profound impact on research directions within the Hydrogen Sorption CoE.
- If sorption-based processes were within range of meeting ambient temperature gravimetric and volumetric hydrogen storage targets, this project would get an even higher score for relevance.
- A sorbent with a high hydrogen capacity at room temperature would be a very significant breakthrough. Hydrogen spillover effects in carbon-based sorbents have real potential for the development of room temperature hydrogen sorbent materials with capacities suitable for vehicular applications.
- Project as presented and described is outstanding and attempts to understand kinetic issues limiting the use of carbon materials.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- The approach has potential to meet DOE gravimetric storage targets for 2010.
- Use of platinum at anywhere near these levels will be too expensive – need nickel or a cheaper metal.
- Isotope studies can help define doping levels needed and effective distance of spillover effect.

- Need a mechanistic model and estimate of maximum - can you go beyond one hydrogen/carbon atom with spillover? Is the hydrogen atom occupying a carbon coordination site, or can more than one hydrogen atom occupy a coordination site?
- This project is empirically investigating the addition of platinum/carbon catalyst particles on several types of activated carbons in addition to metal organic framework (MOF) compounds to allow for hydrogen spillover onto the main carbon sorbent. They are also looking at the degradation effects of water and air on stabilities of the metal organic framework materials.
- They have also used deuterium isotope effects to investigate the mechanisms to the spillover effect into splitting hydrogen molecules into atoms for chemical adsorption on carbon materials and also facilitate reversible desorption. These analysis methods, as used by the investigators, are certainly informative but further in-situ spectroscopy would be useful.
- The methods of study applied in this research are very cleverly orchestrated; the demonstrated concept of bridge-building and the tracer experiments provide pathways for understanding and enhancing spillover.
- Spillover in the high surface area templated carbons and metal organic frameworks is an excellent approach.
- Efforts to develop non-noble metal catalysts for spillover are important.
- Understanding spillover is highly relevant and is the key to advancing the state-of-the-art in sorption materials. Why synthesize materials when so many others in the CoE are synthesizing novel carbons that could use used in your study?

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.4** based on accomplishments.

- Have achieved 1.5 weight percent at room temperature with platinum-doped metal organic frameworks.
- Have increased heat of adsorption in IRMOF-8 to 21 kJ/mol.
- Technical accomplishments to date are outstanding providing solid progress towards understanding storage systems costs.
- The PI showed several examples where the bridged 5%Pt/AC catalysts not only enhanced the room temperature storage capacity by factors of 2-3 but also leads to the desirable increase in the heat of reaction. The kinetics are still rather slow while the capacities are also beyond upper levels theoretically expected.
- Showed that spillover-storage is influenced by surface area and binding energy.
- Made the case that spillover-storage on nanostructured carbon is "far" from reaching theoretical limits.
- Presented data showing that ambient temperature discharge rates for selected sorption materials are now in the range of the DOE target.
- Performed some interesting deuterium tracer results that provide direct evidence of molecular hydrogen dissociation, and "last-in-first-out" behavior during spillover/reverse spillover procedures.
- Relatively little progress on room temperature hydrogen capacity since the excellent result of 4 weight percent hydrogen at room temperature in IRMOF-8.
- Current work with the templated carbon and new metal organic frameworks looks interesting for the possibility of increasing the hydrogen capacity at room temperature.
- Technical accomplishments to date are outstanding.
- Mechanistic understanding of spillover with deuterium isotopes will lead to a new understanding of how carbon sorbs hydrogen.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- Some collaboration with the National Renewable Energy Laboratory and National Institute of Standards and Technology, spillover seems to be spilling over to other projects in the sorption center.
- Collaborations extend across all CoEs and national laboratories.
- The University of Michigan investigators are interacting with several of members of the Hydrogen Sorption Center of Excellence for samples sources and characterizations.

- Numerous partners were listed on slide 2 of the presentation but it was not clear, as the PI went through the accomplishments/results, which ones were done at the University of Michigan and which ones were done by a partner.
- Other collaborations were mentioned by the PI during the presentation but are not well documented in the slide file.
- Clearly, many in the hydrogen storage community have picked up on the findings from this project.
- Relatively little interaction with other members of the Hydrogen Sorption Center of Excellence. This project would benefit greatly from increased center theoretical interactions, particularly as to the mechanisms of hydrogen spillover and how theory might guide experimental progress to increase hydrogen capacity at room temperature.
- Collaborations need to be elaborated upon, showing a list of collaborators is not enough.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Future work should look at using nickel or cheaper metals; platinum use is price prohibitive.
- Proposed future work is very promising.
- The plans of this project to address mechanisms of the spillover kinetics with emphasis on understanding and improving the kinetics are just where they need to be as the details of the actual processes are still obscure and the models are not yet substantiated.
- Furthermore, development of improved metal dopants and dispersion methods on metal organic framework and other carbon compounds is also needed if hydrogen adsorption storage capacities above 6 weight percent are to be obtained.
- Spillover measurements with bridge-building for other promising metal organic frameworks and high surface area carbons.
- Synthesis of carbons with surface areas >3500 m^2/g.
- Exploration of metal doping to facilitate spillover and enhance storage capacity.
- Emphasis on achieving 6 weight percent and 48 g/L hydrogen storage at ambient temperature.
- Will address fueling rate issues.
- The metal organic frameworks and templated carbons to be studied have significant potential.

Strengths and weaknesses

Strengths
- Broad-based collaborations with both private and public institutions.
- Observations of reversible hydrogen storage capacities greater than 1 weight percent at room temperature are promising for developing metal organic framework or activated carbon materials that might reach DOE storage targets.
- The demonstration of larger bonding energies with spillover suggests better sorbents may be possible.
- The PI is a world renowned expert in the field.
- All the essential expertise and facilities required to make significant progress on this project are available within the project team.
- Spillover optimization (perhaps maximization) is absolutely essential if sorption-based hydrogen storage "systems" are going to simultaneously meet DOE capacity and rate targets - so, this project has the right focus.
- Original discovery of the hydrogen spillover effects that may increase hydrogen capacities at room temperature in carbon-based sorbents.
- Isotopic studies to determine spillover charge and discharge mechanism and kinetics are beneficial to determining viability of carbon materials.

Weaknesses
- There is a great need for better understanding of the detailed spillover mechanisms that observations of just macroscopic adsorption capacities and general rates do not provide. While the isotope exchange experiments do indicate breaking of molecular hydrogen bonds, these do not give a complete picture.

- In general, it will be very difficult for any sorption-based material to meet the ambient temperature hydrogen storage targets set by DOE; to meet the 2010 "system" targets, a sorption material had better demonstrate at least 9 weight percent and 64 g/L at ambient temperature to give it a credible chance in a "system" context; December of 2010 is just 30 months away.
- Not enough theoretical guidance associated with this project.
- Kinetics of processes are currently too slow to be of use. Paths forward to solve this problem need to be explained.
- The real storage capacity of carbon is far from the theoretical limit. Need explanation on how to bridge today's results to tomorrow's achievement.

Specific recommendations and additions or deletions to the work scope

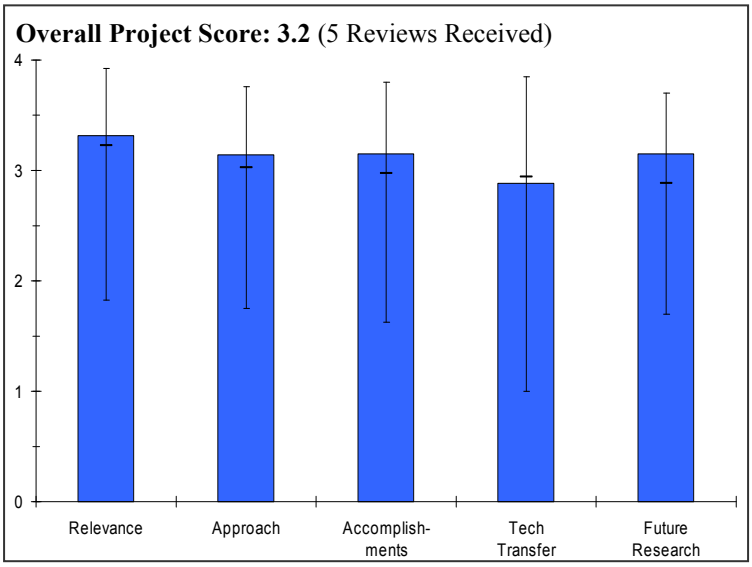
- Modeling of spillover on metal organic frameworks would be useful, because it not clear how "spillover" to an unsaturated metal center would improve adsorption; is it spilling over to the framework organic portion of the metal organic framework?
- Should look more closely at effects of metal catalyst particles (composition and morphology) on room temperature hydrogen storage via spillover.
- Strongly suggest this team work more closely with other HSCoE partners such as National Institute of Standards and Technology or University of North Carolina to include comprehensive spectroscopic characterization via neutron and nuclear magnetic resonance techniques.
- To what extent is it possible that the principles of spillover could be implemented in a meaningful way in chemical and/or metal hydride storage systems, e.g., to speed up the rehydriding rates?
- Could in situ small angle x-ray or neutron scattering provide any useful information on the spillover process, e.g., the effect on the morphology of the adsorbing surface? A real time, in situ measurement of the initiation and progression of spillover seems like something worth doing.
- Discontinue moisture effects on metal organic frameworks.

Project # ST-18: Theoretical Models of H_2-SWNT Systems for Hydrogen Storage and Optimization of SWNT
Boris Yakobson, presenting; Robert Hauge (Co-PI) both of Rice University

[NOTE: This project is part of the Hydrogen Sorption Center of Excellence.]

Brief Summary of Project

The overall objectives of this project are 1) to model materials structures' interaction with hydrogen, optimize their makeup for storage and assess the volumetric and gravimetric capacity; and 2) provide recommendation for the synthetic goals (e.g. pore/channel size, metal enhancement routes). The 2007-2008 objectives are to 1) identify the obstacles (thermodynamics and kinetics) for spillover and suggest material designs to overcome them; 2) enhance the binding of hydrogen by introducing charge into the carbon lattice by adding a highly stable superacid anion that also acts as a spacer; and 3) explore doping as an anchor to metal/metal cluster, role of bridges and dopants on the threshold of spillover.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Relevant to DOE storage goals and targets.
- This project involves both first principles computations and simulations of hydrogen interactions with metal clusters and defects on carbon surfaces as well as production of various carbon nanostructures and foams to assess their hydrogen adsorption behavior via gas adsorption experiments. A major goal of the theory effort is to identify and define whether hydrogen spillover behavior can be enhanced to reach DOE storage targets as well as advance understanding of the mechanisms.
- The experimental work is exploring different options for producing carbon nanostructures and fluorination treatment to possibly enhance adsorption energies where hydrogen reaction would be assessed by their Sorption Center of Excellence partners.
- The project addresses the objectives of the storage program in general terms without reference to the specific goals set by DOE.
- Most of the theory work is relevant.
- Various tasks within this project have varying degrees of relevance; the work on spillover is quite important, and focused on materials that have the potential to have high capacities; the work on foams is not as clearly targeted towards materials which are likely to exhibit good storage properties (though the PIs have demonstrated a high gravimetric density at 77K).

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- Modeling approach using ab-initio and experimental potentials to bracket adsorption between maximum and minimum is OK, but feedback from adsorption experiments being done at the CoE should allow them to validate models and arrive at correct potential to use.
- The work on metal clustering effect is important.

- Modeling work suggests that vertically aligned nanotube arrays (VANTA) are not as productive an area to work on as carbon "sponges".
- Modeling of spillover starting with palladium clusters rather than platinum. I believe platinum is more active in hydrogen spillover in catalysis.
- While the theoretical and experimental tasks are not explicitly correlated, they do share common objectives and features to enhance effective reaction sites for the adsorbing hydrogen coupled to modifications of the host carbon matrix and metallic additives.
- Not much was presented on experimental approach, so this is hard to quantify.
- Good combination of theory/experiment; however, in many cases, the experiments and theory are working on different problems. It would be good to have a closer connection between the theory/experiment, e.g., particularly on the spillover work.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- Modeling is making good progress.
- Modeling results indicate carbon foams are a good area to pursue.
- Synthetic/experimental progress on vertically aligned nanotube arrays (VANTA) is slow (efforts focused on calculations?).
- The majority of information presented at this review concerned simulations of hydrogen adsorption where particular emphasis was on interactions with simple clusters of palladium metal. The trends are suggestive of possible spillover processes but future assessments are needed.
- Relatively limited experimental adsorption data was given for 77K tests. This data was mainly of zeolite-templated carbon foams, which yielded capacities similar to the better metal organic framework materials. The other suggested candidates remain to be prepared.
- Nice work on spillover modeling (score of 3.6).
- Little progress apparent on experimental work (score of 2.4).
- Theoretical/computational work has had a lot of excellent technical accomplishments this year; the experimental work has produced interesting new results on the foams, but in general, seems to be lagging behind the theoretical work.
- Work on spillover is highly imaginative, and is currently the only detailed proposed mechanism of this phenomenon in hydrogen storage. The implications of this nucleation-and-growth picture of spillover should be more fully explored.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.9** for technology transfer and collaboration.

- Collaborations evident.
- Collaborations/interactions with others modeling the effects of charged centers on hydrogen storage at other centers of excellence may be useful (for example, Hwang at Michigan Technological University).
- The presentation indicated fruitful collaborations and interactions not only with several partners within the Hydrogen Sorption Center of Excellence and other active carbon materials research groups being supported by DOE/EERE.
- The theory effort, while focused on an important topic (spillover) seems to be conducted largely in isolation.
- No experimental collaboration with center partners apparent.
- Theory work seems closely connected with external partners and the CoE. Not clear how the experimental work is connecting.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Modeling of spillover with less expensive metals like nickel is necessary.

- The theoretical efforts address a number of detailed mechanisms and possible diffusion processes involved with spillover behavior. These appear to be logical next steps.
- The proposed geometries and modified compositions for the carbon materials do not appear to be duplicated elsewhere where the rationale for improved hydrogen adsorption behavior is reasonable if not overwhelming.
- Computational study of impact of catalyst in spillover process is the next logical step.
- Experimental next steps are poorly defined.
- Good plans for the spillover work. This area should be the top focus for the theoretical work.

Strengths and weaknesses

Strengths
- Extensive theoretical modeling effort of hydrogen interactions with palladium metal clusters and possible processes in the spillover mechanisms.
- Exploring methods to fabricate and alter bonding within carbon foams and nanophases are key features of the experimental growth of these materials as possible improved hydrogen adsorbents.
- Highly imaginative and differentiated from other efforts in the center (except for the metal-carbon work, which is somewhat redundant with other efforts).

Weaknesses
- Metal cluster sizes and geometries look to be chosen more for computational ease rather than reflecting actual configurations achieved during doping.
- Model calculation primarily involved palladium clusters rather than platinum clusters that are being used in most spillover studies and it is not evident that conclusions drawn in these calculations actually pertain.

Specific recommendations and additions or deletions to the work scope

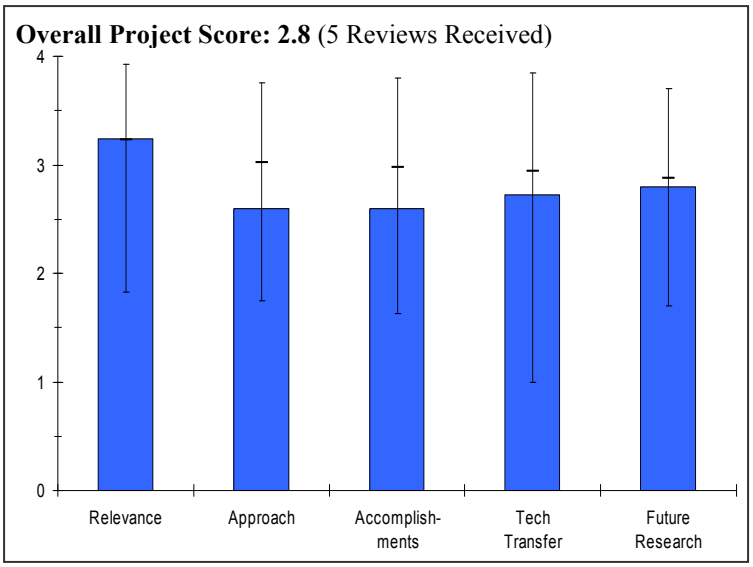
- It would be good to have a closer connection between the theory/experiment, e.g., particularly on the spillover work.
- Suggest that calculations of spillover mechanisms be extended to include platinum and nickel metal clusters to allow direct comparisons with current results obtained on palladium/carbon systems.
- Effort on "non-starter" approaches (e.g., storage within fullerene pores) to storage should be eliminated.
- Focus efforts on spillover.
- The spillover work should be the focus for theory; the metal-carbon work seems less important since (a) it is somewhat redundant with other efforts in the Center, and (b) it is proving extremely difficult to synthesize these theoretically-predicted structures anyway.

Project # ST-19: National Renewable Energy Laboratory Research as Part of the Hydrogen Sorption Center of Excellence

Anne Dillon; National Renewable Energy Laboratory (NREL)

[NOTE: This review is for NREL's technical contribution to the HSCoE.]

Brief Summary of Project



The objectives of this project are 1) develop stable high surface area, minimally macroporous, light materials that can either stabilize large quantities of hydrogen directly (by physisorption), or provide frameworks for incorporating/stabilizing other species; 2) increase concentration of substitutional dopants (e.g. B and N) in lattices to adsorb dihydrogen directly (via donation), stabilize active species (e.g. transition metals) against agglomeration, or provide anchor points for building more complex sorbents; 3) synthesize sorbents which can bind multiple dihydrogen ligands through metals that are capable of "Kubas binding"; and 4) develop methods to prepare catalytic species, bridges, receptors and the activation processes to reproducibly prepare spillover materials with high capacities and good kinetics.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- Very relevant.
- The objectives are aligned with DOE R&D objectives.
- The project works toward enhancing the binding energy and the hydrogen weight percent to reach the DOE objectives.
- It is clear that the project is aimed at discovering new, high-density hydrogen storage materials.
- Emphasis of project is currently on binding energy, which is extremely important, but not the only consideration.

Question 2: Approach to performing the research and development

This project was rated **2.6** on its approach.

- Approach proved to be not particularly successful.
- General chemical behavior of fullerenes is not quite in line with calculations used to justify this research.
- The research cluster approach is OK in general and they are grouped together well.
- Some of the specific approaches in material design are not based on the fundamental understanding of material need.
- The PI seemed to still work on impractical material.
- The approach to support the four research clusters shows interaction and collaboration.
- The concept of using theory to guide experiments is a well-established and promising strategy. However, in practice, many (if not all) of the theoretical predictions produced by this project have focused on exotic materials which have not been amenable to experimental synthesis.
- It would be very helpful to have a set of criteria in place to guide whether a given theory prediction should be pursued experimentally.

- Theory seems to be operating only in a "forward prediction" mode. Theory could also be employed to help decipher why various experimental efforts have thus far not yielded synthetic or storage goals.
- NREL defines their own objective, "efficiency", which translates to binding energy of 15-20 kJ/mol.
- NREL contributes to all 4 research clusters in the center, so materials being studied cover a wide range of properties and characteristics.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.6** based on accomplishments.

- A lot of experimental work without sufficiently positive results.
- Model systems may need some additional adjustment.
- Only modest progress over last year, not proportional to the large funding.
- Lack of fundamental understanding and lack of the attempt for fundamental understanding of the material system.
- Difficulty in synthesizing materials per the theoretical estimation for enhancement the binding energy of hydrogen in C_{60} by adding dopants (organometallic fullerenes) was illustrated. It is suggested to have a clear path forward prior to materials selection based on solely theoretical estimation and to enlist challenges to achieving the targets as a first step.
- The concept of co-intercalation of Li/metal within graphite using THF/benzene has to be carefully considered to avoid hydrogen solubility situation or simply liquid evaporation!
- The discrepancy between the University of Michigan and NREL results is suggested to be resolved.
- Many systems have been explored, but there has been relatively little progress in identifying materials with promising properties.
- Wrapping up organometallic fullerenes and finally going to simpler structures. Theoretical structures found to be difficult to synthesize.
- Intercalated graphites have been synthesized. Li/THF shows some modest hydrogen uptake.
- Has expanded spillover approach using wet chemistry - NaSWNT shows ~4 weight percent.
- Provides measurements for center partners.
- Materials synthesis lab is operational.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.7** for technology transfer and collaboration.

- Very good collaboration.
- Some collaborations exist.
- The PIs should really extensively collaborate with some expert in catalysis field to get better understanding of the spillover effect.
- Collaboration with others within the center is visible.
- Good collaboration with center partners, but no external collaborations identified in the presentation.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.8** for proposed future work.

- Reasonable plans; hope they will materialize.
- The material design should be based on the fundamental understanding of the system. There is little attempt in understanding the science behind the results.
- Path forward for the Li/solvent intercalated graphite is suggested to be more clarified to avoid the C60/metal scenarios where calculations predictions do not match with synthesis/formation feasibility.

Strengths and weaknesses

Strengths
- Strong expertise in chemical synthesis.
- Organized research cluster approach.
- Visible collaboration with others within the center.
- Trying to create truly new hydrogen storage materials.
- Collaboration between theory and experiment.

Weaknesses
- Model systems are not particularly efficient.
- Lack of fundamental understanding in material design.
- Relying on theoretical estimations.
- Lack of devising a strategy for material synthesis and identifying the challenges as the materials estimated by the theory are selected.
- The research direction is dictated too strongly by modeling predictions on "unrealistic" exotic compounds.

Specific recommendations and additions or deletions to the work scope

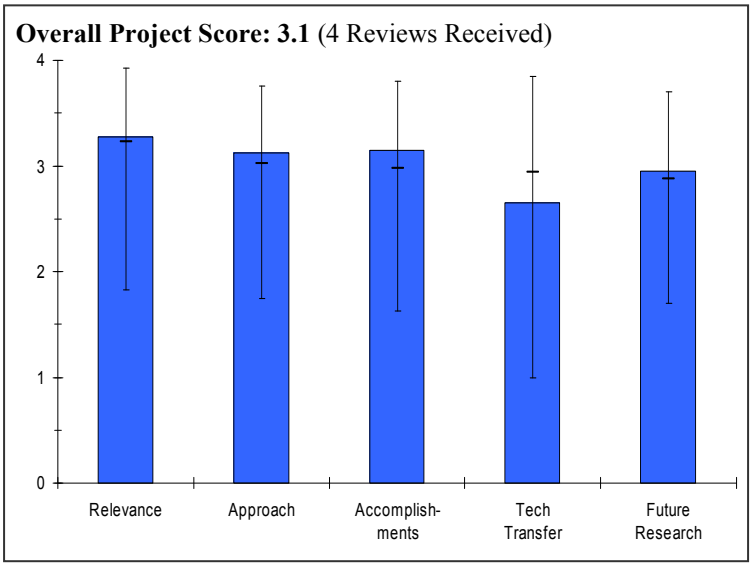
- Suggest keeping the project; however, a clear plan for materials selections and synthesis needs to be presented.
- Suggest increasing efforts on mechanistic studies of spillover.
- Suggest careful consideration of efforts exerted towards synthesizing exotic compounds.
- Overall, it is suggested to identify challenges as the materials are selected for synthesis based on theoretical estimations and create a plan towards achieving the targets.
- NREL could help the development of spillover for storage if they would include some studies related to understanding the phenomena, e.g., looking more at the temperature dependence of uptake and release, using analytical techniques to ascertain the hydrogen atom sites.

Project # ST-20: Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports
David Geohegan; Oak Ridge National Laboratory (ORNL)

NOTE: This project is part of the Hydrogen Sorption Center of Excellence.

Brief Summary of Project

The overall objective of this project is to exploit the tunable porosity and excellent metal supportability of single-walled carbon nanohorns to optimize hydrogen uptake and binding energy. The 2008 objectives are to 1) improve surface area to 2,200 m^2/g for >3.0 wt% at 77K; 2) adjust pore size controllably to <1 nm; 3) quantify effects of pore size; 4) theoretically investigate origin of binding energy increase; 5) search for alternative metals to enhance binding energy; and 6) develop new synthesis/decoration approaches for these materials.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Project addresses relevant hydrogen storage goals and targets.
- The objectives are aligned with DOE R&D objectives.
- The project addresses the objectives of the hydrogen storage program in general terms. Without specific reference to the DOE targets.
- Carbon nanohorn structures may provide an effective storage material, but there are many obstacles to overcome; specifically, volume and weight density, binding energy and other target-related metrics.
- The project involved both experimental and theoretical efforts in tailoring the pore size and morphology of carbon nanohorns and understanding the nature of bonding in metal coated fullerenes. High surface areas and small pore sizes were achieved, but the gravimetric density of hydrogen fell far short of the DOE target.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- Addressing appropriate issues such as clustering and dispersion of metal dopants.
- Unclear how CaH_2 formation will be prevented at higher temperatures (room temperature and above - CaH_2 is thermodynamically favored) - CaH_2 is fairly stable and may trap hydrogen, not leading to spillover but leading to hydrogen that is not releasable until high temperature.
- The material synthesis approach is unique.
- The PI should work with theory group to predict the best pore size combination of this type of materials.
- Well orchestrated approach.
- The approach of using charge effects to enhance binding energy is a good, promising alternative to other techniques being examined in the center.
- The search for dispersed metal coatings is important for spillover development.
- Both experimental and theory have used state-of-the-art techniques, but there has been a disconnect between the two.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- Demonstrated spillover in single walled carbon nanohorns (SWNH). Demonstrated up to 3.5 weight percent hydrogen storage at 77K in short SWNH.
- Have prepared calcium decorated nanohorns but need to demonstrate enhanced adsorption with these materials
- Good progress toward objectives.
- Pathway to achieve higher capacity has been identified.
- Publications resulting from experimental work are not comparable with that of theory. The progress in overcoming barriers is modest although the progress in the synthesis of materials with small pore size and high surface area is good.
- Developed "short" nanohorns with high surface area; hydrogen capacity is consistent with C surface. Binding energy ~6 kJ/mol.
- Studied decorated long nanohorns.
- Charged nanohorns. Theory calculations indicate Ca, Sr can generate good binding energy and sites.
- Experimentally was able to decorate nanohorns with Ca that also may show some intercalation.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.7** for technology transfer and collaboration.

- Collaborations within the center are apparent.
- More collaboration with Ralph Yang's group [University of Michigan] could be beneficial.
- Some collaboration with group at Michigan Technological University looking at interactions with charged species (metal perhydrides) may be mutually beneficial.
- Some collaborations exist, but only in materials characterization part.
- The PI should expand the collaborate area to include some theory prediction.
- Tech transfer and collaborations not discussed in the presentation.
- Partnerships used for analytical work on materials.
- The team has worked well with other members in the center.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.0** for proposed future work.

- People have looked at metal intercalated graphene previously – unless there is some new insight regarding optimum spacing, what will be new?
- The general research direction is good.
- The PI should include the theory prediction in defining what is the maximum pore volume can be created by this approach and which metal carbide can provide the best pore size desired.
- Focus on charged nanostructures and spillover is good, as is the objective for fundamental understanding of spillover.
- Consideration of kinetic properties of spillover good.
- Dispersion of metals on nanostructures an important aspect of using these materials for storage.
- Studies of graphene flakes and graphite nano-particles with metal doping will provide further insight into the effect of structure and composition on hydrogen binding but unlikely to lead to a material sought by DOE for hydrogen storage.

Strengths and weaknesses

Strengths

- The research approach is novel.

- Addressing the efficiency and thermal management issue through design of materials with high thermal conductivity is important.
- Synergy between theory and experiment plus efforts to control pore size. Understanding of the spillover mechanism.

Weaknesses
- Lack of theory work in predicting what the technology limit is.
- Theory and experiment should be better coordinated. Experiment was carried on Ca coated nanohorns while theory was on Ca coated fullerenes. The stability of materials with Ca coated C_{60} should be investigated.

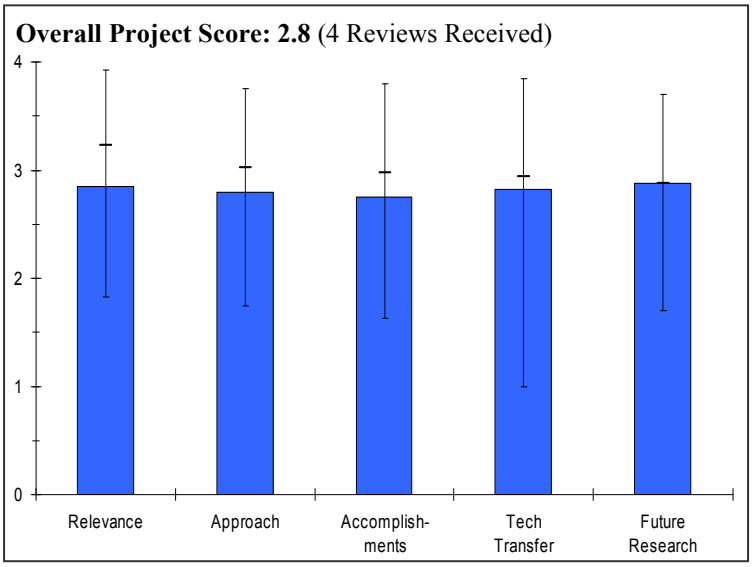
Specific recommendations and additions or deletions to the work scope
None.

Project # ST-21: Hydrogen Storage through Nanostructured Polymeric Materials
D.J. Liu, presenting; Argonne National Laboratory (ANL) and Luping Yu; University of Chicago, Co-PI

NOTE: This project is part of the Hydrogen Sorption Center of Excellence.

Brief Summary of Project

The objectives of this project are to 1) design, synthesize and evaluate nanostructured polymeric materials (NPM) as new hydrogen storage adsorbents for transportation applications; and 2) support polymer materials development with modeling/simulation and advanced structural characterizations. Polymer surface properties such as specific surface area and porosity can be controlled at the molecular level. Polymer-hydrogen binding can be enhanced through incorporating different functional groups and atomically dispersed metals. Polymers are generally stable under the temperature and humidity required for hydrogen storage application.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.9** for its relevance to DOE objectives.

- This project has the objective of developing porous polymers from conductive and polyimide skeletons with various functional groups added to enhance hydrogen adsorption capacity. However, initial results indicate that rather low surface areas (i.e. < 1000 m^2/g) are being formed and the hydrogen adsorption capacities measured at 77 K are not any larger than found for most other common carbon materials. While improvements are possible, the current materials will not meet the DOE mass or volumetric targets. There was no indication that any significant enhancement is available from these specific materials.
- Polymers are inexpensive materials with a number of tailoring options for improving hydrogen storage capacity.
- This project, based on designed nanostructured polymers, aims at the DOE targets and barriers, especially gravimetric capacity.
- The potential for meeting volumetric and other targets (e.g., kinetics) is not addressed in any quantitative sense.

Question 2: Approach to performing the research and development

This project was rated **2.8** on its approach.

- It does not appear that the program is absorbing the body of data on delta-H, spillover and other findings that have been established in the field.
- The Argonne National Laboratory and University of Chicago team is well balanced to address polymer design and synthesis and materials characterization and hydrogen storage measurements.
- The approach is a pretty conventional combination of selecting attractive functional molecular groups and components to produce a polymeric material that is then reacted with hydrogen gas at 77K. Based upon empirical observations and modeling analyses, iterations in components would be used to make further polymers for assessment of their hydrogen storage properties.
- At some point it might be interesting to look at hydrogen spillover effects in the polymers.
- What are the rationales being employed for enhanced hydrogen storage via the incorporation of "metallic" conductive features and selected functional groups?

- Are hydrogen permeability and polymer free volume being considered as possible guiding rationales for polymer hydrogen storage materials?
- The approach to explore new molecularly designed polymers, in particular controlled structures and porosity, is a convincing one.
- The ability to add metallic "backbones" will hopefully improve the storage capacities of the basic polymers via spillover-like phenomena.
- The direct collaboration between Argonne National Laboratory and University of Chicago is obviously synergistic.
- The project directions and chances for success will be helped by the modeling component.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- In comparison with the current state of storage the results appear well below the targets.
- Setting up and producing at least three series of polymers with moderate surface areas and narrow pore distributions were done within less than a year of this project.
- Initial storage capacities are OK but not suggestive of a high performance storage media even at 77 K.
- A good deal of progress has been made in a relatively short time, although initial hydrogen storage capacities are unremarkable.
- Although the project is new (< 1 yr), much preliminary work has been accomplished so far.
- Three multi-composition series of polymers have been synthesized and evaluated (along with a reference carbon material) in a relatively short time.
- The gravimetric storage results are not very good, so far, and may not bode well for the future. However good understanding has been made that should hopefully help to accelerate progress.
- Hydrogen testing well-established and is giving very credible results.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.8** for technology transfer and collaboration.

- Is it possible to interact with Southwest Research Institute for expedited and independent testing?
- Not clear how this project interacts with the Hydrogen Sorption Center of Excellence or perhaps there is no connection.
- The Argonne National Laboratory/University of Chicago team has been working with several members of the Hydrogen Sorption Center of Excellence on behavior during their first year and indicate plans for more detailed characterizations via neutrons, nuclear magnetic resonance, etc. in the future as they generate more favorable storage candidates.
- There appears to be little or no interactions with other hydrogen storage research organizations.
- Collaborations to identify hydrogen bonding sites in the polymers will be useful.
- The joint project combination of Argonne National Laboratory and University of Chicago seems excellent.
- There should be good collaborations within the Hydrogen Sorption Center of Excellence.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- There is divergence between the plans and the program goals.
- Will there be a critical analysis of the approach? A go/no-go decision at some point?
- In general, this team looks from their stated Fiscal Year 2008 and Fiscal Year 2009 plans to follow the course of analyzing and tweaking polymer designs to produce samples then test their hydrogen adsorption properties as they soldier on towards the goal of higher capacities.
- The plan seems good. Alternative directions are available.
- The milestones are good and have been met to date.

Strengths and weaknesses

Strengths

- Complementary interaction between the University of Chicago polymer synthesis group and the Argonne National Laboratory characterization and modeling members to proceed toward possibly developing better hydrogen adsorption materials.
- Hydrogen storage in polymers is an area that has been little explored.
- Excellent knowledge of polymers and ability to design and synthesize old and new families.
- Project will be a thorough test of polymers and polymeric porosity.

Weaknesses

- The technical approach appears to be behind the current state of scientific discoveries in the field.
- At the moment, there does not seem to be any rationale for devising materials that could adsorb greater quantities of hydrogen gas at temperatures between 77K and room temperature (i.e., stronger H-C bonding with effective surface areas >> 1000 m^2/gram).
- Predictive rationales for hydrogen bonding site construction in the polymers should be enhanced.
- Not enough focus on volumetric targets.

Specific recommendations and additions or deletions to the work scope

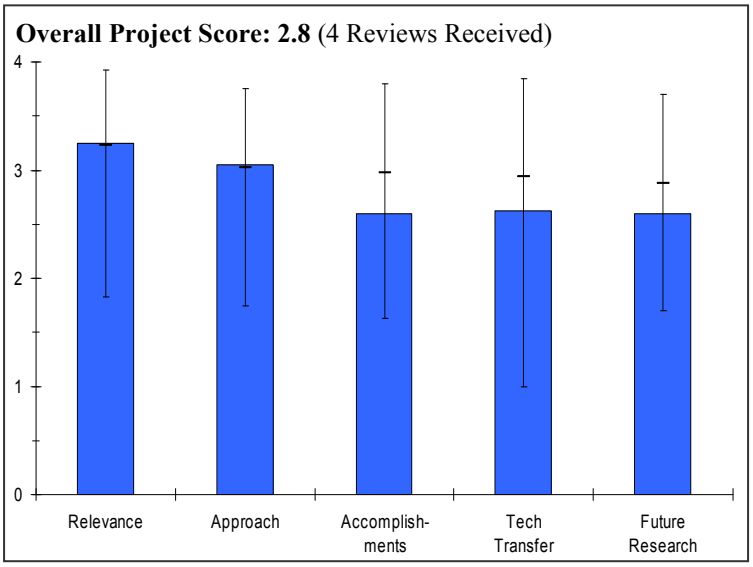
- Do not spend too much time on polymers that do not show promise relatively quickly.
- The program needs to re-address the technical approach and streamline (eliminate) areas with limited strategic success.
- This team should more actively seek assistance of other sorption groups to explore feasibility of activation processing such as KOH processing and other methods to increase effective surface areas and internal porosity.
- Given the rather low H-capacities measured so far, it would be wise to start the metal-doping part of the effort sooner than originally planned (sometime in Fiscal Year 2009).
- There should be at least one quantitative go/no-go gate put in place for early Fiscal Year 2009.

Project # ST-22: Enabling Discovery of Materials with a Practical Heat of Hydrogen Adsorption
Alan Cooper; Air Products and Chemicals, Inc. (APCI)

NOTE: This project is part of the Hydrogen Sorption Center of Excellence.

Brief Summary of Project

The objectives of this project are: 1) development and testing of new materials with high hydrogen storage density and appropriate enthalpy of hydrogen adsorption; and 2) development of enabling technologies for hydrogen storage materials development. Air Products' goal is the reversible adsorption of hydrogen at near-ambient temperatures at densities that will enable meeting the 2010 Department of Energy system-level targets for hydrogen storage. Air Products has leveraged existing materials science and chemistry capabilities in carbon materials and fluorine chemistry to generate new hydrogen storage materials for testing.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Project as presented and described is good.
- The work is focusing on a key problem in the DOE hydrogen program - hydrogen storage. There is currently no effective means of storing hydrogen via chemical/physical storage techniques. Gas/liquid tank storage seems to be the best route which takes up valuable space. An effective alternative, such as what is proposed in this project, is necessary.
- Clearly trying to develop new hydrogen storage materials and improve understanding of existing materials (e.g., spillover).
- Much of the project supports the DOE objectives.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- Approach is sound; project's results are poor.
- The project is attempting a relatively unique approach. The materials being examined are very novel, and this is probably necessary to achieve any success (F-based materials). Air Products and Chemicals, Inc. is proposing a number of unique concepts that are currently not be examined elsewhere - for example the effects of anion-hydrogen interactions in intercalated carbons. The approach is well thought out and appears to be scientifically acceptable. The approach is conceptually very solid.
- The project, as proposed, would use a balance of modeling and experimentation to achieve the project goals. This is a rational approach to develop new materials at a molecular level.
- The work is considering new materials that APCI has had success in synthesizing in the past.
- Unclear whether the $C_{32}F_8$ compounds are thermodynamically stable or will be able to be synthesized in a morphology consistent with theory.
- Thermodynamic predictions (slide 10) suggest only weak bonding of hydrogen at high loading -- (~4kJ/mol at 8 weight percent hydrogen); this does not appear to be a viable material. Unclear why experiments conducted given expected poor performance.

- Modeling of mechanisms of spillover is valuable.
- Although the modeling of spillover phenomenon is important, its impact on the development of the approach for hydrogen storage is not clear.
- The emphasis on intercalated graphite materials may not lead to a viable storage material.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.6** based on accomplishments.

- Approach to add N to C is novel and should be explored as N tends to make C more basic in nature.
- The project has had some general success in developing computer based models for several different aspects (spillover mechanism, conceptual materials, etc.). The models appear to have a big value to the Hydrogen Sorption Center of Excellence.
- However, the work appears to lack any solid experimental results at this time. The only results appear to be some low level hydrogen results on the F-carbon materials. All are well below 1 weight percent - which is well below the DOE targets. It is unlikely that these materials will ever be developed up to a reasonable level. This is a major concern as this project has been ongoing for about 2 years and based on the opening slide - is 60% complete.
- It is not clear that APCI has yet been able to synthesize the necessary materials. Attempts have been made - but the analytical data tends to suggest that the attempts were unsuccessful.
- A balance of modeling and experimental work is a good approach - but this project needs to provide some experimental results.
- The surface area of the materials under consideration is too low (75 m^2/g). Considering the poor hydrogen weight percent, it is unlikely that this material will have any use for hydrogen storage.
- Modeling work seems to be progressing at a reasonable pace.
- Several attempts at synthesizing materials have been performed, but no promising leads thus far.
- The intercalated materials may be promising candidates for storage, but they are a long way from the performance (e.g., capacity) achieved with other materials.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.6** for technology transfer and collaboration.

- Anticipated collaborations need to be explained or removed. When unexplained they appear as fluff.
- Tech transfer and collaboration are acceptable.
- The work appears to involve a number of outside participants with needed special skills.
- The work appears to be highly coordinated with the Hydrogen Sorption Center of Excellence. In particular, it appears that the modeling work is of considerable interest to the center.
- Seems to be significant overlap with Rice University's efforts on spillover on graphene. Redundant?
- Some interaction and collaboration with center partners, but external collaborations not apparent.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.6** for proposed future work.

- Consider adding more detail in work for next year and leaving out work for current fiscal year.
- The work is suggesting the investigation of some new materials - N based. However, it appears that the work is being conducted on few potential materials and others need to be considered.
- The work needs to concentrate on completing some experimental work.
- Unclear if using other graphitic carbons will increase accessibility of hydrogen
- Limited hydrogen accessibility could be endemic to these intercalated materials.
- Intercalation of N doped C may be promising.
- Not clear what the MD ab initio calculations on BC_3 intercalated compounds will yield in terms of developing these materials.

Strengths and weaknesses

Strengths

- The project is based on some unique scientific concepts that could have significant benefit if the work is successful.
- The modeling effort has been successful and is providing insight into potential mechanisms and conceptual materials.
- Good connection between theory and experiment.

Weaknesses

- There is a significant lack of any solid (or positive) experimental results.
- The results provided thus far tend to indicate that the current material has little chance of success.
- Theoretical predictions are for "exotic" compounds that may not be thermodynamically stable and/or realized experimentally.

Specific recommendations and additions or deletions to the work scope

- The project needs to identify (and test) other material compositions - including materials with high surface area.
- Consider balancing synthesis and characterization for hydrogen uptake. Project heavy on synthesis and light on results for uptake.
- Suggest clarifying role of Air Products and Rice University regarding spillover modeling to avoid redundancy.

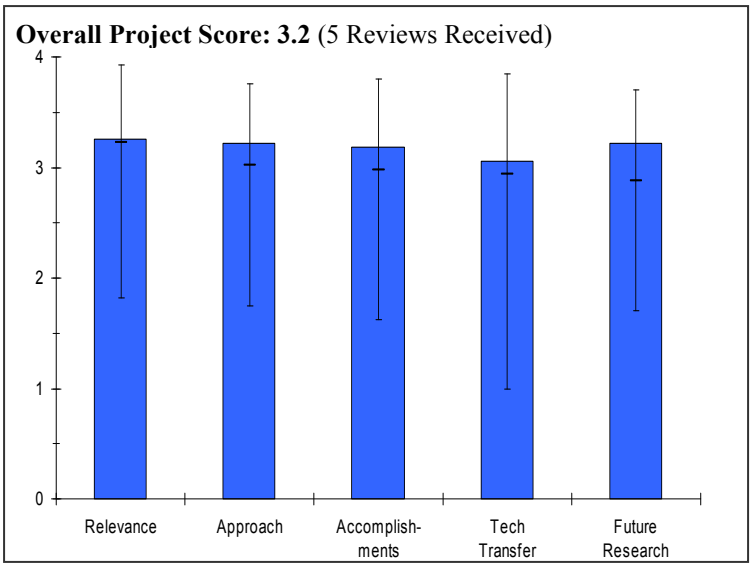
Project # ST-23: Enhanced Hydrogen Dipole Physisorption: Henry's Law and Isosteric Heats in Microporous Sorbents

Channing Ahn, California Institute of Technology

NOTE: This project is part of the Hydrogen Sorption Center of Excellence.

Brief Summary of Project

The objectives of this project are the 1) synthesis of framework structures via normal solvo-thermal routes; 2) evaluation of aerogel properties in collaboration with Lawrence Livermore National Laboratory; 3) evaluation of microporous activated carbon properties; 4) adsorption/desorption evaluation with volumetric Sieverts apparatus capable of measurements of samples at 77, 87, 195, and 298K temperatures; 5) thermodynamic evaluation of sorption enthalpies via Henry's Law region of isotherm and/or isosteric enthalpy of adsorption; and 6) neutron scattering (diffraction and inelastic) of promising systems in collaboration with the National Institute of Standards and Technology.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- The project is aligned with DOE R&D objectives.
- The objectives of this project need to be better defined.
- The project like so many others addresses the objectives of the hydrogen storage program in general terms without reference to the specific targets set by DOE.
- The emphasis of this project is on several key aspects of the hydrogen storage goals that align with the hydrogen vision and DOE RD&D objectives.
- More specifically, the project seeks to develop understanding of critical issues for hydrogen sorption processes.
- It appears that important new knowledge about hydrogen sorption is emerging from the work of this project.
- Synthesis of frameworks structures and measurement of the isoteric heats of adsorption and pore sizes is very relevant to DOE objectives in enhancing the room temperature weight percent hydrogen by increasing the binding energy.
- This program is highly relevant to the DOE Hydrogen Storage Program.
- It is concerned with improving the properties of high surface area materials with respect to hydrogen storage.
- Activated carbon, aerogels and metal organic frameworks (MOFs) are the materials of interest.
- This program has the capability to synthesize and characterize complicated MOF materials.
- This capability is highly relevant to the DOE objectives.
- Surface packing density of hydrogen was achieved in a newly synthesized MOF.

