Hydrogen Storage
Summary of Annual Merit Review Hydrogen Storage Subprogram

Summary of Reviewer Comments on Hydrogen Storage Subprogram:

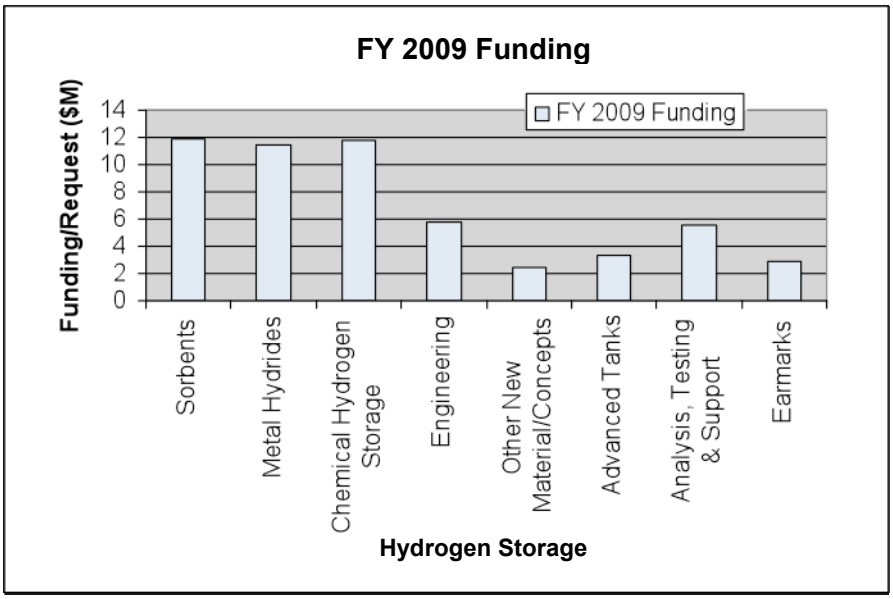
Reviewers indicated that the Hydrogen Storage subprogram area is focused, well managed, and effective; and has a diverse R&D portfolio addressing the technical system targets. Significant advances have been made for the various material systems, bringing materials closer to the vehicular system targets of the DOE Hydrogen Program. Effective communications and coordination between DOE, Center of Excellence (CoE) managers, and CoE partners, has allowed for cross-fertilization of ideas and focus of technical efforts. Although the subprogram strategy, goals, and achievements were well defined, some reviewers suggested that the remaining challenges were not adequately addressed and that greater attention to critical issues, obstacles, and challenges still facing each of the specific materials technology areas (i.e., chemical hydride, metal hydride, and sorbents) is needed to put progress to-date into proper context. It was also suggested that a "lessons learned" and gap analysis be performed to better assess progress made and the status of the portfolio. Some reviewers expressed concern regarding the 2010 Congressional budget request for the subprogram and the lack of clear future plans for Storage R&D.

In general, the reviewers thought that the revised vehicular performance targets, based on current fleet data and future projections, are an improvement and that re-evaluation of the hydrogen storage system targets was essential to both the real and perceived success of the Hydrogen Program. Some reviewers still had questions regarding the relevancy of the targets to the existing technical and economic challenges and recommended that further revisions be considered. The reviewers also urged DOE to identify storage systems and performance targets for early market applications.

Finally, the reviewers stressed the importance of the Hydrogen Storage Engineering CoE in providing feedback to the material research community regarding materials' characteristics critical for hydrogen storage and effective system design. This CoE can also provide valuable input on the important materials parameters in addition to gravimetric and volumetric capacities (i.e., heat capacity, thermal diffusivity/conductivity, packing geometries, agglomeration effects, etc.). Continued interactions between the Materials CoE partners and the Engineering CoE were strongly encouraged, and it was recommended that data generated to-date in the subprogram be properly recorded and archived to ensure conservation of the data and results from the Materials Centers.

Hydrogen Storage Funding by Technology:

The Hydrogen Storage subprogram portfolio remained focused in FY 2009 on materials-based R&D for onboard transportation applications. The primary goal has been development and demonstration of commercially viable hydrogen storage technology to enable greater than 300-mile vehicle driving range, while meeting safety, vehicular packaging, and cost and performance requirements. A new goal introduced in FY 2009 is to develop storage options to facilitate deployment and market growth of fuel cell power systems for early market applications. R&D efforts remained focused on applied, target-oriented research of materials systems including high-capacity metal hydrides, chemical hydrogen storage carriers, and high-surface area adsorbents with the potential to meet the vehicular technical targets. In addition, the subprogram continued to support advances in physical storage (e.g. compressed hydrogen gas) for nearer term applications. The initiation and funding of the Engineering CoE in FY 2009 reflects a growing programmatic emphasis on engineering and systems integration issues. The following chart illustrates the appropriated funding in FY 2009 for each major activity.



Majority of Reviewer Comments and Recommendations:

The Storage portfolio was represented by 34 oral and 46 poster presentations in 2009. A total of 60 projects (32 presentations and 28 posters) were reviewed. In general, the reviewer scores for the storage projects were good (1=poor, 2= fair, 3=good, 4=outstanding) with scores of 3.8, 3.0 and 2 for the highest, average, and lowest scores, respectively. The projects were reviewed by two (for one project) to six reviewers each with an average of 4.3 reviewers per project. Reviewers remarked favorably on the coordination and management of the Storage Materials Centers of Excellence. It was suggested that the Materials Centers focus on summarizing results, trends and lessons learned to-date, and on making recommendations for future hydrogen storage materials R&D. Key recommendations and major concerns for each project category are summarized below.

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, and is well focused on many DOE vehicle targets and technical barriers including cost. The chemical hydrogen storage material R&D has made good progress toward addressing issues related to ammonia borane (AB) by reducing foaming and release temperature, as well as increasing capacity and the kinetics for the release of hydrogen during the stoichiometric reaction. Continued R&D is required to further improve these AB release parameters as well as to address hydrogen purity, heterogeneous catalysis, liquid fuel formulation, and cost effective first fill. Recommendations were made to continue the down-select process with a focused effort on winning strategies, and to coordinate with the Engineering CoE to address onboard system requirements. Significant progress was made in AB regeneration chemistry and the associated cost analysis where separation steps were identified as the dominant cost factor and new approaches were developed to address the issue. It was recommended to further advance and complete the AB regeneration scheme and update the cost analysis. It was also recommended that the boron demand market projection be updated based on worldwide adoption of fuel cell vehicles.

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-managed and coordinated group of quality researchers focused on relevant research to the Hydrogen Storage subprogram. The MHCoE was commended for their flexibility and adaptability in refocusing on promising materials while moving away from less promising materials. However, the reviewers felt even further materials down-selection could be useful in some projects. In addition, reviewers recommended more communication and coordination between the MHCoE and the independent research projects on advanced metal hydrides to minimize duplication and maximize effectiveness of the program. The reviewers found the use of computation modeling to aid in materials research direction well coordinated and effective. The computational modeling efforts were also praised for incorporating gas phase species into their modeling. With the limited time remaining for most of the projects, it was recommended that the projects focus on the materials and activities that are expected to yield the most promising results and reduce efforts in higher risk areas.

Sorbent Materials: The goal of sorbent applied materials R&D is to develop materials with high hydrogen volumetric and gravimetric reversible net available capacities at closer to ambient temperature and at moderate pressure. The general approach is to identify and design (often via theoretical modeling) high surface area porous materials with increased hydrogen uptake capacities and higher binding energies for molecular hydrogen that will enable storage above cryogenic temperatures (e.g. 77K). The DOE portfolio for sorbent materials includes the Hydrogen Sorption Center of Excellence (HSCoE) and independent R&D projects. A number of new sorbent materials (i.e., various polymers, MOFs, COFs) have been synthesized and their hydrogen uptake capacity characterized. The reviewers noted that while many of these materials do show promise, issues still remain with achieving "net available" volumetric and gravimetric capacities that can meet DOE vehicular targets. "Net available" means that the temperature, pressure, energetics, and transient delivery/uptake rates are taken into account to determine the amount of fuel available to the power plant. Furthermore, retaining these properties at closer to ambient temperature/moderate pressure has proven difficult, as hydrogen/adsorbent site binding energies remain too low. Reviewers also pointed out the limited success for either or both the syntheses and experimental performance verification of improved storage from several materials that had theoretically predicted high capacities. The reviewers suggested more inputs from experimental results should be incorporated into the theoretical efforts in order to improve the latter's predictive potential. The reviewers remarked that while members of the HSCoE have provided some significant new theoretical insights into the mechanisms for hydrogen spillover behavior associated with selected metal dopants (i.e., Pt or Pd), issues remain with reproducibility in experimental studies of this phenomenon with often contradictory observations from different groups on hydrogen uptakes and the kinetics for adsorption and discharge. The reviewers emphasized that integrated efforts should be made by the researchers to prepare and process samples that can provide reproducible measurements of the reactions during hydrogen spillover to establish viable mechanisms that may enhance reversible uptake and increase the kinetics. The reviewers recommended that instead of using idealized (i.e., single crystal) densities to estimate material volumetric capacities greater efforts be made to consider powders or compacts/monoliths of porous sorbents as practically configured for vehicle storage. Down selection of sorbents from further evaluation should be based upon criteria rooted in laboratory measurements rather than upon theoretical predictions that had not been previously validated by experiments.

Advanced Tanks: The advanced tank R&D is conducted by a small but diverse group of researchers from industry, universities, and at national laboratories. Gradual progress has been made in conventional high-pressure tanks toward reducing cost, weight, and volume of the systems. However, this advancement has not been communicated in the clearest manner possible. Although Lawrence Livermore National Laboratory has made good technical progress in all the areas mentioned above, there are still concerns with respect to energy use, specifically for liquefaction. It was recommended that more than one OEM partner be included in this effort.

Analysis, Testing and Support: Reviewers noted that Argonne National Laboratory and TIAX LLC have made good progress this year. They are finalizing reports on systems that have been under evaluation since the beginning of the program. As in past years, the reviewers commented on the value of this work to an understanding of the relative merits of materials with respect to the requirements of the entire storage system. This work also allows screening of materials before the physical integration stage. This year the Engineering Center initiated complementary analysis work on integrating storage and fuel systems.

The National Testing Laboratory at Southwest Research Institute was considered to be essential for the National Hydrogen Storage Project; however the reviewers felt that more effort is needed to develop methods to verify extraordinary results, especially related to "spillover" effects and to understand the cause of irreproducible or spurious measurement results.

Notes on Storage Report Structure:

Chemical Hydrogen Storage
ST – 15 to 21 and STP – 17 to 20 are partners in the Chemical Hydrogen CoE
STP – 21 is an independent project

Sorbent-based Materials and Other New Materials and Concepts
ST – 22 to 31 and STP – 25 to 29 are partners in the Hydrogen Sorption CoE
ST – 32 to 33 (Sorbents) and STP – 2 and 3 are independent projects

Advanced Metal Hydrides
ST – 1 to 11 and STP – 36 to 42 are partners of the Metal Hydride CoE
STP – 44 is an independent project

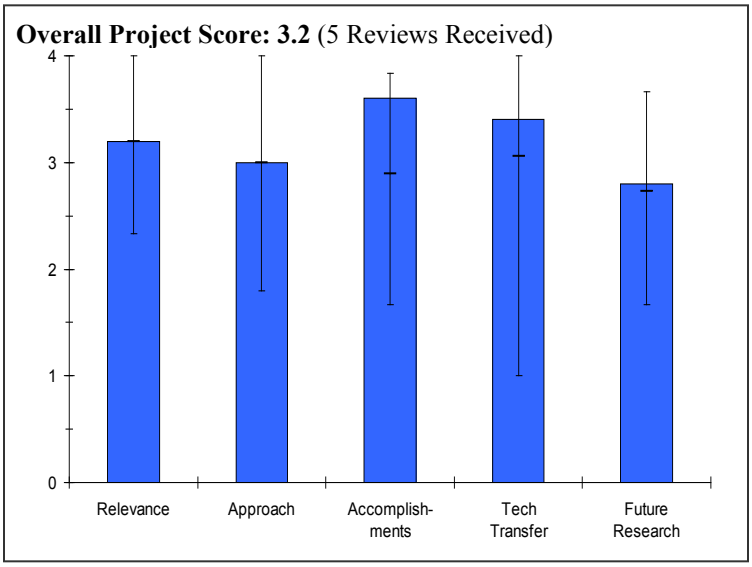
Advanced Tanks
ST – 34, STP – 1, and STP – 4 (Advanced Tanks Projects)

Analysis, Testing and Support
ST – 12 to 13, STP – 30 and STP – 45

Cross-Cutting
STP – 22 to 23, 43, 46

Project # ST-01: Metal Hydride Center of Excellence
Lennie Klebanoff and Jay Keller; Sandia National Laboratories
[NOTE: This presentation was to evaluate the entire Metal Hydride Storage Center of Excellence as a whole. A separate review form was used and can be found in Appendix C.]