Question 2: Approach to performing the research and development

This project was rated **3.2** on its approach.

- The approaches are OK in general but nothing unique. The slit pores have been known for long time.
- Lack of systematic approach in selecting the materials for testing.
- Synthesis and characterization of framework structures, including electron microscopy where appropriate.

- Measurement and evaluation of the hydrogen sorption properties of framework structures, aerogels, and microporous activated carbons.
- Measurements include temperature dependencies and sorption thermodynamics.
- Neutron diffraction and scattering measurements to identify hydrogen positions.
- Good approach in identifying relevant materials properties.
- The approach is highly scientific and professional.
- While MOF-74 has a high surface packing density (SPD), the weight percent hydrogen is still well below that of competitive materials.
- Efforts to improve gravimetric density are planned and should be encouraged.
- A more negative adsorption enthalpy should be a goal.
- A less time consuming MOF synthesis should be devised.
- An important barrier is the low gravimetric density at room temperature.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- The PI made some progress toward objectives.
- Pathway to achieve higher capacity has been identified through the available data.
- Showed that sorption enthalpies approach a constant value as pore size distribution narrows.
- Elucidated several of the causes for sorption enthalpy heterogeneity.
- Found that when sorption enthalpy is high, a majority of the sorbed hydrogen is retained at pressures less than 2 bar and 77K; as temperature increases, a larger fraction of the sorbed hydrogen is available at pressures greater than 2 bar.
- Made projections about optimum pore size and size distribution.
- Identification of pore/slit geometry of 1 nm and careful examination of surface area effect is very good approach in the identification of key frameworks properties which would help in frameworks design.
- The successful synthesis of MOF-74 is an impressive feat. Its structural determination is also impressive.
- The determinations of the isosteric heats of adsorption for MOF-74 and activated carbon materials are of wide interest.
- Although still in the early research stage, the cost of the subject materials should be of concern.
- Similarly it appears that soon a choice must be made between MOFs, aerogels and activated carbon adsorbents.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- Some collaborations exist, but only in the materials synthesis and nuclear magnetic resonance measurement part.
- A substantial number of collaborations and interactions were mentioned during the course of this presentation.
- Some collaborators provide materials for study (e.g., Lawrence Livermore National Laboratory); others provide characterization capability (e.g., National Institute of Standards and Technology [NIST]).
- This research appears to be well recognized and respected within the Hydrogen Sorption Center of Excellence.
- Professor Ahn seems to have many collaborations within the Center of Excellence.
- Visible good collaboration with theory group at NIST.
- This program has extensive collaborations both within and outside the Metal Hydride Center of Excellence.
- A cited publication in "Langmuir" is a fine paper.
- Several presentations are also noted.
- Technology transfer with members of the Metal Hydride Center of Excellence as well as industry could be improved.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- The general research direction is good.
- The PI should feed some of the experimental data into theory prediction.
- The PI needs to pay more effort in better understanding how to design a material with maximum usable hydrogen on board.
- Optimization of pore size and pore volume to maximize volume density. Otherwise, much of the future research will be a continuation of Fiscal Year 2008 activities involving framework structures, aerogels, and microporous carbons with emphasis on those materials displaying homogeneous sorption enthalpies.
- Continued evaluation of thermodynamic properties, including differential enthalpy of adsorption near zero coverage.
- Good plan to support several members in the center. However the approach towards enhancing the adsorption by tuning the pore sizes needs to be clarified and addressed more.
- Plans noted are logically based on past progress, but in view of the DOE time-line, it is time to choose the most advanced material and concentrate the effort on it.

Strengths and weaknesses

Strengths
- Accurate experimental measurement techniques.
- The PI is very knowledgeable about the systematics of sorption processes and is keenly aware of the ongoing progress in the field regarding hydrogen sorption.
- The emphasis of this project is heavily weighted towards developing understanding of the influence of all relevant properties and parameters as opposed to just making lots of materials and doing lots of sorption measurements.
- Well established collaborations and well respected PI.
- Systematic approach.
- A very strong scientific effort.
- The resources appear adequate.
- The MOF effort is novel with implications beyond hydrogen storage.
- The expertise demonstrated in the thermodynamic studies is most impressive.
- The scientific credentials of the PI and his collaborators are excellent.

Weaknesses
- Lack of a general strategy in selecting the materials for measurement.
- No obvious weaknesses other than the daunting task of meeting DOE's ambient temperature hydrogen storage capacity targets using sorption-based materials and processes.
- Addressing materials design and synthesis by utilizing the results obtained.
- Practical problems involved in the use of microporous adsorbents as hydrogen fuel sources not addressed.
- Difficulty in synthesizing MOFs.
- Overall costs may be prohibitive.
- Cycling stability of MOFs not addressed.
- Low gravimetric capacity at room temperature.
- Safety issues have not been addressed.

Specific recommendations and additions or deletions to the work scope

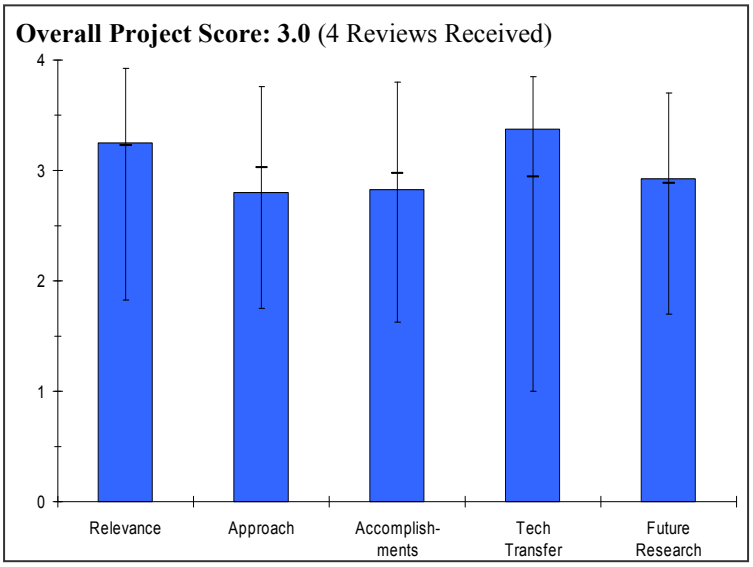
- The PI should expand the collaborations to include experts in other field, such as catalysis.
- Avoid expending too much effort on achieving high hydrogen uptake at ambient temperature; continue to focus on elucidating the interrelationships among the key parameters--pore size and pore distribution, enthalpies, temperature effects, and pressure effects--and how they collectively influence hydrogen uptake and release.
- The project showed good progress in designing catalysts and it is recommended to keep the project.
- The items discussed under "Project Weaknesses" should be addressed.
- While this effort is still in applied science stage the DOE time is short. Thus the following should be addressed; reversibility, cost, kinetics, storage capacity at 298K, and cycle stability.
- The above likely requires that a specific material be chosen.

Project # ST-24: Carbon Aerogels for Hydrogen Storage
Ted Baumann; Lawrence Livermore National Laboratory (LLNL)

NOTE: This project is part of the Hydrogen Sorption Center of Excellence.

Brief Summary of Project

The objective of this project is the design of novel carbon aerogel (CA) materials that meet the Department of Energy system targets (6 wt%, 45 g/L) for on-board vehicle hydrogen storage. The focus is in two areas: 1) engineering of CA-based spillover materials and 2) design of new CA materials as porous scaffolds for metal hydride materials. The specific objectives are 1) to optimize structure for enhanced hydrogen uptake and improved kinetics; 2) storage at reasonable operating temperatures; and 3) the potential to improve kinetic and thermodynamic performance of metal hydrides.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Project relevant and addressing DOE goals and targets.
- Relevant in several ways, both as a storage media and a catalyst. Only lack is that the odds of meeting 2015 goals are low.
- The project is nicely focused toward the DOE goals and barriers, especially weight and volume.
- Future work will focus increasingly on kinetics.

Question 2: Approach to performing the research and development

This project was rated **2.8** on its approach.

- High surface area of carbon aerogels together with spillover effect has potential, overlap with use of carbon aerogels as scaffolds for metal hydrides.
- Use of platinum for spillover leads to cost issues, should focus on cheaper metals (nickel) for the spillover effect.
- Decision to discontinue work on undoped carbon aerogels (CA) is appropriate.
- The re-focus on spillover is indicative of good tactical change.
- Scaffolding appears to become less significant.
- ALD Vacuum Technologies approach does not appear of much value. It is not clear why the PIs decided to purchase their own system versus collaborating with other groups. This is not a good resource utilization and no justifications were made why this was done.
- Good that program has two routes to success.
- Methods used are suitable. Team is expert in doing this sort of material design.
- Project includes two worthwhile objectives: (1) M-doped carbon aerogels for maximum spillover performance; and (2) carbon scaffolds for containment and performance enhancement of metal hydrides.
- Aimed at optimization of pore structure for two applications.
- PI has long experience on the control of aerogel structures.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- With spillover, achieved only 1.2 weight percent at 100 bar at room temperature.
- Doubled thermal conductivity of carbon aerogels with carbon nanotubes composites.
- Increased kinetics for hydrogen uptake in platinum-doped carbon aerogels.
- Made spillover materials but not much success, but did show 1 nm diffusion distance likely a limit. Also apparently improved kinetics.
- Made highly regular pores in carbon for hydride scaffold.
- Starting to alter heat transfer character, though a long way from meaningful results in this area.
- Really great work on getting an incredibly tight distribution of pores in an aerogel.
- New M-doped aerogels have been developed and significant new data has been generated on their microstructure and hydrogen storage properties.
- Some structures show promise for spillover and some are disappointing. There has clearly been increased understanding during the last year.
- Understanding the needs for hydride-scaffold aerogels has developed considerably during this preliminary stage.
- Synthesis of nanoporous metal hydride-aerogel scaffolds has been improved by templating.
- The interesting possibility of including C-nanotubes for increased thermal conductivity has been explored.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- Collaborations within Metal Hydride Center of Excellence are good.
- Collaboration with Metal Hydride Center of Excellence for carbon aerogel scaffold work is present.
- Need more interactions with Southwest Research Institute (SWRI) for testing samples.
- Exemplary, working with 2 centers and outside people and making a difference to them all.
- Several useful collaborations have been established in the Hydrogen Sorption and Metal Hydride Centers of Excellence.
- Samples are being prepared for validation testing.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- Proposed spillover work with nickel is appropriate, platinum is too expensive.
- Plans to investigate stability/durability of carbon aerogels (either for scaffolds or with metal spillover) addresses a major barrier and need - with metal catalysts present, reaction with the carbon aerogel structure is a concern.
- Suitable.
- Given recent results, future work looks very reasonable and logical.
- Project will be completed during Fiscal Year 2009. At least one quantitative go/no-go gate (based on volume and weight) should be inserted for consideration of the concept beyond 2009.

Strengths and weaknesses

Strengths

- High flexibility in approach.
- Several avenues to success.
- Good experience and skills in custom designing of aerogels.
- Project is concentrating on M-doping for spillover.
- Project provides good synergistic contributions to the CoEs. In particular, the HRL Laboratories hydride destabilization project should be greatly helped.

Weaknesses

- Really challenged on heat and cost.
- Volume efficiency in question, too.

Specific recommendations and additions or deletions to the work scope

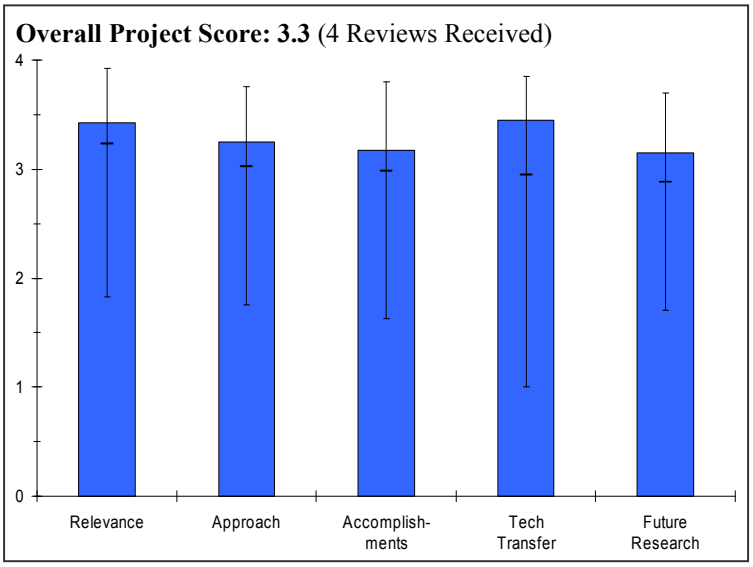
- If spillover is the pathway of future, need to establish more collaboration with University of Michigan and Rice University teams.
- Is there a synergistic effect between carbon aerogels and metal hydrides ($LiBH_2$ etc.)?
- ALD Vacuum Technologies may not be the right approach as the platinum/palladium clusters need to be loosely bonded with the substrate.
- The more pressing question would be is the carbon aerogel the right substrate with the spillover?
- Probably need to start looking for new catalysts. Need to start thinking about how to improve volumetric storage which may be inherently a problem.

Project # ST-25: Characterization of Hydrogen Adsorption by Nuclear Magnetic Resonance
Yue Wu; University of North Carolina

NOTE: This project is part of the Hydrogen Sorption Center of Excellence.

Brief Summary of Project

The overall objective of this project is to provide nuclear magnetic resonance (NMR) support to the Department of Energy Hydrogen Sorption Center of Excellence team members in developing reversible adsorbent materials with the potential to meet Department of Energy 2010 system-level targets. The 2008 objective is to use NMR porosymetry analysis to obtain detailed information on the micropore structures. This approach is based on the information of local magnetic field inside micro- and meso-pores probed directly by hydrogen.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Project as presented and described is good.
- Project is highly relevant and has a good potential for becoming critical.
- The approach developed should find applications in other energy related areas which employ porous material and hydrogen reactive gases including hydrocarbons.
- The microscopic characterization of pore sizes via nuclear magnetic resonance allows more detailed evaluations of the adsorption interactions of hydrogen with carbon surfaces as well as its binding energy and quantity of adsorbed hydrogen. While this information does not directly lead to higher performance levels for storage, it does let one compare local adsorption properties to predictions and modeling of structures. Hence, the more promising candidates can be emphasized in future development studies while less promising materials are down selected with greater confidence.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- Approach is sound.
- Not focused enough on promising systems or materials.
- Linkage to real need for this approach is missing.
- The project is well-designed, technically feasible, and integrated with other research.
- In-situ proton nuclear magnetic resonance provides unique information of hydrogen adsorption and porosity.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Qualitatively, the results presented are quite convincing.
- Mass calibration requires further improvement, including calibration of a broader variety of systems and standards.

- A number of materials with different local structures have been evaluated using these proton nuclear magnetic resonance measurements and self consistent results were obtained.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.5** for technology transfer and collaboration.

- Collaborations should be expanded to other CoE team members.
- Good coordination with other institutions; partners are participants.
- The nuclear magnetic resonance team has worked closely with several hydrogen sorption center groups to assess adsorption behavior and porosity.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Future research is not well defined.
- Is the group planning to wrap up the ongoing research only?
- The nuclear magnetic resonance group will look at a number of the more promising sorbent systems to assess their porosities and distribution between surface adsorbed and gas phase (bulk and confined) hydrogen species. These results will give useful insights into performance potential.

Strengths and weaknesses

Strengths
- Strong understanding of theoretical background and experimental techniques used.
- Good collaboration with other members of the CoE.
- A highly qualified nuclear magnetic resonance analysis team with dedicated spectrometer for evaluating hydrogen sorption behavior under in situ conditions over a range of temperatures.
- They have well established procedures and analysis methods to evaluate a variety of carbon-based adsorption samples.
- The use of nuclear magnetic resonance porosymmetry analysis is an innovative approach.

Weaknesses
- Project very limited in scope.
- Mass calibration requires further work.
- Future goals are not well defined.
- The current nuclear magnetic resonance porosymmetry analysis methodology lumps a complex distribution of interactions for the pore dimensions into a single parameter, which is OK for narrow size distributions but could be misleading for materials with complex wide or binominal distributions.
- The nuclear magnetic resonance shift depends strongly on the distance between hydrogen and the surface as pointed out by the presenter; L.E, the technique is sensitive only to surface layer. Is this a potential problem?

Specific recommendations and additions or deletions to the work scope

- Compare with nuclear magnetic resonance results with neutron scattering results where available (National Institute of Standards and Technology [NIST]).
- Consider isotopic studies to evaluate spillover and hydrogen or D in pores.
- The in-situ nuclear magnetic resonance facility should have its temperature range extended to lower temperatures (i.e., down to < 20K) to allow evaluations of more heterogeneous pore size distributions as well as more weakly bound hydrogen species.

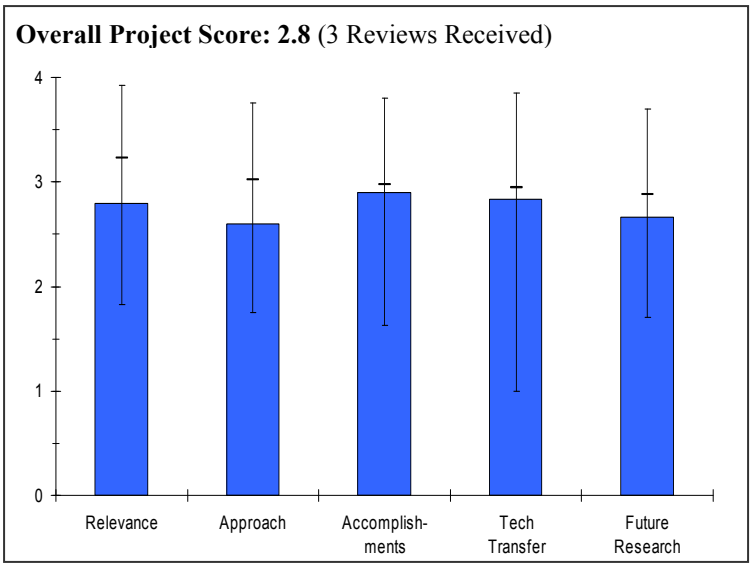
Project # ST-26: Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

Juergen Eckert; University of California - Santa Barbara

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The overall objective of this project is to develop hydrogen storage materials for reversible on-board application with hydrogen binding energies intermediate between physisorption and (dissociative) chemisorption. The University of California, Santa Barbara demonstrated the presence of molecular chemisorption of hydrogen in number of porous materials. Also, porous material with fluorinated organic and open metal sites was synthesized.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.8** for its relevance to DOE objectives.

- This project focuses on modifying the chemisorption properties of transition metals to either increase the number of bound hydrogen molecules or change their binding energies. Since stabilization of the active metals usually require large and massive organic support framework, these systems have very low storage capacity by either weight or volume. Unless, these metal complexes can either enhance hydrogen reactions with the framework group or serve as highly efficient catalyst to promote further adsorption, this approach has little potential to yield the needed improved hydrogen storage materials to meet DOE targets.
- The project addresses the objectives of the storage program in general terms without reference to the specific goals set by DOE.
- Relevant towards the discovery of a hydrogen reversible adsorbent with a "delta H_2" of about 20-25 kJ/mole hydrogen.

Question 2: Approach to performing the research and development

This project was rated **2.6** on its approach.

- The approach to give enhanced chemisorption bonding on metal is primarily to alter the functional groups and framework geometry to alter electron density and accessibility for hydrogen molecules to bond.
- Structural characterization of these materials is by a combination of x-ray diffraction and neutron scattering with occasion hydrogen adsorption measurements.
- Good to excellent approach of focusing on the most critical property of hydrogen storage via adsorption - the heat that's associated with this reversible process, but capacity needs to be considered more.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.9** based on accomplishments.

- The PI indicated that changes in bonding energy at metal sites can be changed by ~50+ percent yet the total storage capacity for hydrogen storage is rather limited to surface areas of only a few hundred m^2/gram.

- While binding energies around 20 kJ/mol may be possible, the weight penalties seem to be substantial with little option for any real improvements.
- Excellent new science or materials which display a slight improvement in "delta H" but unfortunately usually at a weight penalty. The mud touted effect of fluorinated linkages in metal organic frameworks is a case in point.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.8** for technology transfer and collaboration.

- The project has several international collaborators but relatively little interactions with the DOE hydrogen storage centers.
- The closure of the quasielastic QNES spectrometer at Intense Pulsed Neutron Source (IPNS)/Argonne National Laboratory has apparently restricted assessments of various samples by the PI and his collaborators.
- Good collaborative work.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.7** for proposed future work.

- The investigator has identified several candidate combinations of metals with organic linkers for evaluation of stronger bond formation that include chemical modification to increase surface areas as well as other properties.
- Needs more "new thinking'" to focus on higher "delta H" materials with a more favorable weight capacity.

Strengths and weaknesses

Strengths
- This project looks into details of single and multiple adsorption sites for molecular hydrogen as a possible method to produce bonding interactions that lie between conventional physisorption and chemisorption.
- The PI has long history in research and evaluation of the systems with insights into what modifications would alter adsorption behavior.
- The choice of Probins hydrogen interactions with host using inelastic neutron scattering is very sound.

Weaknesses
- There is little chance that practical high performance adsorption materials will be discovered from these combinations of transition metals and large framework of organic linkers.
- Project progress is highly depend upon accessibility to neutron scattering centers with limited capabilities or allocated testing times.
- The shut down of quasielastic neutron scattering capability at IPNS/Argonne National Laboratory will have a negative impact on the project.

Specific recommendations and additions or deletions to the work scope

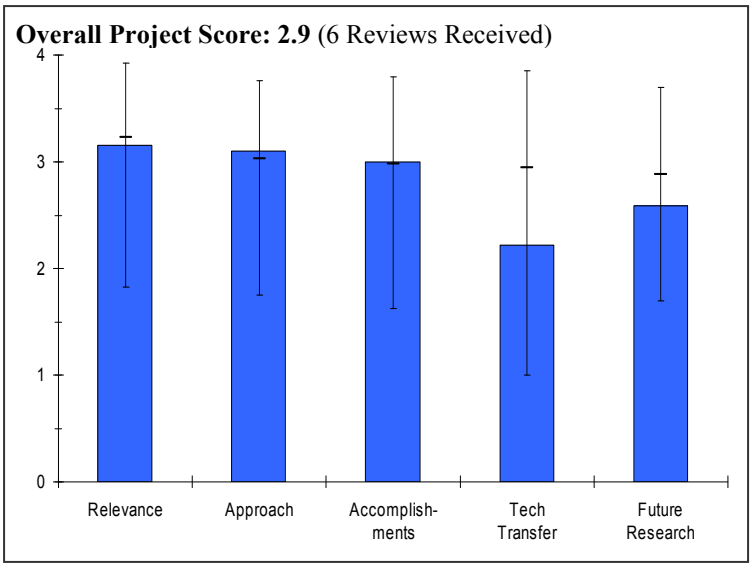
- For near term neutron scattering studies, the PI should apply to the National Institute for Standards and Technology (NIST) neutron center for measurement time.

Project # ST-27: A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part I
Jeffrey Long, presenting; University of California-Berkeley. Jean M. J. Fréchet and Martin Head-Gordon, UC-Berkeley, and Sam Mao and Tom Richardson of Lawrence Berkeley National Laboratory (LBNL), Co-PIs

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objectives of this project are the 1) synthesis of porous polymers; 2) synthesis of porous coordination solids; 3) calculations of hydrogen binding energies; 4) synthesis of destabilized hydrides; 5) hydrogen storage characterization instrumentation; 6) metal/metal hydride nanocrystals; 7) synthesis of nanostructured boron nitrides; and 8) theory for boron nitride materials.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- An apparent comprehensive effort out of Berkeley that addresses the programmatic efforts of the Office of Energy Efficiency and Renewable Energy.
- Long's group in particular synthesizes and analyzes a more interesting range of materials than other groups.
- Richardson and Head-Gordon appear to be contributing little relevance to this program and this is reflected in the publication record.
- No apparent contribution by Mao.
- Very innovative, cutting edge ideas about novel materials for hydrogen storage.
- Provides fundamental chemical insight into the molecular interactions that may optimize H+ support interactions and thus H+ storage density.
- Unclear whether or not improved hydrogen storage materials come out of this program since the concepts being explored are untested and in some cases unknown at this point.
- The goals of the research tasks that comprise this project are generally well aligned with the hydrogen vision and the DOE RD&D objectives.
- The nature of the work is mostly basic science aimed at identifying new types of materials with the potential to enable hydrogen storage systems that could conceivably meet the overall DOE hydrogen storage "system" capacity and performance targets.
- All the subtopics in this project do address and align with DOE objectives. Some aspects appear to be "hail Mary" efforts with little real hope of developing promising new leads (e.g., Cr doping), other aspects appear to be incremental efforts also with little real hope of promising new leads (e.g. differently-crosslinked polyaniline).
- Difficult to assess the "relevance" of this project, since it is composed of several distinct topic areas each of which have very different relevance to DOE objectives.
- Metal-organic framework materials (MOFs) are one of the most promising materials for hydrogen storage by physical adsorption and therefore are relevant to meeting the program goals.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- Approach behind the work on porous materials is strong with interesting data. The volumetric densities that are calculated for the Zn benzene dicarboxylate are particularly interesting.
- Exploration of hypercrosslinked polymers looks like a good avenue to pursue.
- The work on destabilization should have a better grounding in thermodynamics/kinetics. It is not clear what the overarching theme is here. Many of the ideas at Mg destabilization are being addressed by other groups and in much more comprehensive ways.
- The computational effort also appears to be rather poorly focused. It appears to be directed at finding metals to put onto linkers but the rationale for this given the synthetic challenges and the gravimetric penalty associated with transition metal additions makes this pursuit of limited technological value and not very interesting from an intellectual standpoint. While the title of the presentation says synergistic, the integration with other parts of this program is weak.
- This is a basic science study grounded in the fundamentals of solid-state chemistry and coordination chemistry.
- The PI is a well-established young investigator in the area of coordination solid synthesis and is now demonstrating excellent skills in the area of organic polymer solid-state structures.
- The approach both for the metal-organic solids and the pure polymer systems are scientifically solid both from the synthesis and characterization points of view.
- Synthesis and characterization of porous polymers, porous coordination solids, and destabilized hydrides.
- Calculation of molecular hydrogen binding energies.
- Emphasis is placed on optimizing synthesis methods and on precise measurements of hydrogen uptake characteristics.
- Approaches to the R&D in the subtopics are generally sensible, but seem to be scattered and poorly integrated.
- It is difficult to review the "approach" for this project, because it almost seems like 3 completely disconnected projects (cross-linked polymers, MOFs, and destabilized hydrides).
- The destabilized metal hydride work does not seem to build on (but, rather seems to be redundant with) the considerable amount of work done on Mg-containing alloys and intermetallic systems in the metal hydride community.
- The cross-linked polymer and MOF work seems to be carefully thought out, and builds on (and surpasses) previous work in many respects.
- The efforts to increase the binding in MOF materials (e.g., via Cr incorporation) are likely to give a substantial penalty in gravimetric density.
- The PI has a well thought out approach to new materials development and has a good emphasis on new materials with high hydrogen binding enthalpy.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- The work on porous materials by Frechet and Long is interesting and very productive. Most of the presentation and the publications produced over the past year reflect this.
- The work of Head Gordon offers fewer physical insights and may be less relevant to the program.
- The work of Richardson does not cover any new intellectual ground from what has been articulated in this presentation.
- Program is meeting all scientific goals.
- New hydrogen absorption materials have been synthesized and characterized with respect to surface area and hydrogen uptake.
- Novel mechanisms of hydrogen support interaction have been explored.
- Understanding of the hydrogen uptake mechanism and improved solid-state synthesis of the conducting polymer systems.
- Presented results that showed the beneficial effect of polymer crosslinking on effective surface area, sorption capacity, and heat of adsorption.
- Clarified the required conditions for synthesis and stabilization of selected MOF materials; achieved record high effective surface areas with $Zn_4O(BDC)_3$.
- Attempted to incorporate metal carbonyls into MOFs with some preliminary evidence that hydrogen binding occurred.

- Developed a new model for hydrogen binding that facilitates the study of how added metal centers influence binding of hydrogen in MOFs.
- Studied alloying of Mg to reduce the sorption enthalpy; preliminary results with fluoride addition look interesting.
- Seems to have "decent" progress in the subtopics.
- Porous polymers: the idea is intriguing, the reported results are sound but not yet exciting. Has there been any work on hydrogen uptake in crosslinked polyanaline as a function of extent of oxidation?
- MOF: Glad someone has paid attention to sample variability and stability. Ability to make Cr-hydrogen form is very interesting, its inability to release hydrogen is disappointing but not really surprising.
- Theory: Not clear that there is any new insight here.
- Hydride destabilization: Fluoride doping could be interesting but the reported results are not exciting.
- The work on cross-linked polymers seems promising, as this is a fairly unexplored area for hydrogen storage, and there is a huge "library" of possible polymers/crosslinkers.
- Very different surface areas found for MOF-5, depending on synthesis procedure, and found that exposure to air could be a controlling factor, and established a new synthesis and activation method, treating the samples as air sensitive (whereas others previously have not). This new synthesis procedure has led to substantially greater absorption than previous measurements on MOF-5.
- For MOF-5: Measured a volumetric density of 66 g/L at 77K and 100bar, approaching the density of LH_2, though they are at 77K. Also found an excess absorption of ~7 weight percent, much larger than previously measured. However, the volumetric densities reported are a combination of the (measured) gravimetric density combined with the (ideal) single crystal density. So, actual volumetric densities will be reduced from this idea number by a factor of the packing density.
- Used quantum chemistry calculations to help identify more suitable binding metals. Similar to other predictions in other materials (e.g., at the National Renewable Energy Laboratory (NREL)), they are predicting things like transition metal (e.g., titanium). Synthesis is (like in the NREL predictions) a huge challenge.
- There has been good progress on making new MOF materials with higher hydrogen adsorption enthalpies. The conducting polymer materials do not show great promise for meeting the storage targets.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.2** for technology transfer and collaboration.

- Nature of collaborations has not been made very clear in any of this work.
- It appears that some collaboration takes place between the efforts of Long and Head-Gordon but they would benefit from better direction.
- Unclear that this requirement applies to the described study.
- Several partners are listed on slide 2 but it is not obvious how they interact with the project.
- Little was said about how this project connects to or communicates with the relevant CoEs.
- 5 investigators, 5 separate sub-projects. There is no evidence of any real attempt to integrate effort within this project itself, let alone with any other institution in the Hydrogen Program. This despite some potential opportunity.
- No collaboration/tech transfer identified. Also, the various portions of these projects (except the computational work) seems largely disconnected to the other parts of the project.
- Good collaboration with the National Institute of Standards and Technology (NIST) and other groups that perform characterization. Additional collaborations may be helpful for accelerating materials development.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.6** for proposed future work.

- Future work has not been addressed.
- The described studies are on track and will continue probing issues fundamental to synthesis and molecular interactions.
- The path is well defined and tracking well.

- The future plans are not well documented in the slide file.
- It was reasonably clear from statements made during the oral presentation that future work will proceed in directions that are sensible extensions of the work done in Fiscal Year 2008.
- Porous polymers: no communication of any future plans.
- MOFs: pi-complexation of different metals is further along in this project than in other projects of which this reviewer is aware, and some promising new directions are outlined. (If the dicarboxylate were anthracene-based instead of benzene-based, could Mg atoms be incorporated re Mg-anthracene? and what would happen then with hydrogen sorption?)
- Metal hydrides/fluorides: future plans seem rather pedestrian: more fluoride?
- No proposed future research was articulated.
- The PI's emphasis on new materials is very good and the attention to high adsorption enthalpy is consistent with the DOE program goals.

Strengths and weaknesses

Strengths
- Work of Long and Frechet.
- Solid chemical foundations.
- Good molecular insight.
- Innovative materials and concepts for hydrogen-surface interactions.
- Successful identification of potential new hydrogen storage systems.
- Prof. Long and the other faculty working on this project are taking a scholarly approach to their research; the level of science is very high.
- The detailed study of what's important in the successful synthesis of MOF materials is much appreciated by the community.
- Well-known and respected investigators, excellent resources, further along in intentionally and advantageously functionalizing MOFs than other projects.
- The PI and his team have excellent capabilities in materials synthesis and characterization.
- The project is focused on new materials with high hydrogen binding enthalpies.

Weaknesses
- Work of Head Gordon and Richardson.
- Understanding of hydrogen-support interactions (proposed charge transfer mechanism appears unlikely) conducting polymer system.
- Synthesis of high surface area polyaniline systems.
- Misguided concept that a $Cr(CO)_2H_2$ system might be capable of releasing hydrogen under mild thermal conditions. (This idea violated known coordination chemistry). But, one can imagine other coordination systems where this might work.
- Needs better coordination with the CoEs; if substantive collaboration/communication does exist, it is not obvious from the presentation materials.
- Hydrogen storage based on sorption methods has no clear chance of meeting DOE's "system" storage targets at ambient temperature; the investigators working on this project are smart people who are capable of doing the type of back-of-the-envelope calculations that can readily show what it will take to store sufficient hydrogen by sorption methods at ambient temperature to meet DOE "system" targets for 2010 and more importantly beyond 2010.
- Sub-projects are too independent; insufficient effort to open new territory.
- Various portions of project are disjointed, and it's not completely clear (other than proximity) why they are together.
- The porous conducting polymer materials are unlikely to reach the necessary weight and volume targets for hydrogen storage materials.

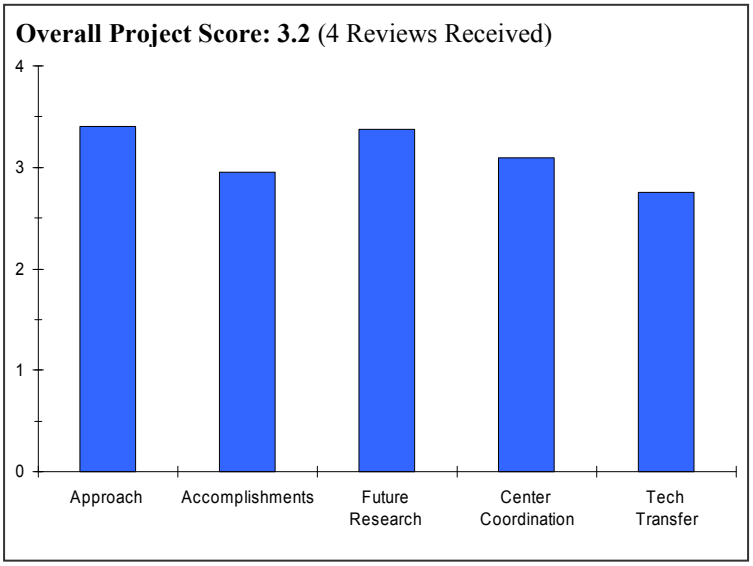
Specific recommendations and additions or deletions to the work scope

- Work of Richardson should not continue.
- Mao's contribution has not been presented and should not continue.
- Computational effort is poorly directed and doesn't appear to address program goals in any meaningful way.
- Continue program as is.
- Next year include summary slides for accomplishments and future plans.
- Elaborate on nature and effectiveness of collaborations with other related projects.
- Achieving Cr-doping by arene complexation in MOFs, begs the question of metal-arene complexation in the polymer systems. Could bis-arene-metal coordination be achieved as a "dehydrogenated" state, then the polymer subjected to strain while under hydrogen, resulting in metastable mono-arene-metal-$(H_2)_x$ form? This is only one hypothetical example of how attempts to integrate the sub-projects might open new leads or concepts.
- Work on destabilized Mg alloys is not novel; this type of work has been extensively studied in the metal hydride community. No compelling justification was made to pursue this line, and it is not clear that the PI is aware of large amount of the previous work in this field.
- The PI should focus on new MOF materials and fundamental investigations on modifications to increase the hydrogen adsorption enthalpies.

Project # ST-29: Metal Hydride Center of Excellence
Lennie Klebanoff; Sandia National Laboratory-Livermore

[NOTE: This presentation was to evaluate the entire Metal Hydride Center of Excellence as a whole. A separate review form was used and can be found in Appendix C. Sandia's technical contribution to the center is evaluated in ST-36.]

Brief Summary of Project



The overall objective of the Metal Hydride Center of Excellence is to research, develop and validate reversible on-board metal hydride storage materials and systems that meet the 2010 DOE system targets for hydrogen storage, with a credible path forward for meeting the 2015 DOE storage targets. The approaches to meet the hydrogen capacity targets of 6 wt%, 45 g H_2/L volume density are to 1) synthesize and characterize hydride materials with high hydrogen capacity and favorable thermodynamics; and 2) use state-of-the-art theory to guide the materials discovery effort. The approaches to meet the chare/discharge rate target of a 3 min system fill (5 kg) are to 1) develop materials that are fully reversible; 2) develop catalysts that aid reversibility; 3) assess nanoengineering promotion of kinetics; and 4) investigate the role of contamination on reaction rates. The approach to meet the hydrogen purity target of 99.99% is to assess release of NH_3, B_2H_6 and other volatile species from metal hydrides during desorption and cycling. The approach to meet the cycle life target of 1,000 desorption/adsorption cycles is to investigate durability of materials, cycling behavior, effects of contaminants, structural stability, and release of volatiles.

Question 1: Approach to performing the R&D including Center Management

This project earned a score of **3.4**.

- Materials go/no-go decisions that were done in September 2007 are extremely effective. The project in a good shape.
- The center has demonstrated flexibility, for example dropping engineering focus based on new engineering center picking up the work but maintaining a liaison (exactly what was indicated); appropriate use of partners' skills and that partners have good skills in the area. The center has down-selected a large number of materials based on a combination of experiment and theory. They do review progress and ability to meet goals, and there are internal down-selects based there-on with clear criteria to get further support.
- Clearly focused on the key challenges and renewing that focus regularly.
- Work is being carried out by some partners on systems that initial favorable theoretically predictions have since been shown to have been in error.
- The theory team still needs to be pushed to include carbon compound outputs (methane).
- Based on the amount of work that has already been done on metal hydrides and the results achieved versus the challenging storage targets, including the results achieved in this center of excellence, it appears that metal hydrides have a significantly lower probability of meeting the on-board storage targets than other approaches. Although more is being learned about them, how to improve them, and to how find better metal hydride systems, they appear to have specific limitations that will be very difficult to overcome. Therefore funding this area of storage research to the extent it is funded may not be the best approach to meet the Department of Energy Hydrogen Program overall objectives.

- This center of excellence is taking a broad, aggressive, and state of art approach to this research effort. The science being done is outstanding. They are including computational chemistry modeling to help screen and find new materials, nano-confinement, catalysis, as well as other important aspects to try to overcome the challenges for a metal hydride storage system. This is all very good work. This center of excellence is very well organized and following a good down-select process. There is an excellent process for gathering new ideas and materials, screening them against well defined criteria, and placing them in the appropriate part of the center of excellence if research on them is warranted.
- There is no mention of the storage cost target in the presentation. This also needs to be in the forefront of this effort.
- The center appears reasonably well managed. This reviewer's biggest concern is the amount of effort directed at a material system ($AlH_3 = Al + {}^3/_2\ H_2$) that is already known to be irreversible; this effort is justified owing to this system being a potential learning tool. But this reviewer believes the effort would be better spent delving into the minute details of other systems that do have the thermodynamic possibility of being reversible: therein lies what really needs to be learned, what happens across solid-solid phase boundaries, how catalyst entities disperse and how they manage to function if non-dispersed, and etc.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **3.0**.

- The materials that meet the 2010 target and can be recharged on-board have not yet been proposed. However, the center of excellence has made go/no-go decisions and clearly selected potential materials to be studied.
- The confinement scheme is good progress. Determination of $B_{12}H_{12}$ blocking intermediate is a key item that needs to be further understood. The alane (AlH_3) work is important and looking at several ways to regenerate it. The theory group shows a good ability to learn and improve the quality of predictions based on experiment results and outside work. Calcium borohydride ($CaBH_4$) work is important even if the material might not practical.
- The presentation could have done a better job of clearly stating in greater detail what the center of excellence has achieved over the past 12 months versus the Hydrogen Storage Subprogram's targets. Additionally it could have better described how and why the center of excellence believes it can fill the gap between current metal hydride systems' performance and the DOE targets.
- Based on the results that were presented, it is not clear that metal hydrides have a reasonable chance of achieving the DOE storage targets.
- There was no real detail in any area of the effort. The achievement statements were quite general and did not provide enough information as to the depth and level of the efforts. A few examples within the effort could have been very affective to clarify this.
- It is clear from the presentation that excellent science is being done in this project relative to computational chemistry modeling, nano-confinement, catalysis, and other areas. More detail on these would have been very welcome to get a better sense of these efforts.
- There is a decent record of publishable findings, however it has not been quite so good at focusing the "progress engine" toward making the vital findings in kinetics and thermodynamics of the hydrogen release/uptake cycle. One bright spot is Professor Robertson's demonstrated ability to focus on catalyst/material-phase interactions. Another is the apparently aggressive de-selection of some concepts that are not able to achieve DOE targets.

Question 3: Proposed future research approach and relevance

This project was rated **3.4**.

- This year the center of excellence showed the go/no-go decision for the materials and distinguished individual scientists who lead each subject. It is a good direction that theoretical activities to explore novel materials will be coordinated by a talented scientist.
- Areas of future work are correct for their current position and the upcoming engineering center. In these areas the approach seems appropriate. I think it this is a good plan.
- The path forward and list of efforts for the future work fits well with what this center of excellence has accomplished and learned to date. The center of excellence efforts are well organized and utilize an excellent

process to gather new ideas and materials, screen them, and establish efforts on them in the appropriate parts of the center of excellence when warranted. The areas being pursued should yield continued advances in this area.
- There was nothing in the future work, nor details within the accomplishments to date, that suggests a strong likelihood that through these efforts, a metal hydride system could be developed that would meet the DOE on-board storage targets.
- Future plans appear reasonable. This reviewer accepts the premises of the Director, that only nanostructure and/or catalysis will improve the rates of hydrogen release/uptake for any material system, and that only composition (and perhaps nanostructure?) will improve the thermodynamic parameters for hydrogen release/uptake. Given the capacity requirements, a focus on boron materials appears sensible. Nitrides do not look as promising owing to the need for additional complexity (in material & chemistry, possibly also in system engineering) to mitigate ammonia (NH_3) loss.

Question 4: Coordination, collaborations and effectiveness of communications within the CoE

This project was rated **3.1**.

- There are a large number of collaborations among projects under the Metal Hydride Center of Excellence.
- The partners are communicating regularly. This is good. The intellectual property (IP) agreement does seem to lead to less than full disclosure and thus inhibits cross fertilization. Structure is good. Interaction outside is quite good. There is a history of experiment guided by theory. Now that the communication going both ways between the experimentalist and theoreticians, it is clearly paying off in better theory.
- There appears to be good interaction, coordination, and communication within the members of the center of excellence based on the presentation, the project organization, and the results to date.
- Coordination and cooperation among partners appears to be good. Other center partner talks (e.g., Robertson, Johnson) offer more insight into the communication/coordination than the center talk itself.

Question 5: Collaborations/Technology Transfer Outside the CoE

This project was rated **2.8**.

- International collaboration has not been included in the presentation.
- Very good outside collaboration. Collaboration is on several fronts and not isolated to one area. Work with other centers (e.g., Vajo-Baumann) is great. They are also publishing with outside groups.
- The project has resulted in an impressive number of publications and talks at important conferences.
- It is not clear if there is any collaboration outside of the center of excellence. The center of excellence is quite large by itself but some collaboration with the private sector, especially perhaps with the OEM stakeholders could be very valuable.
- There is little evidence that the center is coordinating outside of itself.

Strengths and weaknesses

Strengths
- The go/no-go decision is a very strong point of the Metal Hydride Center of Excellence. This is a good example that the management of the center of excellence works effectively. There are a large number of world-class scientists in the center of excellence and they carry out their research intensively.
- The center has strong players.
- They are willing to learn from errors.
- Theory, experiment, and to some extent engineering all interact.
- A large collaborative group of excellent scientists are applying state of the art techniques and chemistry to try to find a metal hydride system that can meet the very challenging targets of the DOE on-board Storage Program.
- This center appears to be the best one poised to orchestrate the discovery and development of a lightweight, high capacity, truly rapidly reversible, metal hydride storage system.