Brief Summary of Project



The overall objective of the Metal Hydride Center of Excellence (MHCoE) 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 charge/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 **3.2** for its approach to R&D and CoE management.

- The CoE is generally well managed. A lot of activities are directed to address the regeneration/reversibility issue of the materials.
- The overall impression of this CoE is good but not perfect.
- There are good connections between theory and experiment.
- The down-selection process is very impressive, but there are still a large number of materials being studied − perhaps too many?
- The CoE is well focused on the many DOE targets and barriers.
- The CoE does not seem to be focusing enough on materials cost. This is not referring to systems cost, which is the proper domain of the new Engineering CoE; but to the absence of preliminary cost studies on the metal hydride materials being studied in this CoE by the materials experts that are best suited for this work, at least in a preliminary sense.
- The CoE appears to be well managed and has adapted over the years of the center's operation as progress has been made on various materials. Essentially, there have been continuous down-selections of different materials during the project.
- New center members have been effectively included. Extensive utilization of new member, UTRC, is particularly noteworthy.
- This is mostly basic research.
- The industrial partnership(s) is insufficient.
- Scalability of studied materials has not been established.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **3.0** on its accomplishments and progress.

- There have been some interesting basic results especially on boron-based materials.
- DOE targets have not been met yet; more work is needed to meet them.
- This task may require refocusing on alternative hydride systems such as carbon hydrides.
- The overall CoE activities showed good progress in overcoming the technical barriers.
- Very good technical progress has been made on many fronts.
- The down-selection process was nicely done.
- Good progress has been made this last year.
- Material properties for reversible materials to date continue to be problematic (e.g., enthalpy too high, kinetics slow, release of contaminant phases, less than complete rehydriding and/or loss of capacity).
- Good productivity based on papers and presentations.

Question 3: Proposed future research approach and relevance

This project was rated **3.6** based on future plans.

- Future work plans build on past progress, but more should be done to meet the DOE targets.
- With the remaining CoE life, the proposed future research is reasonably good; however, there is still no well-defined pathway to achieve DOE targets.
- The CoE has only a limited time remaining. In that sense, the list of remaining work is the best it can do. It cannot all be completed in time.
- Good planning.

Question 4: Coordination, collaboration and effectiveness of communication within the CoE

This project was rated **3.4** for collaboration and communication within the CoE.

- Collaborations within the CoE are excellent. This has improved over the years and has continued to improve this past year.
- Good coupling between modeling and experimental efforts in certain areas.
- Center partners have established reasonably good coordination within the CoE.
- The CoE seems to collaborate well internally, but it is hard to fully see this from the Director's presentation.
- Are the CoE members adequately open to each other? Are there any IP problems or conflicts that limit communication?
- It is not clear how much of the progress is synergistic (i.e., from internal CoE communications and collaborations rather that individual efforts). Is it clear to the CoE management that the overall progress of the CoE is more than the sum of the individual parts?

Question 5: Collaboration/Technology Transfer Outside the CoE

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

- National and international collaborations seem to be very extensive and valuable, including joint
- publications.
- Good interactions with outside collaborators in certain areas (e.g., modeling).
- Limited interactions with other CoE.
- The Metal Hydride CoE contribution to the newly formed Engineering CoE will be critical.
- Industrial collaboration is limited.
- It is not clear how the progress outside of the CoE is filtered through the center activities

Strengths and weaknesses

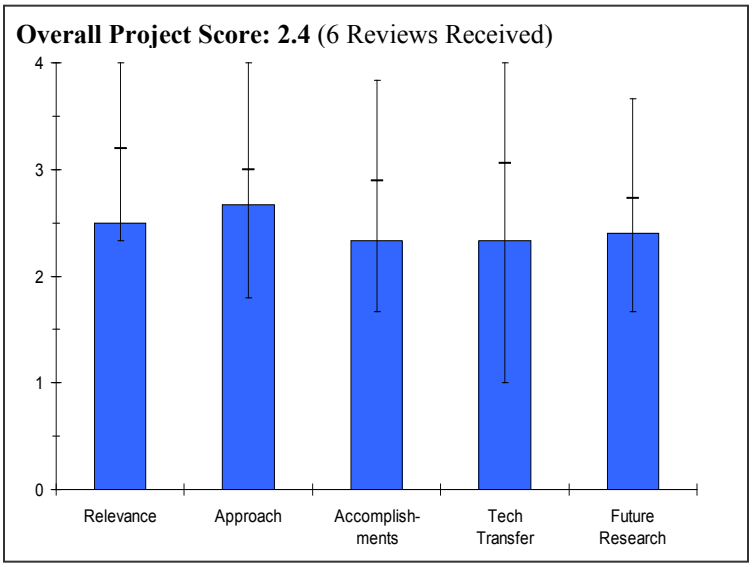
Strengths
- Interesting basic research – especially in the area of the solid-state chemistry of metal borohydrides.
- The CoE structure and materials down-select process are strengths.
- This is an excellent group of technically skilled individuals.
- This is a strong research team whose members complement one another in certain areas.

Weaknesses
- The focus has changed several times during the last few years. Unfortunately, these changes did not conclude in generating sufficiently new ideas.
- New approaches and non-trivial ideas could really benefit the research at the CoE.
- Poor collaboration with the industry is definitely a weakness.
- It is not clear how progress outside of the CoE – addressing the same issues as the CoE – is linked to the CoE plan.
- The material down-select criteria should be discussed with the Engineering CoE in order to incorporate the engineering input.
- The group may be a bit large for the most effective communication and interaction.

Specific recommendations and additions or deletions to the work scope

- Research on hydride materials as hydrogen sources should continue.
- Reconsider research directions toward non-conventional ideas and new approaches, which may include hydrogen storage in organic materials, combining photo-chemical generation of hydrogen with hydrogen storage, etc.
- Review the previous materials that did not make the down-select criteria based on the revised DOE target.
- Other than more cost thinking, no suggested changes for the duration of the effort.