Weaknesses

- The engineering part will be dissolved and the activities will be moved to the new Engineering Center of Excellence. Therefore engineering applications, such as large scale preparation, may be lost. Collaboration with the new Engineering Center of Excellence will be indispensable.
- There is more secrecy internally than is good with some partners not appearing to fully collaborate.
- There is still a need to upgrade theory to be fully helpful.
- Metal hydrides have been studied for some time. There may be fundamental characteristics of this approach to hydrogen storage that make it unlikely that it can ever meet the DOE on-board Storage Program targets.
- It is not at all clear that Nature will cooperate in allowing the existence of a metal-hydride storage system that meets all DOE expectations.

Specific recommendations and additions or deletions to the work scope

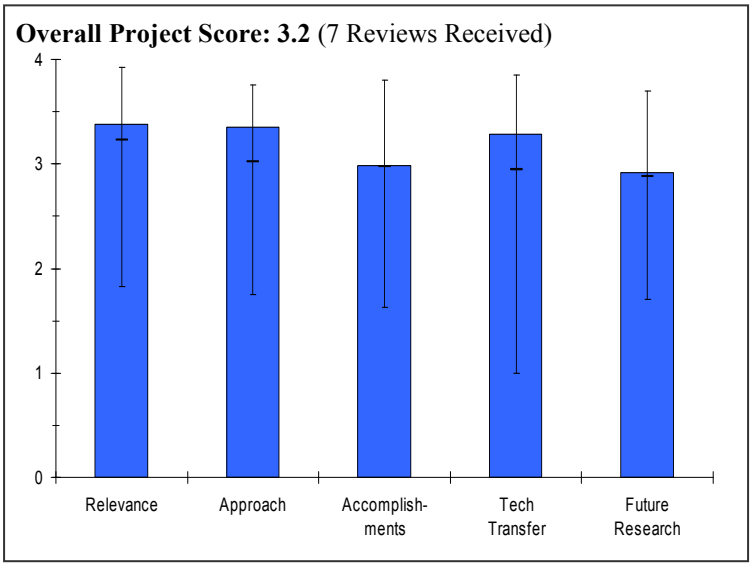
- Strong collaboration with the new Engineering Center of Excellence is highly recommended.
- Include carbon products in the theory package.
- Discontinue work on materials that will never be reversible.
- De-emphasize this storage center of excellence relative to other storage research and development by reducing its funding level.
- Recommend the Center give very careful consideration to whether Al/alane really makes sense, and to whether the work on it will give truly useful knowledge. Put more emphasis on atomic-scale understanding of interphase and intra-phase atom mobilities and catalytic effects.

Project # ST-30: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage
Ping Liu; HRL Laboratories

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project

The overall objective of this project is to develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for reversible on-board hydrogen storage. The 2007-2008 objectives are to 1) identify and test new high capacity Li- and Mg-based destabilized hydrides; 2) screen candidate $LiBH_4$ + MgX destabilized systems and evaluate energetics and kinetics; 3) down-select systems for additional work; 4) evaluate sorption kinetics and thermodynamics of $LiBH_4$ and Mg in carbon aerogel scaffolds; 5) investigate effects of pore size and pore size distribution on reaction rates of $LiBH_4$; and 6) incorporate Mg into the aerogel and measure its kinetics.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- This program is highly relevant to the Department of Energy Storage Subprogram.
- It is concerned with novel, thermodynamically destabilized, nanophase materials for hydrogen storage.
- The introduction of carbon aerogels as scaffolds to preserve the nano-scale properties of the active materials is innovative.
- Systems of interest are $Li(BH_4)$, MgH_2, $Li(BH_4)/Mg_2NiH_4$, MgX(X=Ni or Si) as well as aerogel properties.
- This program has the capability to synthesize and characterize theses materials. This capability is highly relevant to DOE objectives.
- The project is very relevant.
- The project objectives and respective work plan are very well aligned to the hydrogen vision and they are of high relevance to the DOE research and development strategy.
- This project to develop and test new high capacity lithium- and magnesium-based destabilized hydrides is clearly contributing to DOE's objectives.
- The project is aligned with the hydrogen vision and DOE research and development objectives.
- The objective to screen lithium- and magnesium-based hydrides is good.
- Incorporating magnesium into the carbon aerogel is a unique objective.
- The project is focused on $LiBH_4$ system, which has a potential for high hydrogen capacity.

Question 2: Approach to performing the research and development

This project was rated **3.4** on its approach.

- The approach is highly scientific and professional.
- A compilation of attractive destabilized systems was carried out.
- The pertinent properties of selected systems were characterized.
- Aerogels of various pores sizes were synthesized.

- The selected systems were or will be incorporated into aerogels.
- This is an interesting experimental approach that focuses on existing barriers.
- The project is well-designed.
- This is a solid, well thought-out approach. The project is moving with clear steps to address the key issues and closely following up progress against set milestones and implementing go/no-go decisions.
- They are fully exploring possibilities offered by advances in hydride destabilization methods and nanoengineering.
- The approach for MH destabilizing and nanoengineering seems to be well thought-out and feasible.
- The principal investigator presents adequate experience to perform the proposed research.
- The focus to enhance reaction rate by nano-engineering is good.
- The focus on destabilized system will help in lowering enthalpy (ΔH).
- This project is focused on kinetic enhancements that are critical to practical use as well as thermodynamic destabilization and hydrogen content.
- A much stronger integration with other efforts within the center is needed, specifically with respect to advanced characterization.
- There is little to no focus on efficiency.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- The system $Li(BH_4)/Mg_2NiH_4$ was found to be reversible at 350°C with a hydrogen storage capacity up to 8 weight percent.
- The reactions and product phases were determined.
- A $Li(BH_4)$ - aerogel system was characterized.
- High loadings of magnesium in an aerogel were achieved with no change in thermodynamics with an associated improvement of reaction kinetics.
- Aerogel temperature and pore size effects were determined.
- Good progress.
- The approach may require a significant adjustment if degradation of the hydrogen storage component is due to the formation of B_2H_6.
- Satisfactory accomplishments and sound progress, particularly taking into account the degree of complexity and level of challenge of this research.
- Encouraging data from the use of aerogel scaffolds with destabilized hydrides for lowering desorption temperatures and improving kinetics.
- Screened a new class of destabilized material systems; progressed in nanoporous scaffolds and starting to understand the effect of pore size and distribution.
- The principal investigator has made significant progress towards developing a new $LiBH_4/Mg_2Ni$ system for hydrogen storage.
- The success of the destabilizing and nanoengineering techniques in lowering reaction temperatures and improving kinetics contributes towards improving the performance of these materials.
- Significant progress has been made as evidenced by publications and presentations.
- Improvement in kinetics by use of nanopore materials is demonstrated in this project. This result is very instructive to research and development activities of metal hydrides with practically high desorption temperature.
- Finding of ternary borides shows possibility of other metal hydrides with high capacity and low desorption temperature.
- Successful impregnation of aerogels with magnesium.
- No improvements in dehydrogenation temperature of magnesium hydride.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- This program has extensive collaborations both within and outside the Metal Hydride Center of Excellence.
- A total of two refereed publications over the period of 2007 to 2008 have been produced.
- Similarly a total of three presentations have been given.
- A provisional Patent application "Metal Filled Porous Carbon" has been filed.
- Good collaboration.
- Limited industrial collaboration.
- Strong collaborations within the Metal Hydride Center of Excellence, but also with other DOE-funded projects (carbon scaffolds work) and international collaborations (access to unique testing facilities and expertise).
- The cross-center collaboration is particularly important when expertise developed in one center can benefit the others.
- There is a large degree of interaction between the principal investigator and partner institutions in this project.
- Impressive collaboration with center of excellence and other intuition.
- This project has contact with research groups of nanomaterials in other centers of excellence as well as the theoretical research group in the Metal Hydride Center of Excellence.
- Even though multiple partners are listed, actual partnering is obscure, if at all existent.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- The incorporation of $Li(BH_4)$-MgH_2 in an optimized aerogel scaffold.
- The following systems will be candidates for scaffolding: $Li(BH_4)$-Mg_2NiH_4, $Li(BH_4)$-MgF, $Li(BH_4)$-MgS, $Li(BH_4)$-MgX where X = O, OH, Ni.
- Adopt nano-engineering to improve kinetics.
- Research plans are well defined and realistic.
- The approach presents a clear idea of current material system limitations and is well structured, with carefully drawn future plans. Very useful project progress and future direction matrix.
- Opening a new research avenue with the exploration of oxide-based destabilization reactions supported by the theory group.
- The principal investigator seems to have a good plan for building on the work already accomplished.
- The research should continue as planned.
- Plans built on past progress.
- Nano-engineering to reduce diffusion distance should help reaction rates.
- Theory to address oxide-based destabilization is essential.
- Future research into new destabilization agents is lacking reason. Why MgX with X = O, OH, and Ni? Especially Ni since the $LiBH_4/Mg_2NiH_4$ system has been already investigated. Is there a reason to expect that MgO will be so much different from MgS?
- How will the fully destabilized $LiBH_4/Mg_2NiH_4$ system be incorporated into scaffolds? How will the stoichiometry be controlled/varied from one pore to another? With an expected broad distribution of stoichiometries, what will be the utility of future work?

Strengths and weaknesses

Strengths
- A very strong scientific effort.
- The resources appear adequate.
- The technology transfer is good.
- The use of a scaffold to preserve physical integrity and prevent dissemination nano particles.
- The realistic appraisal of critical problems and issues.
- The demonstrated reversibility of the $LiBH_4/Mg_2NiH_4$ system.
- Solid experimental work.
- Good collaboration.
- Strong team, highly skilled, with an open mind and a clear vision.
- The principal investigator presents adequate experience to make the project successful.

- Nano-engineering.
- The results in this project are totally analyzed according to appropriate structural and thermal analytical data.
- This project considers kinetics, thermodynamics, and hydrogen capacity.
- Using scaffolds to control diffusion distances.

Weaknesses

- The prospect that any of the scaffold systems will meet the 2010 DOE targets is unlikely.
- The possible evolution of borane has not been addressed.
- The question arises, what are the safety issues involve with aerogels and their incorporated materials?
- Due to high processing temperature, carbon aerogel offers limited opportunities for functionalization/doping.
- Practical considerations with respect to aerogels, capacity limitations and, cycling performance, have not yet been addressed. Is it possible to have scaffolds of high enough specific porosity volume to "balance"/mitigate the capacity penalty for instance?
- Feasibility of developing a destabilized material system able to meet all thermodynamic targets for application; theoretically calculated values have not been experimentally confirmed.
- Even if the project succeeds, the materials barely have enough hydrogen holding capacity to meet DOE's 2010 goals.
- Lack of theory group.
- Conclusion that lowered kinetics in 4nm pores is due to limited access of hydrogen is unsupported by the data. 40 angstrom holes are still much larger than hydrogen molecule.
- A claim about "beginning to understand pore size/distribution effects" is unsupported by the data. No actual understanding provided.
- Dissemination of results (publications/presentations) is low.
- NMR, FTIR characterizations have been planned but have not been done.
- Work on scaffolds appears to be separated from work on destabilized systems.

Specific recommendations and additions or deletions to the work scope

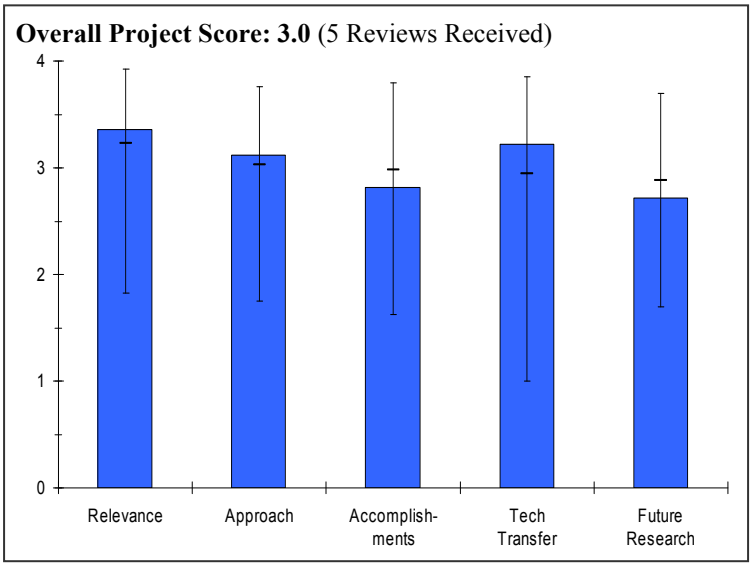
- It is likely that high melting point alloys will have very poor phase separation kinetics when the product phases require long range metal atom rearrangement. Thus some effort should be diverted to low melting point systems that do not require large metal atom diffusion distances. In the latter case very small nano particles ameliorate such problems as shown in this project but they also introduce other difficulties.
- Further emphasis on borohydrides should include the determination of whether evolution of borane is a problem.
- At this point the type of safety issues which may arise should be addressed.
- Increase emphasis on the $LiBH_4/Mg_2NiH_4$ system.
- Closely collaborate with theoreticians and modelers to refine the destabilization predictions so as to better guide further investigations.
- Explore the effects of incorporated catalysts on the sorption kinetics.
- Much better integration with theory.
- Focus on scaffolds and nanostructuring.

Project # ST-31: Chemical Vapor Synthesis and Discovery of H_2 Storage Materials: Li-Al-Mg-N-H System
Zak Fang; University of Utah

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project

The overall objectives of this project are to 1) discover new solid hydrides that meet reversibility and kinetics requirements; 2) develop the chemical vapor synthesis process (CVS) for production of nanosized solid metal hydrides; and 3) demonstrate the effectiveness and unique properties of nanosized solid hydride materials. Objectives for fiscal year 2007-2008 are to 1) understand reaction mechanisms of materials based on lithium alanates destabilized by light metal amides, and LiMgN; 2) establish capability and quantify NH_3 co-production during dehydrogenation; 3) synthesize new materials using high-energy, high-pressure reactive milling process; and 4) synthesize nano precursor and hydride powders using the CVS process.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- The project is partially aligned with Department of Energy research and development objectives.
- Based on the stated objectives, this project seems to be highly relevant to DOE's goal of discovering new high capacity materials for hydrogen storage.
- Enhancement of compound reversibility is relevant to the DOE objectives.
- Project is quite relevant to DOE program objectives, especially in relation to the Metal Hydride Center of Excellence work program and aims. Important results are expected with respect to the applicability of certain material types (especially Li-Al-Mg-N-H systems).
- Materials based on the Li_3AlH_6 + $_3LiNH_2$ system should be abandoned from further consideration since the temperatures required to achieve reversibility are much too impractical.
- The principal investigator has made a good effort to realign the program objectives by focusing on the LiMgN system, which has proven to be reversible with a theoretical capacity of 8.2 weight percent. However, the dehydriding temperature for this system also appears to be impractically high (~200°C) and, hence, may warrant focusing efforts on a different, more promising system.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- The approaches are good in general if these reactions can ever work for on-board usage.
- The chemical vapor synthesis and high-pressure high-energy synthesis route are effective.
- There is a lack of overall structure in approach.
- There is a lack of creativity.
- The project is well designed and incorporates rapid screening tools such as TGA, XRD and FTIR as well as PCI and NMR for in depth characterizations.

- The principal investigator plans to demonstrate feasibility based on characterizations of the thermodynamics and kinetics. This is important.
- Good usage of the theoretical estimation results with regards to the LiMgN compound.
- Mechanistic understanding and visible collaboration with other center members (i.e. NMR, effects of O_2) is good.
- Overall approach is sound and focused on the project aims. Important milestones lie ahead (September 2008) and quite rightly a go/no-go decision on LiMgN and (Li_3AlH_6 + $_3LiNH_2$) suitability is to be taken in September 2009.
- While chemical vapor synthesis of hydride materials is a potentially useful approach, it is not evident from the presentation what scale of throughput may be achieved by the system. If found to be important in synthesizing nano-sized powders of a highly-active metal hydride, what is the practical scalability of the process?

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- The principal investigator made some good progress toward objectives.
- Some new synthesis routes have been validated.
- It was confirmed that LiMgN is reversible with 6.6 weight percent capacity. This is good but the ammonia production poses a significant problem that must be solved.
- MgLiN could not be reversed such that the total 8 weight percent was obtained. This could imply a multi-step decomposition with observed ammonia formation. For future work, it is not clear how this could be improved.
- Promising results have been obtained on two fronts (Li_3AlH_6 + $_3LiNH_2$) and LiMgN (although the latter is relaxed to the (MgH_2+$LiNH_2$) system that is no longer pursued at the Metal Hydride Center of Excellence level). Rehydrogenation of the former system is found to depend on heating rate and this should be further explored. LiMgN is shown to be a 6.6 weight percent reversible material and this justifies further work on it.
- Now that the principal investigator appears to have both analytical and synthetic capabilities well in hand, progress toward discovering and screening new hydride materials with acceptable sorption temperatures should proceed at an accelerated pace. More frequent collaboration with the theory group of the Metal Hydride Center of Excellence is strongly encouraged to aid in the selection of potentially promising systems for experimental studies.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.2** for technology transfer and collaboration.

- Some collaborations exist.
- The PI works closely with the theory group.
- Collaboration with the Metal Hydride Center of Excellence Theory Group to identify promising candidates has been an asset to this project.
- Collaboration with the other center members researching amide-hydride mixtures is suggested to avoid duplication.
- Good interaction for mechanistic understanding, such as NMR.
- Several collaborations exist and complement nicely the work done at the University of Utah. Close interaction and good coordination is shown.
- As mentioned above, more frequent collaboration with the theory group is encouraged in order to help select additional hydride chemistries of potential interest.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.7** for proposed future work.

- The general research direction should be aligned with potential on-board usage.
- Chemical vapor synthesis is a proven approach for synthesizing nano-sized. However, the principal investigator needs to expend more effort in determining what is the phase and chemical composition of the end product.

- The plan to focus on LiMgN and $Li_3AlH_6 + {}_3LiNH_2$ and to develop techniques to minimize the release of NH_3 are reasonable and this will address a key barrier to using these materials for hydrogen storage.
- Nano particles of LiMgN: Using methods such as CVS could help solve the kinetics problem initially but sintering as the material is cycled could occur. Careful tracking of particle size is highly recommended. It is also not clear how the particle size relates to the potential multi-step decomposition path.
- Overall path forward for NH_3 mitigation needs to be more clarified (i.e., to avoid scenarios similar to $LiNH_2$:LiH).
- Future research plan makes sense and builds properly on progress achieved so far. NH_3 emission is an issue but the finding that it depends on heating rate provides interesting hints on how to fight it. The high pressure, high energy ball milling process can be further explored. The Mg-Ti system on which it is applied is an interesting one, especially with regard to the differences observed between film and bulk material.

Strengths and weaknesses

Strengths
- Experimentally validated the predictions from the theory group.
- The applicant has the resources needed to complete the proposed work.
- Utilization of theory to guide materials selection and following systematic approach.
- Promising results on the two systems investigated. Findings about heating rate dependence of rehydration process and ammonia release may have important implications.
- The principal investigator has strived to obtain detailed, mechanistic characterization of candidate metal hydride systems, leading to a better understanding of the attributes and pitfalls of such systems.
- Establishment of an apparatus for chemical vapor synthesis of nano-size hydride precursors provides a potentially useful venue for rapidly synthesizing new materials and screening their viability.

Weaknesses
- There is a lack of a systematic approach in selecting the materials to be studied.
- The use of a pH meter to detect NH_3 formation is not the best way to do this. An RGA has more sensitivity and it can detect a variety of other gases that may be produced. The principal investigator could send samples to a partnering institution for RGA analysis if one is not available on site.
- Further clarification of path forward and how current problems will be tackled is needed.
- Further collaboration with other members working on amides and alane is needed.
- Issues related to NH_3 emission need to be dealt with. Maximum capacities expected range between 6.6 to 8.0 weight percent and are therefore low.
- Materials that are found to be thermodynamically non-viable are not being abandoned early enough in the program to allow a more aggressive pace in the investigation of other candidate materials/chemistries.

Specific recommendations and additions or deletions to the work scope

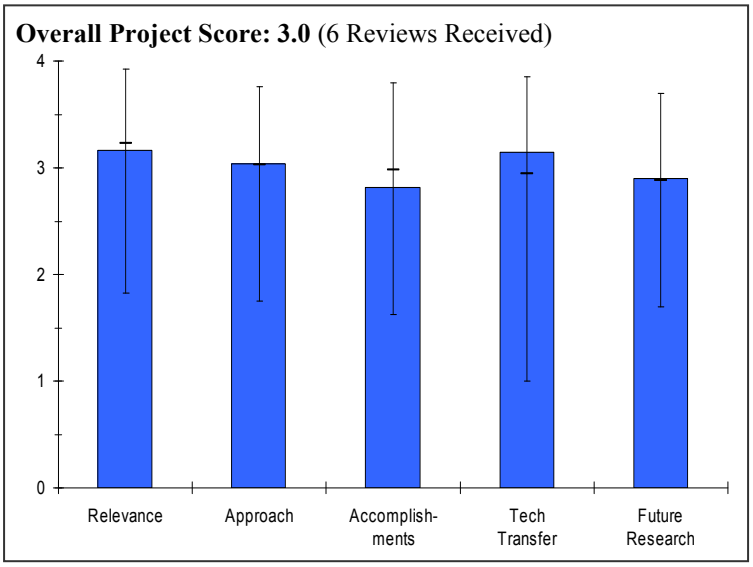
- A go/no-go decision should be made within the current fiscal year on whether or not NH_3 evolution from the LiMgN system exceeds acceptable limits. If the results show that NH_3 exceeds acceptable limits, further study of this system should also be abandoned in favor of new chemistries as predicted by theory (e.g., Li_2CN_2).
- Further characterization studies on the $Li_3AlH_6 + {}_3LiNH_2$ system should be abandoned.
- Potential formation of CH_4 from the amide-carbon mixture should be carefully addressed.
- Clarification on how the nano structures, for both Al and LiMgN, could enhance the decomposition temperature and decomposition route is suggested.
- The Mg-Ti system presents interest. It would be nice to explore further the HPHE milling facility to try to understand the observed differences between films and bulk material in this case.
- Abandon the $Li_3AlH_6 + {}_3LiNH_2$ from further study.
- Abandon the LiMgN system if NH_3 evolution is confirmed to exceed the acceptable limits.

Project # ST-32: Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure
Ian Robertson, presenting; Duane Johnson, Co-PI, University of Illinois-Urbana-Champaign

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project

The main objectives of the University of Illinois, Urbana-Champaign within the Metal Hydride Center of Excellence (MHCoE) are to 1) advance the understanding of the microstructural and modeling characteristics of complex hydrides; 2) provide feedback and knowledge to partners within MHCoE framework; 3) provide more reliable theoretical methods to assess hydrogen-storage materials, including key issues affecting materials under study; and 4) help achievement of specific targets and milestones.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- The project supports the DOE objectives.
- Catalyst study (distribution) in response to barrier A; theory work in response to barrier C; not clear how barrier B has been addressed directly by the project.
- This project to develop new theoretical models for studying hydrogen storage systems aids partnering institutions in their efforts to understand these materials and therefore supports DOE's goals.
- Experiments on catalyst dispersion are relevant (score 3.0).
- Theoretical calculations are mostly irrelevant since it is not clear they add anything beyond what Georgia Tech/Pitt project is already providing (score 1.0).
- Claims that they have developed a "new theoretical method" are unfounded.
- Quite good. Comes closer than other projects to developing a nano-, almost atom-, scale understanding of how the material constituents and their catalysts function in a metal-hydride storage system.
- Experimental work on micro structural analysis and location of catalyst particles is critical towards improving these materials, and making current high-capacity (but irreversible) materials more practical. Theoretical work does not have as clear a relevance to the Hydrogen Fuel Initiative.
- Project is essential to supporting materials discovery efforts within the Metal Hydride Center of Excellence by providing advanced characterization and theoretical modeling capabilities.
- The project provides scientific support for characterization and microstructural analysis of complex hydrides and theoretical work aimed at prediction of new crystal structures.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- The project is technically feasible and is well integrated with other research in the Metal Hydride Center of Excellence. It contributes to overcoming some barriers.
- Experimental approach score 3.0.
- Theory score 1.5.

- Also quite good. Very impressed by the emphasis on detailed understanding at the scale of smallest-detectable phases, and below.
- Experimental work combining a variety of techniques to locate catalyst particles in various hydride materials is really unique and important work. However, it would be helpful to see more of a connection as to how this information is being used to guide experimentalists towards new catalysts, processing, materials, etc. At the moment, this connection is not clear.
- Not clear how the theory work here is differentiated from other work in the center of excellence, and what true value it is providing.
- Imaging techniques developed to characterize catalyst-particle dispersal will provide much needed information about the effectiveness of processing steps, such as ball milling.
- The development of DFT-based methods to predict reaction enthalpies and, ultimately, the Van't Hoff plots are a significant accomplishment that should find broad use for predicting such properties in novel materials prior to experimental measurements.
- It is not clear what specific new methods were developed in connection with this project.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- The development of a theoretical model suggesting that reversibility is affected by intermediates is valuable information to researchers who seek to understand the mechanism.
- Since last year there seems to be only minimal experimental progress, and essentially zero theoretical progress.
- Good techniques developed in electron-microscope imaging, but could use more progress toward exploiting the understanding of catalyst and phase effects in improving kinetics.
- Measurement of catalyst dispersal in a variety of materials is an excellent accomplishment.
- Theoretical work on $LiBH_4$ seems very similar to what was presented last year (the figure is the same), and even to what was presented in 2006.
- Significant technical accomplishments have been made thus far in the program.
- Understanding of intermediate phases and prediction of reaction enthalpies.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- The principal investigator has worked closely with partners within the Metal Hydride Center of Excellence to provide a theoretical framework for their investigations.
- There are some minor collaborations with Dr. Ronnebro and Sandia National Laboratories on materials. Wider collaboration with other center partners should be encouraged.
- Appears to coordinate and communicate well with other center partners.
- Experimental work is closely connected with other portions of the center of excellence. Theoretical work seems largely unconnected.
- Imaging methods developed to characterize catalyst dispersion are relevant to physisorption materials, and collaboration should be extended to the respective center.
- Collaboration between theory and experiment, particularly leading to joint publications, should be improved.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- The principal investigator plans to continue the modeling work that is underway and to build on past progress.
- The proposed future work is okay but seems on the "passive" side.
- The aim is to continue work as before. While the previous published work is of good quality, I would have liked to see some novel approach towards discovering new materials/catalysts.

Strengths and weaknesses

Strengths

- The team operates in support of the center and in close coordination with other center partners.
- Determination of catalyst distribution (and Alane precursor).
- Characterization methodology is versatile and has qualified and quantified the efficiency of the dispersion of the catalysts.
- Reaction enthalpy calculations have been validated.
- Accurate and better prediction of reaction enthalpies in molecular solids by adding corrections.
- Demonstrated ability to quantify efficacy of ball-milling and mixing for dispersion of catalyst reversibility and starting phases.
- Integration with center activities.
- Accurate predictions of reaction enthalpies of destabilized reactions.
- None noted.
- Good experimental techniques. Good at asking important questions about the materials and driving toward some answers.
- The methods being developed under this project are capable of providing important insights into the structural and thermodynamic properties of candidate storage materials, and would serve as important screening tools for many investigators.
- The project benefits from theoretical input and seems to be driven by theory. The prediction of alloy phase diagrams is an asset to the program.

Weaknesses

- There are some limitations due to beam damage in “low-dose” STEM mode.
- The project is currently understaffed.
- None noted.
- Theory project seems to be irrelevant.
- Theory component does not seem as well advanced nor integrated nor as adept at asking the critical questions.
- The project's ability to ask critical questions has led to some improved understanding, but the next steps (from understanding to improvement to breakthrough) does not seem to have happened - yet.
- No significant weaknesses on which to comment.
- The record of publications is disappointing, particularly from the experimentalists.

Specific recommendations and additions or deletions to the work scope

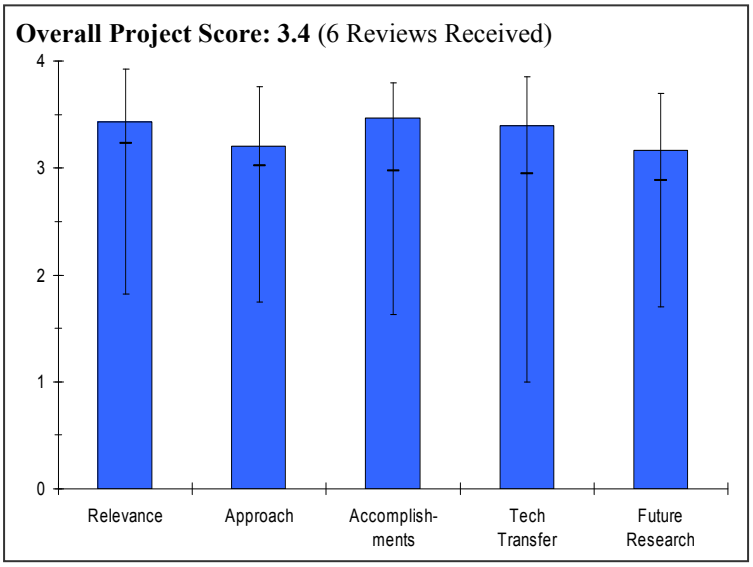
- Expand interaction with the Metal Hydride Center of Excellence efforts to help individual investigators screen the predicted properties of new materials under consideration.
- Given the strong contributions of the Georgia Tech/Pitt and Majzoub (U. Missouri) theory projects, it is recommended to eliminate this theory project and redirect efforts towards experiments.
- The dehydrogenated form of boron-based materials is usually a boride, and most borides have extended boron-boron networks that are absent in the hydrogenated form. The need to disrupt and re-form such boron-boron networks has to be a contributor to poor kinetics. Find a new way to mobilize boron atoms and facilitate the formation/disruption of boron-boron networks. Or find a boron-based material that doesn't need to have them.
- The PI’s should broaden the scope of their research. I do not see how more funding can enable the PI’s to be more innovative.
- Coordinate with the physisorption center . Plan for future work should be expanded to include characterization studies on promising physisorption materials; namely, such materials that take-up hydrogen via a spillover mechanism. Structural characterization relative to catalyst dispersion and interfacial region between catalyst and substrate in these materials is needed.

Project # ST-33: First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems
Karl Johnson, presenting; University of Pittsburgh, David Sholl, Georgia Tech

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project

The overall objectives of this project are to 1) compute the thermodynamics of metal hydride systems; 2) compute interfacial properties of hydrides; and 3) address fundamental processes in hydrogenation. Specific objectives for fiscal year 2007-2008 were to 1) develop an automated approach for screening complex hydrides by gravimetric densities and heats of reaction, ΔH; 2) explore nanoparticle thermodynamics through calculation of surface energies and Wulf construction calculations; 3) screen doped hydrides for phase stability; 4) compute surface reactions as relating to poisoning and initial kinetics of hydrogenation/dehydrogenation; and 5) investigate the structure and thermodynamics of $Mg(BH_4)_2$.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Highly relevant in that it can greatly reduce the experimental load in identifying new tests to do with higher chance of getting good thermodynamics and hydrogen capacity.
- This project addresses aspects of hydrogen storage that are crucially important to meeting the hydrogen vision and Department of Energy research and development objectives.
- Specifically, these computational studies greatly facilitate the screening of candidate hydrogen storage materials, thus simplifying and accelerating the process of selecting materials for development and testing.
- Computational prediction of effectiveness of solid state hydrogen storage materials.
- Clearly relevant.
- Theoretical work is focused on predicting high capacity reactions with suitable thermodynamics; this is exactly what theory is most useful for at this "materials discovery stage."
- The work is relevant to DOE objectives as it deals with predictive theory and directs experimentalist toward discovery of new materials.

Question 2: Approach to performing the research and development

This project was rated **3.2** on its approach.

- The team has a good approach and is doing all the right things. Could use more validation of modeling approach.
- DFT and temperature scan is a good a method as is known. Using libraries of functions calculated to make things more efficient is wise.
- Limiting to single step reactions is not appropriate and the movement to multi-step reactions is an improvement.
- Theoretical studies are based mainly on density functional theory methods; thermodynamic and interfacial properties are calculated.
- Reaction screening is a major focus of this work.
- Investigating nanoscale effects on the reaction thermodynamics of metal hydride particles.

- A creative application of computational methods for screening hydrogen storage materials limited to solids of known structure.
- Many of the predicted reactions, in particular those involving elemental carbon as a reactant, are clearly incorrect. Because of the large exothermic formation enthalpy of methane, all carbon will be converted to CH_4 as a first thermodynamic step in these reactions. Hence the proposed reactant combination is unstable, and for all practical purposes the hydrogen bound in CH_4 will be inaccessible at temperatures of realistic interest.
- Use of DFT to screen through many reactions is a good idea.
- The approach is focused on overcoming the barriers of high storage capacity at reasonable (de)hydriding conditions. The computational approach is built on the work of others (which the principal investigators credit adequately), and is an excellent use of theory to screen through a large number of candidate reactions.
- The PI is using standard codes and DFT-formalisms for the calculations. No new methodology is being developed.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.5** based on accomplishments.

- Addition of considering multi-step reactions correctly is a big improvement.
- The project scanned a huge number (millions) of discreet compositions and narrowed those of interest to dozens grouped by major chemical classes.
- Evaluated nanometer-sized particles for improved thermodynamics and only magnesium and sodium are better and then only at 3 nm or less.
- Millions of dehydriding reactions have been screened since inception of this project.
- The project has identified 43 single step reactions with greater than 6 weight percent H and dehydriding enthalpies in the 15 to 75 kJ/mol range.
- Several interesting multi-step reactions have been identified.
- The effect of particle size on dehydriding temperature and thus dehydriding thermodynamics has been elucidated.
- Excellent progress on a large-scale computational search for hydrogen storage materials - not previously published. Would like to see a more explicit indication of correspondence with experimental data.
- Good progress.
- Good use of the linear programming approach to predict new reactions; excellent discussion of the "caveats" associated with these predictions, and where they might go wrong. This is a very important, candid, discussion to have for the experimentalists.
- Screened millions of possible reactions along with studying nano-size effects through surface.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- Good tie-in with universities, national labs, and companies. There is no apparent corporate tie-in now that General Electric is no longer a center partner.
- Very good both within the center and outside the center, and more to the point is that there is two-way exchange of information.
- Many institutions within and outside the Metal Hydride Center of Excellence have taken direction from this project in formulating their work plans.
- This work has had major impacts on the choice of materials for study and on developing understanding of the dehydration of metals.
- The principal investigator and his team seem to be readily willing to make computations for systems proposed to them by other organizations where ongoing work can benefit from computational studies, e.g., planned computations on $Mg(B_{12}H_{12})$.
- Good collaborative work - particularly as stimulating experimental studies on the computationally predicted systems.
- Project seems to be well-connected to experimental efforts within the Metal Hydride Center of Excellence.

- Work seems to be well-connected within the center of excellence and obviously excites many of the experimental groups to test the predictions.
- The PI has worked very well with others in the center and the synergy between theory and experiment has been very good.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Continuing predictions for multi-step reactions is appropriate.
- The proposed contaminant work is also good.
- Plans to search for metastable/multi-step dehydriding reactions.
- Plans to continue work on dehydriding thermodynamics at the nanoscale.
- Plans to investigate the energetics and kinetics of surface reaction pathways involving poisoning agents, like H_2O and O_2.
- Hopefully, they will continue to be responsive to the community at large as interesting issues arise that theory may be able to address in a substantive way.
- Good future work plan shown. Suggest relating more to experimental data, even if it involves applying persuasive effort to experimentalists for acquiring it!
- The future plans are somewhat vague.
- The proposed future work is a bit weak. The discussion of the caveats associated with these predictions was really excellent, but the future work does not really provide a clear pathway to address these caveats. The future plans really look like largely a continuation of the activities, with no clear plans for where the future critical needs will come.
- The PI plans to continue work as before. The publications have been modest and no publications exist jointly with experiment.

Strengths and weaknesses

Strengths
- This is important work that should be funded.
- This is a strong team with good "bang-for-the-buck".
- Continuing upgrade of the theory and the mechanism of implementation is a major strength.
- The efficiency of the library method.
- Recognition of limits of technique.
- Scholarly, enthusiastic, collegial principal investigator.
- Very effective and extensive collaborations.
- This project is saving the metal hydride program lots of time and effort.
- Automated approach for screening complex metal hydrides and understanding their phase-stability.

Weaknesses
- There are no obvious weaknesses.
- Calculations of properties of nano-particles through consideration of surface energies and Wulf construction may not be valid for small nano-particles. Effect of detailed surface structure is important.
- Lack of inclusion of hydrogen carbon products in the thermodynamic database may lead to incorrect conclusions.

Specific recommendations and additions or deletions to the work scope

- More tie-in to experimental work.
- Keep up the good work.
- The first priority for future work should be inclusion of CH_4 into the thermodynamics database.
- The database of phases should be periodically updated so that the proposed reactions can be re-assessed. This will aid in the accuracy of the predictions.
- The PI should be critical of using standard techniques for nano-particles.

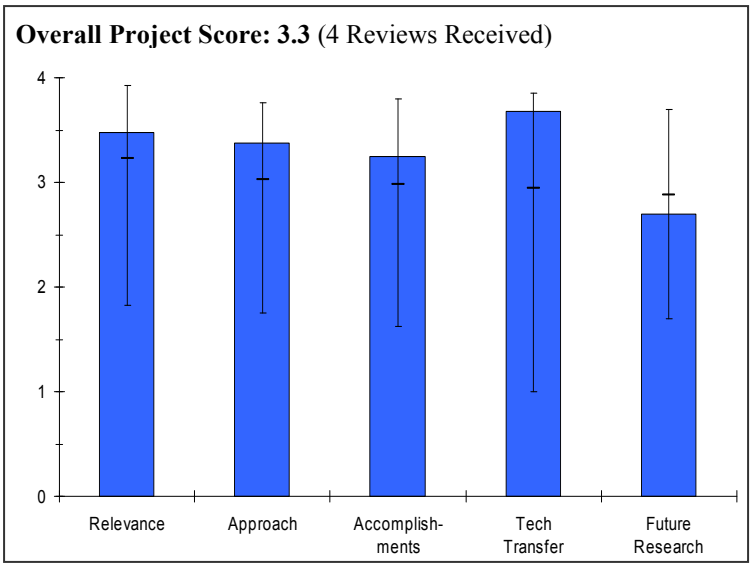
Project # ST-34: Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

Bob Bowman; NASA Jet Propulsion Laboratory

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project

The overall objective of this project is to develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage.
The Jet Propulsion Laboratory objectives are to 1) validate storage properties and reversibility in light element hydrides including: a) nanophase, destabilized hydrides based upon LiH, MgH_2, and $LiBH_4$; b) complex hydrides (e.g., amides/imides, borohydrides, and AlH_3-based hydrides); and c) samples provided by numerous Metal Hydride Center of Excellence partners; and 2) support developing lighter weight and thermally efficient hydride storage vessels.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- The principal investigator employs a valuable analytical technique [nuclear magnetic resonance (NMR)] to assist metal hydride center partners in characterizing new materials. The principal investigator's experience, knowledge and lab skills are clearly a benefit to the whole center.
- The project addresses fundamental aspects of hydrogen storage.
- As a general service to the Metal Hydride Center of Excellence members and their project groups, this particular project indirectly supports the Department of Energy objectives to the high extent the center of excellence itself does.
- Very relevant to DOE objectives. Finally someone is sorting out the chemical species that participate in, and perhaps disrupt the desired pathways of, hydrogenation/dehydrogenation.

Question 2: Approach to performing the research and development

This project was rated **3.4** on its approach.

- NMR is a valuable technique to characterize amorphous type materials (many of the materials studied in the metal hydride center are amorphous rather than crystalline in structure). Even crystalline materials may begin to exhibit amorphous characteristics after cycling or other undergoing other stresses. The NMR technique should better help researchers to understand these mechanisms and design more robust materials with improved capacity.
- Systematic approach is effective.
- This project provides much needed services to all five project groups of the Metal Hydride Center of Excellence: (A) Destabilized Hydrides, (B) Complex Ionic Materials, (C) Amides-Imides, (D) Alane, (E) Engineering Analyses and Design.

- The main support effort is in the specialty field of NMR, valuable for understanding hydrogen-bonding, phase content, and reaction pathways. The principal investigator is a high-level expert in this field and has access to valuable NMR equipment and services.
- The other principal area of center of excellence contribution is hydride container design, evaluation and modeling, very useful to Project Group E.
- Done right, NMR is a magnificent method for identifying chemical constituents that elude diffraction and other means.
- Identification is only a part of the battle, who is going to use effectively this identification?

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.3** based on accomplishments.

- The principal investigator's work has been crucial to the identification and understanding of $B_{12}H_{12}$ intermediate kinetically inhibited compounds in the cycling of borohydride based materials. The mechanism of this intermediate step must be understood in order to overcome many of the cycling issues currently associated with boron-based materials.
- An overview of state-of-the-art of storage systems is important.
- The identification of $B_{12}H_{12}$ as a key intermediate is significant.
- During the relatively short time this project has existed, a large quantity of new data has been generated on a variety of storage media.
- The extensive NMR data obtained has added to the fundamental understanding of most of the materials being developed within the center of excellence. For one example, it has been useful in phase identification of amorphous species (not amenable to XRD or Neutron Diffraction study) and reaction pathways.
- The confirmation that $B_{12}H_{12}$ is an intermediate in the decomposition of borohydrides may help to set the directions for the development of practical reversibility of same.
- The Metal Hydride Storage Survey Report will be useful when it is completed.
- The container modeling effort is new, but it is not yet clear what it will add to other DOE-supported efforts or other similar worldwide efforts.
- Identifying $[B_{12}H_{12}]^{-2}$ as a borohydride dehydrogenation product is an important accomplishment and identifying different M-BH_4 entities will prove to be useful in understanding dehydrogenation of mixed-metal borohydrides.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.7** for technology transfer and collaboration.

- The principal investigator clearly communicates with nearly every other principal investigator in the Metal Hydride Center of Excellence.
- The project has collaborations across the Metal Hydride Center of Excellence.
- The project provides important characterization to significant number of center of excellence members, as well as to other researchers.
- The collaborations within the center of excellence and outside are outstanding. Information is getting transferred.
- Publications are quickly getting out to the public.
- Project appears to be collaborating and cooperating well with a number of the Metal Hydride Center of Excellence partner institutions.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.7** for proposed future work.

- Continue work and continue to offer characterization techniques to the center as a whole.
- Both the relevance and approach are good.

- Given that the principal investigator is leaving, the future work is in doubt.
- Future work follows along the same directions as the recent past.
- Many things are being worked on at once. Some down-selection may be necessary as other center of excellence projects may falter.
- The principal investigator is soon to "retire."
- Hydride-bed design: This work appears to be useful, but not as essential as understanding how the hydriding/dehydriding material chemistry is happening, and how to improve it.

Strengths and weaknesses

Strengths
- Excellent technique for characterizing amorphous type materials.
- Project offers a means of characterization which is independent on material morphology.
- Project offers support to all center of excellence researchers.
- Provides a much-needed and powerful NMR service.
- Works well as a service within the Metal Hydride Center of Excellence.
- The NMR studies, and the discoveries thereby enabled, are extremely important. Keep this capability!

Weaknesses
- The project is not incorporated in upfront strategy of the center.
- Technique is limited to NMR active nuclei.
- It is difficult to do in situ characterization.
- The project does not seem to be fully integrated with other projects aimed at exploiting the chemical reaction discoveries.