Project # ST-02: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials
Bruce Clemens; Stanford University



Brief Summary of Project

The objectives of this project are to 1) develop a fundamental understanding of metal hydride reaction kinetics, 2) develop an understanding of metal hydride nanostructure thermodynamics, and 3) develop an 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) (e.g., Mg, Al), and continuum modeling suggests that reaction thermodynamics should be modified by reducing particle size to the nanometer regime. Material structure can play an important role in reaction kinetics, especially during solid-state phase transformations such as those in metal hydride reactions. 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 **2.6** for its relevance to DOE objectives.

- The project is completely in line with and in full support of the DOE objectives. It aims to develop a fundamental understanding of reaction mechanisms in metal hydride transformations. It addresses the kinetic limitations that hinder the performance and hydrogen storage potential of metal hydride systems. This is of great value for the design of new materials with improved kinetics and storage properties with potential to meet the targets for the Hydrogen Program.
- One of the goals of this project is to develop an understanding of metal hydride reaction kinetics. This aligns well with DOE's goals because kinetics are an important aspect of the hydrogen storage element.
- Storage targets/barriers addressed include stored hydrogen gravimetric/volumetric capacity and reversibility.
- From a fundamental point of view, the work would help develop an understanding of the kinetic limitations of existing hydrogen storage systems; however, from an applied point of view, it does not strongly relate to the objectives because it utilizes highly ordered systems that might not relate to the bulk (real) materials.
- This project seems to be more like a Basic Energy Sciences (BES) effort. Focus on conventional metal hydrides has no direct connection to the complex hydrides being studied in the rest of the MH CoE. (Complex hydrides are not interstitial hydrides, at least some fundmental elements of the kinetics are expected to differ significantly between these materials.)
- This work is more fundamental in nature compared to the work of the rest of the CoE that is focused on developing high capacity hydride materials.
- Specific important contributions to the CoE efforts have not been demonstrated.
- This project does not appear to be well integrated into other CoE activities.

Question 2: Approach to performing the research and development

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

- The approach is well thought out, concentrating on modeling geometrically simpler systems and coupling theory with strong experimentation and verification. This work can contribute to a better understanding of the interplay between structural changes in materials and reaction kinetics and their limitations during hydrogen charging and discharging.
- In general, the approach seems to be well thought out; however, it is not clear why the PI is using thin films of Mg coated with Pd to model hydrogen absorption by Mg. Mg, more typically, might have an oxide coating on the surface, not Pd.
- The project develops the understanding of metal hydride reaction kinetics and thermodynamics at the nanostructure level and phase change/structure relationships.
- The project team employs microbalance, X-ray diffraction, and synchrotron X-ray methods.
- Experimental measurements and modeling are combined to resolve issues affecting hydrogen storage capacity, hydrogen diffusion limitations, and reaction kinetics during charge and discharge.
- Generally, work is on simple systems (i.e., single metal and binaries); work on more complex systems is planned.
- For a basic understanding it's definitely useful, especially for Mg-based materials; however, when it comes to more complex systems (i.e., Mg alanates), a thin film approach might be difficult based on the current results.
- Although the stated purpose of this project is to gain an understanding of hydride reactions and properties, the work has focused on thin films that have not been shown to be necessarily representative of other hydride structures.
- Work was continued on simple systems (e.g., MgH_2), which are very different materials compared to the complex hydrides studied by the rest of the center.

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

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

- The project team has shown a satisfactory degree of accomplishments and good progress. The team developed model systems for seeing the hydrogenation reactions and successfully identified and modeled the hydride formation kinetics. This included determining the size of the critical dimensions for the structures (threshold) in order to improve kinetics and avoid the activation of a diffusion controlled hydride growth. Equally encouraging are the results from the quartz crystal microbalance (QCM) experimental setup while the neutron reflectivity data should be throwing more light into the thin film hydride growth model.
- The PI was successful in developing a model to describe the hydriding kinetics. This model needs to be backed up with further studies.
- Work on Mg_2Si showed that H_2 uptake is not H_2 diffusion limited, but rather that it is limited by Mg and Si diffusion.
- The Mg-Al system seems to be H_2 diffusion limited; Mg/Al layers inter-diffuse resulting in complex super-lattice diffraction.
- The model was further developed to investigate hydride growth kinetics; application to experimental data indicates that there is a critical dimension (<120 nm) to avoid diffusion control. Examined transition from interface to diffusion limited growth.
- Observed loss of solid phase epitaxy on cycling for Mg/MgH_2 system.
- Postulated that for metal hydrides it is necessary to shift thermodynamics to add relative stability to metal phase. Initial attempts to demonstrate the effect with nano-level films were made. So far, no changes in thermodynamics.
- For Mg-Ti, a 10-fold increase in P_{eq} was observed with Ti addition.
- The neutron results with NIST are just now showing interesting results. What are they?
- There is one paper in press.
- For the MgH_2 system, this is a very good study and results.
- The publication of results has not improved since last year − only one paper is mentioned as being in press after 4.5 years of effort.

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

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

- The PI fully explores links within the MHCoE and gains access to unique facilities and expertise.
- Collaborations are reported with two CoE partners, but it is expected that they would have had a few more collaborators because this project is part of the MHCoE.
- Collaborators are listed as being HRL Laboratories, the University of Pittsburgh, and NIST.
- There is nothing significant shown regarding work with HRL Laboratories and the University of Pittsburgh; the NIST collaboration is a work in progress.
- Collaboration seems to be limited to working with HRL Laboratories' systems.
- Aside from the NIST work, connections to the rest of the CoE's work are not apparent.
- Some specific interactions on the Mg-Si system, but not much collaborations with others in the CoE.

Question 5: Approach to and relevance of proposed future research

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

- The future research plan builds on current experience, and it is appropriately drawn for further progress toward reaching the objectives.
- It is good that the PI plans to develop a general model to describe the reverse reaction and phase growth with cycling. It would be interesting to see if the thin films can endure continued cycling. It would also be useful if the PI would compare the kinetics results of his thin film to kinetics studies done on bulk samples.
- Plans include continuing to study particle size effects.
- Plans include completing work on Mg/MgH_2, Mg-Al, and Mg-Ti.
- Plans are to continue work with NIST on neutron reflectivity study of Mg/MgH_2 thin films; model specifics of reaction kinetics and MgH_2 film growth.
- Plans to move to the complex hydrides systems, using the thin film approach could be difficult.
- With half a year left in this project, there is little in the proposed future work suggesting that a more relevant approach will be followed.
- Not applicable.