Specific recommendations and additions or deletions to the work scope

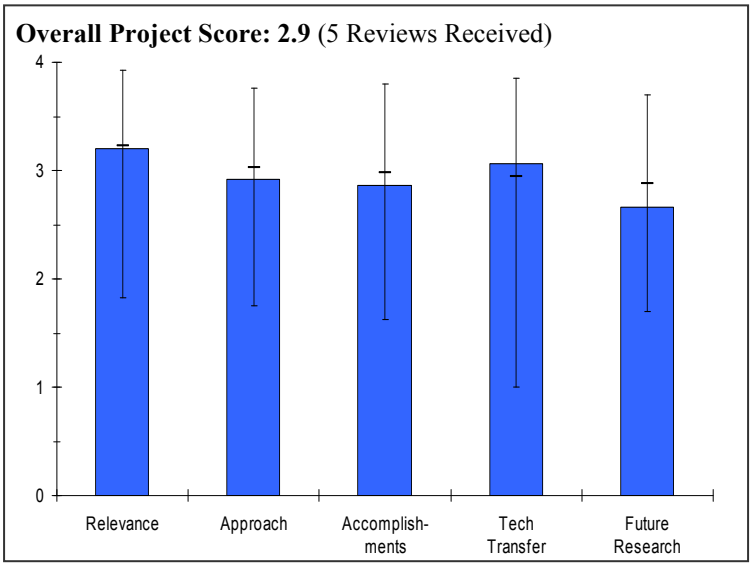
- Perhaps the center could incorporate the principal investigator in upfront discussions about material strategies, etc.
- The project should be prepared to abandon any materials that do not show promise.
- Leave a time slot for possible new materials that are suddenly discovered.
- Consider offering NMR services to the other centers of excellence.
- Be prepared to transfer the engineering services to the Engineering Center of Excellence, if and when it is established.
- Send the bed-design scope to another project. Add more solid-state boron chemistry to the scope of this project.

Project # ST-35: Complex Hydrides for Hydrogen Storage Studies of the $Al(BH_4)_3$ System
Gilbert Brown; Oak Ridge National Laboratory (ORNL)

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project

The overall objective for this project is to develop the chemistry for a reversible hydrogen storage system based on borohydrides, amides/imides, alane, and the light alanates. Target materials and processes are 1) complex anionic materials (Metal Hydride Center of Excellence [MHCoE] Project B); 2) amide/imide (M-N-H) systems (MHCoE Project C); and 3) regeneration of alane (MHCoE Project D). The Oak Ridge National Laboratory goal is to employ solvent-based procedures appropriate for scale-up to production and practical application with a focus on high hydrogen content materials (>10 wt% hydrogen).



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- The materials studied are those given a "go" by the go/no-go decision.
- The project is very relevant.
- The project covers the correct area of materials but unclear what they really intend to do.
- The project is relevant in that it is investigating fundamentals of hydrogen storage materials. However, there seems to be a lack of focus or urgency.
- Discovery of new ways to utilize aluminum-borohydride and aluminum-hydrides is relevant to the Department of Energy objectives as these materials are hydrogen-rich compounds.

Question 2: Approach to performing the research and development

This project was rated **2.9** on its approach.

- To understand the reaction mechanism is critical to explore novel materials and to improve performance of existing materials.
- The project focuses on technical barriers.
- The strong chemical component is a plus.
- The approach or plan is fairly obscure, they will use schlenk lines to make materials and test it, but the actual chemical approach or guiding principles were not at all clear.
- The projected seems very curiosity driven. No energy analyses were performed to see if they are technically feasible.
- The presenter demonstrated a very good approach and new ways towards overcoming diborane gas formation from aluminum-borane.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.9** based on accomplishments.

- The reaction mechanism of $Al(BH_4)_3$ and $Mg(BH_4)_2$ has been clarified.
- Good progress.
- Interesting experimental results.
- I am not sure that Al_3Ti is the true catalyst; what happens to Ti-H compounds, which may form as intermediates?
- B_2H_6 often forms during thermal decomposition of metal borohydrides (shown by VV. Volkov et al.).
- Looked at $Al(BH_4)_3$ and confirmed previous results of large B_2H_6 formation and extended to various temperatures.
- Initial work on ammonia adduct of the aluminum borohydride seems to have less diborane.
- Claim that B_2H_6 is inherent but the method and evidence was very sketchy at best. They may well be right but they have assuredly not proven it!
- Suggestion that hydrogen pressure suppresses diborane has been known for some 4 years.
- Progress is slow and all over the map. They need to focus and use energy analysis to guide activities. The work seems very preliminary and more suited for Basic Energy Sciences.
- Remarkable progress in understanding mechanisms and materials performance needs.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- This work is carried out in the network of the Metal Hydride Center of Excellence.
- Good collaboration with DOE partners.
- Collaborating well and in fact much of the value in what was presented was from partners however it is not clear that partners are benefiting though!
- The collaborative aspects are not apparent in the presentation.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.7** for proposed future work.

- The future plan presented is not clear about the research targets.
- Future work is well defined.
- Probably suitable but the plan again is not clear.
- Future work plans were not very clear.
- Understanding intermediate steps towards decomposition is a very good proposal.

Strengths and weaknesses

Strengths
- The reaction mechanism of borides has been analyzed experimentally.
- The advantage of expertise in handling air/moisture sensitive materials is well utilized for the activities of the Metal Hydride Center of Excellence.
- Very solid experimental work.
- Good understanding of chemistry involved.
- Good lab technique.
- Very good synthetic approach.
- Devising methodologies to allow for $Al(BH_4)_3$ utilization by mitigating B_2H_6 formation.

Weaknesses
- The mechanism analysis did not show the research direction for material development. Suggestions and proposals for other material scientists are highly recommended.
- An additional theoretical component may be a plus.
- The project seems to be just wandering around looking for something to do, there seems no underlying plan or understanding.

- Presentation probably obscured what progress and understanding they have.
- It was not clear they are up to date on the literature.
- By this time the project should have settled on something to go with. It is still at very preliminary stages.
- Insufficient interactions with theory group.

Specific recommendations and additions or deletions to the work scope

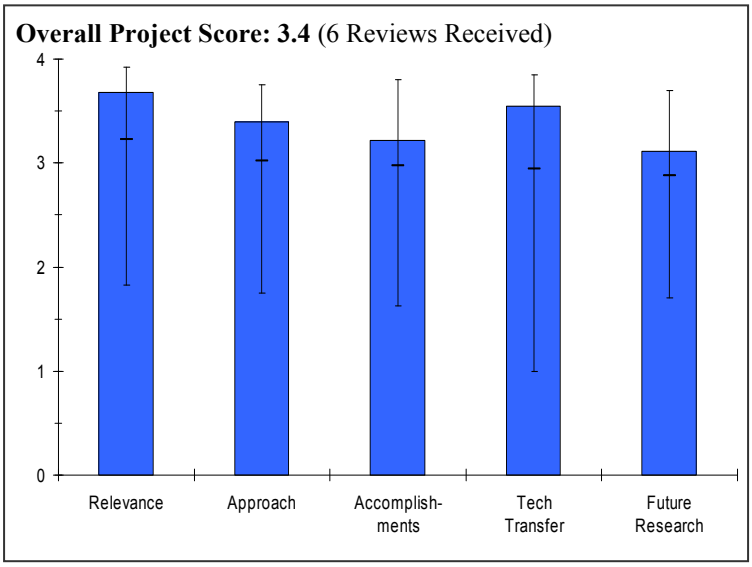
- The results of the mechanism should be transferred to the scientists who explore novel hydrogen storage materials.
- The PI needs to develop a clear plan and direction.
- The project should choose a system and go with it.
- Definitely keep the project.
- For the AlB_4H_{11} compound decomposition, diborane formation needs to be tracked and checked.
- Collaboration with the theory group within the Metal Hydride Center of Excellence is recommended.
- Close collaboration with the alane reversibility groups is also recommended.

Project # ST-36: Discovery and Development of Metal Hydrides for Reversible On-Board Storage
Ewa Ronnebro; Sandia National Laboratory-Livermore

[NOTE: This review is for Sandia's technical contribution to the MHCoE.]

Brief Summary of Project

The primary objective of this project is to discover new complex hydride materials. The experimental objective is to establish a synthesis route that combines high-energy milling followed by hot-sintering under high H_2-pressures. A new start as of July 1, 2007 was work on improving kinetics, cycling life and desorption properties by incorporation of hydride materials in nanoframeworks. The theory objectives are to 1) employ the Prototype Electrostatic Ground State technique for structure determination and ΔH estimates to provide Metal Hydride Center of Excellence partners with theoretical support regarding Al-N bond energies for AlH_3.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.7** for its relevance to DOE objectives.

- This project is very important for the Hydrogen Fuel Initiative and fully supports Department of Energy objectives.
- Efforts to synthesize new borohydride related materials for hydrogen storage supports the DOE's objectives.
- Discovery of metal hydrides which are reversible (moderate ΔH) is an important activity and relevant to the DOE targets.
- This project is clearly relevant.
- There is a correct focus on high capacity materials.

Question 2: Approach to performing the research and development

This project was rated **3.4** on its approach.

- The project focuses on new materials and barriers.
- There is a good combination of theory and experiment.
- The principal investigator has several well designed projects that are integrated with other research going on with partnering institutions in the Metal Hydride Center of Excellence. These efforts utilize the strengths of each institution.
- The principal investigator presents more than adequate experience to perform the proposed research.
- It is likely that the characterizations of $Ca(BH_4)_2$ will be completed and that nanoengineering will improve the hydrogen storage properties of these new materials.
- Some activities have been terminated. To try new material based on new ideas is quite important for finding better hydrogen storage materials. No-go decisions do not indicate a poor job.
- The presenter demonstrated good integration between theory and experiment which is well guiding their discovery work.
- The PEGS approach is promising.
- There is a nice connection between theory and experiment.
- The project address kinetics and reversibility.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Significant progress in 2007 and 2008.
- The regeneration mechanism for $Ca(BH_4)_2$ still requires explanation.
- Group reports interesting research on multi-metal systems, which have limited applications potential.
- The principal investigator has made significant progress towards the objectives of synthesizing new hydrogen storage materials.
- Reversible re-hydriding for $Ca(BH_4)_2$ system with an additive is an outstanding result in this field which may solve the reversibility problem in complex metal hydrides, although the present results do not achieve the DOE 2010 target.
- Enhancements of the kinetic performance of $Ca(BH_4)_2$ with additives is interesting.
- Utilizing the PEGS modeling to discover a potential alane adduct is a good effort.
- There have been no breakthroughs experimentally. It appears that only modest progress has been made on $Ca(BH_4)_2$ after more than a year's worth of effort. Disappointing that the enthalpy for $Ca(BH_4)_2$ has yet to be measured by experiment.
- Theory work seems to be the headliner.
- Experiment: $Ca(BH_4)_2$ has been shown to be reversible. Reversibility optimized with several additives.
- Theory: Numerous useful predictions that are being verified by experimentalists.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.6** for technology transfer and collaboration.

- Good collaboration that includes international collaboration.
- The collaborations and interactions with other the Metal Hydride Center of Excellence partners are excellent and ongoing.
- The presenter showed very good collaboration with others for $Ca(BH_4)_2$ (i.e. discovery of the polymorphs).
- Its advisable for the modeling to have a closer collaboration with the experimental Brookhaven National Laboratory group working on alane adducts.
- Good job with collaboration.
- This is a well coordinated effort. Numerous useful collaborations.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Insufficient details about future work were presented.
- It is not clear how the nanoframeworks will be created.
- What are alternative "nanostructured metal hydrides"?
- The principal investigator has several projects planned for the future that involve additional studies on borohydrides, nanoengineering and continued collaboration with the theory group.
- The research should continue as planned.
- Fundamental studies for kinetics and reaction mechanism (rate determining step) of $Ca(BH_4)_2$ system is required to judge its practicality for a hydrogen storage tank. Its cycle life is also important to know its practicality, but it is the second priority.
- Emphasis on the kinetic enhancement for $Ca(BH_4)_2$ is very important.
- Will $Mg(BH_4)_2$ be explored experimentally?
- Future work is based on prior results.

Strengths and weaknesses

Strengths
- Good experimental work.
- Good combination of theory and experiments.
- Good collaboration.
- The principal investigator has access to all the equipment and financial resources needed to complete the proposed work.
- Intimate collaboration between the experimental group and the computational group.
- Experience in synthesis of complex hydrides and their analysis.
- $Ca(BH_4)_2$ is an illustration of excellent interaction between theory and experiments.
- Enhancement of kinetics with different additives for $Ca(BH_4)_2$ is a very good progress.
- Good connection between theory and experiment.
- Thorough analysis of results obtained to date.
- Right decision-making about what to pursue and what not to pursue.
- Excellent coupling with theory.
- Strong publication record.

Weaknesses
- The project has somewhat slowed down compared to the previous year.
- New materials ideas are needed.
- Collaboration with industry is still insufficient.
- None noted.
- Interactions with the group working on alane synthesis and reversibility.
- The high throughput screening facility is not functional and therefore could not be used for combinatorial work.
- Vaguely stated "alternative nanostructuring." What would be the alternative(s)?

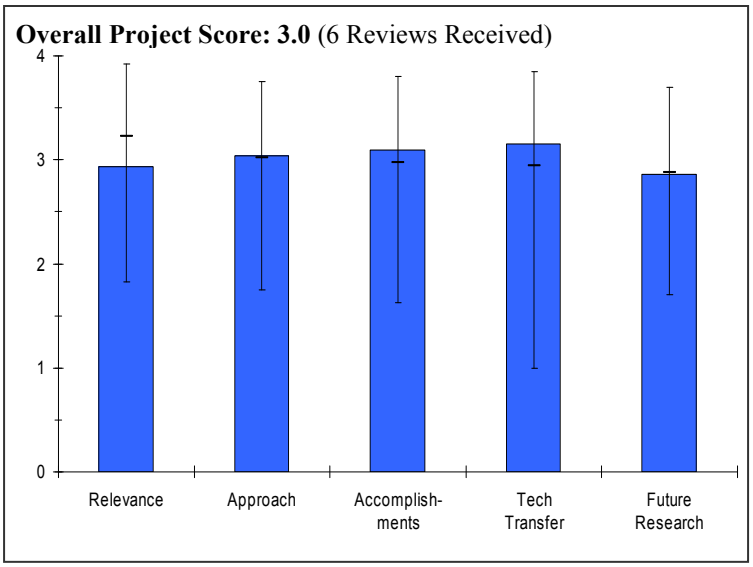
Specific recommendations and additions or deletions to the work scope

- Definitely keep the project.
- Incorporate experimental comparison of thermodynamic stability of $Ca(BH_4)_2$ polymorphs to validate theoretical predictions.
- Incorporation of materials inside nanostructures could lower the gravimetric and the volumetric capacities and therefore it is suggested to have this addressed as the frameworks are researched.
- None.

Project # ST-37: Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

Dhanesh Chandra; University of Nevada-Reno

NOTE: This project is part of the Metal Hydride Center of Excellence.



Brief Summary of Project

The primary objective of the project is to determine the effects of gaseous trace impurities such as O_2, CO, H_2O, CH_4, etc. in H_2 on long-term behavior of the complex hydrides/precursors by pressure cycling and/or thermal aging with impure H_2. Secondary related objectives are 1) vaporization behavior of hydrides; and 2) crystal structure studies. Earlier objectives have included 1) construct high pressure (up to 100 bar) cycling equipment; 2) perform hydrogen cycling studies on amide-imide and mixed alanates; 3) initiate vapor pressure behavior of Li_3N and $Mg(BH_4)_2$.; and 4) perform HP DSC experiments, in situ neutron, and X-ray diffraction studies. Objectives for 2007 and 2008 (May 15, 2007 – April 1, 2008) have been to perform thermodynamic and crystal structure studies.

Question 1: Relevance to overall DOE objectives

This project earned a score of **2.9** for its relevance to DOE objectives.

- The project addresses issues of storage material degradation.
- The material studied is problematic when it is unclear which material will find future applicability.
- The project is aligned with hydrogen vision Department of Energy research and development objectives.
- The objective to determine the effects of gaseous impurities in hydrogen is essential on long-term behavior of hydrides/precursors.
- The project is relevant to DOE goals.
- It is not clear whether this should be done when there is still a need for better and new materials that may be susceptible to other impurities.
- Although this project itself contributes little to the improvement of hydrogen capacity of materials, durability against impurities and loss of materials by vaporization are important to estimate "practical" capacity over the life time of the tank using the materials.
- The scope of work for this project addresses several important aspects of hydrogen storage material behavior that are well aligned with the hydrogen vision and DOE research, development and deployment objectives.
- This project specifically addresses impurity effects on storage material performance and cycle life issues.
- The effects of trace impurities on the long-term performance of candidate storage materials is an important aspect of the program that should be investigated judiciously using standard practices.
- The choice of complex hydrides for study should be selected among materials that have a reasonable chance of meeting the thermodynamic targets.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- The approach is reasonable.
- A larger number of different materials should be studied.

- The approach of the project is focused.
- The approach is uniquely addressed using Knudsen Torsion Effusion Method.
- The project adequately addresses targeted technical barriers and demonstrates technical feasibility.
- The effects of trace impurities on the stability and cyclability of metal hydride storage materials are being investigated.
- Vaporization thermodynamics are studied at moderate temperatures.
- The long-term behavior of metal hydrides and their precursors during pressure cycling and thermal aging are tested.
- In situ phase transformations are studied by high-resolution x-ray diffraction.
- Analytical approaches are excellent, but choice of candidate materials is not compatible with thermodynamic targets. For example, while the theoretical capacities of amide-imide and amide-alanates are high, the desorption temperatures are unrealistic relative to the targets. Hence, detailed impurity studies for these systems seem moot.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- Identification of O_2 as a major impurity is important.
- More materials need to be addressed.
- Significant progress was made in addressing the effect of impurities in hydrogen.
- Progress is good. The project demonstrated effect of common contaminants on hydrogen sorption and desorption properties.
- The durability against impurities obtained in this project is instructive to the research and development of similar hydrogen storage material, although the materials tested do not meet the DOE target.
- Lots of testing and measurements were performed in the past year.
- The effect of gaseous impurities on Li_2NH-$LiNH_2$ cycling properties was determined.
- The vaporization behavior of $Mg(BH_4)_2$ was studied.
- Phase transformations in $Ca(BH_4)_2$ were investigated by synchrotron x-ray diffraction.
- Technical accomplishments for the materials selected for study is excellent.
- Further progress could be made on materials exhibiting more promising thermodynamic properties than those selected up to this point in the project.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.1** for technology transfer and collaboration.

- There is collaboration with some center of excellence researchers.
- Collaboration with more researchers would provide access to more/different materials.
- Some coordination with partners exists.
- Good collaboration with ESRF, Grenoble, and Sandia National Laboratories.
- Technology transfer appears weak. Are the results being applied?
- The information coming from this work answers many of the kinds of questions that have been raised in prior merit reviews.
- The breadth and the nature of collaborations are obvious and impressive.
- This research impacts many of the other research projects conducted under the umbrella of the Metal Hydride Center of Excellence.
- The principal investigator has established and planned broad collaborations with other investigators, particularly in the area of theory.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- The scope of future work is good.
- The next stage of where to go with this work is not clear.
- The project is lacking in optional paths.

- The plans are built on past progress.
- Addressing phase diagram determination of mixed complex hydride will be useful but may take away from the main program.
- This project is still very academic. Where is the technology transfer?
- Influence of impurities to the materials studied in the Metal Hydride Center of Excellence is predicted.
- The proposed future work (Slide 17) is very ambitious; it extends in a logical way and expands upon the fiscal year 2008 accomplishments.
- Several new types of measurements (neutron diffraction, differential scanning calorimetry, phase diagram determinations) are in the future plans.
- Broadening of the collaboration profile to include International Energy Administration [Hydrogen Implementing Agreement] and the International Partnership for the Hydrogen Economy inspired interactions is also planned.
- The principal investigator has made reference to "other" borohydrides for future studies. These undefined systems should be selected judiciously relative to thermodynamic targets.

Strengths and weaknesses

Strengths
- Addressing the effects of impurities on materials will be important in the future.
- The principal investigator is well suited to address the problems stated in the project.
- The project contains good science and well designed experiments.
- Cycle durability of reversible hydrogen storage material can be tested with impurity under practical conditions.
- The principal investigator seems very knowledgeable and most aggressive in tackling the impurity, cycling, and aging issues.
- The cadre of tools being employed in this work provides the flexibility to study a broad range of issues; some of the research involves state-of-the-art measurements at neutron and synchrotron x-ray sources.
- The project team has access to excellent sources of well characterized materials to examine through its participation in the Metal Hydride Center of Excellence.
- Project has the potential to provide much-needed data on the stability of candidate storage materials when exposed to real-world levels of common gas impurities.

Weaknesses
- The type and number of materials studied for impurities effects should be broadened to better cover future possibilities.
- It is difficult to study the effects of impurities on storage materials, when the type of storage material which will ultimately find merit is as yet unknown.
- Future plans are too ambitious.
- The project is academic in that it is not connected to the end user.
- There are no obvious weaknesses.
- Evaluation of the effects of gas impurities on storage materials with sorption-temperatures within practical ranges has not been achieved.

Specific recommendations and additions or deletions to the work scope

- Further studies (e.g., cycling, impurities, and thermodynamics of vaporization) on $LiBH_4$ should be abandoned since the sorption temperature for this system is much too remote from the targets.
- Impurity studies in the future should focus on materials exhibiting sorption temperatures at or near practical targets.
- Add some customer input.
- Keep up the good work but don't out stretch your resources.
- Try to resolve lingering uncertainties in some of the results (like in the $H_2 + O_2$ versus $H_2 + H_2O$ results) as discussed during the question period.
- Abandon further work on pure $LiBH_4$ and $Mg(BH_4)_2$.
- Conduct impurity studies on the LiMgN system, which has been shown to be reversible at temperatures slightly below 200°C.

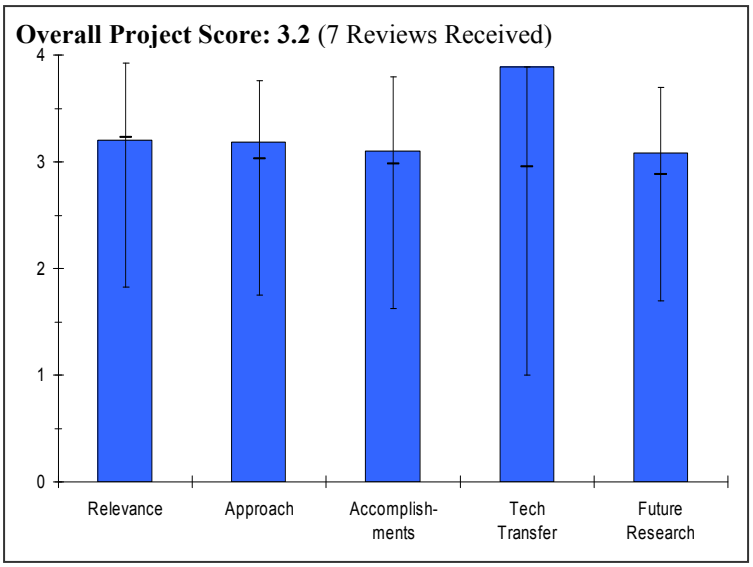
Project # ST-38: Fundamental Studies of Advanced High-Capacity Reversible Metal Hydrides/ Recharging of Light Metal Hydrides Through Supercritical Fluid Hydrogenation

Craig Jensen, presenting; University of Hawaii, Sean McGrady, University of New Brunswick, Canada, Co-PI

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project

The objectives of this project are to 1) develop new materials with potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets such as novel borohydrides that can be reversibly dehydrogenated at low temperatures and Al and Mg nano-confined in carbon aerogels; and 2) develop a method for the hydrogenation of Al to alane, AlH_3 at moderate pressures in hydrogen containing supercritical fluids.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- This program is highly relevant to the Department of Energy Hydrogen Storage Program.
- This project is concerned with novel, reversible metal hydrides with the potential to meet 2010 DOE targets with respect to hydrogen storage.
- Aluminum and magnesium nano particles in aerogels, transition metal borohydride complex, hydrogenation and reaction catalysts, and alanes are the materials of interest.
- This program has the wide capability to synthesize and characterize these materials.
- This capability is highly relevant to the DOE objectives.
- A novel effort concerns the synthesis of alane (AlH_3) and Mg alanate in supercritical fluids.
- The project is well aligned with the hydrogen vision addressing key issues for overcoming some of the main barriers.
- The project objectives are dynamic and flexible enough to continuously remain of high relevance to DOE research and development strategy, as demonstrated by the down-selection performed and the inclusion of a new promising research area in this project on alane regeneration with supercritical fluids.
- This project is clearly contributing to, and is in good agreement with, DOE's goals.
- The project is aligned with the hydrogen vision and research and development.
- The objective to develop new material to meet DOE 2010 system gravimetric capacity and kinetic targets is essential.
- Both objectives address key problems in promising routes to storage.
- Work is scattered among many subjects, some of which are not really relevant to the Hydrogen Fuel Initiative (e.g., LiSc-borohydride which may be a good ion conductor, but is irrelevant to the Hydrogen Fuel Initiative simply because of the cost of scandium).

Question 2: Approach to performing the research and development

This project was rated **3.2** on its approach.

- The approach is highly scientific and professional.
- The reduction of borane contamination in the decomposition of anionic borohydride is an objective of the program.

- Efforts to improve reversibility of borohydrides are also addressed.
- Borohydride reaction products are characterized by panoply of techniques.
- Various supercritical fluids are of interest for synthesis reactions under relatively mild conditions.
- A rather well-focused approach, with set milestones and decision points, is employed. This is valid for both the novel borohydrides discovery subproject and for the development of a hydrogenation method of aluminum to alane, at moderate pressures in hydrogen containing supercritical fluids.
- There are at least three distinct projects underway, each of which is well-designed and integrated with research going on at partner institutions within the Metal Hydride Center of Excellence.
- The approach to develop new materials is sharply focused.
- The program's neat organometallic approach to achieve high loadings of carbon aerogels is unique.
- Another unique approach employed is hydrogenation of aluminum in supercritical media.
- Supercritical method is unique and worth trying.
- Confinement is known but a good approach.
- The use of ions to change stability makes sense.
- Synthesis of AlH_3 under mild condition is strongly expected to improve energy efficiency of its off-board rehydrogenation path.
- A whole slew of borohydrides is being synthesized but sometimes without enough rationale. For example, it is not clear why these syntheses are relevant and which barriers they are addressing.
- Actual syntheses have not been described in enough detail to determine whether or not they are geared towards addressing any of the technical barriers.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- $Na_2Zr(BH_4)_6$ has undergone decomposition up to 110°C with no detectable B_2H_6 contamination.
- The structure of $LiSc(BH_4)_4$ was determined.
- The reaction MBx - $M(BH_4)x$ was found to be reversible at 1000 atm and 230°C.
- High loadings of magnesium in carbon aerogel were achieved.
- Initial supercritical syntheses indicated the presence of small amounts of alane produce from aluminum.
- The project is making excellent use of powerful experimental techniques and of its collaborations with expert groups in the field. As a result, sound progress is being made toward objectives.
- A particularly interesting result is the confirmation that there are low levels of diborane contamination as hydrogen evolves from anionic borohydride complexes, at relevant temperatures for operation.
- The work with supercritical fluids is innovative and very interesting and could offer new ways for improving the thermodynamics of the system.
- It is noteworthy that some new reversible borohydride materials have been identified and that a new method for rehydrogenating [spent] alane has been identified.
- Excellent progress has been made as evidenced by publications and invited presentations.
- Mixed transition metal BH_4 complexes have been shown to desorb hydrogen with no B_2H_6 loss and at low desorption temperatures.
- A good lithium ion conductor was found in the bargain.
- The program was able to get magnesium into carbon aerogel.
- The project was able to make surface hydrogenated aluminum using supercritical fluids.
- Synthesis in supercritical fluids has been demonstrated as a promising technique for AlH_3 production.
- Work on alane in supercritical CO_2 is positive. If alane may be synthesized this way in high yields this would present a much needed breakthrough.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.9** for technology transfer and collaboration.

- This program has extensive collaborations both within and outside the Metal Hydride Center of Excellence.
- A total of 10 refereed publications over the period 2007 to 2008 have been produced.

- Similarly a total of 14 invited presentations were given.
- Technology transfer with members of the Metal Hydride Center of Excellence as well as industry should be improved.
- Impressive lengthy list of strong collaborators including international experts in the field. Such interactions really reinforce the project and return high value for money.
- The degree of interaction and collaboration with other institutions is outstanding.
- Impressive collaborations with the center of excellence and other institutions.
- Good connections to many groups with mutual benefits.
- The project is conducted with interaction of the International Partnership for the Hydrogen Economy countries as well as the laboratories of the Metal Hydride Center of Excellence.
- A highly collaborative work.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Borohydride calorimetric studies are planned.
- Collaboration with Sandia National Laboratory (Ronnebro) in the dehydrogenation of borohydrides is planned.
- The effects of catalyst compositions upon borohydride reactions will also receive attention.
- The effect of aerogels upon the enthalpy and reaction kinetics will be addressed.
- The exploitation of the properties supercritical fluids for synthesis of alane and magnesium alanate will continue.
- Solid future plans, building on past experience and taking the research steps forward. There may be too many areas to cover now given the resources available and the time left.
- Looking forward to hearing more next year about the collaborative discovery with Sandia National Laboratories on the reversibility achieved for one compound through high pressure experiments (patent pending).
- The work planned for the future with partner institutions is well thought out and feasible.
- Continue the work as planned.
- Plans are clearly built on past progress.
- The project focus seems diversified.
- Future plans seem suitable. Preference would be for more clarity of plan rather than general area of work.
- Strategy for improvement of AlH_3 yield is not clear. Fundamental study of the behavior of AlH_3 and etc. in supercritical fluids is required.
- There is no contingency planning.
- No go/no-go decision points are foreseen.

Strengths and weaknesses

Strengths

- A very strong scientific effort.
- The resources appear adequate.
- The technology transfer is outstanding.
- The use of supercritical fluids for synthesis of metal hydrides is very innovative and should be vigorously pursued.
- The principal investigator's expertise in the field is a strength. He has a strong team and a well-organized, consolidated network of collaborators.
- The large number of partnering institutions adds strength to the project.
- The principal investigator is well suited to address the problems stated in the project.
- This is the best presentation of their work that this reviewer has seen.
- An interesting, new approach that there is reason from industrial practice to think that it could work.
- Strong team.
- International cooperation is actively conducted.
- The project leader has much experience in organometallic, organic, and inorganic chemistry.
- The project is broad in scope.
- Innovative approaches, especially for the synthesis of alane.

Weaknesses

- The prospects of borohydrides meeting the 2010 targets are dim.
- Similarly dim are magnesium intercalated carbon aerogels.
- Rather ambitious future plans - probably too many areas to cover given the available resources.
- None noted.
- Focus is too diversified.
- The project falls out of focus with so many subjects and research avenues.
- There is not enough concentration on the promising candidate materials, except for work on alane.

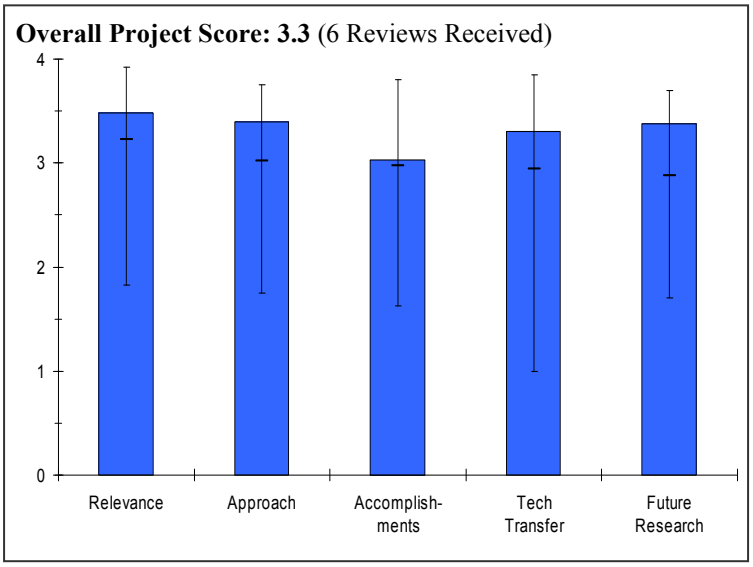
Specific recommendations and additions or deletions to the work scope

- The items discussed under "Project Weaknesses" should be addressed.
- The DOE time is short, thus, the following should be addressed: reversibility, cost, kinetics, storage capacity at 298K, and cycle stability.
- The above likely requires that a specific material be chosen.
- The program should increase the effort on super critical fluids even if it decreases the effort in other areas.
- It is recommended that it would really be good to do some sort of thermodynamics to show there is sufficient energy in the process to actually accomplish the regeneration of aluminum to alane.
- Identify the most promising research avenues and concentrate the efforts there.
- This program would benefit from an analysis of the energetics. What sort of energy must the supercritical process provide into the aluminum to make alane and compare that to what can be provided (at reasonable energy input required to generate the supercritical fluid).
- Likewise it would be good to see some more quantified analysis of the use of ionicity to alter the stability, and perhaps a ranking of logical ions to try based on that theory.
- There is no need to continue work on pure magnesium in aerogels. This may be relevant for basic science but has little relevance to the Office of Energy Efficiency and Renewable Energy mission.
- Focus and expand the effort on improving yields of alane.
- Establish quantitative go/no-go targets, especially with regard to improved yields of alane. If 10 percent or more conversion can be shown, then pursue further improvements with vigor.

Project # ST-39: Aluminum Hydride Regeneration
Jason Graetz, PI, presenting, Jim Wegrzyn, co-PI; Brookhaven National Laboratory

NOTE: This project is part of the Metal Hydride Center of Excellence.

Brief Summary of Project



The overall objective of the project is to develop a material that supports the 2010 DOE technical performance targets using aluminum hydride (AlH_3), by fully elucidating the nature of hydrogen desorption from AlH_3 and developing an efficient regeneration method. Objectives are to 1) develop new routes to prepare pure crystalline α-AlH_3 from Al (spent fuel) with minimal energy cost; and 2) assist the engineering design for an off-board system based on AlH_3. The challenge is that AlH_3 is thermodynamically unstable below 7 kbar (at 300K). In an AlH_3 system H_2 evolution is controlled by temperature (rather than pressure) so the ability to tune decomposition kinetics will be critical. Various routes exist to adjust kinetics (e.g. size, coatings and catalysts). The key issue is regeneration (hydrogenation of Al metal), and multiple regeneration pathways are being investigated.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Very relevant and timely project, clearly addressing the goals of the Hydrogen Program.
- The project is exploring possibilities for new cost-effective and energetically efficient methods to regenerate or recycle the hydride from the spent fuel and reaction products.
- This project is responsive to the Department of Energy's objectives in so far as the principal investigator plans to develop ways to regenerate alane, a very promising hydrogen storage material.
- The project addresses a fundamental step in the adoption of hydrogen technologies, according to the Hydrogen Fuel Initiative.
- AlH_3 is one of the few materials with a realistic chance at achieving storage gravimetric, volumetric, and kinetic targets. Regeneration is one of the key obstacles and deserves substantial focus.

Question 2: Approach to performing the research and development

This project was rated **3.4** on its approach.

- The results with $LiAlH_4$ are encouraging.
- The success metrics are not clear.
- The project uses a systematic approach appropriately using the expertise from the Metal Hydride Center of Excellence.
- The link to and integration with the Metal Hydride Center of Excellence is instrumental for overcoming the scientific and technical barriers in aluminum hydride regeneration.
- The titanium was shown to be well dispersed, but does the form matter? The form of titanium might be titanium particles, $TiAl_3$, solid solution or even change during use. Does it matter? At some point this should be looked at.
- There needs to be costs estimates done, such as for adduct formation.

- Very good overall.
- The technique of alane harvesting is a novel technique for overcoming the technical barriers that may prevent it from being a reversible storage material.
- The approach is clear and concise.
- The project integrates with other research.
- Highly imaginative schemes (both at the Brookhaven National Laboratory and elsewhere within the center) towards the regeneration of AlH_3. One question I have about the Brookhaven National Laboratory approach of regeneration of solvated AlH_3 that I would have liked to hear discussed is: The temperatures for separation of the solvent and dissociation of hydrogen will need to be clearly separated in any future process (i.e., one cannot have the AlH_3 dissociating during the process of removing the solvent) and, the dissociation temperature for hydrogen cannot be brought down too low, since the equilibrium pressure above it is so high. What is the plan to deal with these thermodynamic/kinetic issues?

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- Clearly much technical work is done and much has been accomplished but it is difficult to gauge how much closer the project is to its internal milestones.
- Satisfactory progress has been made with respect to objectives.
- Theory guided choices of adduct were made, and overall energy cost considerations were attempted, following up on last year's recommendations.
- Further progress was made with the hydrogenation occurring at lower pressure of less than 13 bar and at room temperature. Separating the alane from the organometallic without decomposition is still challenging.
- The program managed to reverse the reaction of lithium alanate at moderate pressure and temperature. It will be interesting to see how this develops.
- The principal investigator has worked with others to identify and test organic stabilizers that may be suitable for alane harvesting. Results from gas phase calculations can be used to predict the most likely prospects for this.
- There are a number of significant technical accomplishments.
- The work has been done effectively and efficiently.
- Good progress with the TEDA, showing a complete reversible cycle, and also in the analogous work regenerating $LiAlH_4$. It would be nice to more clearly compare this latter work to the analogous work from Ritter's group at the University of South Carolina.
- The use of theory to predict new ligands is quite useful; it will be interesting to see whether these predictions are verified.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- This research work is strengthened by the collaborations established within the Metal Hydride Center of Excellence, the Chemical Hydride Center and by the interaction with international partners, through the International Energy Administration.
- Close collaborations with partnering institutions is adding overall strength to the project.
- The number of collaborations, both within the Metal Hydride Center of Excellence and externally is good.
- Good connections with other partners within the center. As this regeneration scheme is "off-board", it might be useful to have a closer connection with some of the regeneration efforts in the Chemical Hydrogen Center of Excellence.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.4** for proposed future work.

- Clear work program was presented with set down-selection pathways and go/no-go decision points for the regeneration via organometallics and for recovering of the hydride from alane-adducts. Identifying the energy penalties also planned.
- Milestones planned for 2008 and 2009.
- The principal investigator has a well thought out plan for continuing the alane harvesting, building on past progress.
- The proposed future work is well thought out.
- It is nice to see some self imposed go/no-go targets.
- The inclusion of a process energy efficiency goal is nice.
- Proposed future research seems like a reasonable path forward.

Strengths and weaknesses

Strengths
- Networking and inter-collaborations within the center of excellence.
- Good team, good approach.
- The key personnel in this project have the experience working with alane that is necessary to make this project successful.
- The concise methodology used is impressive.

Weaknesses
- The alane on-board/off-board storage concept requires a radically different infrastructure system. While regeneration is correctly identified as one of the barriers, there are many other significant barriers which could diminish the probability of the success of this concept (under Grand Challenge program). So this begs the question that at what point and under what conditions a go/no-go decision should be made. This comment reflects on all alane regeneration projects and not just this work. What are the success metrics?
- Engineering aspects and associated regeneration costs, respective energy penalties, remain an issue.
- The applicant does not appear to have much experience or expertise in working with organic stabilizers, which are essential materials for this project.

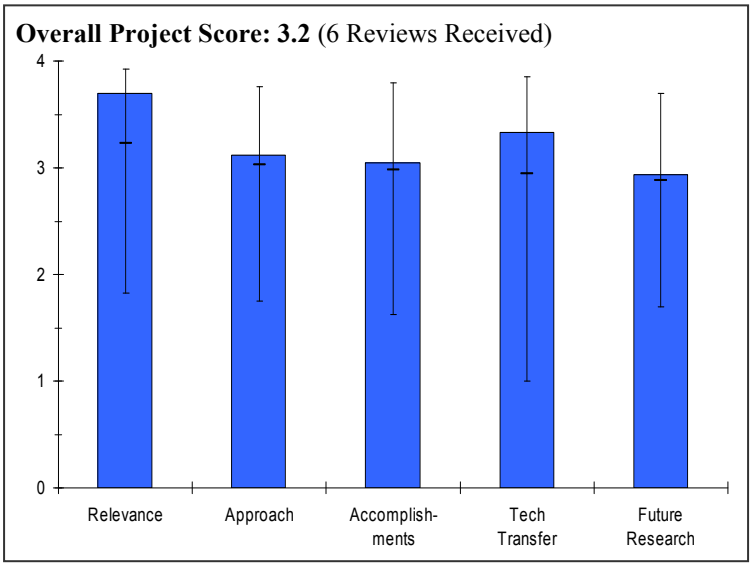
Specific recommendations and additions or deletions to the work scope

- This comment is for the entire effort on alane (not just this project). Would it be more appropriate to fund these projects under the Office of Basic Energy Sciences?
- While the alane concept is far from storage device development, can the system analysis project review the feasibility of the concept (under optimistic assumptions) and obtain the well to tank (WTT) efficiency and on-board storage metrics?
- Need to conduct even at this stage a preliminary energy analysis, over the life cycle, to get a feeling where the project stands and how it progresses with respect to regeneration costs and energy penalties.
- This project needs to be connected to the soon to be established Engineering Center of Excellence to investigate the alane system engineering aspects and practical application issues.
- There needs to be costs estimates done, such as for adduct formation.

Project # ST-40: Fundamental Reactivity Testing and Analysis of Hydrogen Storage Materials and Systems
Don Anton; Savannah River National Laboratory

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project



The objectives of task 1 – risk assessment are to 1) assess the potential risks of using solid-state hydrides; 2) develop test protocols and experimental designs to aid in characterization of hypothetical accident scenarios; and 3) test six compounds in three discharge states using standardized semi-quantitative test methods. The objective of task 2 - thermodynamics and chemical kinetics is to quantitatively assess chemical reactions of compounds with air, water and other engineering materials. The objectives of task 3 - risk mitigation are to 1) quantitatively assess chemical reactions of compounds with potential inhibitors; and 2) evaluate efficacy of inhibitors in laboratory scale tests. The objective of task 4 – prototype system testing is to design assemble and test prototype storage systems to evaluate effectiveness of inhibitor systems.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.7** for its relevance to DOE objectives.

- The project is critical to Department of Energy's hydrogen initiatives.
- The overall objectives of this project are well defined although most of them are premature.
- It is very important to determine the chemical and environmental reactivity characteristics of the materials and systems to be used for on-board storage which is the overall objective of this project.
- It may be too soon to initiate significant effort on the chemical and environmental reactivity characteristics of the materials and systems to be used for on-board storage. Most of the effort should be after materials have been identified that have a high probability of meeting the storage requirements.
- Critical to the Hydrogen Program both for risk mitigation and an effective down-selection process.
- A highly relevant project, addressing the development of solid low-pressure hydrogen storage via metal hydrides, chemical hydrides and sorption hydrides.
- As a materials characterization center, this project helps to put the various DOE storage projects on an even plane.
- This project is critical to ensuring that systems can be developed for safely utilizing hydrogen storage materials and fully supports the relevant multi-year program plan.
- Tasks 3 and 4 are imperatives for assessing the potential risks of solid-state hydrides and other materials as well as the mitigative technologies/techniques.
- Important work to (as UTRC pointed out) put more meaning in the DOE safety target of "Meets or exceeds applicable standards."

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- The approaches are good and effective in general.