Strengths and weaknesses

Strengths
- Strong analytical/computational skills and development of potentially excellent experimental techniques and instrumentation.
- The PI seems to be well equipped to continue kinetic studies on thin films.
- The project team has carefully performed research at the nanoscale.
- The PI is knowledgeable.
- The project team has shown very good capabilities.
- Good capabilities have been employed to study material interactions in clean systems.

Weaknesses
- Need to demonstrate how representative the thin films examined are of the material systems which are of interest.
- The PI could develop additional collaborations with others in and outside the MHCoE.
- Progress seems slow and productivity could be better. The results so far are interesting but not compelling in terms of eliminating barriers.
- There is only one paper (in press); the publication record of this project still needs improvement. (This is the reason for the "Fair" score on Technical Accomplishments.)
- It is not obvious how collaboration with University of Pittsburgh played a role this past year.
- Also, it is not obvious how the results from this project are fed into MHCoE planning and decision making.
- The unclear relation to the bulk systems is a weakness.

- So far, the approach has only focused on one partner system.
- The complex hydrides thin film approach might prove to be difficult.
- Efforts have not focused on materials of interest to the CoE or the program.

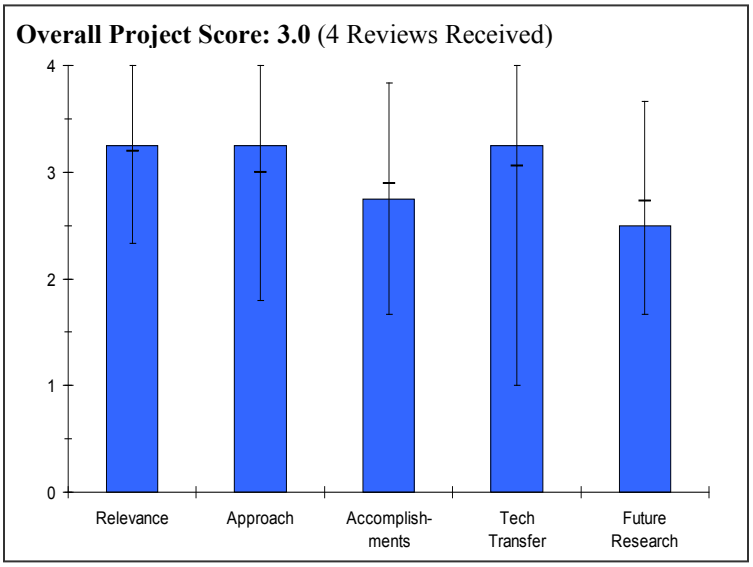
Specific recommendations and additions or deletions to the work scope

- The project should demonstrate how the thin film results and conclusions drawn from this work can be translated to the more advanced material systems examined within the Metal Hydride CoE.
- Nanoscale work needs to be validated on suitable nanostructured systems. The PI has also identified this as a critical assumption issue.
- The PI needs to justify key assumptions, such as why it's necessary to have a Pd coating on thin films.
- The PI should bring the work in progress to logical and meaningful conclusion, then publish it.
- In the time that remains, the PI should steer away from systems that hold no promise of meeting hydrogen storage system targets (e.g., Mg_2Si).
- The PI should emphasize how collaborations are enhancing the output of this project and how the project results are having an impact on the hydrogen storage element's quest to meet its goals.
- The project team uses a good approach to fundamental understanding, however, it seems that this type of research could fit better in the basic research program.

Project # ST-03: Discovery and Development of Metal Hydrides for Reversible On-board Hydrogen Storage
Mark Allendorf, Vitalie Stavila, and Eric Majzoub; Sandia National Laboratories

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 hydrogen pressures. The project works on improving kinetics, cycling life, and desorption properties by incorporating hydride materials in nanoframeworks. The theory objectives include employing the prototype electrostatic ground state (PEGS) technique for structure determination and hydrogen estimates to provide MHCoE 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 **3.3** for its relevance to DOE objectives.

- The discovery and development of reversible metal hydrides for on-board usage is very critical to the Hydrogen Program.
- Discovery of high potential materials with support of modeling is needed to help meet the DOE targets.
- This is a solid effort to solve a difficult problem (onboard reversible materials).
- The project basically supports DOE needs and targets.
- Although the key barriers are listed in slide 2, that list seems rather *pro forma* because there are almost no actual demonstrated relationships between the quantitative results of the project and the DOE system.
- There is a little on media gravimetric capacity, but almost nothing on any system targets (e.g., volume, cost, refueling times, quantitative purity of H_2).

Question 2: Approach to performing the research and development

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

- Good connections were made between modeling and experiments.
- Experimental work guided by modeling is a good approach.
- This solid approach combines excellent theoretical aspects with sound experimental efforts.
- The project is a complicated mix of candidate materials, theoretical (modeling), synthesis, and materials evaluation. It is not completely clear how this large spectrum of activities avoids overlap with other numerious groups from around the world working on similar techniques and materials.
- The various theoretical (modeling) activities seem especially complimentary and coordinated.
- The important experimental components of the project seem a bit haphazard and not as coordinated as the theoretical components.

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

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

- It is clear that many good theoretical and fundamental understandings have been made on the borohydrides, alanates, amine systems, and etc.

- A lot of work has been completed in one year.
- It is necessary to incorporate all the phases possible to the modeling work to determine material suitability. However, it seems that only one system has been examined so far.
- Synthesis of the $B_{12}H_{12}$-anion-based compounds and comparison with theory is very helpful as it gives insight into the borohydrides decomposition intermediate to support a go/no-go decision.
- It is not at all clear how much (if any) progress has been made toward solving the system barriers. The large array of interesting results is simply not related to progress toward the DOE goals. One gets the feeling that little real (practical) progress has been accomplished during this project.
- The negative no-go on $Ca(BH_4)_2$ is nicely documented, clear, logical, and appreciated.
- There are some serious implications of theoretical and experimental results that are not fully discussed:
  - Is the $B_{12}H_{12}$ intermediate going to be a potential barrier to most borohydride practical reversibilities?
  - Will the general presence of impurities (e.g., B_2H_6, NH_3) mean the on-board purification will always be necessary, or is there any hope of the <10 ppb impurity levels required by proton exchange member fuel cells? In other words, there should be more in the way of practical implications of the results.

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

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

- There has been good collaboration both within and outside of the CoE.
- There has been visible collaboration between theory and experiments.
- Collaborations are outstanding, and the many multiple-party publications clearly show that.
- What are the mechanisms of communications among the many collaborators?
- There are many collaborations within and outside of the CoE.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.5** for proposed future work.