- The principal investigator should also consider the difference between pelletized material and powdered material at early stage of the project.
- United Nations methods and procedures are being used to measure pyrophoricity, self heating, burn rates, and impact of water contact. These methods do not appear to be state of the art approaches. Savannah River National Laboratory is developing additional more scientific methods as well. It seems that there should be more scientifically based tests that have been previously developed and standardized to characterize the chemical and environmental reactivity of solid materials that could be used.
- Many of the methods being used do not include capturing the products of the reactions and determining their composition. It would seem this would be possible and important to do. Separate calorimetry experiments are being developed that include identification of the reaction products but these do not seem to be state-of-the-art either. For example there are differential scanning calorimetry (DSC) instruments connected to gas chromatography-mass spectrometry (GC/MS) that could be used.
- Future work includes developing some predictive models relative to material chemical and environmental reactivity in on-board vehicle applications. These will be empirically based. This may prove to be very challenging at best.
- Mitigation strategies are discussed in the future work but no examples are provided. The speaker mentioned pelletizing and the use of inhibitors or retarders but admitted there had been little thought about this aspect of the project.
- The approach is very safety-centered – a major positive.
- Very thorough approach in determining thermodynamic and kinetic properties of materials.
- Involving the centers of excellences is a plus.
- Good combination of standard tests and innovative self-developed tests.
- If they are going to look at sorption materials, they may need a different set of tests.
- The technical approach is good and will systematically address key properties of the materials being studied.
- The "connections" and interactions with the storage centers of excellence are functioning well, but it is less clear how the material down-selects from the centers of excellence are taken into consideration. The approach of looking at classes of materials seems very reasonable at this point in time.
- Testing of a few specific metal hydrides following standard United Nations protocols for the transport of dangerous goods. Augmented by developing a scientific basis for the often arbitrary criteria for these United Nations tests.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- The principal investigator made some good progress toward objectives.
- The established thermodynamic and kinetic database will provide valuable insight for material development work.
- The experimental data really helped the theory group to build an effective model.
- Given the approach taken, significant effort has been made and considerable results on one metal hydride system has been obtained, all of which is in keeping with the funding available to date.
- The value and extent of the results could be much greater if better approaches were taken (see comments under the approach section).
- Small comment: Reviewer is not convinced that the reaction of the storage solid after hydrogen evolution is pyrolysis only. It can also be diffusion limited oxidation, where the reaction and heat release rate is limited by the rate of oxygen diffusion into the powder. This is the same as ash combustion.
- A very thorough assessment of thermo-sensitivity of $LiBH_4/MgH_2$.
- Work with this material sets out a good protocol for future testing.
- Predictive modeling should help to determine a pathway to mitigation.
- It may have been valuable to have seen some comparative results with other materials.
- Progress on tasks to date is good.
- Good, careful studies of a few metal hydrides. Instructive results for the thermal and other behavior of the particular examined compositions, information which is not confidently transformable to other than the most closely related systems. Nevertheless, at least the demonstration and use of the standardized U.N. tests for metal hydride materials is of broader value.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- Some collaborations exist.
- The collaborations should be expanded to include some combustion experts outside the center.
- There is some good collaboration with other members of this International Partnership for the Hydrogen Economy project and with the DOE Storage Subprogram centers of excellence.
- Working with United Technologies Research Center and Sandia National Laboratories provides a thorough characterization of materials.
- There appears to be good coordination with the centers of excellences.
- Very good international component.
- This project has a very strong team of partners that includes international participation through the International Partnership for the Hydrogen Economy.
- Good collaboration with partners.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- The general research direction is good.
- Small scale system-level testing should be considered at current stage of the project.
- The mitigation strategies should be considered at an early stage of the project.
- There is a well-defined plan for additional work that will continue to characterize on-board storage materials for their chemical and environmental reactivity, utilizing the approaches that have been taken for metal hydrides that have been evaluated.
- The project plan includes work on mitigation strategies but very little thought has gone into this part of the project.
- Since the principal investigator is doing the primary effort in understanding risks and mechanisms for reactivity, it is important for the principal investigator to suggest mitigation strategies.
- Task 2 seems somewhat limited. It would be good to do more testing of various storage materials from all the centers.
- Risk mitigation task is next logical step, and this group is well qualified to perform it.
- Priority attention should be given be given to Tasks 3 (Risk Mitigation) and Task 4 (Prototype Systems Development).
- Since we are far from practical hydrogen storage materials, investigators should try to make the results of this work as broadly applicable as possible. Focus more on the development and "illustration" of techniques than in-depth analysis of a few specific hydrogen storage materials.

Strengths and weaknesses

Strengths

- The overall approach of accessing potential risks of solid state hydrogen storage materials is effective.
- Good set of experiments done well to identify chemical and environmental reactivity issues with metal hydrides using UN test procedures.
- Generally good approach to understanding the reaction risk factors for hydrogen storage materials.
- Very strong project leader.
- High safety consciousness.
- Thorough set of tests.
- The principal investigator and partners have the requisite expertise to achieve the project goals.
- The principal investigator fully recognizes the importance and need to develop sound and even novel technologies and techniques for risk mitigation associated with the use of these materials.

Weaknesses

- The scope of this project should not only be limited in material level testing. Small scale system-level testing should be considered at early stage.

- It does not appear that this project is utilizing state-of-the-art test methods and analytical techniques that are likely already well established for testing the chemical and environmental reactivity aspects of solid materials.
- It may be too soon to initiate a significant effort on the chemical and environmental reactivity characteristics of the materials and systems to be used for on-board storage. Most of the effort should be after materials have been identified that have a high probability of meeting the storage requirements.
- There needs to be some comparative tests with other materials to at least better understand the qualitative tests (e.g., water drop, surface contact).
- Less specific attention has been given to-date to the specific risk mitigation technologies/techniques than I think is desirable.
- The principal investigator did not include feedback comments on 2007 Annual Merit Review recommendations in the back-up slide section of the presentation material.

Specific recommendations and additions or deletions to the work scope

- Find and utilize the best state-of-the-art test methods and analytical approaches available for this effort.
- To the three water tests: Immersion, Surface Contact, and Water Drop, the project should add a credible 4th test. A Dense Slurry test, which is an extension of the Immersion test, where the possible heat release in immersion is not quenched by the water heat capacity, and there is a potential for ignition, with larger heat release per unit volume should be added. It is suggested to drop 1-10 ml solid powder into 1-10 ml of water. The results of "contact" and "drop" tests imply this immersion could ignite, possibly with "interesting" results. The mechanics expected may be where ignition occurs at the interface, where some of the powder has yet to sink and propagates into dry powder. The released heat diffused downward may evolve hydrogen and/or evaporate water, allowing combustion propagation downward into slurry as well.
- In the "Predictive Models" slide (slide 27): add tasks of "Predict combustion rate during hydrogen evolution" and "Predict reaction rate during pyrolysis or diffusion-limited combustion of material."
- Use these tests as screening tests for more materials.
- Work on identifying and testing appropriate fire suppression agents for these classes of materials should be considered in cooperation with the other companion projects being funded by the Storage Subprogram.

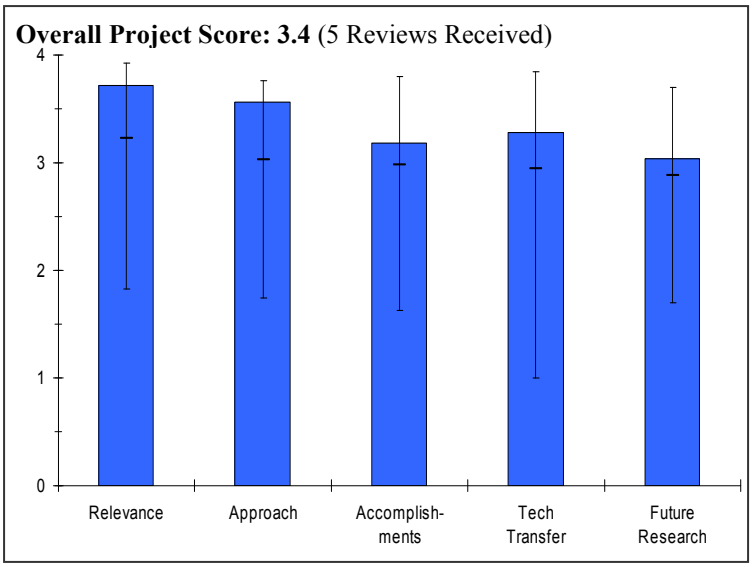
Project # ST-41: Quantifying and Addressing the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems

Dan Mosher; United Technologies Research Center

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objectives of this project are to 1) quantify the DOE On-Board Storage Safety Target: "meets or exceeds applicable standards"; 2) evaluate reactivity of key materials under development in the Materials Centers of Excellence; 3) establish generalized and specific risk analyses between reaction characteristics and satisfaction of acceptance criteria; 4) reduce reactivity consequences of candidate materials and systems through development of mitigation methods; 5) determine the trade-offs between performance and residual risk; and 6) support risk informed choices for codes and standards activities.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.7** for its relevance to DOE objectives.

- This program is highly relevant to the Department of Energy's Hydrogen Program.
- It is concerned with the chemical and environmental reactivity analysis and testing of hydrogen storage systems.
- Candidate systems are based on $2LiBH_4/MgH_2$, AlH_3, NH_3BH_3 and activated carbon materials.
- This program has a wide capability to test and characterize these materials.
- This capability is a valuable asset to the Metal Hydride Center of Excellence effort.
- The project is critical to DOE hydrogen initiatives.
- The overall objectives of this project are well defined although most of them are premature.
- The project attempts to quantify and address the DOE Material Reactivity Requirements with Analysis and Testing of Hydrogen Storage Materials and Systems.
- The presentation stated that the project addressed code and standards as well as system weight and volume but it is not clear from the materials presented how the system weight & volume were addressed.
- Setting "meet/exceed standard," mitigation strategies, trade-off process, and codes and standards efforts in this project are critical to meeting overall program objectives.
- This project is also critical to ensuring that systems can be developed for safely utilizing hydrogen storage materials and fully supports the relevant multi-year program plan.

Question 2: Approach to performing the research and development

This project was rated **3.6** on its approach.

- The approach is highly professional.
- It is concerned with risk analysis, material testing, reaction kinetics, risk mitigation and prototype implementation.
- There are four material candidates; $2LiBH_4/MgH_2$, AlH_3, NH_3BH_3, activated carbon which will be tested as charged/uncharged, as synthesized, both with and without contamination, before and after risk mitigation.
- A task structure has been set up the program partners and collaborators.

- Risk analysis will carried out on quantitative basis.
- The approaches are good and effective in general.
- The mitigation strategy and results need feed back to modeling work.
- Ball milling agglomerated materials is counter to automotive experience.
- The approaches used appear to be adequate.
- Risk analysis framework effort is well done and valuable to program success.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.2** based on accomplishments.

- Finely divided $2LiBH_4/MgH_2$ hydrided was tested with respect to various criteria.
- This material was found to be highly reactive and comparable to $NaAlH_4$.
- In the partially discharged state, coarser powder (100-200 mesh) was less reactive.
- Air exposure tests in the hydrided and partially dehydrided state of $2LiBH_4/MgH_2$ were carried out. A complex reaction sequence involving H_2O was defined.
- The principal investigator made some good progress toward objectives.
- The experimental data helped theory group to build an effective model.
- The risks need to be distributed and prioritized over different factors, especially at system level.
- The project is making adequate progress.
- The dust explosion work was well done, and integrating the testing with Sandia National Laboratories modeling and Savannah River National Laboratories TR-XRD is very well done.
- The project has made reasonable progress.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- This program has many collaborators both within and outside the Metal Hydride Center of Excellence. These include Savannah River National Laboratories, Sandia National Laboratories, Forschungszentrum Karlsruhe (FZK, Germany), the National Institute of Advanced Industrial Science and Technology (AIST, Japan), and the University of Quebec at Trois Rivières (UQTR, Canada) each of which are responsible for several tasks.
- An expert panel will advise on the organization of the Risk Analysis Framework.
- No reports or papers were listed in the presentation, but the program began June 2007 and as of March 2008, is only 10 months old.
- Some collaborations exist.
- The collaborations can be expanded to include some combustion experts outside the center.
- Well integrated into DOE the centers of excellences and International Energy Administration and International Partnership for the Hydrogen Economy programs.
- This project has an extensive and strong set of collaborators.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.0** for proposed future work.

- For fiscal year 2008, plans include: Compile input from the expert panel on risk assessment for on-board storage; Initiate quantitative ETA/FTA risk assessment; Define AlH_3 and NH_3BH_3 system configurations and perform risk analysis; Material testing and modeling for the $2LiBH_4/MgH_2$ will be completed. Modeling will involve collaboration with Sandia National Laboratories and Savannah River National Laboratory; and Initiate testing of AlH_3.
- For fiscal year 2009 plans include: Involve risk studies of activated carbon for on board and off-board regeneration; Conduct dust explosion and air reactivity tests for activated carbon, AlH_3 and NH_3BH_3 and Develop risk mitigation methods.
- The general research direction is good.

- Small scale system-level testing should be considered at current stage of the project.
- The cycled materials might have different behavior compared to fresh materials. Therefore the proposed test should include accessing the cycled material behavior.
- The proposed future research builds on the past progress.
- Increased emphasis should be placed on ensuring that the system configuration which drives the failure mode and effects analysis (FMEA) for components and sub-systems is truly representative of what is likely to be designed/built as a first generation.

Strengths and weaknesses

Strengths
- A very strong engineering effort.
- The resources are adequate.
- The collaboration arrangement is exceptional.
- The principal investigator is highly respected and has prior experience in conducting similar studies with $NaAlH_4$.
- This program is very relevant to the storage program's Centers of Excellence effort and should be vigorously supported.
- The overall approach of accessing potential risks of solid state hydrogen storage materials is effective.
- The project involves a wide range of new materials that were not routinely dealt with. Developing codes and standards to handle the materials in research and development and in future wide-spread application is critically important.
- The principal investigator and collaborators have established a methodology and assembled a team capable of meeting the objectives of quantifying and addressing the material reactivity requirements.
- The principal investigator clearly explained and illustrated the task breakdown for various collaborators. (Note: It would be more effective if this overview were given before the first talk or as part of the first talk, rather than in the second talk.)

Weaknesses
- Other than the lack publications or written reports, there are no weaknesses.
- The scope of this project should not only be limited in material level tests. Small scale system level testing should be considered at early stage.
- Although the work of all partners is relevant and well-illustrated in the task matrix, it is less clear how this interaction is managed, how technical progress is integrated and how priorities are set in a coordinated fashion.

Specific recommendations and additions or deletions to the work scope

- I have no recommendations for either additions or deletions to the program scope at this time.
- The team should focus on one type of material and develop a complete set of codes and standards.
- The activated carbon effort may have moving targets regarding the pressure, presence of metals and lower temperatures that should be included in analysis and testing.

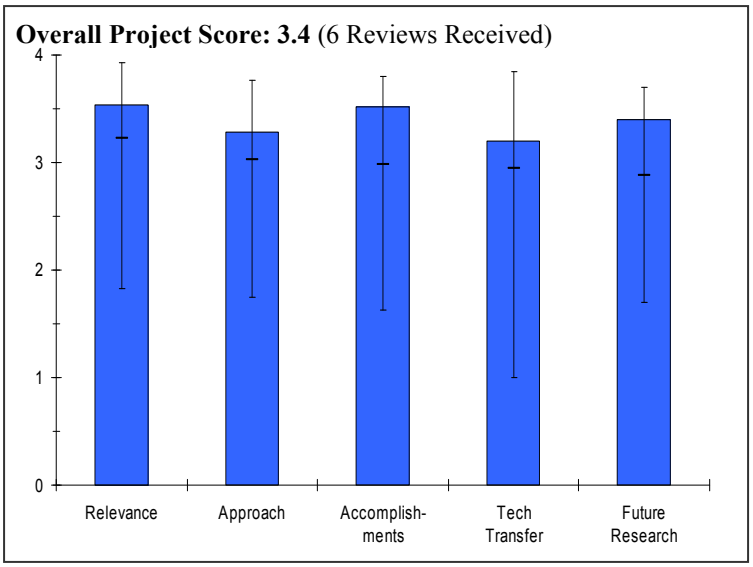
Project # ST-42: Chemical and Environmental Reactivity Properties of Metal Hydrides within the Context of Systems

Dan Dedrick; Sandia National Laboratory-Livermore

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objective of this project is to develop generalized methods and procedures required to quantify the effects of hydrogen storage material contamination in an automotive environment. The eventual impact of the project will 1) provide technical basis for C&S efforts when appropriate technology maturity has been attained; and 2) enable the design, handling and operation of effective hydrogen storage systems for automotive applications.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- The project is critical to the Department of Energy's hydrogen initiatives.
- The overall objectives of this project are well defined although most of them are premature.
- This project seeks to develop fundamental tools for quantifying the chemical reactivity related hazards of hydrogen storage materials is critical for committing their ultimate safe implementation. However, their work does not relate to health and environmental concerns of hydrogen storage materials.
- The project is addressing important basic material behavior characteristics from a chemical and environmental reactivity standpoint that should enhance the development of appropriate hydrogen storage safety requirements.
- The project addresses hydrogen storage in low pressure systems - a high Hydrogen Program need.
- Trying to look at real world contamination scenarios - this is also appropriate.
- This project is critical to ensuring that systems can be developed for safely utilizing hydrogen storage materials and fully supports the relevant multi-year program plan.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- The approaches are good and effective in general.
- The off-road of developing generally applicable tools, providing a scientific basis for standard United Nations tests (rather than testing individual hydrogen carriers) is appropriate at the present state of the development of the field of hydrogen storage.
- The four tasks in project, experimental methods and analysis will be effective in understanding the contamination effects for hydrogen storage materials.
- Task 4, mitigation strategies appropriate for a broad spectrum of storage materials may not provide the best mitigation strategy for a particular storage material finalist. Some attention to material specific mitigation strategies should be considered.
- The project plan is well-structured but could better address how to migrate results to standard or code requirements.
- The project focuses on contamination scenarios and has developed their own group of scenarios essentially covering tank breach and contamination. Breach and then air or moisture entry is a good scenario pathway.

- Contaminated refueling is a separate scenario that is not necessarily connected to others; it is fine to look at this, but it should not be made to look like part of same scenario path. (It's just a problem with the way the approach is presented rather than a real approach fault.)
- In the project plan, it is not entirely clear from the presentation that Sandia National Laboratories is addressing all four tasks.
- This project specifically adds contamination aspects to work of the associated partners in the areas of mechanism studies, life-cycle implications, etc.
- Task 4 (assessing the fundamental usefulness of fire suppression chemicals) acknowledges the importance of this topic as referenced in the white paper recommendation of the Hydrogen Safety Panel ("Potential Fire Suppression Agents for Metal Hydride Fires") and in the April 2008 report of the NFPA Hydrogen Research Advisory Council, "Research Needs in Support of Hydrogen Safety Standards."

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.5** based on accomplishments.

- The principal investigator made good progress toward objectives in a relatively short time frame.
- The generalized methods and procedures developed in this project to quantify the effects of hydrogen storage material contamination are very useful.
- Impressive development of techniques, in particular the STMBMS apparatus which may be regarded as the scientific data providing equivalent of the U.S. Kaemen Test for the effect of heating in a confined environment.
- Generally good results. Results for reaction products from alane heating in air exposure are well done.
- The project, in its early stages, is making good progress against the project plan.
- New flow cell seems to be a powerful tool to measure effects of contamination.
- Very interesting result on differences between alanes. (With many labs investigating alanes, this system could be very useful.
- Scale-up bulk reactor is also very appropriate.
- It is unclear how the dust cloud combustion effort fits with the rest of the work. It is not addressed sufficiently in the presentation.
- Project team's progress is milestone-based and appears to be appropriate for the one-year point.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.2** for technology transfer and collaboration.

- Some collaborations exist.
- The collaborations can be expanded to include some combustion experts outside the center.
- Good coordination.
- The project team is well-designed to address the project plan.
- Later in the project, representatives from Code Development Organizations (CDOs) and Standards Development Organizations (SDOs) should be engaged to help address issues related to migration of results to codes and standards.
- Collaboration with the United Technologies Research Center (UTRC) and the Savannah River National Laboratory is very good.
- Good international component with the International Partnership for the Hydrogen Economy.
- The principal investigator fully recognizes the importance of sourcing materials from collaborators to ensure relevance and continuity.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.4** for proposed future work.

- The general research direction is good.
- System level testing is not addressed at current stage of the project.

- The predicted accident scenarios need to be validated by OEMs.
- Continuing the development of tools. It is suggested to provide where possible some "linkages" to standardized United Nations tests.
- The future work plan is appropriate but later stages need to engage codes and standards experts.
- Risk mitigation work is a logical next step.
- It was not adequately explained as to whether existing systems will be used, new ones built, or etc.
- Task plan fully embraces milestones and go/no-go decision points.

Strengths and weaknesses

Strengths
- The overall approach of accessing potential risks of solid state hydrogen storage materials is effective.
- The project represents an opportunity to build an appropriate technical structure from which future safety requirements can be developed.
- Seems like very good development and use of powerful diagnostic tools.
- Strong collaboration.
- The project is addressing an important area.
- The principal investigator has considered credible contamination scenarios based upon NFPA, ISO and SAE draft language.

Weaknesses
- The scope of this project should not only be limited in material level tests. Small scale system level testing should be considered at early stage.
- Once sufficient progress has been made, experienced codes and standards representatives should be engaged.
- The presentation needed to be a little clearer on what diagnostics were being applied to what tasks.

Specific recommendations and additions or deletions to the work scope

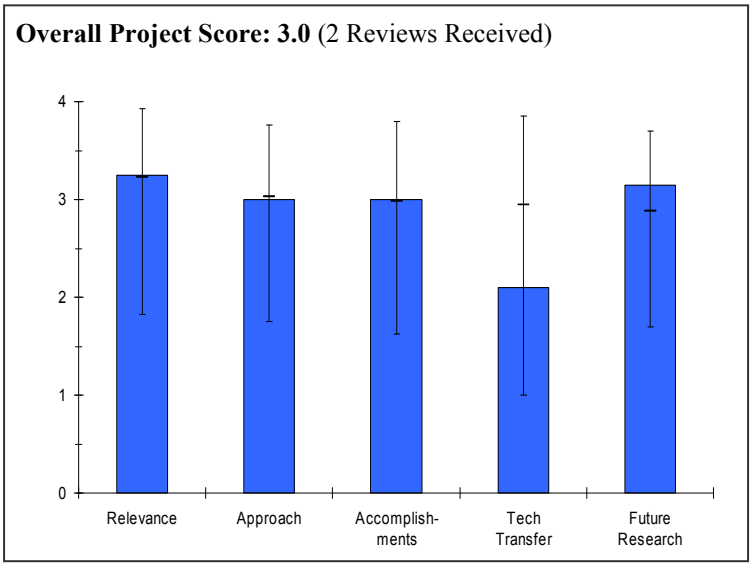
- For dust cloud combustion, the approach for step one of predicting gas/particle flow field needs to be done for several failure scenarios. Resulting burn velocity data for step two will likely depend somewhat on failure mode.
- Addition of a consultation link to CDOs and SDOs is recommended.
- The principal investigator/project team should consider outlining (perhaps in a short white paper) how they would approach the study of fire suppression agents. Such a document, which could incorporate other collaborators, could be provided for external review and feedback in advance of specifically planning Task 4.

Project # STP-04: Purdue Hydrogen Systems Laboratory
Jay Gore; Purdue University

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objectives of the project are to 1) improve the extent, rate and control of hydrogen release from ammonia borane (AB) by hydrolysis reactions; 2) discover practical uppermost hydrogen storage density of the AB hydrolysis approach; 3) understand engineering properties of the AB hydrolysis approach; 4) characterize the dehydrogenation products and develop new methods for AB regeneration; 5) investigate reaction mechanism and effect of process parameters on yield of hydrogen generation by novel noncatalytic AB hydrothermolysis; 6) determine parameters that maximize anaerobic biological hydrogen production; and 7) understand energy balance for a local modular energy system using biological/solar technology.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.3** for its relevance to DOE objectives.

- Only the storage portion of this project is evaluated - not the hydrogen production portion.
- Addresses the Department of Energy hydrogen storage targets.
- Apparently no consideration of cost of this storage approach.
- Ammonia borane slurry storage research shows promise as a high hydrogen capacity storage method, which is clearly relevant to overall DOE objectives.
- The relevance of the "local modular energy system" using anaerobic biological hydrogen production was not made clear.

Question 2: Approach to performing the research and development

This project was rated **3.0** on its approach.

- Clearly aware of the DOE storage performance targets.
- Appears to be focused except for the work on hydrogen production which deflects attention and effort from the hydrogen storage effort.
- Has looked at two approaches for hydrogen release of hydrogen from ammonia borane and also regeneration of ammonia borane from spent fuel.
- Engineering analysis of ammonia borane storage shows focus on meeting DOE system weight goals.
- Experimental results appear to be conducted using good practices.
- Ambient temperature ammonia borane hydrolysis and noncatalytic ammonia borane hydrothermolysis (at ~117-170°C) being researched in parallel.
- The anaerobic biological hydrogen production part of this project lists feedstock cost and hydrogen yield as technical barriers and neither seemed to be addressed in the report.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- Progress seems to be slow. Results to date indicate hydrogen material storage capacity that is marginal to meet system capacity targets and needs to be improved.
- Thermal release under increased pressure appears to be interesting.
- Experimental data indicates high storage density of ammonia borane hydrolysis approach at ambient temperature.
- Promising preliminary results for noncatalytic ammonia borane hydrothermolysis approach, provisional patent application filed.
- Demonstrated hydrogen production from waste using fermentation, and developed initial "modular local energy system."

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.1** for technology transfer and collaboration.

- General Motors and General Atomics are claimed to be partners in this project but no detail is given and it is not clear what contributions, if any, these partners have made.
- This work needs to be coordinated with the Chemical Hydrogen Center of Excellence.
- The ammonia borane storage research team is aware of the Pacific Northwest National Laboratory ionic liquid approach as a lower energy regeneration approach.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Future plans appear to be reasonable but are stated only in general terms - need to be more specific. From a hydrogen storage perspective, there is nothing to be gained from the plans to develop a storage system that is integrated with a fuel cell stack. This seems to be a diversion. The emphasis should remain on improving hydrogen storage capacity and regeneration.
- Team recognizes the need to improve regeneration yield, and thus reduce energy. Currently at 64 percent yield, goal of 80 percent by January 2009.
- They have a plan to reduce the water/ammonia borane mixture ratio.
- Optimize parameters for noncatalytic ammonia borane hydrothermolysis for maximum hydrogen yield.
- Maximize anaerobic biological hydrogen production.

Strengths and weaknesses

Strengths
- Identification of system level targets, and understanding that the material capacity needs to be well above system targets.
- Parallel approaches to ammonia borane hydrogen storage (hydrolysis and hydrothermolysis).

Weaknesses
- Lack of coordination with other DOE efforts in hydrogen storage - coordination with the Chemical Hydrogen Center of Excellence.
- Energy requirements for regeneration not clearly stated.
- Anaerobic biological hydrogen production yield status/baseline/benchmark not reported; feedstock cost not addressed at all.

Specific recommendations and additions or deletions to the work scope

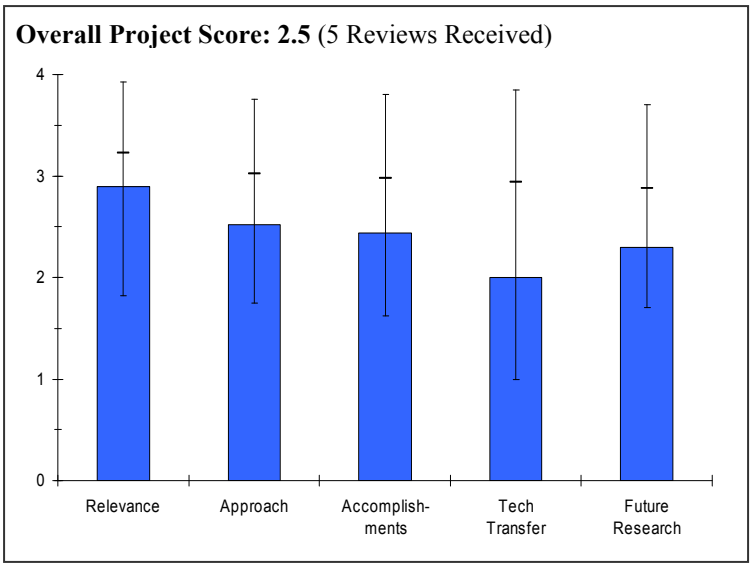
- Develop a relationship with the DOE Chemical Hydrogen Center of Excellence.
- Make regeneration energy requirements (and carbon emissions) more transparent.
- Show similar systems analysis for volume target, as you have done for weight.
- As hydrothermolysis research progresses, keep track of the amount of energy needed to sustain temperature and pressure requirements. Identify if this energy can be provided by fuel cell waste heat.
- Clearly address anaerobic biological hydrogen barriers of hydrogen yield and feedstock cost.

Project # STP-05: Development of Regenerable, High-Capacity Boron Nitrogen Hydrides For Hydrogen Storage

Ashok Damle; Research Triangle Institute

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project



The overall objective of this project is to develop a boron-nitrogen hydride-based hydrogen storage system to meet U.S. DOE's 2010 technical (6 wt%) and cost targets ($4/kWh). The hydrogen release objectives are to: 1) develop an energy efficient process of on-board thermal decomposition of ammonia-borane (AB) (NH_3BH_3) to release pure hydrogen suitable for proton exchange membrane fuel cells; and 2) discover catalysts to improve efficiency of hydrogen release and to produce decomposition products that are amenable to regeneration of AB. The AB regeneration objectives are to 1) develop an energy efficient process for catalytic regeneration of AB decomposition products; and 2) discover catalysts to promote regeneration of partially dehydrogenated products, preferably using only H_2 pressure and temperature.

Question 1: Relevance to overall DOE objectives

This project earned a score of **2.9** for its relevance to DOE objectives.

- Project is relevant to the main objectives of ammonia borane hydrogen storage option.
- Ammonia borane has high hydrogen material capacity and the potential to meet DOE 2010 targets.
- OEMs have stated their strong dislike for cartridge based storage systems- principal investigators should concentrate on liquefying storage materials if they cannot be charged on-board the vehicle.
- Regeneration of ammonia borane systems is key to the use of these materials as hydrogen storage media. Today, the lack of a good catalyst for this process is a major weak link to any practical implementation scheme. This work offers one approach to solving this critical issue. While the approach being explored in this grant is of interest, the current work has not identified any potential catalyst systems at this point.
- This project was redirected into catalyst development for ammonia borane hydrogen release and regeneration.
- Hydrogen storage using ammonia borane.

Question 2: Approach to performing the research and development

This project was rated **2.5** on its approach.

- Characterize non-catalytic thermal decomposition of ammonia borane.
- This process has long been a well understood phenomenon.
- This process clearly does not operate within the envelope of automotive operating conditions.
- Conduct combinatorial high-throughput screening of the catalyst libraries to identify catalysts. This is an important task however there are many more qualified principal investigators conducting this work in the Chemical Hydrogen Storage Center of Excellence.
- Evaluate promising catalysts and process conditions for regeneration of decomposition products to AB (with up to two moles of hydrogen released). This process will likely require more than just catalyst work to achieve reversibility.

- The cartridge approach should be abandoned completely. OEMs strongly prefer to avoid such systems to system complexity – (seals connections, logistics at the forecourt, etc.).
- The thermochemical analysis employed is good.
- The high throughput screen that has been developed is very clever.
- The concept of an internal multifunctional catalyst in continuous intimate contact with reactants and products is a well developed idea.
- Combinatorial high throughput screening is a sound approach to address hydrogen release and Spent fuel regeneration.
- Good integration of theory and experiment.
- Intematix screens catalysts and RTI determines their effects on release and spent fuel regeneration.
- There appears to be no clear rationale for catalyst selection for release and spent fuel regeneration.
- Reasonable approach to the catalytic and non catalytic dehydrogenation ammonia borane. Futile attempts to directly re-hydrogenate "spent" ammonia borane-due to the unfavorable thermodynamics.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.4** based on accomplishments.

- The principal investigator is utilizing a high throughput screening of ammonia borane using a 16 cell library method sputtering different catalysts. Using an RGB signal to implicitly determine if hydrogenation/ dehydrogenations are occurring although they can't elucidate on exactly what reactions are truly occurring (potential undesirable side reactions). The technique is limited to hydrogen inert materials which is desirable however they will not be able to determine how the catalyst is behaving on hydrogen.
- Library screening techniques have been implemented (but not totally perfected).
- One potential catalyst has been identified and carried through a bulk analysis that indicated it was not a successful candidate.
- The accomplishments indicated above appear less than expected for a project that is time marked to be 70% complete.
- Good accomplishments in hydrogen release tests up to 500°C.
- Only one set of catalysts screened for dehydrogenation and one set for rehydrogenation, would have liked to see more.
- Spent fuel regeneration is a major hurdle for ammonia borane as a hydrogen storage material, while disappointing yet not too surprisingly, the first attempt at catalytic rehydrogenation of decomposition residue failed.
- Much of the work on the ammonia borane release looks like a duplication of effort with the Pacific Northwest National Laboratory work.
- Has done a good job at finding ways to release hydrogen from ammonia borane and demonstrating the considerable exo-thermicity of this process. But it should have been evident from their thermodynamics that the spent fuel regeneration process, a direct re-hydrogenation with hydrogen, would be futile.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.0** for technology transfer and collaboration.

- Neither the principal investigator nor the partner Intematix is significantly connected to the Chemical Hydrogen Storage Center of excellence.
- This project has not proceeded to a point where technology transfer can be considered.
- The limited work completed to date is collaborative in nature.
- Intematix is the only external collaboration partner (for catalyst screening).
- There appears to be no interactions with the solid ammonia borane work at the Pacific Northwest National Laboratory.
- RTI and Intematix.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- With screening techniques in hand, work will now focus on the search for a catalyst. However, with the very limited data that has been produced to date, it is unclear if the selected search parameters have merit.
- Future plan is appropriate.
- Need to focus on rehydrogenation and demonstrate some success, absence of which renders the project less relevant to DOE objectives.
- This project ends in November 2008. It is unlikely that significant catalyst development will take place between now and then.
- As said there is no point in searching for catalyst to effect the highly thermodynamically unfavorable one step rehydrogenation of "neat" ammonia borane.

Strengths and weaknesses

Strengths
- High throughput library technique should allow the principal investigator to evaluate many catalyst combinations quickly.
- A good high throughput screening for hydrogen evolution and catalyst oxidation state have been developed.
- Good experimental methods.
- Ability to generate large number of metal catalyst compositions.
- None.

Weaknesses
- Lack of collaboration with leaders of ammonia borane catalysis and regeneration.
- No catalyst or potential catalysts have been identified, and an updated strategy has not been presented that might improve the productivity of the project.
- Limited interactions with the Metal Hydride Center of Excellence partners.
- RTI does not have a rationale for catalyst development.

Specific recommendations and additions or deletions to the work scope

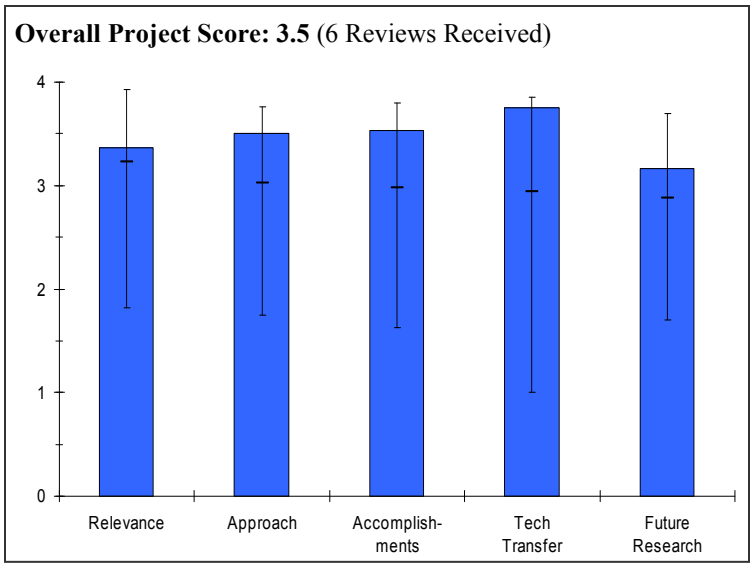
- Continue high throughput screening. Either the rate of screening must be upgraded or a more clever parameter space needs to be identified (or both).
- None.

Project # STP-06: Neutron Characterization in Support of the Hydrogen Sorption Center of Excellence
Dan Neumann, presenting Terry Udovic and Craig Brown, Co-PIs, NIST

[NOTE: NIST is a member of the Hydrogen Sorption and Metal Hydride Centers of Excellence.]

Brief Summary of Project

The overall objectives of this project are to 1) support the development of hydrogen storage materials by providing timely, comprehensive characterization of center-developed materials using neutron methods; and 2) use this information to speed the rational development and optimization of hydrogen storage materials that can be used to meet the 2010 DOE system goal of 6 wt% and 45 g/L capacities. Objectives are to 1) provide Calphad calculations of phase relationships of potentially promising hydrides (Metal Hydride Center of Excellence only); and 2) contribute within the Center and with independent projects if it furthers the Center goals.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Strength: NMR is a wonderful tool, critical to understanding the mechanisms of adsorption in physisorbents by providing detailed structural information, binding locations, binding energies and even transport (diffusion) information. [DOE NOTE: NMR work is done at UNC, a partner of the Hydrogen Sorption Center of Excellence.]
- This project is providing a fundamental understanding of the structures of some hydrogen storage materials. To the extent that this understanding leads to developing new materials, it supports the Department of Energy's objectives.
- This project is providing outstanding structural and other analysis to the Storage Hydrogen Sorption Center of Excellence, is a key enabler to understanding these sorption materials and designing improved materials. Sorption-based materials offer perhaps the greatest chance of meeting the very challenging on-board storage targets for hydrogen fuel cell vehicles.
- Neutron scattering is critical to understanding the behavior of hydrogen in materials.
- The project scope is to provide a set of uniform characterization techniques applicable across multiple material samples. Within this scope, the project is quite relevant as the techniques definitely provide useful information on how and where hydrogen is sorbed. Whether this information leads to breakthroughs in achieving hydrogen storage goals rests in the hands of collaborators; it seems unlikely that this project itself will lead directly to such breakthroughs.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- This project is a critical tool in support of Hydrogen Program sorption-based storage projects. It provides deep insight into the sorption phenomena and can contribute significantly to determining go/no-go decisions.
- The neutron facilities for determining the elemental composition of materials and for determining the locations and bonding of adsorbed hydrogen are state-of-the-art. The principal investigator presents adequate experience to do the work.

- The project's neutron scattering and other techniques are elucidating the exact structure and hydrogen placement of the sorption materials being researched. This is elucidating the reasons for the thermodynamics and performance being achieved; greatly advancing the science in sorption based materials for hydrogen storage and should enable the development of improved materials.
- The project provides much needed basic understanding of which centers are critical for improved hydrogen absorption.
- Again, within the project scope, the characterization techniques are well-focused on providing the expected information, and the project is reasonably well integrated with other activities.
- Greatest concern: This project's capabilities appear to have been applied most heavily to systems that are already reasonably well understood, and that are unlikely to be improved despite the additional understanding these capabilities provide. Can these capabilities be applied to more controversial materials where higher-than-typical capacities are claimed? That way, erroneous claims might be corrected sooner, and genuine new leads might be recognized and advanced more rapidly than has been the tendency.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.5** based on accomplishments.

- Strength: Technical achievements such as the experimental identification of adsorption sites in MOF-74, the effect of binding on the length of the H-H bond, the observation of a "denser than solid hydrogen" monolayer for MOF-74, and the confirmation of the breathing effect in materials such as the MIL-53 are very impressive.
- Strength: The results are outstanding and show pathways to achieving higher storage densities using physisorbents.
- Strength: The use of NMR as a non-destructive element analytical method to determine the degree of incorporation of various elements in nanoporous carbons before and after activation is interesting. (To what degree is this technique unique in that respect?)
- The work done to determine the structures of MOFs, including a "breathing" MOF, is excellent.
- The neutron methods have provided a valuable service to partnering institutions in the center.
- Has shown packing densities of hydrogen greater than in solid hydrogen in MOF-74 and has helped elucidate how and why this occurs through neutron scattering as well as BET surface area measurements along with sorption measurements.
- Discovered "breathing" in MOF MIL-53. This is a newly identified phenomenon that may enable further improvement in sorption material for hydrogen storage.
- Elucidated how boron and platinum affect nanoporous carbon hydrogen sorption through neutron scattering experiments.
- The project provides highly reliable structural data that can be and are used by partners in their materials design work.
- The project provides rapid access to neutron scattering facilities as requested by partners.
- The principal investigators are highly qualified experts in neutron scattering.
- There has been good progress using the techniques and capabilities, within project scope. Perhaps the most promising progress has been in contributing to understanding "phase breathing" material modes; a complete understanding of these modes may lead to new temperature/pressure cycles that can be exploited for storage. Also intriguing is the hint from inelastic scattering (slide 13) that "free" 1-d motion of hydrogen might occur in longer channels, although how this will contribute to meeting DOE capacity goals is unclear.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.8** for technology transfer and collaboration.

- The project is by its nature collaborative and fulfills its mandate with the Sorption Center of Excellence and other partners.
- The National Institute of Standards and Technology (NIST) has fulfilled one of its major objectives by providing characterization of materials, using neutron methods, to several institutions in the center.
- This project is collaborating with and aiding many parts of the Sorption Center of Excellence.

- The project is publishing many papers and presenting at conferences so that the knowledge being gained is getting transferred to a broad scientific community.
- The nature of work is highly collaborative.
- Excellent relationships with the Hydrogen Sorption Center of Excellence.
- Collaboration is inherent in this project's scope, and appears to be happening as intended. As mentioned in other comments, applying these capabilities to more controversial samples could be valuable.
- Some coordination exists.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Strength: The project has a clear plan for future research that is consistent with past research and partner and program requirements.
- Strength: Infirming/confirming the role of "Kubas" interactions in doped physisorbents would be an important contribution.
- The principal investigator presents adequate experience and capability to continue neutron scattering studies on various adsorbents.
- Some contingencies to the future work could have been mentioned.
- A well defined plan for future work is in place for fiscal years 2008 and 2009.
- It is suggested that this project might try to define a clearer strategy with the Sorption Center of Excellence as to the areas, types of samples, etc. it should focus on to most efficiently aid in the development of sorption based hydrogen storage materials.
- The project clearly builds on prior accomplishments.
- Within the present scope, this project may not have much room to overcome barriers. The project appears to be constrained to provide more "service" than "guidance."

Strengths and weaknesses

Strengths
- This project has managed to achieve important technical achievements.
- This project is an essential characterization method in support of understanding sorption properties and mechanisms, performing non-destructive element analysis of modified materials, and guiding the development of materials that could attain DOE storage goals.
- NIST is providing access to neutron facilities to a large number of partners in the centers, as well as to several external partners.
- This project is providing outstanding structural and other analyses to the Sorption Center of Excellence that is a key enabler to understanding these sorption materials and designing improved materials. Sorption-based materials offer perhaps the greatest chance of meeting the very challenging on-board storage targets for hydrogen fuel cell vehicles.
- A whole suite of neutron scattering capabilities is utilized.
- Excellent publication record.
- High visibility of research.
- Solid and reliable data are disseminated quickly.
- Very good characterization within defined scope. Provides interesting insights into phenomenology of hydrogen sorption; insights that appear to be uniform and readily compared across different samples and sample types.
- Theoretical calculations look interesting.
- Some experimental results may be of certain practical value.

Weaknesses
- Weaknesses (refer mostly to the presentation provided for the review): Are the storage densities referred to net or excess densities? How are they obtained?
- Pressure and temperature information should be stated everywhere a storage density is mentioned.

- NIST should make more of an effort to extend its collaborations and partnerships to include some small independent DOE-funded institutions that are not part of the Hydrogen Sorption Center of Excellence or the Metal Hydride Center of Excellence.
- I noted that collaborations with the Metal Hydride Center of Excellence have not been presented. If these were simply not reviewed, this is fine. If these have been discontinued, then I think they should be restored.
- Insights into phenomenology, especially phenomenology of materials already empirically optimized, are unlikely to teach how to proactively design new, breakthrough, materials.
- The poster focuses on a limited set of materials provided by a few collaborating institutions. If possible, studies of a more diverse set of materials could lead to a greater likelihood of advancing progress toward DOE goals.
- I am not sure that this project is presented in the best possible way.

Specific recommendations and additions or deletions to the work scope

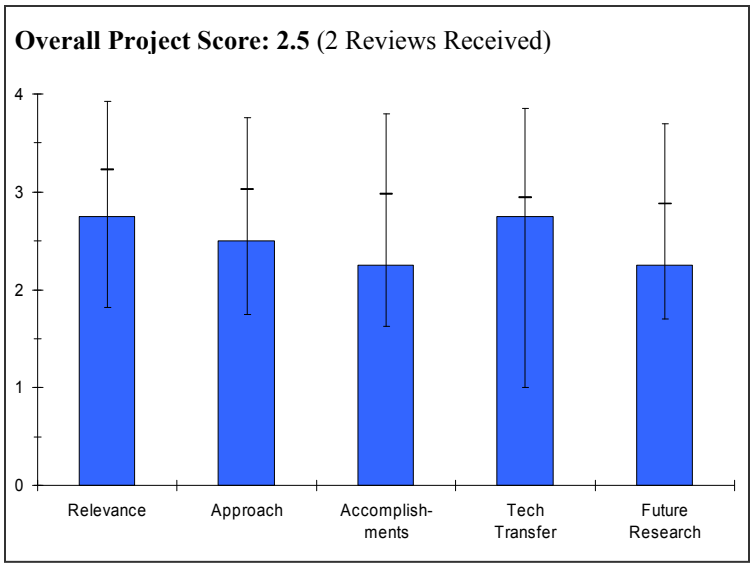
- The SPD analysis provided in the slides is very interesting; it would be nice to compare with pure carbon nanostructures as a baseline reference (activated carbon for example).
- This method could likely make an important contribution in understanding and characterizing the spillover effect.
- It is suggested that this project might try to define a clearer strategy with the Sorption Center of Excellence as to the areas, types of samples, etc. It should focus on how to most efficiently aid in the development of sorption based hydrogen storage materials.
- Given the excellent results, I recommend expanded collaborations with the Metal Hydride Center of Excellence, and if possible, with added funding.
- If possible, put these capabilities to work on controversial samples or materials. That way, erroneous claims of unusually high capacity can be disproved sooner, and accurate claims can sooner be recognized and advanced.