- The future work is planned reasonably well for the upcoming year.
- The new materials investigation path forward is rather vague. Is it screening-based, modeling-based, etc.?
- Strong focus on hydrides NH_3 stabilization, however, formation of NH_3 is likely.
- It's unclear why $Ca(BH_4)_2$ received a no-go, while $Mg(BH_4)_2$, which has the same thermodynamic decomposition issue, will be further researched wihin the CoE.
- The past *modus operandi* will continue.
- It is only partially clear why the future work activities selected are the most important to the overall objectives aimed at breaching of practical system barriers.
- The outline of proposed future work on slide 22 was somewhat vague.

Strengths and weaknesses

Strengths
- The experimental work is guided by theory.
- There are good connections between modeling and experiments.
- The project team has employed PEGS, and modeling in general.
- The project team has a good, comprehensive and coordinated understanding of the theory. Very good theoreticians have been involved.
- Attempts have been made to verify model calculations with experimentation.
- It is very nice to see the incorporation of gas-phase species into the computational predictions.

Weaknesses
- There seems to be no theory prediction of what is the best nanoframework in terms of pore size distribution for incorporation of metal borohydride.
- There is almost a complete lack of effort to correlate theoretical and experimental results with their potential (or lack thereof) for meeting DOE system targets. Fundamentals should be better coordinated with practicals.

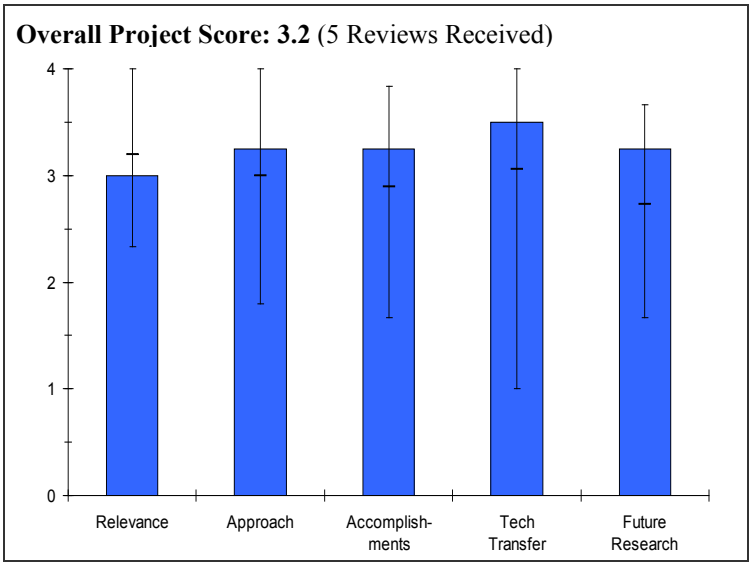
Specific recommendations and additions or deletions to the work scope

- With the remaining time left for this project, it is not clear why the team would like to further explore new mixed-metal borohydride systems.
- Modeling is needed to determine decomposition paths for the NH_3 stabilized systems.
- The project must invoke some practical systems thinking: mass, volume, cost, kinetics, reversibility, quantitative purity, etc. Some simple calculations on systems projections will suffice.
- There are too many materials being considered. More go/no-go decisions are necessary, particularly aimed at the many DOE on-board targets.

Project # ST-04: Chemical Vapor Synthesis and Discovery of H_2 Storage Materials: Li-Mg-N-H System
Z. Zak Fang and H.Y. Sohn; University of Utah

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 chemical vapor synthesis process for production of nanosized solid metal hydrides, and 3) demonstrate the effectiveness and unique properties of nanosized solid hydride materials. Objectives for FY 2008-2009 were to 1) determine the thermodynamic properties of hydrogen storage using the ternary nitride material, LiMgN; 2) understand mechanisms of hydrogenation and dehydrogenation of LiMgN; 3) quantify NH_3 content during dehydrogenation of hydrogenated LiMgN; and 4) demonstrate effects of nanoscale particle size on properties of metal hydrides.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- The research performed supports DOE RD&D objections.
- Very relevant work to DOE storage objectives.
- The PI has found a very good system in LiMgN that has the potential to meet DOE's short term goals for hydrogen storage.
- The PI and his group have performed a detailed hydrogen storage performance study of LiMgN; measured the thermodynamic properties, kinetics, and cycling properties; and explored the complex desorption process. They also have performed impressive cycling experiments on $MgH_2 + TiH_2$ nanoparticle system.
- Domain of materials was too narrow.

Question 2: Approach to performing the research and development

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

- The approach used is adequate.
- The approach of using "low-energy" ball milling to produce pure LiMgN, and thereby achieve reversibility, is a very good one.
- This is a good approach that uses multiple characterization methods.
- The approach uses more than one material preparation technique: both low-energy and high-energy milling techniqus, as well as chemical vapor synthesis.
- The approach looks at cycling properties as well as the first few cycle performances.
- The project team has considered a number of different material systems.
- The project team has demonstrated a number of reversible systems.

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

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

- The PI has developed a method for making the LiMgN system absorb and release hydrogen reversibly and this is a significant accomplishment.
- An extensive amount of work has been completed on different material systems.
- Important progress has been in the understanding of the LiMgN system by focusing on pure material preparation.This is interesting fundamental research on a Li-Mg-N system.
- The understanding of mechanochemical reactions is incomplete.
- The results on the MgH_2-TiH_2 system are interesting.
- The PI measured enthalpy and kinetics of materials, which many PI's fail to complete.
- The PI measured impurity release (i.e. NH_3) in gas stream of LiMgN system.
- Stability was determined in the nanoscale Mg-Ti system after 100 cycles.
- This project has very good accomplishments and progress. However, it could be improved by 1) investigating the long-term cycling performance of LiMgN and 2) looking into particle size effects on the MgH_2+TiH_2 system.

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

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

- Collaboration with others is adequate.
- This project is well coordinated with other partners in the MHCoE.
- Good collaborations within the CoE.
- The project team has excellent collaborations with other groups in the CoE.

Question 5: Approach to and relevance of proposed future research

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

- The MgH_2+TiH_2 system is quite promising.
- The kinetics and cycling studies that were mentioned are crucial in determining if this material will be of use in practical applications. The cycling studies will help determine if the ammonia production leads to significant degradation of this promising material.
- The project team has a good plan for future work.
- For the future plan, there are few places that are not so certain:
    - The project team wants to use a nanoengineering method to change the structure of LiMgN to improve the hydrogen sorption performance and NH_3 release, but what would be the appropriate method they will use? High energy milling for MgH_2+TiH_2 system is not appropriate for the LiMgN system.
    - What will be the guideline for them to find additive to the LiMgN system to minimize NH_3 release?