Project # STP-08: Optimizing the Binding Energy of Hydrogen on Nanostructured Carbon Materials through Structure Control and Chemical Doping
Jie Liu; Duke University

[NOTE: This project is part of the Hydrogen Sorption Center of Excellence.]

Brief Summary of Project

The objectives of this project are to 1) design and synthesize carbon-based materials with optimized binding energy to hydrogen molecules that will show storage capacity meeting the Department of Energy 2010 goal in hydrogen storage; and 2) design and synthesize microporous carbon-based materials with enhanced binding energy to hydrogen including: pore size control; surface area increase; metal doping of microporous carbon materials; and B-doping of microporous carbon materials.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.8** for its relevance to DOE objectives.

- This project as presented and described does not appear unique. Needs direction by center of excellence leadership to improve relevance.
- The project objectives are aligned with Department of Energy research and development objectives.
- Improving the binding energy of hydrogen and carbon is one of the critical factors to improve the hydrogen uptake for carbon-based materials.
- One aim is to increase surface area: but generally this will decrease volumetric density (which is already low for these materials); is there any way to achieve the 2010 volumetric densities with these materials? The PIs do not report any measurements of volumetric density, and do not comment on this issue. Thus, it seems as though they are unaware of this important drawback of their materials?

Question 2: Approach to performing the research and development

This project was rated **2.5** on its approach.

- Objective does not set this project apart from others in the Sorption Center of Excellence - what new research and development is this project doing?
- Micropore activation can be accomplished by steam, CO_2 or chemical means. Steam leaves OH^- on surface, KOH tends to leave both K^+ and OH^- and CO_2 leaves dangling oxygen bonds. The principal investigator needs to characterize surface to determine if there is an impact of microchemistry on outcomes. There are numerous tests to characterize the carbon surface within the center of excellence and correlation of the surface chemistry would strengthen this project and shed light on hydrogen sorption.
- The approach does not demonstrate how this project will add to the state-of-the-art.
- The principal investigator did not show how theory group can help them in the design of nanostructured carbon.
- The experimental approach is more like a trial and error approach rather than an engineered bottom-up approach.
- Very interesting surfactant approach to control pore size; it appears that the researchers have achieved sub-nanometer pore sizes using this approach!

- The PIs assert that continuous control of the binding energy should be possible by controlling pore size. However, they have not demonstrated that the binding energy is actually a function of the pore size (and since they have different pore sizes in their samples, it seems that this demonstration should be possible).
- The PIs say that there are problems associated with too weak or too strong a binding energy, and that they are trying to tailor their materials towards the optimum binding energy. However, they don't give any indication of what this optimum binding energy is? Could the PIs comment on this?

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.3** based on accomplishments.

- Technical progress is minimal for a project in its second year.
- Data presented does not look like new additions to art or literature. Most of data presented can be found in existing literature.
- The principal investigator has demonstrated modest progress on overcoming the barriers.
- There is not enough data to demonstrate the relationship between surface area, pore size, and binding energy.
- Though PIs show hydrogen weight percent adsorbed higher than the "Chahine rule," they still do not have any results above 2.5% at 77K, which is not anywhere near even state-of-the-art for activated carbons.
- Why are all the "super high surface area" samples tested at a different facility than the National Renewable Energy Laboratory? This raises some suspicions about the consistency of the various surface area measurements.
- The 8kJ binding energy is substantially higher than is typical for sorption materials; so this result is significant. However, the process used to obtain this binding energy [NMR measurements by HSCoE partner UNC] seems to have the strong possibility of experimental error (i.e., peaks from voids/pores first have to be separated, then integrated, and the resulting intensity from the pores is then fit to a Langmuir isotherm). It seems as though the experimental error bars on this binding energy are likely to be quite large, but the PIs do not report this error.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.8** for technology transfer and collaboration.

- Need to establish stronger collaborations within the Sorption Center of Excellence. Some collaborations are listed but could not be fully explained.
- The principal investigator did not demonstrate a close coordination with a theory group in defining the design parameters of a nanostructured sorbent material.
- The experimental results need to be independently verified, especially when a sample showed higher hydrogen uptake than expected.
- Good to see they are sending samples to the National Renewable Energy Laboratory for testing. Why are all of the samples not sent there?

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- Proposed future work (boron doping) duplicates on-going work at Penn State carried out by T. C. Chung and needs to be re-evaluated and relevant.
- The current experimental method is based on lab scale 1" diameter tube furnace. The potential scale-up issue of optimized experimental parameters needs to be addressed at this stage.
- The sample lost about 80 percent weight during activation process alone. The low yield will in turn increase the product cost and the issue should be addressed in future research plan.
- The proposed future work is not sharply focused on overcoming the barriers associated with these materials. The PIs are focused on achieving 6 weight percent (presumably at 77K) in their materials, but this is not the DOE 2010 target (which is a system target for *useful energy*, not a material target at 77K). Also, the proposed future research does not mention any attempts to increase volumetric density, which is just as important a DOE goal as the gravimetric target.

- Theoretical modeling work is proposed to study the effect of doping on binding energy. However, this modeling work is already ongoing in other parts of the CoE. (And, the PIs say they will collaborate with Rice and Air Products on this.) So, it is not completely clear whether or not this modeling is proposed to be part of the Duke project, and if so, what is the rationale for duplication of this effort?
- The work on doping of these carbons (e.g., with boron) seems to be somewhat redundant with other efforts in the CoE.

Strengths and weaknesses

Strengths
- The concept is aligned with DOE Hydrogen Program objectives and some of the results will help in understanding the relationship between binding energy and surface morphology.
- The main strength of this project is the successful synthesis of microporous carbons with variable pore sizes. This is an interesting accomplishment, and its implications towards hydrogen storage in these materials are not fully explored.
- Relatively modest budget for the work being performed.

Weaknesses
- The project has shown minimal progress and characterization of the carbons synthesized is lacking. The project could be strengthened by carbon microchemistry, surface activity/basicity, and other relevant characterization.
- Future work needs to be completely rethought and realigned to avoid duplication and to improve relevance.
- Lack of theory guided experimental design.
- The main weakness is the complete focus on gravimetric density (with a lack of attention on the volumetric density). The PI's approach for increasing gravimetric density is highly likely to actually reduce the volumetric density, which is arguably a larger obstacle for these materials.

Specific recommendations and additions or deletions to the work scope

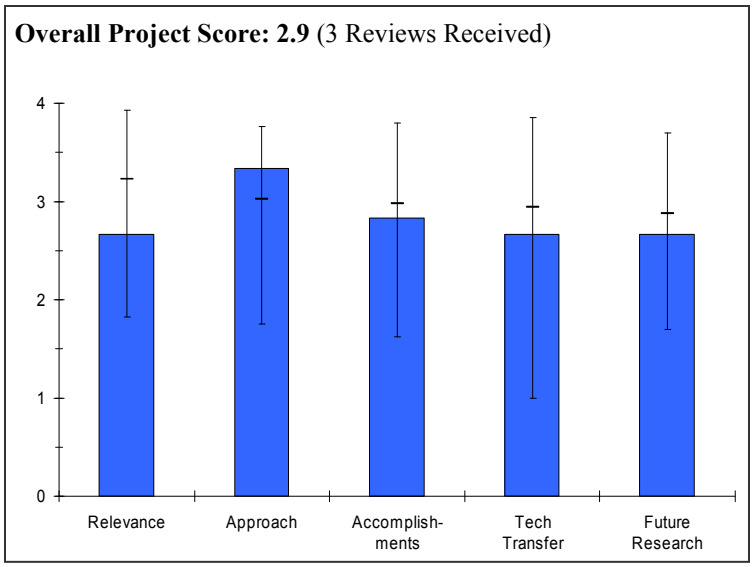
- The principal investigator can also try to activate the carbon with NH_3 other than CO_2.
- It is not clear whether the PIs are proposing to do theoretical modeling work in the future, but if so, I would recommend deleting this from the project scope. The PIs do not have expertise in this area, and it appears to be redundant with other activities within the CoE.

Project # STP-11: Advanced Boron and Metal Loaded High Porosity Carbons
Mike Chung, Presenting; Peter Eklund, Hank Foley, Vincent Crespi, Co-PIs, Pennsylvania State University

[NOTE: This project is part of the Hydrogen Sorption Center of Excellence.]

Brief Summary of Project

The primary objective of this project is to achieve the 6 wt% H_2 storage goal by increasing binding energy (10-30 kJ/mol) and specific surface area (SSA) (>2,000 m^2/g). Boron substitution in carbon structures has the advantages of: lightness of boron, enhancing H_2 interaction, no serious structural distortions, catalyzing carbonization, and stabilizing atomic metal. Activities for FY 2008 include 1) synthesizing the desirable B/C and M/B/C materials with B content (>10 mol%), M content (>3 mol%), and SSA (>2,000 m^2/g), and 2) studying structure-property relationships.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.7** for its relevance to DOE objectives.

- This project offers a unique approach to modifying the carbon structure with boron that could be an important breakthrough in understanding structure changes on hydrogen binding.
- The project claims to be ultimately aimed at a variety of DOE barriers, but only gravimetric capacity and adsorption enthalpy are covered in the presentation. Information on volume and kinetics would have been helpful to hear, even in a preliminary sense.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- Very good approach demonstrating strong modeling coupled with novel synthesis.
- Could/should be strengthened by broadening approach to consider other dopants to graphite structure and their impact on hydrogen binding energy.
- The overall approach, to increase the enthalpy of hydrogen adsorption on carbon, is good.
- Substitution of boron into the carbon structures has a good theoretical basis.
- The subsequent substitution of metal atoms provides a catalytic (spillover) component.
- Interesting approach to boron incorporation, and demonstrated significant levels of incorporation, coupled with a better than "Chahine-like" adsorption behavior.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.8** based on accomplishments.

- Good accomplishments.
- When is the go/no-go to determine when boron does not improve hydrogen storage and whether project should move on?

- The project has been successful in developing techniques to partially substitute boron for carbon in the structures.
- The addition of fine metal particles (~2 nm) has also been successful.
- The project has been successful in increasing the hydrogen adsorption enthalpy by 100 percent, a significant achievement and the confirmation of theoretical predictions.
- In spite of this, the 77K hydrogen-capacities seem on the low side relative to DOE targets, at least at 1 bar pressure. It would be interesting to see some higher pressure data.
- Have produced boron-doped materials with approximately 10 percent boron.
- The boron/carbon structure obtained as a function of pyrolysis temperature seems quite unusual. Do the principal investigators have some hypothesis to explain the proposed model? Is this model based solely on the XRD data of the d-spacings? If so, are there alternate explanations?
- The principal investigators have achieved a significantly increased binding energy of 11-12 kJ/mol. However, they should report error bars associated with the process of extracting these numbers.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.7** for technology transfer and collaboration.

- Collaborations are not clear. Need to elucidate collaborations, not just list or explain.
- There are some collaborations within the Hydrogen Sorption Center of Excellence, but they seem somewhat limited.
- There are no apparent collaborations outside the center of excellence, or internationally.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.7** for proposed future work.

- Proposed future work needs to be clearly delineated and expanded upon. Much of future work looks similar to work already ongoing in the center of excellence. Show uniqueness.
- Future work is a logical extension of the past results.
- The description of the actual work planned is not very detailed.
- There should be a go/no-go target.
- The proposed future work is not sharply focused on overcoming the barriers associated with these materials. The principal investigators are focused on achieving 6 weight percent (presumably at 77K) in their materials, but this is not the DOE 2010 target (which is a system target for *useful energy*, not a material target at 77K). Also, the proposed future research does not mention any attempts to increase volumetric density, which is just as important a DOE goal as the gravimetric target.
- The future work relies on "finding the right metal M". How do the principal investigators propose to find this metal?

Strengths and weaknesses

Strengths
- This project offers a unique approach to modifying the carbon structure with boron that could be an important breakthrough in understanding structure changes on hydrogen binding.
- The project is looking in detail at the boron approach for increasing hydrogen adsorption enthalpy.
- The project combines synthesis advances with property evaluations.
- The group has excellent synthesis capability and understanding.
- Interesting approach to boron and metal incorporation; good synthetic approach.

Weaknesses
- Catalyst decoration needs to be expanded past current materials (i.e., Ti and Zr). Look at more relevant catalysts.

- Carbon structure can be modified with more than boron. Other cations have been shown to change surface catalytic properties and should be evaluated in this project.
- Apparently not working on specific properties other than weight.
- It seems this approach will have difficulty reaching any system target. Carbon may have insurmountable limits.
- Progress seems somewhat slow, given the amount of time spent, and the budget involved.
- The project should have an equal focus on volumetric and gravimetric densities (right now, volumetric densities are not mentioned).
- No rational course is proposed for deciding which metal is the best to incorporate in these materials.

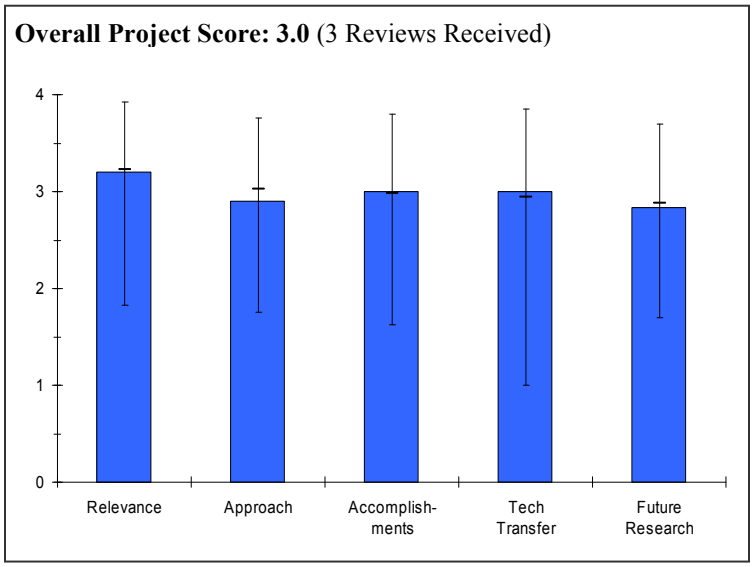
Specific recommendations and additions or deletions to the work scope

- Look past boron to other additives to carbon.
- More consideration to cost, volumetric capacity, and kinetics.
- Add some higher pressure measurements, if necessary through Hydrogen Sorption Center of Excellence partners.
- Add one or two measurements at room temperature. Would boron show some advantage there?

Project # STP-12: Nanoengineering the Forces of Attraction in a Metal-Carbon Array for H_2 Uptake at Ambient Temperatures

James Tour, PI; Carter Kittrell, co-PI; Rice University

[NOTE: This project is part of the Hydrogen Sorption Center of Excellence.]



Brief Summary of Project

The primary objective is to design and produce layered carbon-metal media with nanoengineered attractive forces capable of exceeding 80 g/L volumetric uptake of dihydrogen at -20°C. Nanoengineering the structure is conducted to effect the forces of attraction for dihydrogen. Four attractive forces are designed to act cooperatively to "pull dihydrogen" into the pore; these include: 1) Van der Waals attraction to a pi cloud of sp^2 (graphene or CNT) carbon surface; 2) dipole induced-dipole attraction between a charge separated (+) metal atom layer and a (–) graphene layer; 3) charge induced-dipole attraction near charged metal atoms; and 4) "Kubas-type" interactions for transition metal atoms. Regarding force design parameters, each of the binding energies are intentionally chosen to be inadequate to bind H_2 at room temperature, but collectively will "pull H_2" into the pore.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- A large number of promising and unique nanoengineered materials have been designed and synthesized. However, as observed last year, virtually no hydrogen storage measurements were presented. While the materials synthesis and characterization efforts are understandably time-consuming, some preliminary hydrogen storage data is highly desired. If it is a matter of coordinating with the sorption CoE to facilitate these measurements, then these interactions should be better developed.
- The project has a sharp focus on the need to develop hydrogen storage materials with volumetric hydrogen densities and enthalpies of dehydrogenation that are adequate to meet US DOE targets. However, this project suffers from a lack of careful consideration of the gravimetric hydrogen densities and the cost of the envisioned materials. The cost issue has not been addressed including presenting an estimate of the cost of the final, functionalized, metal-loaded material.
- Layered nanostructures assembled from well-studied graphene and further modified to elicit higher binding affinities for dihydrogen in the pore structure is precisely the theme of research on which the Sorption CoE should focus its efforts.
- Effort is consistent with other researcher's renewed interest in the manipulation of graphene or graphitic carbons to prepare oxide functional groups.
- Proposed concepts for modifying internal pore structure merge well with other, highly ordered nanostructures such as metal organic frameworks, thus establishing a common tactic for future research efforts.

Question 2: Approach to performing the research and development

This project was rated **2.9** on its approach.

- It was not clear in the presentation how meaningful and to what extent Rice is interacting with other collaborators in the sorption CoE.
- It is anticipated that additional collaboration with center partners would be particularly valuable in the area of hydrogen storage measurements. Could/should be strengthened by broadening approach to consider other dopants to graphite structure and their impact on hydrogen binding energy.
- The project is directed towards a establishing a synergism between hydrogen-graphene Van der Waals interactions and the coordinative interaction in dihydrogen metal complexes. This is an interesting premise. The investigators seem to be very knowledgeable in the art of functionalization of CNTs and graphene. However, the project suffers from the lack of any real understanding of dihydrogen ("Kubas") complexes. As Kubas himself has repeatedly pointed out, a very special electronic environment must be established at the metal center in order for dihydrogen to bind to a metal center without rupture of the H-H bonding. There seems to be no appreciation of this in the planning of this project as it is proposed to introduce Pd(0) (which very unlikely supports dihydrogen ligands) into a ligand environment that is not conducive to stabilization of dihydrogen ligands.
- The approach, though ambitious, should establish a benchmark for comparing surface- and pore excess effects in "doped" physisorption materials as it is aimed at employing all non-bonded (classically) forces of attraction which, heretofore, have been studied only individually.
- One potential pitfall of the approach is that the end product becomes over-engineered to the extent that the cost of synthesis is prohibitive even though the starting materials and proposed dopants may be of low cost.
- Need to accelerate synthetic and bulk analytical efforts in order to validate at least one or two aspects of the energy "tunability" of the layered pore structures.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- In general, future plans are a logical extension of current work. This reviewer would advise placing much more emphasis on testing storage properties (e.g. uptake, binding energy calculations, cycling, etc). Additionally it is recommended that collaborations with center partners be clarified.
- Excellent progress has been made in single sheet graphene functionalization chemistry and the introduction of lithium into the modified materials. It remains to be seen if this progress is an important step towards overcoming technical barriers in the hydrogen storage problem.
- Very significant and impressive progress relative to the development of the nanoengineered slit pore concept, but more rapid transition of chemistries from nanotubes to graphene is needed to validate conceptual approach
- Overall program is 60% complete of budget or milestones (not indicated). If 60% complete of budget, the remaining 40% must be expended on probably the most labor and time consuming aspects of the technical approach. Should this be of any concern?

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.0** for technology transfer and collaboration.

- It was not clear in the presentation how meaningful and to what extent Rice is interacting with other collaborators in the sorption CoE.
- It is anticipated that additional collaboration with center partners would be particularly valuable in the area of hydrogen storage measurements.
- Limited collaborations within the CoE.
- Collaboration with other important theory- and experiment-based teams (e.g. NREL, ORNL, Air Products, etc) is evident.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.8** for proposed future work.

- In general, future plans are a logical extension of current work. This reviewer would advise placing much more emphasis on testing storage properties (e.g. uptake, binding energy calculations, cycling, etc). Additionally it is recommended that collaborations with center partners be clarified.
- Future plans address several fundamental issues that will contribute to a finer fundamental understanding of the nature of the interaction of hydrogen in functionalized graphene. However, a sharper focus to bring these materials towards a go/no-go decision is necessary.
- Proposed future research adequately addresses concerns about the need to obtain experimental validation of proposed "nanopump" concepts.
- It will become particularly important to assess, theoretically and experimentally, the relative contributions of attractive forces engineered into the pore of the layered structure. For example, dipole-induced-dipole interactions may prove to be sufficient for dihydrogen pumping without charge or “Kubas-type” functionalities. This delineation should be included in the plan.

Strengths and weaknesses

Strengths
- Diverse approach and strong materials synthesis capabilities/expertise.
- Recognized leader in nanoengineered carbon-based materials.
- The PI is clearly working toward room temperature storage and high volumetric capacity, two of the major challenges with this class of materials.
- Expertise in graphene functionalization chemistry.
- Concepts are well thought out and supported, in part, by theoretical predictions.
- Engineered layered structures of the kind proposed enables one to explore many different options to enhancing room temperature uptake of dihydrogen in nanoporous materials. The best options which emerge are likely to be relevant to engineering storage materials based on other highly ordered nanostructures.

Weaknesses
- Hydrogen storage property evaluations need to be performed routinely for all promising materials.
- The whole project rests on the to be assessed premise that the dihydrogen metal complexes will be formed within these materials and if they do, that the materials will have adequate gravimetric hydrogen storage densities at room temperature.
- The weakness in the approach is one of potential over-complexity if all modes of binding are eventually implemented. This may lead to a costly material to synthesize even if it meets or exceeds the storage goals.

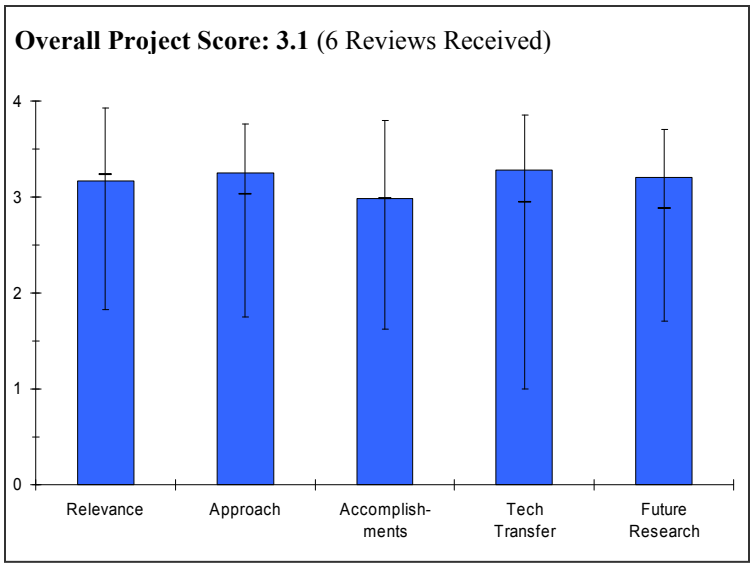
Specific recommendations and additions or deletions to the work scope

- In the next year it should be established if these materials actually storage hydrogen at room temperature and if so, what gravimetric and volumetric capacities have been achieved.
- While the goal of nanoengineering the forces of attraction in pores of metal-carbon layered structures is to attract dihydrogen without dissociation, the realization that dissociative uptake of atomic hydrogen is possible should be explored further as an alternative mechanism. In particular, one should ask whether or not a dissociative mechanism would be more favorable, thermodynamically, than non-dissociative binding within layered pores, and should structures be engineered to purposely affect this mechanism?

Project # STP-16: Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

Dan Mosher; United Technologies Research Center

[NOTE: This project is part of the Metal Hydride Center of Excellence.]



Brief Summary of Project

The objectives of this project are to: 1) design and synthesize hydride/nano-framework combinations to improve a) reversible capacity, b) desorption temperature, and c) cyclic life; and 2) build upon successes previously demonstrated in the community and extend to a wider range of doped, functionalized and catalyzed framework chemistries to a) advance the understanding of behavior modification by nano-frameworks, b) obtain/maintain nano-scale phase domain, c) tune hydride/framework interactions to decrease desorption temperature for highly stable compounds, stabilize high capacity compounds – ligand elimination, and influence desorption product formation, and d) activate H_2 dissociation on highly dispersed catalytic sites.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- The project is well aligned to the program objectives and relevant to the President's Hydrogen Fuel Initiative. It is well committed to reach the Department of Energy objectives and focused on addressing the big challenge of improving reversibility of high capacity hydride candidates.
- Work is relevant to DOE objectives.
- Development of nanoframework is one of the ways to increase kinetics in metal hydrides.
- Partially supports the hydrogen vision and DOE research, development and deployment objectives in the areas of charging/discharging kinetics, reversible capacity, and cycle life.
- Seeks to lower desorption temperature, stabilize desired phases, and increase rehydriding rates.
- Is focused on exploring metal hydrides that have relatively high hydrogen weight percentages (e.g., $LiBH_4$).
- The project is well-directed toward solving the weight, volume and thermodynamics targets and needs defined by the Program.
- Reversibility is a troublesome, yet very important property to achieve for on-board vehicular storage applications. Project correctly aims at this property.
- Mostly relevant.

Question 2: Approach to performing the research and development

This project was rated **3.3** on its approach.

- Well thought out, reasonable approach, with a clear direction and focus on technical barriers, using atomistic, thermodynamic modeling to identify promising as well as unfavorable system characteristics to guide the work.
- Getting the most out of previous experience and expertise and fully engaging modeling and experiment.
- Theory and experiment are well integrated. Atomistic and thermodynamic modeling to screen framework design and interaction with metal hydrides is very helpful before synthesizing materials.

- Experiments are well designed and conducted.
- Ability to tune nanoframeworks with dopants to enhance stability and interaction with metal hydrides is important to research.
- Conceptually interesting approach that involves dispersing metal borohydrides in nanoframework structures (NFSs) formed by aerogel techniques; this methodology provides an enhanced surface-area-to-volume for the borohydride that facilitates dehydrating and rehydriding.
- Theory (simulation) and experiment are combined to identify compatible NFSs.
- The NFS approach also offers the possibility to incorporate catalysts and to take advantage of beneficial interactions between the borohydride and the NFS.
- Eventually they hope to identify NFS/borohydride systems that exhibit target level cycle life and kinetics.
- Carbon NFSs have shown promise for some storage media. This project should help in testing the generality of the concept, such as extending it to oxide NFSs.
- There is a good coupling between theoretical prediction effort, synthesis and experimental verification.
- A nice spectrum of experimental techniques is in use.
- The inclusion of catalysts into the NFS will be an important component of the project.
- Unclear if theory is really "guiding" the experiment considering the complexity of the sorbent/scaffold interface structure. Have all reasonable interfaces been examined?
- Are the theoretical predictions on slide 13 for the lowest energy pathway? For example, the second reaction has bare Li and H bonded to Al_2O_3 -- is this more favorable than having all Li and H in LiH?
- There seems to be a trial-and-error aspect to the experimental approach of choosing what sorbents to use for scaffolding.
- The approach is based on the hope is that the scaffold will stabilize weakly-stable sorbents, and destabilize strongly-bound sorbents, but there does not appear to be a clear pathway for achieving the desired effect for a given sorbent.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- Some progress already achieved despite that this is a rather new project. NFS material systems have already been developed, and down-selection of the hydrides to be incorporated has been made.
- This is a new project (starting July 2007), yet impressive accomplishments have been achieved in both modeling and experiments.
- Initial data on hydrogen release is very slow. Need to demonstrate faster kinetics as a primary focus.
- Used simulation methods to down-select NFS candidates.
- Identified and investigated a stable combination of $LiBH_4$ in ZrO_2 aerogel;
- $LiBH_4$ compatibility with a series of NFSs was tested.
- This project comes across as a work in progress. (They are one year into the current scope of work.)
- Although the project just started at the beginning of fiscal year 2008, good progress has already been made (e.g., defining the suitability of ZrO_2 and non-suitability of SiO_2 as NFS for Li- and Ca-borohydride).
- Relative values of various screening techniques are being defined.
- No apparent work yet on catalyst inclusion into the NFS.
- I expected to see some preliminary calculations or suggestions as to how much loss in volumetric and gravimetric capacities might be expected from NFS.
- New project - not ranked.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.3** for technology transfer and collaboration.

- Good cooperation with the partners from the Metal Hydride Center of Excellence; a coordinated effort, engaging theory, material synthesis methods and characterization tools for tackling the challenge of improving reversibility of high capacity promising hydrides via advanced NFS chemistries.
- Extensive collaborations with the Metal Hydride Center of Excellence, partners, and industry.

- Principal investigators may want to consider some interactions with Lawrence Livermore National Laboratory on carbon aerogels.
- There are three partners and each has a clearly defined role to play in the project.
- The project is integrated into the Metal Hydride Center of Excellence, so presumably it is coordinated with other related activities in the center.
- This is a good fit for the Metal Hydride Center of Excellence.
- Good collaborations among United Technologies Corporation, Sandia National Laboratories, Albemarle Corporation, and Aspen Aerogels. Duties of each are well defined.
- Collaborations allow access to a very nice array of screening and test equipment.
- Collaboration with Aspen Aerogels will help to quantify ultimate costs of the composites.
- New project - not ranked.
- Since there are now several projects pursuing scaffolding, need to be careful about duplication of effort.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.2** for proposed future work.

- Future work planning builds on past results and includes critical go/no-go decision points.
- The plan for future research is very solid.
- Modeling studies will focus on $Ca(BH_4)_2$ and $NaTi(BH_4)_4$ with emphasis on interactions with the ZrO_2 NFS and catalyzed versions of the ZrO_2 NFS.
- Experiments/testing will focus on ZrO_2 NFS, on identifying other stable NFSs, and on interactions of $Ca(BH_4)_2$ and $NaTi(BH_4)_4$ with NFSs and catalytically augmented versions of selected NFSs.
- Future plans follow the original contract aims.
- Plans are rather vague.
- Milestones are good.
- Go/no-go criteria are not quantitative enough.
- New project - not ranked.

Strengths and weaknesses

Strengths
- Strong team with demonstrated expertise in their respective areas of responsibility - very good, complementary.
- Combining theory and experiment for fine tuning the work program.
- Unique approach with the combination of metal hydride and framework.
- Potential production of cheap, easy mass productions.
- Very solid and promising work.
- Extensive collaboration.
- Good understanding of important issues.
- The lead organization and partners have the facilities and capabilities needed to succeed in this project
- The project is emphasizing metal hydrides that have relatively high hydrogen weight fractions.
- It is a good combination of theoretical modeling, synthesis and screening.
- Collaborative interactions are excellent and provide equipment and expertise.
- The people involved are very well experienced in the field.

Weaknesses
- Need to clarify the path to use for controlling the hydride incorporation into the nanoframework and the associated mass transfer issues
- Approach to reach the target is not clear.
- None identified.
- Very little is apparent in the experimental work done to date that the NFS-based concept will actually work as expected.

- Because of the diluting effect of the NFS, the NFS-based concept is not likely to lead to a material embodiment that will meet DOE's system weight percent and volume percent targets; but it might meet some of the rate and cycle life targets.
- I estimate that roughly $500K was expended on this project over the past year; if that is indeed the case, I would have expected more testing results to have been completed; the score in box 3 above would be higher if more results were obtained in the past year.
- The project is focused entirely on borohydrides, a tough challenge from the perspectives of thermodynamics, reversibility and potential boranes in the exit hydrogen.
- Go/no-go criteria are rather vague.

Specific recommendations and additions or deletions to the work scope

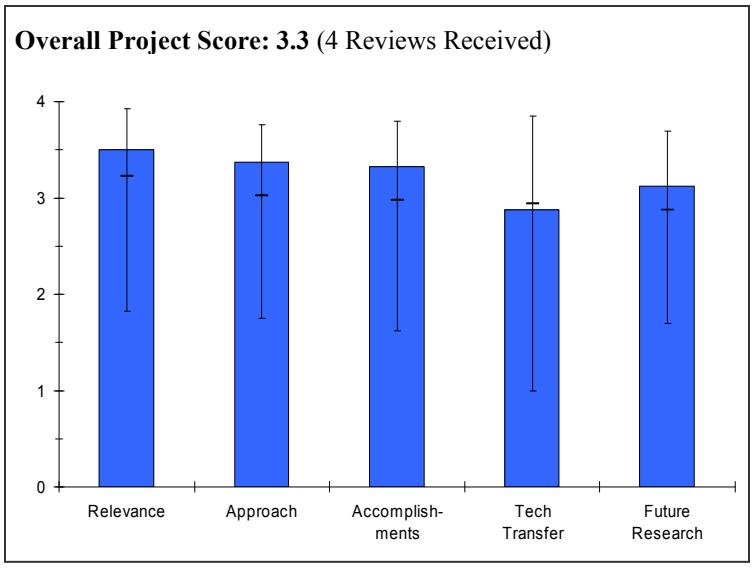
- Consider establishing a cross-center collaboration and interaction to benefit from the expertise developed in the Hydrogen Sorption Center of Excellence on aerogels
- Interact with Lawrence Livermore National Laboratory on carbon aerogels.
- Increase productivity.
- Stick with metal hydrides that have weight fractions on the high end of the possible range (nominally greater than 10 weight percent) because the nanoframework structure will diminish the overall weight and volume percentages of contained hydrogen.

Project # STP-18: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

Bruce Clemens; Stanford University

[NOTE: This project is part of the Metal Hydride Center of Excellence.]

Brief Summary of Project



The objectives of this project are to 1) develop fundamental understanding of metal hydride reaction kinetics; 2) develop understanding of metal hydride nanostructure thermodynamics; and 3) develop understanding of metal hydride structures during phase change. Little is known about the kinetic mechanism present in many promising metal hydride material systems including Mg, Mg_2Si, Li_4Si, $NaAlH_4$, $LiBH_4$+MgH_2, etc. In order to improve the kinetics for any of these metal hydride systems, a sound understanding must be developed. Many systems suffer from inappropriate thermodynamics (equilibrium pressure), including Mg and Al, and continuum modeling suggests that reaction thermodynamics should be modified by reducing particle size to the nanometer regime. Material structure can play important role in reaction kinetics, especially during solid-state phase transformations such as those in metal hydride reactions, and understanding the interplay between material structure and reaction kinetics may provide insight on how to successfully engineer new materials with improved kinetics and storage properties.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.5** for its relevance to DOE objectives.

- Understanding effects of crystal structure on thermodynamics and kinetics of materials is necessary for the design of improved materials for the Hydrogen Program.
- Project as presented and described is outstanding and attempts to understand kinetic issues limiting the use of carbon materials.
- This is a science-based project that seeks to develop insights concerning reversibility, capacity enhancement, physisorption, and chemisorption in hydrogen storage systems.
- The project's principal relevance lies in the opportunity to educate the next generation of scientists needed to advance fuel cell development through at least the first half of the 21st century.
- The results should contribute new knowledge concerning hydrogen reaction kinetics and the thermodynamics of hydrogen uptake and release at the nanoscale.
- This project is developing novel and potentially excellent experimental tools to better understand metal hydride reaction kinetics, thermodynamics, and structural phase changes that should enable the development of improved metal hydride systems for on-board hydrogen storage.
- The techniques being developed in this project are directed only at metal hydride research. Metal hydrides have been researched for a relatively long time. The considerable amount of data already available suggests that metal hydrides have a low probability of meeting the challenging DOE on-board storage targets.

Question 2: Approach to performing the research and development

This project was rated **3.4** on its approach.

- Elegant approach (bottoms up) to understand how crystal structure affects kinetic, etc. Other approaches have used a more brute force of grinding materials to nanoscale and then immobilizing them without truly understanding the morphology of those particles. This technique should help the producers of scaffolds, etc. design more intelligent materials that could perhaps take advantage of effective structures discovered by this work.
- Very good approach demonstrating strong theoretical understanding coupled with strong experimentation and verification.
- While the approach is good, this project is still evaluating pristine surfaces with idealized metal clusters. What is the role of the size and morphology of the metal cluster on spillover? How do intentional changes in the carbon structure through doping with boron or nitrogen or defects affect metal.
- Surface science in a very low oxygen impurity environment.
- The principle research tools are comprehensive x-ray diffraction, quartz crystal microbalance, and neutron scattering with emphasis on oriented and/or epitaxial films, with most work to date done on Mg and Mg containing films.
- The insights from this research could be beneficial to interpreting hydrogen kinetics in ordered structures and nanoscale phases.
- The approaches taken in this research are not likely to identify new types of hydrogen storage materials, but could shed light on novel concepts for kinetics enhancement.
- This project is developing thin film growth techniques, an in-situ hydrogen pressure chamber for use with x-ray studies for real time structural change observations during hydrogen charging and discharging, and quartz crystal microbalance techniques to measure hydrogen uptake on thin films and nanoparticles. These novel techniques should in theory elucidate structural changes and thermodynamic properties of metal hydrides during hydrogen charging and discharging that should enable the development of improved metal hydride hydrogen storage materials.
- The techniques being developed are challenging to develop and it is challenging to prove the results and data interpretation are valid. Results to date on model systems are intriguing but some do not agree with other available data.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.3** based on accomplishments.

- A few thin films have been prepared with sputtering of Mg particles on a sapphire substrate. Proof-of-concept has been demonstrated. The principal investigator must demonstrate the technique on a wider range of substrates and complex hydrides for the technique to be useful to a wide range of material researchers.
- Technical accomplishments to date are outstanding.
- Mechanistic understanding of spillover being developed will lead to a new understanding of how carbon sorbs hydrogen. Identification of spillover as a phase nucleation process allows the temperature and pressure barriers to be modeled. Further allows predictive path forward to overcome barrier to be developed.
- Showed how hydriding/dehydriding of Mg films with preferred orientation causes loss of the preferred orientation, the extent of this loss depending on the degree of hydriding; the interpretation of this result as being related to the retention of some underlying (presumably unhydrided) template layer is an interesting and understandable finding.
- Presented data that indicated hydrogen uptake by nanoscale particles "might" deviate from predictions based on bulk phase thermodynamics.
- Also presented some preliminary neutron scattering data that look very interesting but have not been fully analyzed to derive the attendant surface morphological information.
- Completion/confirmation of measurements done to date will earn a higher score here in the future.
- The development of the novel and potentially excellent experimental tools within the project is progressing well.
- It has taken 3 years to reach the point of beginning to get potentially meaningful data from the techniques being developed.
- The information obtained from the in-situ hydrogen pressure chamber with real time x-ray studies shows evidence of mixed crystal re-growth for the Mg/MH_2 system which may explain its poor performance.

- The quartz crystal microbalance combined with the thin film and nanoparticle techniques is being used to begin to developing information supporting the theory that the smaller the material particle size the better the performance will be, but some of the data being generated is not in line with other available data.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.9** for technology transfer and collaboration.

- Great interaction with Dr. Ralph Yang at Michigan.
- Technology transfer for this project is basically collaborations that provide materials, facilities, or supporting calculations.
- This project is already within the preview of the Metal Hydride Center of Excellence, so insights gained from the Stanford University research should flow smoothly into the center of excellence as a whole.
- Papers are being published and presented relevant conferences.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.1** for proposed future work.

- Continue to expand material and substrate library. The principal investigator should begin to seek partners that can design scaffolds, etc. to stabilize these structures since the materials are not stable under cyclic conditions.
- The future plans build appropriately on where the project stands at this time; several of the experiments presented at the review need to be repeated and there are data analyses that need to be completed.
- Future work will emphasize materials at the nanoscale which is recommended.
- Moving on to new materials compositions will take place, presumably after all the observations presented at the review have been confirmed, formally reported to the center of excellence, and published.
- The future work plan is to complete the development of the techniques and to start to examine metal hydride materials that are more promising relevant rather than the model systems used to date. This is good.

Strengths and weaknesses

Strengths

- Elegant approach (bottoms up) to understand how crystal structure affects kinetic, etc. Other approaches have used a more brute force of grinding materials to nanoscale and then immobilizing them without truly understanding the morphology of those particles. This technique should help the producers of scaffolds, etc. design more intelligent materials that could perhaps take advantage of effective structures discovered by this work.
- The graduate student who presented the poster did so in a scholarly and enthusiastic manner; clearly, he is well directed and is fully engaged in the project - that's a very good sign this project is being conducted the way a university program should be and bodes well for the availability of the cadre of bright young scientists and engineers needed to take fuel cell development through the coming decades.
- The facilities, experimental/computational skills, and understanding needed to study hydrogen interactions at the nanoscale are in place at Stanford and/or through their collaborations.
- Once it is reconfigured and its functional features are fully understood, the QCM should become a very useful tool for exploring hydrogen uptake and release at the nanoscale in well controlled environments.
- This project is developing novel and potentially excellent experimental tools to better understand metal hydride reaction kinetics, thermodynamics and structural phase changes that should enable the development of improved metal hydride systems for on-board hydrogen storage.

Weaknesses

- The principal investigator has not investigated templates that can be overlaid over these new structural configurations in order to maintain performance with cycling. This should be the future focus or at least transfer the knowledge to someone who can perform such work.
- This project is on the verge of producing some nice science, but the confirmatory experiments and the unfinished data analyses need to be completed.

- Reducing the oxygen impurities in experimental systems to levels low enough to allow pristine study of hydrogen in easily oxidized metals is not a trivial problem; clever ways to exclusively getter oxygen in the presence of hydrogen may be needed to effectively measure hydrogen metal interactions.
- Apparently, no peer reviewed publications have been submitted for this work.
- It is not clear exactly how the particular techniques being developed can be best applied to the most promising metal hydride systems.

Specific recommendations and additions or deletions to the work scope

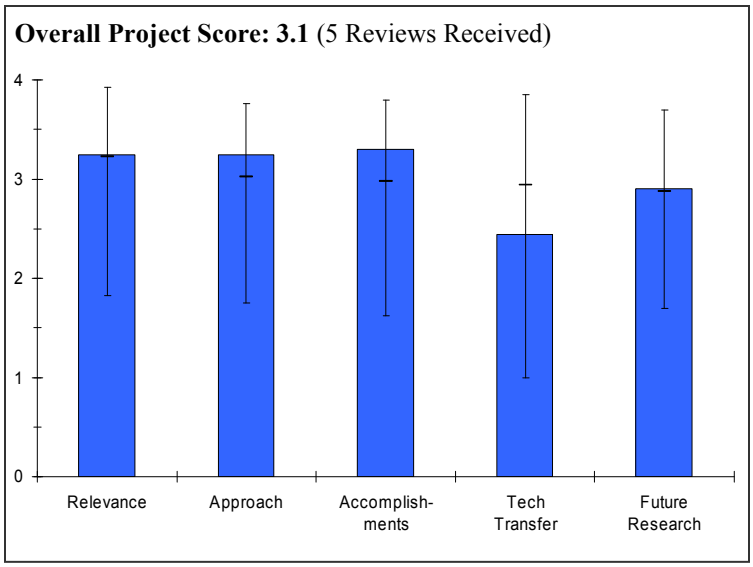
- While very interesting and valuable work, perhaps this should be moved into the Basic Energy Sciences scope.
- The neutron scattering measurements being done with NIST look like they could produce many seminal insights about the impact of hydriding on surface structure - this aspect of the project deserves emphasis.
- Bring reported results to the point where publication is in order.
- The plan to integrate the QCM with the deposition system, characterization of the functional features of that integrated system, and subsequent utilization on nanoscale particles and films is encouraged.
- It might be worthwhile to base the selection of new materials on choices that have already survived down-selection at the centers of excellence.

Project # STP-19: Alane Electrochemical Recharging
Ragaiy Zidan; Savannah River National Laboratory

[NOTE: This project is part of the Metal Hydride Center of Excellence.]

Brief Summary of Project

The objectives of this project are to 1) develop a low-cost rechargeable hydrogen storage material with cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals; and 2) determine that aluminum hydride (Alane-AlH_3), having a gravimetric capacity of 10 wt% and volumetric capacity of 149 g/L H_2 and desorption temperature: ~60°C to 175°C (depending on particle size) meets the 2010 DOE targets for desorption. The specific objective of this project is to avoid the impractical high pressure needed to form AlH_3 by utilizing electrochemical potential to increase hydrogen activity and/ or drive chemical reactions to recharge AlH_3.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.2** for its relevance to DOE objectives.

- To synthesize AlH_3 with around 10 percent capacity is one of the major focuses of the Metal Hydride Center of Excellence.
- This project addresses programmatic goal of hydrogen storage systems to meet 6 weight percent storage with the storage system cost less than 30 percent of the hydrogen cost.
- Alane has high material capacity (10 weight percent) and has the potential to meet Department of Energy 2010 targets.
- Alane regeneration is crucial to its viability as a hydrogen storage material.
- This project is narrowly focused on low temperature/low pressure regeneration of AlH_3, a 10 weight percent hydrogen material that has the potential to meet 2010 hydrogen vision and DOE research, development and deployment targets for gravimetric hydrogen storage.
- Meeting regeneration efficiency and cost targets is also an objective.
- The project is highly focused on one particular topic, that of using electrochemical potential to drive hydrogenation of Al to form alane. Built into this scope is the fact that the project cannot be any more relevant to the Hydrogen Program than alane itself may prove to be. If other difficulties with alane, such as safety considerations or air/moisture sensitivity, force a no-go decision, the project will have little impact on the Program.