Strengths and weaknesses

Strengths
- This is a good research that provides fundermental understanding of the material.
- There is adequate collaboration with others.
- The LiMgN system is a very promising "reversible" system that has the potential to meet DOE's short-term goals.
- This is a good project that is both broad in scope and in examining the details within given material systems.
- There is solid experimental data – very relevant to DOE objectives.

Weaknesses
- The project is well designed; however, materials do not reach DOE targets.
- In the kinetics measurements, a better effort needs to be made to define the reaction conditions. Kinetics are strongly affected by pressure conditions, particle size, surface impurities, etc., and these need to be specified.
- To date, materials continue to have operating temperatures higher than the target.

- Some detailed experiments need to be carried out for structural and hydrogen sorption characterizations. For example, the detailed cycling performance of LiMgH and the structural characterization of MgH_2 and TiH_2.

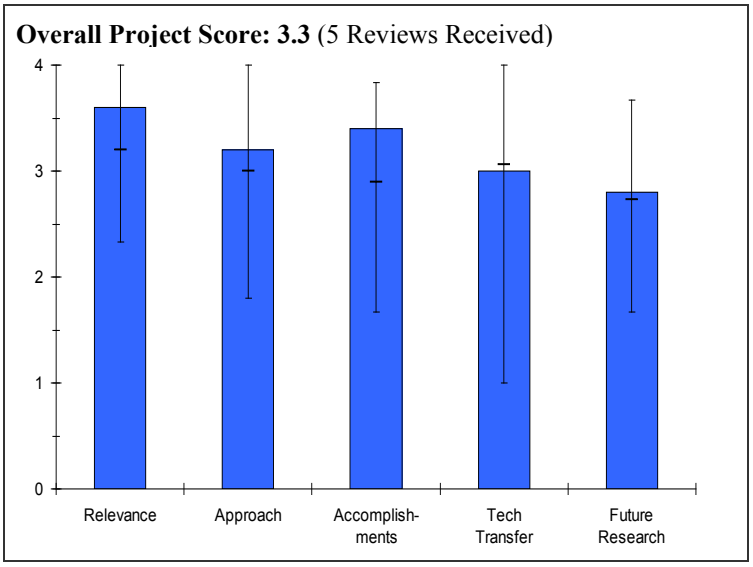
Specific recommendations and additions or deletions to the work scope

- This project should continue.
- Cycling studies should be a part of any future studies on this system.
- None.

Project # ST-05: Aluminum Hydride Regeneration

Jason Graetz, J. Wegrzyn, J. Reilly, J. Johnson, Y. Celebi, and W.M. Zhou; Brookhaven National Laboratory

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 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 (300 K). In an AlH_3 system, H_2 evolution is controlled by temperature (rather than pressure) so the ability to tune decomposition kinetics are critical. Various routes exist to adjust kinetics (e.g. size, coatings and catalysts). The key issue is regeneration (i.e., hydrogenation of Al metal), and multiple regeneration pathways are being investigated.

Question 1: Relevance to overall DOE objectives

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

- The regeneration of AlH_3 is very challenging and critical to the Hydrogen Program.
- The project is well aligned to the DOE objectives and is responsive to the goals of the Hydrogen Program because it addresses a number of key barriers.
- The challenge of off-board regeneration has been addressed, however the challenge of the instability of alpha – AlH_3 for on-board storage did not receive as much attention.
- Particularly relevant to DOE objectives.
- Project seriously considers most DOE on-board system targets: weight, volume, regeneration efficiency, cost, refueling times, H_2 discharge rates, etc. This is an important approach for H_2 storage that should be further explored.

Question 2: Approach to performing the research and development

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

- The high-level electronic calculations and theory-guided approach achieved successful results.
- The ideas for low-energy regeneration routes are very good and effective.
- The project team employs a systematic, well thought out, and quite reasonable approach, which is guided by theory.
- There is very good synergy between calculations and adducts selection.
- Screening of the adducts was well done, but the separation of the pure alpha-AlH_3 remains a challenge. The overall efficiency of the alpha-AlH_3 formation should show superiority against the classical AlH_3 chemistry route.
- The use of AlH_3 liquid slurries for refueling, on-board H_2 generation and spent Al removal is innovative and has immediate practical engineering potential.

- The use of a slurry as an on-board storage medium presents engineering challenges; these challenges include: solvent presence causes the contamination of the fuel cell MEA, lowering of storage capacity in terms of weight percent, the need for continuous mixing in case of solid adducts, etc.
- The approach of low-pressure/temperature synthesis of AlH_3-adduct, followed by separation of the adduct to yield pure AlH_3 is very logical and innovative.
- Experimental work is well guided by theory.
- The approach leverages theory and experimentation.

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

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

- The BNL team has made excellent progress in 2009.
- Progress has been excellent, with the discovery of several new AlH_3 adducts and experimental verifications that some have the potential of practical off-board AlH_3 regeneration schemes
- The demonstration of DOE target discharge kinetics with a liquid AlH_3 slurry is of revolutionary importance and gives the potential for near-term practical vehicular systems.
- Satisfactory progress with respect to the objectives and the eventual improvement of the alane adduct separation and the most challenging step, its recovery. The project fully explores the possibilities for new, cost-effective and energetically efficient methods to regenerate aluminum hydrides and profits from the expertise within the CoE.
- Significant accomplishment with the verification/demonstration of all steps for the two complete regeneration pathways.
- There has been good progress and several new findings.
- The presentation of the results so far, is clear and easy to understand, even for a non-chemist.
- Good connections exist between theoretical adduct thermodynamics and experimental results.
- Nice work on the identification of additional adducts.

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

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

- The networking record is very good and guarantees access to a wide range of top-class expertise and therefore strengthens and greatly benefits the research.
- Some good collaboration exists, but there needs to be more discussion and input from the Engineering CoE.
- Collaboration is visible, especially with SNL.
- Good collaborations with several partners, but some of the results of those collaborations are not fully described.
- The collaboration with ANL for systems analysis has been excellent, and will continue to be important for the remainder of this project.
- Other than collaboration with the SNL modeling effort, there should be more apparent contribution from other partners.