Question 2: Approach to performing the research and development

This project was rated **3.2** on its approach.

- Instead of high pressure direct reaction and complicated chemical reactions, simple electrochemical reaction is one of the ideal methods to synthesize AlH_3.
- The project is an electrochemical approach to developing a rechargeable storage media (aluminum hydride) that has the potential for storing greater than 10 weight percent hydrogen.
- The system will be implemented off-board.

- Very cleaver approach to avoiding oxide formation by forming chloride protective layer
- Electrochemical recharging of Al offers an alternative method to regenerate AlH_3 spent fuel
- Use of ionic solution electrolysis to form AlH_3 is a significant improvement from past years efforts
- Experimental work is consistent with electrolysis technique.
- The calculation of energy consumption need to include energy required to recover AlH_3 that dissolves in ether/THF.
- Electricity requirement to form AlH_3 by electrolysis of $NaAlH_4$ (8.44 kWh/kg H_2 experiment, 5.66 kWh/kg H_2 theoretical minimum) is significant. Regeneration by electrochemical means will not meet the DOE well to tank (WTT) efficiency target of 60 percent.
- Devising methods to electrochemically regenerate AlH_3 and alkali metal alanates using nonaqueous electrolytes.
- Attempting to elucidate reaction mechanisms, and to calculate overall process yields, efficiencies, and alane/alanate production costs.
- Characterizing products of electrolysis tests.
- Technical work has been well focused on identifying and overcoming the initial barriers to electrochemical formation of alane. This reviewer is favorably impressed by the researchers' demonstrated ability to make advances in this complex and difficult system.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.3** based on accomplishments.

- AlH_3 was synthesized but it was mixed with raw material $NaAlH_4$. The hydrogen capacity of the product is about 9 percent. However, there is no direct evidence that AlH_3 is clearly formed.
- Good progress demonstrating potential for over 8 weight percent system storage.
- Developed an understanding of optimal phase for alane.
- Focused in on appropriate solvent system and electrochemical parameters.
- Developed an understanding of the electrochemical cycle and identified reaction products.
- Developed an understanding of dendrite formation and how to avoid (using hydrogen overpressure).
- Demonstrated electrolytic alane formation in small quantities.
- New work using $NaAlH_4$ solution electrolyte is a significant improvement over past years efforts.
- Have successfully demonstrated formation of AlH_3 in $NaAlH_4$ electrolyte, even though the rate and yield are still very modest.
- Despite the success with $NaAlH_4$ electrolysis, unfortunately the WTT regeneration efficiency, even in the best case, has little chance of meeting the 60 percent target (electricity supply based on U.S. grid 2015).
- Demonstrated reversible alane formation and electrodeposition of $NaAlH_4$.
- Provided data that show the hydride production costs are in the range of DOE targets.
- Determined electrolyzer characteristics (e.g., electrode area) required to produce alane at meaningful rates.
- Good progress, within the tightly-defined scope. Investigators have identified "rate" as one critical barrier; using ether to dissolve and remove AlH_3 is one improvement (although it makes removing the ether a necessary subsequent step). Formation of Na_3AlH_6 may be another critical barrier; if so, the path to overcoming it is not presently clear. (Perhaps increasing amount of hydrogen available at cathode, to increase rate of capturing "Na" as NaH?)
- Minimizing electrochemical overpotential will be important for energy efficiency, but this reviewer didn't see this topic mentioned.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.4** for technology transfer and collaboration.

- This is almost an independent project. There are other approaches to synthesize AlH_3 which are being conducted by other members of Metal Hydride Center of Excellence.
- There is one university collaborator and no industry involvement.
- At this stage there seems to be little direct collaboration with industry, universities, or laboratories.

- This project is part of the Metal Hydride Center of Excellence but it is not clear how well integrated into the center of excellence it is at this time.
- Two partners are listed but it is not clear how these partners contributed to the work at Savannah River National Laboratory in fiscal year 2008.
- Collaboration does not appear to be a major component of project scope. If there were similar "electrochemical hydrogenation" needs elsewhere in the Hydrogen Program, collaboration with this team could be useful. The poster mentions partnerships with Brookhaven National Laboratory and Hawaii but not much about what these partnerships entail.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- The target reaction is not direct regeneration of AlH_3 from spent Al but synthesis of AlH_3 from alanate.
- Proposed future work focused on developing larger surface area electrode and use of catalysts to improve efficiency.
- Demonstration that larger surface area electrodes and catalysts can generate larger quantities of alane in larger electrochemical system.
- Will develop more efficient methods of extracting alane.
- The proposed future work to upgrade the electrochemical cell will accelerate the rate and increase yield.
- Working with other partners will be beneficial to the project.
- The proposed future plans build logically on what was done and what was learned in fiscal year 2008.
- Building and testing a larger electrolyzer is in the plan.
- Process optimization will be a major area of emphasis.
- So far, has been focused on "succeed or fail" with the $NaAlH_4 + Al + H_2$ process. While the "scale-up" barrier to operating this process is likely to be overcome, the ultimate workability of alane is hard to predict.

Strengths and weaknesses

Strengths
- To use electrochemical reaction to regenerate AlH_3 is a good idea.
- Sound electrochemical principles. Electrochemistry allows excellent process control capability through the applied voltage.
- Low desorption temperature (60 to 175°C) partially within range of fuel cell waste heat.
- Good understanding of electrochemistry.
- Good experimental techniques.
- The results so far are encouraging.
- The hydrogen storage materials under study are among the more promising ones for meeting DOE hydrogen storage capacity targets.
- The system appears to have formidable experimental challenges. Progress to date appears good.

Weaknesses
- The reaction studied is not AlH_3 regeneration from spent Al.
- Aqueous solution is electrolyzed if the voltage exceeds around 1.4 V considering the over potential.
- At present, hydrogen gas generated by electrolysis is the hydrogen source to regenerate AlH_3 from alanate.
- Off-board regeneration creates potential infrastructure issues.
- Attention must be paid to organic solvent clean-up to avoid unwanted electrochemical reactions/system inefficiencies.
- Overpotential greatly decreases efficiency of process. Need to concentrate on ways to overcome through catalysts. With overpotential, the storage cost for hydrogen approaches that for liquefaction, which is a potential significant drawback
- Electricity cost used for the process ($0.05/kWh) is not realistic in many parts of the country but could be achieved with nuclear.

- Regeneration of AlH_3 using electrochemical recharging will have difficulty meeting the DOE target for WTT efficiency of 60 percent.
- There is little external collaboration.
- A state-of-the-art approach to electrochemical cell design and electrochemical measurement might produce results and understanding beyond what has been established in this project to date and should contribute to making the proposed "optimization" effort in the coming year more successful - systematic electrochemical engineering is required.
- It is questionable whether a process that requires both hydrogen and nontrivial electrical power can be practical on a large scale. If it could be operated so as to need only electrical power it might be more attractive. It would also help if there were more momentum in favor of widespread use of AlH_3.

Specific recommendations and additions or deletions to the work scope

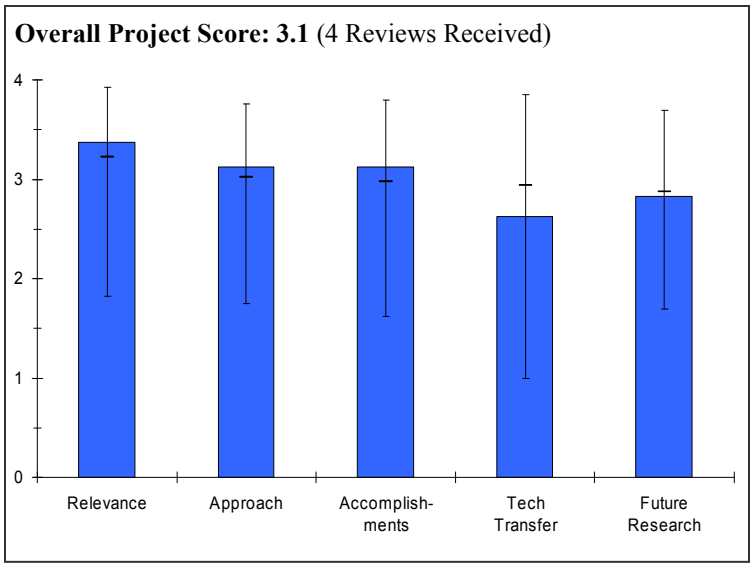
- Proper non-aqueous and stable electrolyte should be selected for further work.
- Close contacts with other AlH_3 regeneration people are strongly recommended.
- Get an industrial collaborator on board to evaluate potential for practical commercialization and costs.
- Accelerate understanding a choice of catalysts.
- Lifecycle systems costs should be examined, including cost of electricity to operate, solvent clean up, etc.
- Need to demonstrate more rapid alane formation rate using higher surface area materials. This should be a go/no-go in next year.
- Demonstrate electrolysis with $AlCl_3$ solutions, the other ionic solution system proposed by the principal investigators.
- Calculate energy requirement to recover AlH_3 from THF/ether.
- It would be good to show more comprehensive characterization results for the electrolysis products.
- Eventually, more detailed electrochemical measurements will be needed to elucidate electrode kinetics in a manner that defines the rate limiting electrode reaction (e.g., transient electrochemical measurements); such measurements can provide insights that aid the design and configuring of practical electrode arrays.
- There is considerable expertise and experience in the design of electrodes for continuous production of a solid deposit. Much has been published on this type of technology.

Project # STP-20: LiMgN Sorption Kinetics and Solid State Hydride System Engineering for the MHCoE
Don Anton; Savannah River National Laboratory

[NOTE: This project is part of the Metal Hydride Center of Excellence.]

Brief Summary of Project

The objectives of this project are to 1) determine heat management requirements for a refueling station based on metal hydrides; and 2) determine sorption kinetics for LiMgN. In 2008, the project will determine the hydrogen sorption kinetics and mechanisms of LiMgN over the temperature and pressure range of interest to DOE for automotive hydrogen storage applications.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.4** for its relevance to DOE objectives.

- Both efforts fit to the Department of Energy's research and development objectives.
- The heating engineering aspects of the project seem more relevant to gas station aspects rather than vehicle aspects.
- The heat engineering work appears more relevant to the new Engineering Center of Excellence and one wonders why it is being pursued at this point in time.
- This project includes two distinctly different efforts of specific value to the Metal Hydride Center of Excellence. Both are aimed at DOE's needs for the Hydrogen Fuel Initiative and DOE's research and development objectives.
- The refueling station heat and mass analysis is critical to answer the question if three minute refueling can be accomplished and how much it will cost in terms of heat removal requirements and cooling costs.
- LiMgN is a new center of excellence material with potential to meet DOE weight and volume storage targets.
- The project will provide confirmation of center of excellence preliminary results by others and obtain required charging and discharging kinetics for future heat load studies needed to achieve the three-minute refueling target.
- Understanding cooling requirements of a fast fill with exothermic materials is important towards developing a material based storage technology for an automotive infrastructure. However the PI proposes nothing new that wasn't understood 5 yrs ago.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- The approach of heat management is very reasonable even though heat management of refueling is only considered.
- The LiMgN study that just started is well organized.
- System analysis, especially from the view point of heat management, is very important to judge practicality and reality of hydrogen storage systems and infrastructure for them.
- This project appears to involve two disparate objectives, which have little interaction. The only thing that they have in common is that they are both engineering-related. That being said, the approach for each of the disparate activities is good.

- The refueling station was modeled in a relatively conventional way to provide useful insight into the massive reaction heat removal needed.
- The synthesis and kinetic work on LiMgN is routine and straightforward.
- Experimental details and planned kinetic parametric analysis are not clearly stated.
- It should be made clear that the kinetic studies on LiMgN will ultimately be used to address the three-minute on-board refueling target.
- PI used typical fueling station to provide model inputs. However, the PI only investigated using an evaporative cooler. Such systems were understood to be impractical due to size and water consumption many years ago- no new information was provided. A more interesting approach would have been investigating other heat sync such as metal hydride beds (as in metal hydride air conditioning systems) etc. An elegant solution to transferring such large amounts of heat must be realized for such systems. Evaporative cooling is not an elegant technique.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.1** based on accomplishments.

- Heat management has been well done.
- The results for LiMgN are preliminary.
- Real system image of infrastructure for hydrogen storage material tanks is very instructive for considering requirements for materials and tank designs.
- Why was LiMgN selected for investigation? Initial results show that its reversible capacity does not seem to be that high, the take-up/release temperatures are on the high side, and it appears to have cyclability problems.
- The heat engineering study has provided useful results for the cooling tower requirements that might be necessary at a hydrogen fueling station.
- The heat/mass transfer modeling work for the refueling has been completed, at least in a first cut. The results are useful in confirming the massive cooling water requirements and associated cooling system investments.
- The basic refueling plant requirements are defined. The bottom line is clear: the plant will work, but will be much larger than a gasoline plant.
- Preliminary LiMgN synthesis work has been reasonably successful.
- The cyclic work has not defined the pressure-temperature-time conditions for complete recharge yet.
- This calculation could be completed in one day by a talented heat exchange designer. Furthermore, a rough estimate could be completed in 15 minutes by almost any engineer sufficient to realize that such a technique for cooling is not feasible. This project should have investigated alternative approaches from the beginning.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.6** for technology transfer and collaboration.

- Input for heat management work has been done but the collaboration and technology transfer is not significant.
- Most of the collaborations are associated with the LiMgN work. No collaborations indicated for the service station work.
- Technology transfer and collaborations are limited to a few partners within the Metal Hydride Center of Excellence.
- Giving the “industrial” nature of the refilling station, an industrially experienced partner should have been included.
- Minimal interaction was required for this analysis. Results won't benefit forecourt designers since the results are self evident and don't provide novel insight to solving this heat rejection problem.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.8** for proposed future work.

- The heat management work has been finished.

- The future plan of LiMgN is reasonable.
- The diameter of pipe to feed coolant to a hydrogen storage material tank should be also estimated.
- Identifying uses for the waste heat seems like the most important aspect for the heat engineering work.
- For the LiMgN, what is the plan for increasing the reversible hydrogen storage capacity?
- The refueling station work is to be continued, but the plan is vaguely focused.
- It is not clear why any further work is needed on the refueling at this time. The basics plant questions have been answered for now and it is probably more important to move toward heat/mass transfer studies of the on-board hydride tank itself.
- The future work on LiMgN seems logical, per se, but not detailed very well.
- Validation of data is always important. The question not clearly answered is to what extent the future work is confirmative in nature. Is similar work being done by others within the center of excellence?

Strengths and weaknesses

Strengths
- In fact, engineering work has only been done in this project.
- None.
- The project has provided much needed information on the refueling plant design and heat requirements.
- Ad hoc work of engineering, validation and fine tuning should be useful to the center of excellence.
- A project which has the ability to respond to center of excellence needs not otherwise available has good value.

Weaknesses
- Only analysis for the heat management has been presented this year. Experimental work to develop total system and/or components of the systems is indispensable.
- Two disparate, non-interacting project activities are being pursued.
- It would seem that the real objective of this project is to enhance competitive posture for the new Engineering Center of Excellence.
- Proposed continuation of work on the refueling plant is doubtful and probably better placed into one of the analysis groups: TIAX or Argonne National Laboratory.
- The present and future LiMgN work is not clearly described: What exactly will be done and how will that generate the data that fits into the upcoming tank study?

Specific recommendations and additions or deletions to the work scope

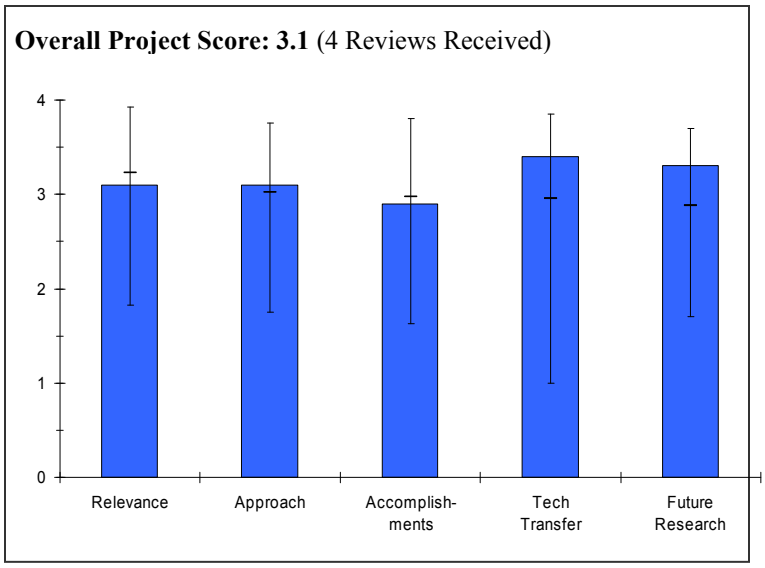
- The activities will be continued at the new Engineering Center of Excellence.
- Pick only one of these activities and concentrate on it.
- Delete any planned work on refueling plant modeling; transfer that to the established analysis groups.
- Set a quantitative go/no-go limit on the NH_3 level reductions of the exit hydrogen gas.

Project # STP-21: Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

Channing Ahn; California Institute of Technology

[NOTE: This project is part of the Metal Hydride Center of Excellence.]

Brief Summary of Project



The objectives of this project are to 1) understand if thermodynamically tractable reactions based on hydride destabilization, that should be reversible but appear not to be, are kinetically limited; 2) enable short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths; 3) address the problems associated with large, light-metal-hydride enthalpies (hydrogen fueling/refueling temperatures) and develop strategies to address thermodynamic issues surrounding the use of these materials through hydride destabilization.; 4) understand issues related to grain growth and surface/interface energies, which are vital in order to understand the kinetics of hydrogenation/dehydrogenation reactions; and 5) follow up on previously studied reactions with phase identification via X-ray diffraction, nuclear magnetic resonance and transmission electron microscopy.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.1** for its relevance to DOE objectives.

- The work is in line with the overall Department of Energy program objectives and of relevance for the attainment of research and development goals.
- Addresses some of the most challenging hydrogen storage targets for overcoming the barriers (B), (M), (N).
- There is a potential for high hydrogen storage capacity in mixed $LiBH_4$ - other hydride systems.
- The project provides technical information on key aspects of some of the potential routes to high capacity hydrogen storage materials.
- Materials studied, in all cases, have the potential to reach DOE weight and volume objectives.
- The project focuses on fundamental mechanisms in relation to reversibility and kinetics.
- The project is relevant to DOE objectives, but not very quantitatively so.

Question 2: Approach to performing the research and development

This project was rated **3.1** on its approach.

- This is a well-planned approach where material systems are chosen through theoretical screening by Metal Hydrides Center of Excellence partners and then predictions are checked in the laboratory.
- It explores the possibilities offered by the coupling of powerful experimental techniques.
- The project may be more sharply focused: either destabilized hydrides or Mg in aerogels.
- Concentrating on potentially reversible systems would improve the project quality.
- A sound approach of applying appropriate experimental studies to the key materials issues.
- There are two distinct experimental efforts to understand reaction mechanisms for materials generally derived from a priori predictive calculations. Both efforts involve nano-sized materials and both are valuable.
- One effort focuses nicely on the reaction pathways and reversibilities of destabilized mixtures.

- The second effort focuses nicely on infusing Mg into nanoporous carbon for potential thermodynamic improvements.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.9** based on accomplishments.

- Good screening of systems and progress towards objectives despite the not so encouraging results.
- In contrast to the calculated reaction enthalpies the large heats of formation of the reactant phases in the systems studied, are, as shown experimentally, still determining the overall kinetics. Additionally the formation of undesirable, stable intermediate phases are jeopardizing the reversibility of the system.
- The direct thermal decomposition reaction pathways are not easy to predict and overall there is still a strong need for understanding the reversibility mechanism.
- Interesting first results on the wetability of Mg in carbon aerogels and the effect of pore size on the reaction enthalpies. New avenues of investigation are now opening.
- Progress on $LiBH_4$-other hydride systems is good.
- Only overall reactions are shown. How about intermediaries? These may be extremely important in identifying rehydrogenation pathways.
- Confusing statements about AlB_2: it is shown as a final product, but x-ray powder diffraction data are inconclusive.
- The destabilizing effects of aluminum-containing species on $LiBH_4$ are interesting.
- Perhaps understanding why liquid $LiBH_4$ wets and infiltrates carbon aerogels so well might be useful in getting other species into the aerogel. What about Mg compounds or alloys with low sessile drop contact angles on graphite or graphene?
- Studies of the ScH_2-$LiBH_4$ destabilized mixture have shown it does not work nearly as well as predicted and why.
- The reversibility of $LiBH_4$ was improved by mixture with AlH_3 or $Ca(AlH_4)_2$. A potentially useful new Al "catalyst" effect was discovered.
- Progress was made on techniques to infuse Mg into carbon aerogels.
- Unfortunately, the principal investigator has not projected his new and interesting fundamental understandings of the materials studied toward the best paths forward to achieving the weight, volume and rate improvements needed for reaching DOE needs.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **3.4** for technology transfer and collaboration.

- Good collaboration record involving a number of laboratories and partners with diverse expertise.
- Not entirely clear if the experimental findings are effectively incorporated by the theorists for fine-tuning their models.
- Collaborations with others appear to be excellent.
- Systems being studied are identified by the Metal Hydride Center of Excellence theorists.
- Good collaboration with aerogel synthesizers.
- There are several good collaborations within the Metal Hydride Center of Excellence.
- With more transfer of information back to the partners, this can develop into a good example of the value of the center of excellence concept.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.3** for proposed future work.

- The project's future plans are logical, reasonable, building up on past experience and moving the research forward. Probably a bit ambitious given the resources available.
- There is some lack of focus. I believe that future work is too vaguely defined.

- Most of the future work appears to concentrate on carbon aerogels, rather than on systems that could destabilize $LiBH_4$.
- Future work should include further studies of the effects of aluminum on the stability of $LiBH_4$, particularly as to mechanisms of beneficial results.
- The proposed future work is reasonable.

Strengths and weaknesses

Strengths
- An enthusiastic team with access to powerful characterization tools.
- Exploring collaboration possibilities with the other Metal Hydride Center of Excellence partners and particularly with the theory group.
- Using a variety of characterization techniques.
- Potentially very high hydrogen capacity materials are under study.
- Excellent knowledge of and experience with carbon materials.
- The principal investigator and his personnel have excellent abilities to do nice, potentially very useful, fundamental work.

Weaknesses
- Investigating systems which may not meet the targets - reversibility, kinetics are limited.
- It is not clear whether the experimental findings are fed back to the theorists for fine tuning their prediction models.
- Relevance of work with Mg in aerogels to future work with "hydrides" is unclear.
- Hydrides may be difficult to impregnate into aerogels using thermal methods/
- None.
- It does not seem to be converting mechanistic results into suggested directions to the rest of the center of excellence for moving these materials toward the meeting of DOE goals and targets.

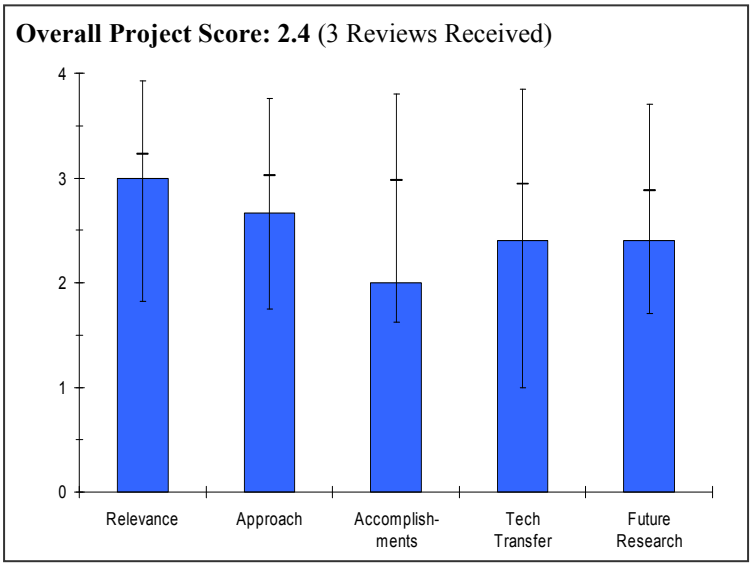
Specific recommendations and additions or deletions to the work scope

- Future plans may be ambitious given the resources available. Could consider to reprioritizing future activities and focus on the few tasks of utmost importance, based on the findings of the rest of the Metal Hydride Center of Excellence groups.
- Keep the communication channels with the theorists open and encourage the feedback of the experimental findings to the models.
- Could benefit from a closer cross-center of excellence interaction with the Sorbents on the aerogels work.
- Concentrate on the reversibility of AlH_3 - $LiBH_4$ system.
- Look into other sources of Al (beyond AlH_3) leading to effective destabilization of $LiBH_4$ and potential reversibility.
- Work with aerogels adds little to none, so it may be discontinued to better use available resources.
- Keep the focus on just a few key aspects identified by other members of the Metal Hydride Center of Excellence. Don't get too overextended.

Project # STP-24: Center for Hydrogen Storage Research at Delaware State University
Andrew Goudy; Delaware State University

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project



The overall objective for this project is to establish a Center for Hydrogen Storage Research at Delaware State University for the preparation and characterization of selected complex metal hydrides and the determination their suitability for hydrogen storage. The 2007 objectives are to 1) identify the most promising types of destabilized hydrides and demonstrate the optimum temperature/pressure range and sorption kinetics of the hydrides under a variety of conditions; and 2) determine their cyclic stability and develop improved sorption catalysts. The 2008 objectives are to 1) extend the studies to include other complex hydrides that have greater hydrogen storage potential than the destabilized hydrides, such as ternary borohydride systems; and 2) perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- The project supports the President's Hydrogen Fuel Initiative.
- One of the objectives of the project, to establish a center for hydrogen storage research at Delaware State University for preparation/characterization of hydrides, was met.
- The identification of potential complex hydrides with improved kinetics and a lower reaction temperature are not satisfactory.
- The project is focused on high capacity $LiBH_4/CaH_2$ systems.

Question 2: Approach to performing the research and development

This project was rated **2.7** on its approach.

- The technical approach is well designed.
- Technical barriers are not addressed to overcome.
- The research and development efforts are not well integrated.
- Weaknesses are described below.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.0** based on accomplishments.

- Results are presented without much insight.
- Publications and presentations are very poor. There was only one presentation at the Materials Research Society meeting in November 2007.

- Technical accomplishments are quite modest. A few "additives" have been examined by using thermogravimetric analysis, but none show improved reversibility or improved capacity.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.4** for technology transfer and collaboration.

- Collaborations are limited in scale.
- Collaborative relationships with other teams/investigators are non obvious.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.4** for proposed future work.

- The proposed future research approach is not addressed adequately based on the results of other Department of Energy projects.
- The approach to future research needs to consider contingencies.
- Future work is vaguely defined. It is unclear how and why future research will lead to meeting DOE objectives.

Strengths and weaknesses

Strengths
- The principal investigator has been involved in hydrogen storage activities for a long time.
- Kinetic modeling is a plus.

Weaknesses
- There is a lack of alignment between the project approach and the DOE goals.
- The project is trailing.
- The provided thermogravimetric analysis data appear to be unreliable.
- The future work is poorly defined. (It is extremely vague and unclear whether it can be accomplished, especially the first two listed goals).
- Due to loss of some B_2H_6, cyclic stability should be continuously deteriorating and low.
- No attempt to understand why the addition of $LiNH_2$ to an apparently reversible $CaH_2/LiBH_4$ system suppresses reversibility. Is it due to a formation of a stable nitride? Are there other reasons?
- It appears that there is no systematic approach.

Specific recommendations and additions or deletions to the work scope

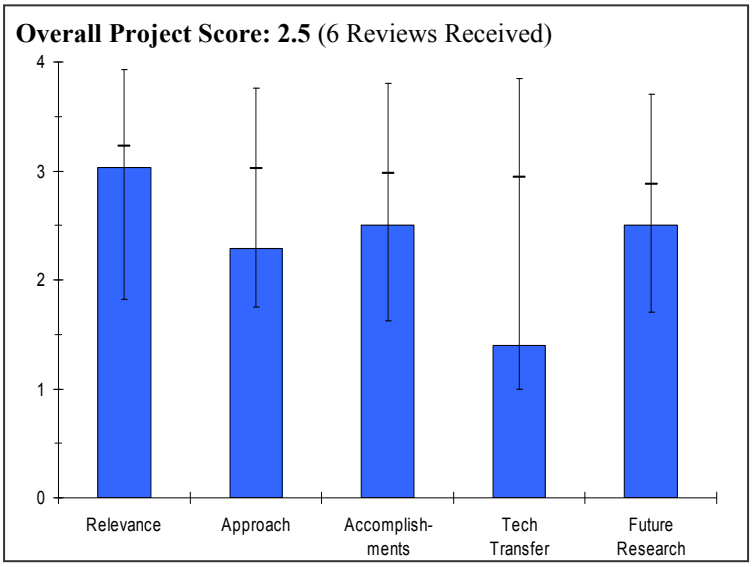
- The approach needs to be realigned with DOE program goals. For example, a storage system that requires 300-500°C for hydrogen release with say approximately 5 to 9 weight percent should be quickly reviewed and dismissed as it will not meet the 2010 overall system goals.
- In deciding on an alternate storage material, one has to consider the end-use system design and functionality. This needs to be shown in the approach.
- Based on the project management plan, the principal investigator is capable but needs to put more effort into the project.
- Given the current status of the project, it is difficult to suggest any meaningful additions/deletions.

Project # STP-26: Novel Metal Perhydrides
Jim Hwang; Michigan Tech University

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The overall focus of this project is to: 1) develop new kinds of materials that are able to bind hydrogen molecules into clusters; and 2) enhance hydrogen adsorption/desorption by means of hydrogen cluster formation/decomposition so that the capacity of materials for hydrogen storage and the kinetics for hydrogen release have the potential to meet the DOE 2010 and 2015 targets. The objective over the past year was to 1) study the potentials and roles of charged/polarized species on hydrogen cluster formation; and 2) examine the interaction behavior of charged species with hydrogen.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- This project addresses hydrogen storage capacity and adsorption and desorption using a unique approach.
- The project addresses relevant goals.
- This is an exceptionally creative idea that is worth evaluating.
- If successful, a totally new mechanism for controlled hydrogen uptake and release will be available.
- High relevance to programmatic goals.
- The concept of charge-induced hydrogen cluster formation has a lot of question based on scientific fundamentals.
- Achieving the President's Hydrogen Fuel Initiative goals seem remote.
- While apparently aligned, it seems exceedingly unlikely that this method can actually work. Therefore it is not really aligned because the money spent here could better be spent on other aligned work.
- The project addresses relevant goals.
- The project supports a major research need for the Hydrogen Fuel Initiative – on-board storage with sufficient volumetric capacity.
- This is an interesting novel concept at the university exploratory research scale.
- Meeting the 2010 target by 2010 will be a challenge based on the technical status. (The principal investigator is optimistic.)
- The 2015 goal should probably be addressed.

Question 2: Approach to performing the research and development

This project was rated **2.3** on its approach.

- Novel approach to hydrogen storage looking at hydrogen adsorption by charged species.
- Calculations of cation perhydrides show promise for this type of material, but not sure how the systems looked at can be approached experimentally without forming some stable metal hydrides. The alkaline earths all form fairly stable hydrides.

- It is not clear from calculations and discussions whether the calculations are performed on isolated cations and anions, or if the conditions simulate cations and anions in a crystal structure, with limited space and geometry for hydrogen molecules in the crystal and additional interactions from neighboring ions.
- There is not much in the way of precedent to support (or not support) the concept.
- There is a potentially supportive mix of density functional theory calculations on molecular metal hydrides and experimental "electrochemical" data.
- It is unclear if the molecular model systems that have been calculated are a reasonable model of the hydrided surfaces that are sought. Given that the rationale for the project is based on the calculations, it is critical to know if the models employed are valid.
- Dissociative adsorption of hydrogen on metal surfaces is well documented, but not considered in this study.
- Presently the electrochemical studies (which are only recently initiated) only monitor electrode potential. Current is not monitored and no surface sensitive techniques are employed to establish the molecular nature of the process(es) being observed. This represents a major weakness of the study.
- The approach to investigate change-induced hydrogen cluster formation is not based on good fundamentals.
- This is unlikely to contribute to overcoming the barriers.
- The approach puts off testing the least probable portions to the end when the money is all spent.
- The use of theory and experiment together is good, but here the theory is not getting any feedback and so it is entirely unchecked for accuracy.
- It is not at all clear that the team has any real idea of the possible storage of the system. They could not clearly tell what the surface to mass ratio was nor the amount of hydrogen on the surface. Nor did they seem able to say if or how much hydrogen would go into the bulk.
- Novel approach to hydrogen storage looking at hydrogen adsorption by charged species.
- The principal investigator is cognizant of the technical barriers that need to be met. The project is focused on addressing feasibility of the concept followed by addressing the technical barriers.
- This is in the exploratory phase of research. The approach is to explore and validate the adsorption and desorption of clusters of hydrogen on anode and cathode materials using an external voltage source, and to evaluate performance of materials screened by computational chemistry. Solid materials will also be included in the hydrogen space between the electrodes.
- External voltage source would be supplied by battery.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.5** based on accomplishments.

- The project looked at the effects of hydrogen pressure on potential but did not measure any hydrogen adsorption in electrodes as a function of applied voltage. Hydrogen uptake needs to be measured directly to determine if there is any, not changes in potential versus a vacuum which could be affected by very small surface adsorption.
- Hydrogen bonding capacities in the cluster calculations appear to be for isolated charged species. Future calculations should look at larger clusters and include interactions with surrounding cations, anions and neutral metal atoms.
- The project has only had serious funding for about one year according to the presenter. Thus, accomplishments must be evaluated in light of the financial limits that have been placed on the project. (But, this comment appears inconsistent with the funding data provided.)
- Laboratory results are very preliminary.
- Two accomplishments exist: 1) density functional theory calculations on molecular hydride models (of questionable value since it is unclear if the systems selected represents what realistically might occur on a metal surface); and 2) Construction and preliminary testing of a capacitive charge/discharge cell to test the hydrogen uptake concept.
- The two noted tasks do not prove (or disprove) the concept at this point.
- Based on computational screening, a number of promising candidates were selected.
- The results are confusing.
- Publications are limited to the proposed work.
- Theory states these materials can be made and will store hydrogen, but at present there is no reason to trust or distrust this theory as there is no confirmation.

- Did not have a very clear explanation of data, nor had they tested for other explanations of the voltage drops.
- Looked at effects of hydrogen pressure on potential but did not measure any hydrogen adsorption in electrodes as a function of applied voltage. Need to measure hydrogen uptake directly to determine if there is any, not changes in potential versus a vacuum which could be affected by very small surface adsorption.
- Hydrogen bonding capacities in the cluster calculations are for charged species which cannot exist in isolation apart from an anionic species.
- Phase 1 is scheduled for five years - with completion stated at 50 percent. (No performance schedule is shown with subtasks.)
- Computational analysis was accomplished for screening materials for anodes and cathods. Conducted initial tests for adsorption and desorption.
- Now planning concurrent electric polarization and hydrogen sorption reactor and new electrode structures to increase hydrogen storage.
- Progress appears to be moderate and meant to be addressing barriers.
- It is too early in research to really address the possibility of meeting the key challenges as identified by the performer (cost, weight and volume, and efficiency).

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **1.4** for technology transfer and collaboration.

- Collaborations are not apparent.
- Nature of the collaboration is unclear.
- Given the state of the project, a consideration of technology transfer is premature.
- Collaborations are mentioned but seem limited.
- There are no clear beneficial interactions.
- Collaborations are not apparent.
- The role of collaborators is to provide materials for testing and evaluation.
- There is no technology transfer collaboration as of this time.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.5** for proposed future work.

- Proposed future work involves experiments to perform needed adsorption measurements.
- Proposal to add pressure change detection to the capacitive cell is important.
- Proposal to add surface analysis is important. (But what analytical techniques will be used?)
- Ideas about adding a "contaminating" gas phase species does not seem to be sound.
- Independent of the calculation results, the reaction of hydrogen with a metal oxide species will likely lead to the formation of metal + water (smelting) not hydrogen storage. This is a not a high probability research track.
- The approach is fundamentally not good.
- Appropriate if and only if they show that the current results mean what they think they do.
- Proposed future work involves experiments to perform needed adsorption measurements.
- The future experimentation will continue to conduct work to achieve an exploratory basis for this novel idea.
- Investigate the effects of applied electric potential on hydrogen adsorption and verify the charge induced hydrogen adsorption/desorption process using a dedicated instrument that is able to measure hydrogen sorption in the hydrogen filled electrode reactor.
- Develop electrodes with large surface area and study the adsorption/desorption enhancement effect.
- Further study the adsorption/desorption enhancement effects of applied voltage and hydrogen pressure, and explore the optimization approaches.
- Examine the adsorption/desorption enhancement effects of different electrode materials (starting from the metals explored by computer calculation), and screen the best candidates.
- Investigate the hydrogen adsorption capability of materials with naturally polar bonds directed by computer simulation, including the exploring of the following material compounds: BeO, Cr_2O_3, Fe_2O_3, NiO, and CoO.

- Investigate the hydrogen adsorption capability of materials being electrically polarized, materials being explored will include: a) Inorganic ferromaterials, b) Organic ferromaterials, and c) Other materials having charge carriers that can be electrically separated. Materials will be placed in the hydrogen space between the electrodes.

Strengths and weaknesses

Strengths
- This is a novel idea
- Some calculation support is provided.
- Reasonable progress over the past year.
- This is a good group of people to address the problem.
- Unique, certainly not just what everyone is doing.
- Unique, exploratory research to investigate the potential and roles of charged/polarized species to form hydrogen clusters - to thereby store significant quantities of hydrogen. The hydrogen would be adsorbed by electric charge and desorbed with the removal of the charge.
- The project has utilized computational chemistry to screen potential material for forming hydrogen clusters.
- Early experimental data shows that the concept may be feasible.
- The goal is to achieve storage capacity of greater than 0.06 Kg H_2/Kg storage system - the Department of Energy 2010 target.
- The principal investigator is competent and knowledgeable, confident of making progress.

Weaknesses
- Lacking measurements showing proof-of-principal.
- No evidence has been obtained that hydrogen uptake or discharge is occurring in the target systems.
- No surface characterization studies are presently in place to demonstrate whether or not hydrogen is interacting with the electrode surfaces and whether or not an observed interaction is consistent with the model systems selected.
- The proposed chemistry is not well-supported by known coordination chemistry.
- The observation of a voltage variation is not proof that hydrogen is being absorbed or desorbed by the system.
- Scientifically weak approach.
- The key problems regarding whether this material be made are not being addressed
- Other interpretations of the data are not being looked at, which is indirect evidence, not direct evidence. This is a major concern.
- Lacking measurements showing proof-of-principal.
- This project needs significant additional information to show the feasibility and to provide a workable concept for use.
- Defining costs for this storage approach will need the additional information.
- Meeting the 2010 Department of Energy target by 2010 seems aggressive overall.

Specific recommendations and additions or deletions to the work scope

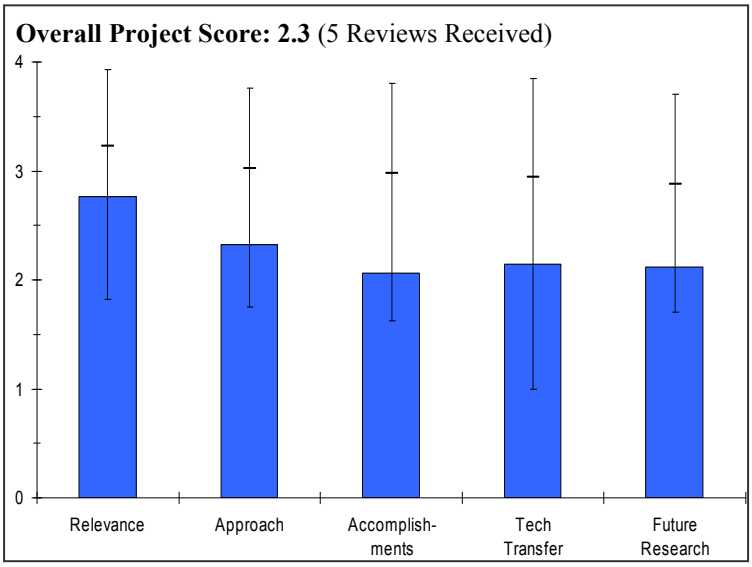
- Continue the work, but focus strongly on determining if hydrogen uptake/release is occurring via a direct measurement (such as pressure swing or IR spectroscopy).
- If hydrogen uptake can be demonstrated (hopefully quickly) then the amount of uptake must be determined.
- Given the accomplishments of points one and two, analytical studies of the surface hydride structure will be important. This will then validate the density functional theory model(s) employed or suggest new models.
- The program needs to prove its assertion and calculate the storage that might be truly possible, not just a proposed stoichiometry.
- No recommendations are made.

Project # STP-27: Glass Microspheres for Hydrogen Storage
Jim Shelby; Alfred University

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The objectives for this program are to: 1) demonstrate that hydrogen storage in hollow glass microspheres is a viable, safe method to meet DOE's hydrogen storage targets; 2) prove that photo-induced hydrogen diffusion results in rapid release of hydrogen on command; and 3) optimize the composition of the glass used to produce hollow glass microspheres for hydrogen storage for maximum crush strength (maximize fill pressure) and minimum reaction time for response to changes in light intensity.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.8** for its relevance to DOE objectives.

- Project partially supports Hydrogen storage goals and vision, unlikely to meet the Department of Energy's research and development objectives.
- Hydrogen capacity must be shown as favorable to meeting DOE targets.
- This project addresses the DOE programmatic goal of developing a solid state hydrogen storage system to meet 2010 target of 6 weight percent on-board storage.
- This project partially supports the hydrogen storage goals and vision, but it is unlikely to meet DOE research and development objectives.
- This project addresses a key barrier - weight percent of hydrogen storage.
- This project does not adequately address hydrogen storage volumetric density.
- The project has the capability to address cost, but has not yet addressed it.
- The project is addressing durability and operability.

Question 2: Approach to performing the research and development

This project was rated **2.3** on its approach.

- This is a well studied approach for storing hydrogen that is unlikely to meet the technical targets for volumetric storage density.
- The approach appears to be unable to meet 2015 gravimetric storage goals at reasonable pressures.
- The study does not appear to be focusing on the relevant issues such as maximum fill pressure of microspheres, optimal sphere diameters and thicknesses, maximizing packing densities, etc. that would maximize storage densities.
- Studies of photo-release of hydrogen do not appear to be addressing mechanism of release, and it is likely release is due to heating of the microspheres. Mechanism of release and things like the extinction coefficients, will determine what size container this type of activation would be effective in. If the distance it is effective over is too short (due to all the light being absorbed or scattered) it will not be useful.
- Other organizations have looked at hydrogen storage via microspheres.
- The project is focused on developing hydrogen storage system using hollow glass microspheres. Several previous investigations have focused on similar systems (without much success).

- The approach is to develop a more rapid method for hydrogen release (photo-induced) and optimize dopants.
- Hollow glass microspheres (HGMS) materials are commercially available, which is an advantage.
- With only 2.2 weight percent (materials only) demonstrated, it is quite a stretch to see how this approach can reach the desired goal of greater than 10 weight percent materials only (necessary to meet 6 weight percent system goal).
- Their approach is based on material weight percent rather than system weight percent. Why?
- The low pressure work is a good screening tool.
- They recognize the importance of size distribution of microspheres.
- Their Phase I/Phase II approach is logical in leading to pressure limits/scale up.
- The length of the project seems rather long, with Phase II lasting an additional four years to get to a working demonstration.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.1** based on accomplishments.

- Made some progress in increasing kinetics of release over thermally activated glass microspheres.
- Progress in demonstrating gravimetric storage density improvements are slow – only 2 weight percent has been achieved. The plan to use 10,000 psi should only lead to a gain of a factor of two; other plans to reach the target were not apparent.
- Progress appears to be very slow. Very low hydrogen capacity has been demonstrated.
- After over three years, only ~ 2 weight percent hydrogen capacities has been demonstrated, indicating it is probably impossible to reach DOE system capacity requirements.
- No spheres have been filled, to date, to 10,000 psi as proposed in project objectives.
- The author presents interesting results for a 5 weight percent CoO doped system with finely divided particles that has rapid hydrogen release rates.
- The mechanisms for photo-induced hydrogen release are not known; no appreciable heating of system was measured.
- Demonstrated fill of microsphere at 5000 psi; 10,000 fill is in progress.
- Demonstrated the ability to obtain 2.2 weight percent hydrogen in HGMS system.
- Narrowed the wavelength region of interest for the photo-induced effect to 1500-2300 nm to see an effect.
- Made some progress in increasing kinetics of release over that of thermally activated glass microspheres.
- They have shown no data that indicate they are reaching the weight targets - especially system weight percent.
- They need to show/produce more data on the effect of type of glass.
- They need to show the effect of hydrogen cycling on capacity.
- Good comparison of dopants.
- They are seriously compromised by the high pressure filling process. They need to better coordinate with Savannah River National Laboratory (SRNL) for the high pressure fill HGMS work.
- They make a statement about the wavelength of light to be used to facilitate the hydrogen diffusion process, but show no data. I would think that the wavelengths used would be more dependent on the type of glass.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.1** for technology transfer and collaboration.

- Collaborations to get microspheres filled to higher pressures are not smooth- delays in getting work done
- Other collaborations are not outlined.
- SRNL has been a partner in this project - but it is not clear what contributions SRNL has made to the accomplishment achieved thus far.
- Commercialization pathway is not clear.
- Collaborations to get microspheres filled to higher pressures are not smooth – there are delays in getting work done.
- Other collaborations are not outlined.

- The coordination with SRNL seems to be a major stumbling block in getting high-pressure fills accomplished and staying on some kind of schedule.
- Appears to be good coordination with Mo-Sci for development of glass microspheres.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.1** for proposed future work.

- Plans do not address a path to meet or address volumetric storage targets.
- Develop an understanding of photo-induced effect is a logical goal.
- Develop a working prototype is a desired goal.
- There is no clear off-ramp decision point in case storage weight percent cannot be increased to more applicable levels.
- Plans do not address a path to meet or address volumetric storage targets.
- They will be addressing some key needs: glass optimization, other dopants, and fill pressure vs. microsphere survival.
- Fill temperature study must include a reality check. That is, refueling at non-ambient conditions may not be practical, and data gathered at these temperatures may not be relevant.
- Doubling the storage capacity will still leave the system short of targets.
- This project is facing a near-term go/no-go decision to proceed to Phase II. Phase II plans seem to address project objectives that should have been demonstrated in Phase I.

Strengths and weaknesses

Strengths
- Demonstrated much more rapid photo-induced hydrogen release rates than from purely thermal.
- Discovery of optimal dopants is quite useful.
- Can use as a base for conventional materials that are sold commercially. The materials are durable and inexpensive.
- The method allows very good control over hydrogen release rates.
- This is a new twist (photo-induced hydrogen diffusion) on an old concept (glass microspheres) that had more or less been discarded years ago.

Weaknesses
- The system will not meet volumetric storage targets.
- The approach does not seem viable to achieve DOE performance targets.
- It is very difficult to determine the hydrogen storage capacity of materials as the researcher is supplied the materials pre-charged; they do not have control over this part of the experiments.
- The very low current status of hydrogen storage capacity (2.2 weight percent materials only) does not bode well for more significant storage. This value is way below all other storage technologies.
- It is not clear that storage is linearly related to fill pressure; that is if double pressure to 10,000 psi will get 4.4 weight percent.
- The potential complexity and cost of the system (with flash lamps uniformly "bathing" materials stored) is in question.
- Need to cool the system and fill at high pressure (e.g., 10,000 psi) for a realistic system.
- The system will not meet volumetric storage targets.
- The length of time needed to perform hydrogen fills (due to transport and scheduling) is unacceptable.
- The amount of data gathered in key areas (weight percent hydrogen storage, ability to cycle hydrogen, rate of hydrogen take up and release) is not commensurate with the length of time this project has been ongoing.

Specific recommendations and additions or deletions to the work scope
- Accelerate discovery of a mechanism for photo-induced hydrogen release – do this in the next year.
- Accelerate development of a working prototype, cut time to two years.
- Off ramp if cannot show at least 6 weight percent hydrogen storage in the next year.

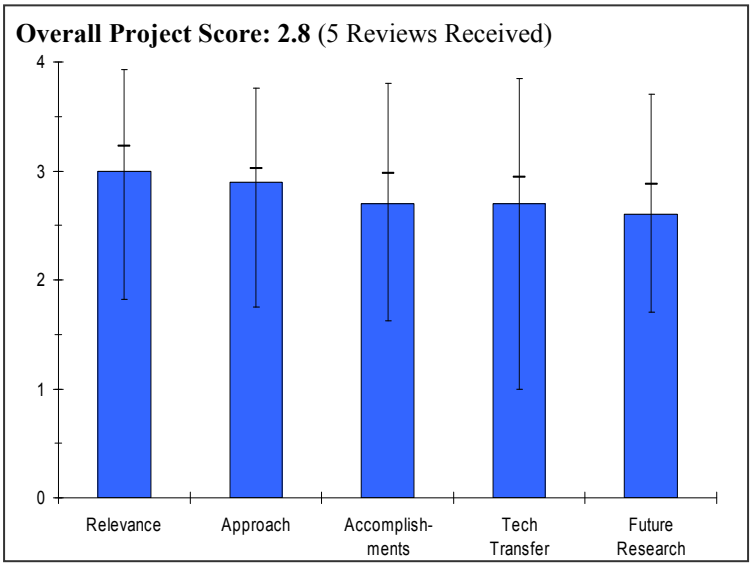
- Develop a strict schedule for getting high pressure hydrogen into spheres at SRNL.
- Develop a plan to study high pressure cycling of hydrogen - this is the key real-world data needed.
- Recommend no-go at the end of Phase II.

Project # STP-28: Electron-Charged Graphite-Based Hydrogen Storage Material
Chinbay Fan; Gas Technology Institute

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

The overall objective of the project is to develop a hydrogen storage material and device for hydrogen quick charge and discharge, high wt% and vol% storage capacities, good durability over many cycles, and safe handling and transport. Objectives for 2007 are to 1) select and synthesize carbon-based materials; 2) test and evaluate cycles for hydrogen storage; and 3) test external electron charge effect on hydrogen storage capacities. Objectives for 2008 are to 1) combine internal electron-charge (doping) and external charge to increase hydrogen storage capacities; and 2) investigate performance optimization and prototype container systems.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- The project objectives are aligned with Department of Energy research and development objectives.
- Introducing electron charge on sorbent is one of the critical factors to improve the hydrogen uptake.
- The overall program objective is to develop a hydrogen storage material and device for hydrogen to quickly charge and discharge with high weight percent and volume percent storage capacities.
- The program is highly relevant to the President's Hydrogen Fuel Initiative.
- It has been clear for some time that carbon can only adsorb modest amounts of hydrogen compared to the targets for on-board storage. The results now available from this project show that the concept of internal doping and/or external means to result in a surface charge on the carbon can increase the amount of hydrogen adsorbed but the results are still far from the DOE targets. It appears unlikely that this approach can ever meet the DOE targets.
- Good emphasis on room temperature hydrogen storage.
- The project generally addresses DOE target and technical barriers.
- No quantitative discussion is made of volumetric capacity.

Question 2: Approach to performing the research and development

This project was rated **2.9** on its approach.

- The principal investigator did not show how much hydrogen uptake is expected through theoretical calculation.
- An optimized experimental design of electron charged sorbent materials should be guided by theory.
- The hydrogen storage is based on hydrogen adsorption with electron shift (physisorption) and electron transfer (chemisorption). The approach uses external electron charge to increase hydrogen adsorption and change hydrogen desorption kinetics. The approach also uses internal electron-rich or poor materials to change carbon-based material surface electron density affects hydrogen storage.
- The technical approaches and concepts are an excellent and novel idea. The carbon materials are very cheap.
- Good science and experimental approaches are utilized in this project to study the impact of electron charging carbon to improve hydrogen adsorption.

- Other researchers have shown 7 weight percent hydrogen at room temperature on a carbon doped with Li, but the system loses its ability to absorb much hydrogen after only a few cycles. Gas Technology Institute (GTI) hopes that doping with a metal in combination with its approach of charging the carbon may yield good results. Based on the GTI data presented in combination with other results from metal hydride and carbon systems, the probability of meeting the DOE storage targets is very low with this approach.
- The system needed to charge the carbon with an external device may prove impractical and/or too costly for on-board storage.
- The project seems a bit weak on the theory of electric field and electrical charge effects on hydrogen storage.
- The approach, namely to control hydrogen physisorption properties of carbon by internal and external electron charges, is not very well explained, a priori. There should be some better physics discussed in order to justify the potential of the approach.
- It is not made clear how the external charge approach, if successful, can be practically applied to vehicle storage. What will the real tank look like and how will it be controlled.
- The concept seems interesting and different, but there seems to be more hand waving than solid physics.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- The principal investigator has demonstrated a modest progress on overcoming the barriers.
- There is not enough data to demonstrate the relationship between surface area, pore size, electron charge, and hydrogen uptake.
- Some of the measured hydrogen uptake improvements (such as 1.185% to 1.476%) are within experimental noise.
- The isotherm of hydrogen uptake should include both adsorption and desorption.
- The hydrogen storage capacity is significantly improved by using charge control agent.
- Partnered with industrial (Superior Graphite Company) and academic (State University of New York at Syracuse and University of Houston) to improve hydrogen capacity with carbon materials.
- Good progress was made. Dopants, different carbons, and external charging were all carefully examined with good repeatable data obtained.
- The project did demonstrate an improvement in hydrogen adsorption with an internal charge control agent and with an external charging approach. However, the improvement still left this system far from the DOE storage targets.
- 1.5 weight percent hydrogen storage demonstrated at room temperature with the charge control agent. But what is the desorption temperature?
- Results with the charge control agent might be indicative of possible interesting capacitive charging effects on hydrogen storage.
- An external electric field appears to have relatively little effect on room temperature hydrogen storage.
- The project is apparently well behind schedule. Although 75 percent of the project time frame has passed, the principal investigator lists it as only 15 percent complete.
- The experimental results so far show only minor improvements, arguably within batch-to-batch and experimental scatter.
- The H-capacity increases shown to date are less than the 50 to 100 percent required to pass the upcoming DOE go/no-go gate.
- Technical details are sometimes withheld, such as the composition of the charge control agent added.
- Based on the results so far, this project offers little hope for meeting DOE targets.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.7** for technology transfer and collaboration.

- The principal investigator did not demonstrate a close coordination with theory group that might play a critical role in this technology.

- The experimental results need to be verified with large sample size when the higher hydrogen uptake is within experimental noise.
- Cooperation with universities and industries are excellent.
- Carbon materials are supported and modified from partners; the technology is easily transferred to industrial company or universities.
- There appears to be only a very modest amount of collaboration and technology transfer with the State University of New York, ATMI, the University of Houston, and a Japanese company.
- Effective interactions with a Japanese company to identify a charge control agent and with the State University of New York on a high surface area carbon material.
- A few industrial and academic collaborators are listed.
- The exact roles of the collaborations are not very clearly stated.
- The names of two collaborators are kept secret: The charge control agent was "obtained from a Japanese company." "High surface area carbon from a partner."

Question 5: Approach to and relevance of proposed future research

This project was rated **2.6** for proposed future work.

- The hydrogen uptake measurement based on larger sample size (10-20 g) should be considered in future research plans to address the measurement noise issue.
- The lower-than-room-temperature measurement should be included in future research plans.
- The future work is clearly stated in the slides and directions are excellent.
- Investigate the electron charge effect on different hydrogen storage materials are very important.
- There is nothing in the Future Work Plan nor the data presented that suggests this approach has any reasonable chance of achieving the on-board storage targets.
- The future work seems somewhat vague on strategies to increase the room temperature hydrogen storage capacity.
- Future work plans are vague and rather qualitative.

Strengths and weaknesses

Strengths
- The concept is well-aligned with DOE Hydrogen Program objectives and some of the results will help in understanding the relationship between surface charge and improved hydrogen uptake.
- Carbon materials are very cheap and easily prepared compared to most alloyed materials for hydrogen storage.
- The concept and idea are novel.
- Good science and experimental approaches were utilized in this project to study the impact of electron charging carbon to improve hydrogen adsorption.
- Innovative approach. This is an area of hydrogen storage that has not been studied a great deal.
- It offers a different idea that was worth trying.

Weaknesses
- Lack of theory guided experimental design.
- It has been clear for some time that carbon can only adsorb modest amounts of hydrogen compared to the targets for on-board storage. The results now available from this project show that the concept of internal doping and/or external means to result in a surface charge on the carbon can increase the amount of hydrogen adsorbed but the results are still far from the DOE targets. It appears unlikely that this approach can ever meet the DOE targets.
- Lack of theoretical guidance.
- The project has not kept to the schedule.
- The physics behind the idea are not clear and convincing.
- The results obtained so far do not look promising.

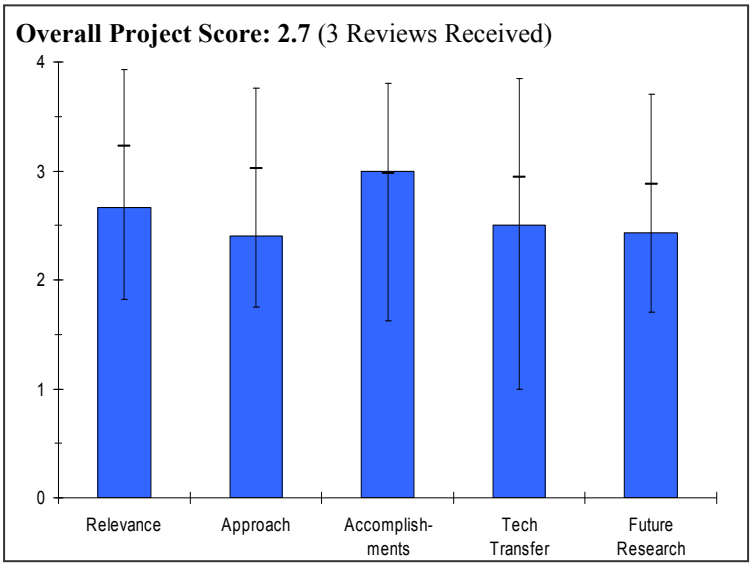
Specific recommendations and additions or deletions to the work scope

- Send samples to independent parties for evaluation.
- This project should be closed out.
- This project would benefit from interactions with the hydrogen storage theoreticians.

Project # STP-29: Polymer-Based Activated Carbon Nanostructures for H_2 Storage
Israel Cabasso; State University of New York

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project



The overall objective of the project is to develop and demonstrate reversible nanostructured activated carbon hydrogen storage materials with materials-based volumetric capacity of 50 g H_2/L, with potential to meet DOE 2010 system-level targets. The objectives for fiscal year 2007-2008 are to 1) develop polymer-based nanostructured carbons with high surface area and high micropore volume; 2) demonstrate reproducibility of 10-gram scale batch production of high surface area carbon; 3) characterize hydrogen storage capacity under various pressure and temperature conditions - target for 2007 >6 wt% and 40 g/L of material-based H_2 capacity; and 4) develop methods for organometallic and multicyclic ligand-doped polymer/carbon.

Question 1: Relevance to overall DOE objectives

This project earned a score of **2.7** for its relevance to DOE objectives.

- The project is relevant to the Department of Energy's Hydrogen Program goals.
- Based on a lot of work that has already been done with carbons, it is very doubtful that a carbon system will be capable of meeting the challenging DOE on-board storage targets. The data resulting from this project shows improvement over prior work with carbon, but is still fundamentally very far from the DOE targets.
- Consistent with the goal of arriving at material for an ambient conditions hydrogen reversible adsorption.

Question 2: Approach to performing the research and development

This project was rated **2.4** on its approach.

- The approach is quite trivial but efficient.
- The approach taken is to develop carbon substrates with optimized nanopore size and very high surface area for hydrogen sorption by carbonizing and carefully processing polymer precursors. The work will also include incorporating doping with organometallics, metal hydrides and multicyclic ligands. Other prior data available and the data from this project make it appear doubtful that this approach can meet the DOE on-board storage targets. The carbon system has been improved to having 6-7 weight percent hydrogen and good hydrogen volumetric density but only at 77K and under 6 MPa hydrogen pressure. This is still very far from the DOE combination of performance and system cost targets.
- The researchers are using excellent science and laboratory techniques to perform this research.
- The use of polymers as precursors and processing them into carbon sorption systems is a novel approach and results in the capability to control pore size and surface area.
- It is well recognized that for an effective ambient temperatures sorption of hydrogen, a heat of about 20-25 kJ/mol is needed. This is not going to be realized by just optimizing the carbon's pore structure and the use of ill-defined, fundamentally unjustified "dopants."

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **3.0** based on accomplishments.

- Impressive surface areas.
- Good repeatability.
- Good storage capacities at 77K.
- The approach being taken has significantly improved the weight percent and hydrogen volumetric density for carbon-based hydrogen storage materials (e.g. from ~2 weight% to ~6 weight% at 77K).
- The hydrogen weight percent and volumetric density at a cost effective temperature is not shown but from the data provided it is clear that it is very far from the DOE combined performance and cost targets.
- Very good to excellent scientific work on optimizing the nanostructure of carbons. Lacking data on hydrogen heat of adsorption which is the critical determining factor for the development of a useful hydrogen solvent.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.5** for technology transfer and collaboration.

- Very limited collaboration with other members of the Hydrogen Program.
- There appears to be only one partner working with the State University of New York researchers.
- Papers and conference presentations are very limited.
- Coordination on hydrogen isotherm measurements.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.4** for proposed future work.

- Future Work is not well defined.
- Goals are very general.
- The future plan is to continue to pursue the same approach pursued to date and to do more doping research. The data already generated along with other data available on similar approaches with carbon materials makes it doubtful this approach will meet the DOE on-board storage targets.
- Investigators should measure their progress by improvements in the isotonic heat of hydrogen adsorption which needs to heat 20-25 kJ/mole. Need to develop a rationale, an underlying basis for choosing metal and other dopants.

Strengths and weaknesses

Strengths
- Very good experimental work.
- Deep understanding of experimental procedures.
- The researchers are using excellent science and laboratory techniques to perform this research.
- The use of polymers as precursors and processing them into carbon sorption systems is a novel approach and results in the capability to control nanopore size and surface area.
- Ability to tailor polymer - derived carbons.

Weaknesses
- Strategic planning can be improved.
- Collaboration needs improvement (include industrial collaboration).
- The approach taken is to develop carbon substrates with optimized nanopore size and very high surface area for hydrogen sorption by carbonizing and carefully processing polymer precursors. The work will also include incorporating doping with organometallics, metal hydrides and multicyclic ligands. Other prior data available and the data from this project make it appear doubtful that this approach can meet the DOE on-board storage targets. The carbon system has been improved to having 6-7 weight percent hydrogen and good hydrogen

volumetric density but only at 77K and under 6 MPa hydrogen pressure. This is still very far from the DOE combination of performance and system cost targets.
- Lack of credible pathway to a room temperature hydrogen solvent. Could be a good solvent for a 100K application.

Specific recommendations and additions or deletions to the work scope

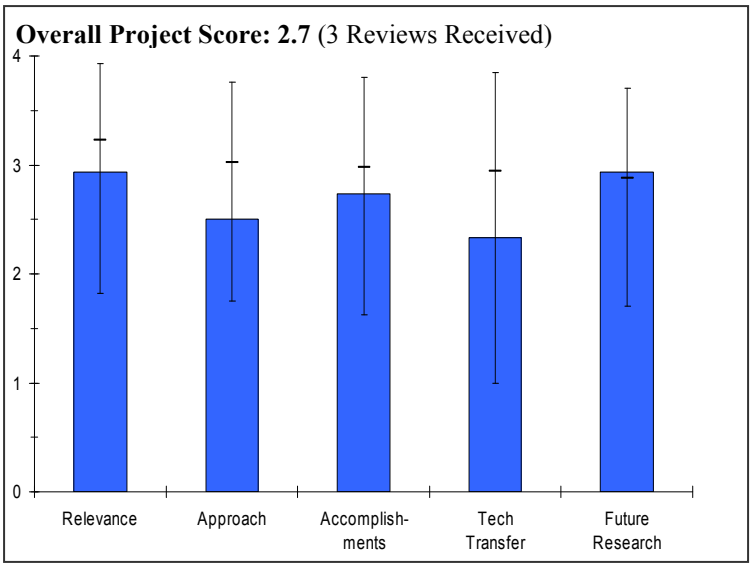
- This project should be stopped.

Project # STP-32: An Integrated Approach for Hydrogen Production and Storage in Complex Hydrides of Transitional Elements

Abhijit Bhattacharyya; University of Arkansas-Little Rock

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project



The objective for this project is to find complex hydrides of transitional elements for hydrogen storage that meet the following project targets by 2010: 6% weight percent; a pressure of 100 bar, kinetics of 3 min; and a temperature of -30/50°C. Objectives for bulk materials are hydrogen storage characterization and development of materials for hydrogen storage, including 1) increasing reversible hydrogen capacity in complex metal hydrides by developing new systems including hydride phases; 2) developing catalytic compounds to enhance the formation and decomposition of complex metal hydrides; 3) investigating hydrogen storage capacity in metal (Ti and Li) decorated polymers; and 4) investigation of enhancement of hydrogen storage capacity in metal hydrides dispersed in polymer matrix. Objectives for nanostructures are the: 1) investigation of maximum hydrogen storage capacity and adsorption/desorption kinetics of thin films and nanostructures of magnesium alanate and magnesium borohydride; 2) utilization of glancing angle deposition technique for the growth of nanorod arrays of magnesium as a model system; 3) construction and utilization of new quartz crystal microbalance gas chamber system; and 4) investigation of effect of catalyst on hydrogen adsorption/desorption properties of Mg, magnesium alanate, and magnesium borohydride.

Question 1: Relevance to overall DOE objectives

This project earned a score of **2.9** for its relevance to DOE objectives.

- The project objectives relevant to overall materials synthesis is relevant to the Department of Energy targets. The objective of building Sievert-type equipment is not relevant and is recommended to be removed from the overall objectives.
- Testing of theoretical predictions is relevant.
- Mostly working on relevant systems.
- The project is relevant to the overall DOE Hydrogen Program objectives. It attempts to build (at low cost) high performance facilities and find ways to increase considerably the uptake of specific materials at room temperature.

Question 2: Approach to performing the research and development

This project was rated **2.5** on its approach.

- Suggested to clarify the approach to increasing the weight percent hydrogen by transition metal polymer decoration, such as using Ti to obtain 4.1weight percent at RT from current 1.8 weight percent.
- Plan to utilize glancing angle deposition synthesis and quantify using a quartz crystal microbalance is suggested to be revisited due to practicality issues in meeting targets.
- Suggest trying to avoid overlap with other projects.

- The work on the polymer side seems well addressed and promising. However, the work on the Mg-based compounds (alanate, borohydride) needs to be put into some perspective with regard to other on-going work, conclusions reached elsewhere about these materials (e.g. Mg-alanate irreversibility; different behavior of films compared to bulk materials), and time left till the project end.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- Ti-decorated PANI's formation appears to be preliminary and requires further confirmation. Care should be taken for "Kubas" type hydrogen bonding resulting.
- The purpose behind the inclusion of hydrides in PANI matrix is not clear and effects are not illustrated.
- Much time is spent on experimental and synthesis capabilities establishment.
- Lots of effort devoted to building apparatus (completed?); should now shift focus on doing science.
- Of great value are the facilities developed in-house by the University of Arkansas research group. The results on Ti-decorated PANI look promising and the work in that direction seems interesting. On the nanostructures side, the work done on thin films could provide some ideas about the observed discrepancy between films and bulk materials (e.g. in the case of Mg-based compounds).

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.3** for technology transfer and collaboration.

- Collaboration with other groups working nanohydrides systems is not visible and its suggested to have more interactions.
- No significant collaborations are evident.
- Some collaborations are mentioned but the role of each of the collaborating institutions (especially the Romanian one) should be further clarified.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.9** for proposed future work.

- Suggest the path forward and the experimental plan to achieve theoretical hydrogen weight percent in polymers per theoretical estimation, such as 4 weight percent at room temperature in decorated PANI systems, should be clarified.
- The practicality could be an issue of using glancing angle deposition and a quartz crystal microbalance for materials synthesis and testing to achieving the DOE targets. A clear plan is suggested to be created on how this would be made possible.
- Looks reasonable.
- The proposed future work on the polymer side is quite interesting and holds promise for useful results. However, the plans on Mg-based materials should account better for work done elsewhere to avoid duplications (given also the limited time left until the end of the project).

Strengths and weaknesses

Strengths
- Promising results and approach for Ti-decorated PANI.
- Good, powerful facilities built by the team at very much reduced costs.

Weaknesses
- Time spent on building equipment like a Sievert's apparatus which is commercially available.
- Plan to achieve targets using the proposed synthetic routes.
- The project finishes in August 2009. While the percentage of completeness is currently only 45 percent. It is questionable if within the remaining time the project can fulfill its aims.

- Some of the materials addressed have already been found to be irreversible (Mg-alanate) or are studied elsewhere ($Mg(BH_4)_2$).

Specific recommendations and additions or deletions to the work scope

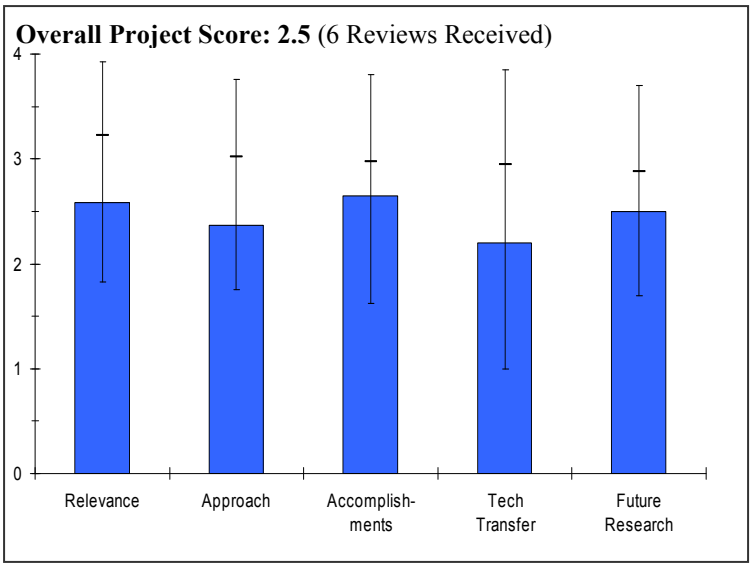
- Suggest shifting from glancing angle deposition system synthesis if no materials upscale plan could be devised.
- It should be reconsidered if the work on Mg-alanate and Mg-borohydride is of real interest to the project and the DOE program.
- The work on thin films could possibly be used to provide hints/clues.
- The work on thin films could possibly be used to provide hints/clues on the different behavior observed between films and bulk materials.

Project # STP-33: Hydrogen Fuel Cells and Storage Technology Project
Clemens Heske; Balakrishnan Naduvalath (Co-PIs); Robert Perret, Project Manager, University of Nevada – Las Vegas (UNLV)

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

Objectives for this project are to perform closely-coupled theoretical and experimental investigations of 1) hydrogen adsorption/desorption in various matrices to establish a solid understanding of optimal storage concepts; 2) the electronic and geometric structure of metal hydrides, nanomaterials (C, B, N, transition metals, alloys), metal adatoms, and adsorbed hydrogen molecules/atoms; and 3) fuel cell membranes and catalytic materials; to predict optimized materials and structures for hydrogen storage and fuel cells in the DOE Hydrogen Program. The project will also collaborate closely with external partners.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.6** for its relevance to DOE objectives.

- Addressing relevant barriers and aligned with Department of Energy goals.
- This project consists of three tasks involving hydrogen storage materials and two tasks on materials and catalysts for fuel cell membranes. While major improvements are needed in both areas, the choices selected by this team for study offer little or no greater performance than existing candidates being done elsewhere.
- Neither the metal doped single wall nanotubes (SWNT) nor palladium (Pd) doped aniline polymers (PANI/Pd) are viable storage materials that are likely to meet the DOE hydrogen storage targets.
- The high Pd levels in the polymers would make these materials much too expensive to meet DOE cost levels.
- While assessment of Co/Pt catalysts would provide a greater understanding in their roles within fuel cells, it doesn't seem to be a direct path for developing lower cost alternative catalysts.
- Addressing relevant barriers and aligned with DOE goals.
- This project seeks to elucidate the fundamentals of the mechanisms that influence the kinetics and thermodynamics of hydrogen uptake and release by candidate hydrogen storage material types - metals, carbon forms, etc.
- The nature of the results produced by this project shed light on what limits hydrogen storage capacity and what controls the charging and discharging rates. In this respect, the quality of the science is quite good in that it produces insights that help to define what limits the storage capacity and the delivery characteristics of selected classes of materials currently under investigation at the Hydrogen Storage Centers of Excellence.
- The degree of relevance to the hydrogen vision and DOE research and development objectives is good in most respects.
- Effort seems to be more interested in understanding changes in electronic structure than with developing materials for hydrogen storage.
- The project bears adequate relevance to DOE program objectives. The statement is more valid with regard to the two tasks related to fuel cell research. The three tasks on hydrogen storage offer some insight to specific material issues but lack overall focus.

Question 2: Approach to performing the research and development

This project was rated **2.4** on its approach.

- Approach is broad in scope, covering storage and fuel cells – a more focused approach might be more productive.
- Modeling addressing relevant materials issues, but need to be more integrated into Hydrogen Program.
- It is not clear what targets the membrane work is addressing. Are they attempting to reduce cost, achieve high temperature low relative humidity targets? Improve durability?
- Fluorinated sulfonamides have potential, but what benefits over Nafion?
- The project has five independent and non-complementary tasks that do not address common goals.
- Good coordination of theoretical modeling of metal clusters on surfaces and experimental spectroscopies of surfaces for both nanophase storage materials and fuel cell catalysts that do suggest synergistic interactions.
- Thermodynamic assessment of Li-Al-H phases has already been reported in the literature and assessments of very high pressure phase transitions of complex hydrides have little bearing on their reactivity or means to improve hydrogen storage properties.
- The approach is broad in scope, covering storage and fuel cells. A more focused approach might be more productive.
- This project is orchestrated to be multidisciplinary and highly interactive within the University of Nevada, Las Vegas. Theory and experiment are closely connected.
- The program is being stretched beyond its originally intended time span through a no-cost extension. This has allowed the principal investigator to focus the emphasis of the remaining funding on the most productive research tasks that evolved from the dozen or so individual tasks that comprised the project at its inception.
- The project also includes work on membranes and catalysts for fuel cells as an add-on to the original project.
- The project seeks to predict optimized materials/structures/approaches for hydrogen storage.
- There is no apparent connection between theory and experimental efforts.
- Should focus more on direct storage measurements.
- There does not appear to be a clear strategy for focusing efforts on achieving DOE goals.
- The approach regarding Tasks 4 and 5 (fuel cells) seems adequate although the present reviewer does not feel experienced enough in the field to provide detailed judgment. With reference to Tasks 1, 2 and 3 (hydrogen storage), although some interesting results are shown, the overall approach lacks focus and convergence on specific objectives. It looks more like a work program in support of other investigations (i.e., it consists of seemingly unrelated packages of work).

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **2.7** based on accomplishments.

- Modeling of Ti-Alloy structures is useful.
- Membrane synthesis work has a good start, but should be aligned with DOE high-temperature membrane working group goals and targets.
- The investigators performed a variety of calculations on surfaces and clusters interacting with hydrogen that resulted in published papers.
- X-ray photoemission spectroscopy (XPS) instrumentation was developed to assess clusters and metals on surfaces that allowed evaluation of interactions with hydrogen with single-walled carbon nanotubes (SWNT) and assessment of Co/Pt catalyst particles.
- A number of PANI/Pd composite samples were prepared and relative hydrogen sorption properties were determined, although thorough measurements of their storage capacities were not measured.
- Several sulfonated polymers were prepared and tested for their potential as proton exchange membrane (PEM) materials; however, no assessment was for actual performance in fuel cells.
- Showed how metal doping of titanium modulates the chemisorption energy.
- Resolved issues about differences in the adsorption of molecular and atomic hydrogen on SWNTs with and without Ti and Li doping.

- Some interesting hydrogen sorption results were obtained for Pd-doped mesoporous polyaniline composite materials.
- Work on partially fluorinated sulfonated co-polyamides showed improved proton conductivity relative to Nafion.
- Studies of Co/Pt clusters are starting to produce some interesting results concerning electronic states and charge transfer within and around the cluster.
- No significant progress.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **2.2** for technology transfer and collaboration.

- Collaborations with United Technologies Corporation (UTC) should be useful.
- Collaborations with hydrogen storage centers of excellence appear to be lacking.
- Collaboration with the DOE High Temperature Membrane Working Group would be beneficial and appears to be lacking.
- This project showed an active collaboration with UTC on characterization of Pt/Co catalysts for fuel cells where UNLV has developed XPS and other analysis capabilities to compare with theoretical modeling work at UTC.
- While there are also indications of fruitful interactions of the UNLV theory team with some other research groups on carbon and metal clusters, the other tasks seemed to be done mostly in isolation from outside hydrogen research organizations.
- Several other organizations are listed as partners, but it is not completely obvious throughout the slides how each of these partners interacts with or contributes to the project at UNLV.
- The project needs access to hydrogen storage measurement capability at an affordable price to provide a means of testing the impact of their findings on hydrogen storage capacity and hydriding/dehydriding kinetics.
- One gets the sense that this project needs to experience more embracement by the centers of excellence.
- There are no significant external collaborations.
- There exist partners but it is not clear how interaction and collaboration among them takes place and how fruitful it has been.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.5** for proposed future work.

- The proposed activities in Tasks 1, 3, 4 and 5 are all reasonable and within the capabilities of the various investigators.
- The assessment of Pt-Co alloy catalysts using in-situ XPS system looks promising when combined with appropriate electronic structure calculations.
- The proposed synthesis and evaluations of both the PANI/Pd and various sulfonated co-polyamides seems more like fishing expeditions rather than system development of high performance materials.
- The plan for future work emphasizes the most informative and productive aspects of the present program.
- The project generally addresses understanding barriers more than overcoming them.
- The material types chosen for study are ones that can provide beneficial insights into hydrogen storage but are for the most part not likely candidates for meeting DOE storage capacity targets.
- Suggest coordinating efforts with one (or more) of the centers of excellence to guide work in more relevant directions.
- Certain plans are mentioned but the remaining time and resources make their realization questionable. Again these plans (especially for the first three tasks) look incoherent and unfocused.

Strengths and weaknesses

Strengths
- Strong modeling component to direct experimental efforts.

- From the description of the scanning tunneling and XPS systems, UNLV has developed a high quality experimental research facility that should be capable of providing valuable in-situ characterizations of surfaces, clusters, etc. that would support strong collaborations in sorption storage materials and fuel cell catalysts.
- The investigators have published a number of research papers in peer reviewed journals that indicate positive contributions.
- Strong modeling component to direct experimental efforts.
- Highly motivated and scholarly principal investigator working with other equally qualified faculty at UNLV.
- Strong peer reviewed publication record and impressive list of presentations is getting their message out.
- Projects like this one produce well educated graduates that will be up to speed in the hydrogen storage field and ready to contribute new approaches and new directions for fuel cell research and development.
- Certain results obtained provide useful data for specific material issues.

Weaknesses

- Apparent lack of interaction and feedback from the storage centers (including data for model validations, etc.). Lack of interaction with the DOE High Temperature Membrane Working Group, which would help define targets for membrane work
- Much of the work described in this report is similar to other DOE-funded projects, especially with regard to the theory of clusters and additives to carbon systems.
- Most of the XPS results pertain to SWNT systems, which have little potential as viable hydrogen storage materials.
- While the results obtained on phases transitions of hydrides at high pressure add to the general fundamental knowledge of these materials, they will not directly impact development of storage materials that can meet DOE targets.
- The properties reported by the investigators for either the PANI/Pd or sulfonated co-polyamides do not indicate any significant advantages over candidates being developed and studied by other groups.
- This project needs to be better integrated into one or more of the centers of excellence for hydrogen storage. Perhaps it is the appropriate center of excellence that should make the overtures necessary to build an effective collaborative relationship.
- Now that the UNLV project has moved into membrane and catalyst areas, some collaborations with fuel cell research and development components of the DOE Hydrogen Program seem in order.
- Remaining time for the project barely sufficient to carry out planned work.
- Work carried out seems rather fragmented and without proper focus (especially for tasks 1,2 and 3).

Specific recommendations and additions or deletions to the work scope

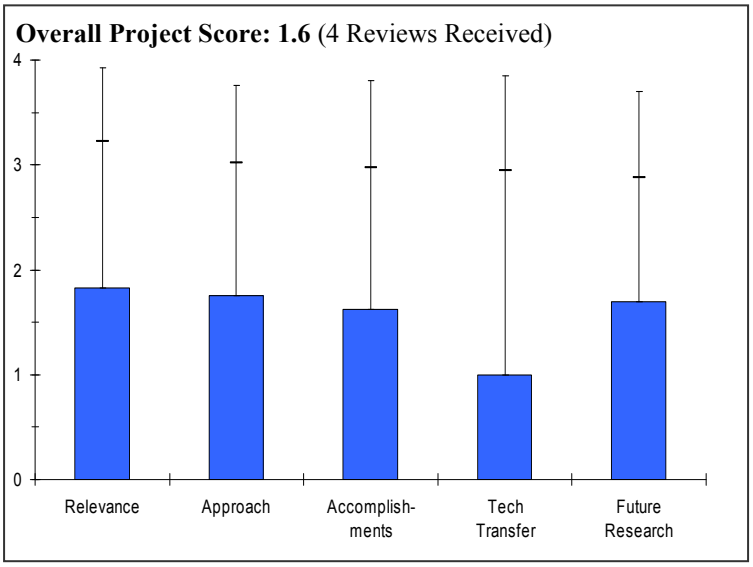
- Interact with the DOE High Temperature Membrane Working Group.
- Increase interactions with hydrogen storage centers of excellence.
- The capabilities of the UNLV surface spectroscopy instrumentation should be explored in partnership with other teams to investigate sorption hydrogenation reactions of clusters and/or catalysts.
- More obvious connection to partners.
- Closer interaction with the appropriate centers of excellence for hydrogen storage.
- Sustain the impressive publication record.

Project # STP-34: Modular Storage Systems
Scott Redmond; Limnia (formerly FST)

[NOTE: This project is not part of the Centers of Excellence; it is an independent project.]

Brief Summary of Project

Objectives for this project are to 1) develop a hardware/software system that stores and releases H_2 at optimum efficiency; 2) implement flexibility that facilitates use of the best available metal hydrides; and 3) provide the following system characteristics: built from readily available materials, scalable for multiple applications, and market adoptable via simple adjustments to existing infrastructure.



Question 1: Relevance to overall DOE objectives

This project earned a score of **1.8** for its relevance to DOE objectives.

- The approach is not in line with the Department of Energy hydrogen storage for vehicular applications.
- This project describes a metal hydride storage container that could be interchanged for filling to minimize thermal effects associated with on-board filling of the hydrogen gas.
- The design and construction of these storage vessels do not address most of the DOE hydrogen storage targets or requirements with respect to mass and many other parameters. The only significant attribute would be potential switching of externally charged and depleted storage vessels.
- Relevance is mixed. It is aimed at storing hydrogen, but it is not all that clear how useful the work is so in that sense it is not so relevant.
- There was no presenter for this poster.
- It is not obvious from the slide file that this project is well aligned with many of the hydrogen vision and DOE research and development objectives for on-board hydrogen storage.
- The stated strategy is to develop a hydrogen storage and distribution technology that is safer, modular, adaptive, regenerative, and transportable.

Question 2: Approach to performing the research and development

This project was rated **1.8** on its approach.

- There is no novel approach.
- A basic model analysis for heat transfer was presented to rationalize a rather naïve bed design for the hydride material. The predicted performance of this bed was compared to high pressure gas cylinders.
- A number of unspecified and hypothetical hydride sorbents were numerically evaluated to compare sensitivity of heat transfer performance and system mass ratios within the same basic design configuration.
- Relatively incomplete analysis and system is nowhere near the full system required for use. Not very impressive.
- The approach involves modeling, evaluation, design, and testing of a cassette-type storage platform.
- Materials selection, storage capacity, thermodynamics, kinetics, heat transfer, and balance of plant issues are addressed.
- The approach appears to be geared more towards transportable power supplies than to on-board storage of hydrogen for fuel cell powered vehicles.

Question 3: Technical accomplishments and progress toward project and DOE goals

This project was rated **1.6** based on accomplishments.

- While a Sieverts type testing station was shown to be constructed for experimental evaluation of both sorbent materials and presumably prototype storage vessels, no test results were presented.
- Fluent modeling results for a conceptual bed design that contains sodium alanate were presented along with some simple mass ratios comparisons to unspecified high pressure gas tanks.
- Essentially built a Sieverts apparatus and did some modeling that replicates well known results from ME/ChemE in heat transfer from finned plates.
- Needed to validate that the system could work, but the system analyzed in the spread sheet is only a portion of the whole system. Results are thus non-instructive for actual application or comparison to goals.
- Parameters selected for hypothetical metal hydride storage material.
- Modeled and compared heat transfer for selected systems.
- Created a "virtual" cassette model and compared to other hydrogen storage methods.
- Designed/constructed "demonstration" cassette system hardware and software to illustrate feature.
- Modified materials and evaluated properties; compared different hydrogen storage systems in cassette test system.
- In the absence of a presenter to clarify what all this means, it is hard to figure out exactly what they really did.

Question 4: Technology transfer/collaborations with industry, universities and other laboratories

This project was rated **1.0** for technology transfer and collaboration.

- The Limnia poster does not indicate any interaction, consultation, or technical exchange with any other organization or individuals other than unnamed patent attorneys.
- None apparent
- No collaborators or partners mentioned.
- No evidence of interaction with one of the hydrogen storage centers of excellence.

Question 5: Approach to and relevance of proposed future research

This project was rated **1.7** for proposed future work.

- Not applicable as this project is completed and no validation test data was provided in review package.
- Actual plans unclear, areas may be appropriate.
- Evaluate two other storage materials; complete study of carbon doped materials; continue studies of material densification.
- Refine balance of plant; adapt cassette to a "slurry system."
- Improve automation of experiments and systems.
- It's hard to appreciate what all of this means from the slides alone.
- Presumably, at some point we will see actual results of heat transfer measurements and cyclic hydriding/dehydriding tests.

Strengths and weaknesses

Strengths
- Modularity for assembly and manufacture.
- Limnia seems to be doing something that is producing both modeling information and testing data; there may be some useful results in this work but without someone to talk me through it, it is hard to appreciate what I'm looking at in the slides.

Weaknesses
- There is little of technical merit in this project as simulation results are for an impractical storage vessel.
- This is not a novel approach. Nor is it practical to address infrastructure issues.

- The storage material is the key to evaluate the system. However very little is devoted to the actual storage material.
- The proposed system is a variation of many different devices that have already been tried and tested.
- Bed design does not address any of the pressure containment issues or the feasibility of fabricating any demonstration vessel for assessment. The critical issues of heat transfer of the hydride powder within the bed during both desorption and refilling does not appear to have been considered.
- Extended shells of many cassettes plus mass and volume of multiplexer and holder.
- Effort at a much less robust level than needed for breakthrough or real progress.
- Electric heat is unlikely to be a good way to get heat. Remember you automatically double the energy requirement this way.
- There are no collaborations or interactions with the greater fuel cell/hydrogen storage community.
- Slide 4 is not overly informative without someone to talk me through it; also, slides 8 through 10 look rather superficial; looked at the tables on slides 11 and 12 for some time without being really sure I understand what their story is. In slide 15, one begins to get a sense of what is actually being done.
- Why are there no collaborations with the centers of excellence? Projects like this need the oversight of a larger group to make sure they are working up to the standard of the rest of the storage program and are using the most up to date information available.

Specific recommendations and additions or deletions to the work scope

- This project does not appear to materially support the DOE goals for developing a storage system for vehicular application as such it is recommended to appropriately phase this project out of the portfolio.
- Not applicable as the project is completed.
- Need to go to much greater analysis to actually improve the storage and performance over simple engineering rules. For example, no performance simulations were shown or suggested, only heat transfer. Mass transfer is also a key factor. The use of electric release is highly wasteful because roughly two hydrogen will be consumed in the fuel cell to get the heat equivalent of one hydrogen in electric resistance. This alone will doom the program to failure visa vie the program goals.
- This project should get an oral review. If Limnia has really done something worthwhile here, it should be made clear to DOE.
- Actual performance results from testing of a real cassette would solve most of the problems I have with this project.