Question 5: Approach to and relevance of proposed future research

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

- The future plans set clear and reasonable steps forward, getting the most out of experiences gained so far in the project.
- Further work plans need to take into account the energy balance of the overall regeneration process.
- Improving the efficiency of the alpha alane separation proposed is very good; the future work should include determining the superiority of this methodology versus other new synthesis and available methodologies.
- The focus on slurries is of concern due to the potential engineering challenges because even a liquid-state adduct still needs solvents present.

- The future work plan cannot be improved upon.
- The energy efficiency of the regeneration process should be assessed as early as possible so that efforts are not devoted to processes that have no reasonable hope of meeting targets.
- Consideration needs to be given to capacity penalties due to slurry formation.

Strengths and weaknesses

Strengths
- Excellent regeneration pathway design and good progress.
- Networking and pooling of expertise and resources.
- Very systematic and good visible progress.
- Excellent practical thinking and focus on virtually all DOE vehicle storage system targets.
- Productive, innovative R&D and positive results.

Weaknesses
- Additional input needed from the system engineering group.
- The engineering aspects and associated energy balance and regeneration costs are still an issue.
- Total energy analysis from Ti activation of Al to separation (for current adducts) is lacking.
- None.

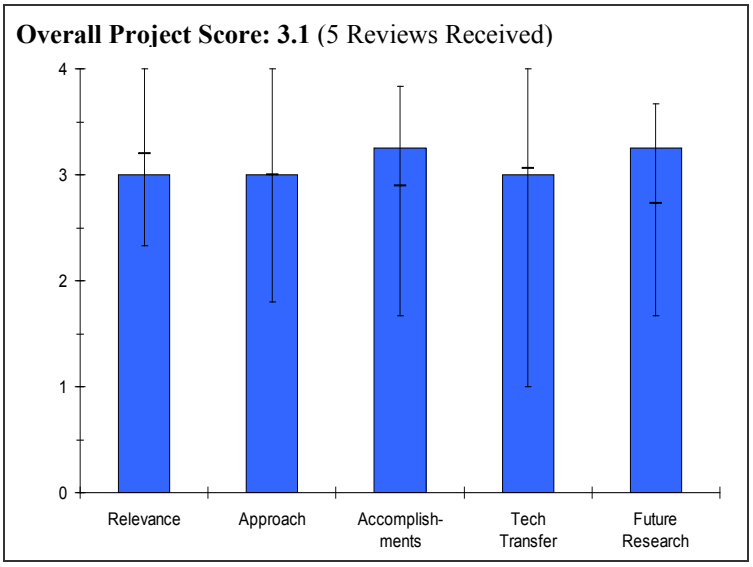
Specific recommendations and additions or deletions to the work scope

- Need to add quick and simple energy balance calculation before the closing of the project and include the calculation in the final report.
- Work together with the established Engineering CoE to investigate the feasibility of the "slurry solution" and all engineering aspects including regeneration energy balance.
- Incorporate efficiency analysis based on current systems and compare with other methodology.
- Slurry for on-board storage is not recommended as a focus.
- No changes are recommended for the remainder of this project; however given the positive potential for this project in reaching the ultimate DOE system targets (if confirmed by ANL systems analysis) a follow-on contract should be anticipated. The objectives of this new project should be the construction of a full-size demo vehicular system coupled with the selected off-board regeneration process.

Project # ST-06: Electrochemical Reversible Formation of Alane

Brenda Garcia-Diaz, Christopher Fewox, and Ragaiy Zidan; Savannah River National Laboratory

Brief Summary of Project



The overall objective of the project is to develop a low-cost rechargeable hydrogen storage material with cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE on-board hydrogen transportation goals. This material is aluminum hydride (alane-AlH_3) that has a gravimetric capacity of 10 wt% and volumetric capacity of 149 g/L hydrogen and desorption temperature: ~60 to 175°C (depending on particle size and the addition of catalysts) which can meet the 2010 DOE targets for desorption. Specific objectives of the work include: 1) avoid the impractical high pressure needed to form AlH_3, 2) avoid chemical reaction route of AlH_3 that leads to the formation of alkali halide salts such as LiCl, and 3) utilize electrolytic potential to translate chemical potential into electrochemical potential and drive chemical reactions to form AlH_3.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- The project is dedicated to the low-temperature/low-pressure, electrochemical reversible formation of alane − a material with a high storage capacity and its regeneration is crucial to its viability as a hydrogen storage medium. The project is therefore focused on the Hydrogen Program goals and addresses key targets of R&D objectives.
- This project addresses one of the critical issues of efficient regeneration of the most promising solid state H_2 storage materials.
- The alane system has very good potential to meet DOE's short-term objectives for hydrogen storage. It has good hydrogen-holding capacity and kinetics.
- This project addresses hydrogen storage system weight, volume, cost, and efficiency, as well as storage material regeneration processes.
- This project is focused on the development of an efficient, low-pressure, low-cost route to regeneration of alane (AlH_3).
- This work supports the regeneration efforts of a promising storage material.

Question 2: Approach to performing the research and development

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

- Very well-thought-out, clear, systematic approach focused on overcoming the initial barriers to electrochemical formation of alane and making significant steps forward.
- The project team demonstrated excellent innovation to overcome the barriers to recover alane with very high energy efficiency using electrochemistry and capture of AlH_3 formed.
- The electrochemical approach to producing alane is a very good one; it is far more realistic than trying to use high-pressure formation. The fact that LiCl production can be avoided is significant. The fact still remains that regeneration must presently be done off board, which is less than ideal.
- Electrochemical recharging of alane ($Al \rightarrow AlH_3$) in a non-aqueous electrolyte.

- Recent emphasis has been on bench-scale electrochemical generation of AlH_3 from pure Al in H_2 atmosphere and on harvesting of pure (adduct free) AlH_3.
- The project includes modeling of electrochemical behavior and process efficiency.
- The electrochemical approach is an important alternative to the study for regenerating spent alane. It eliminates the need for very high-pressure charging.
- The approach considers energy utilization as well as material yield.

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

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

- The project team has made significant accomplishments through a robust approach. The project demonstrated, for the first time ever, a reversible cycle using electrochemistry and direct hydrogenation, with high yield of, isolated and characterized, gram quantities of alane produced under mild conditions.
- The fact that gram quantities of alane have been produced electrochemically is significant. This could lead to more cost-effective ways of producing this material commercially.
- This is the first time alane has been isolated for the reaction system in gram quantities. It is suggested that the project team try and release hydrogen directly from the adducts, bypassing the pure alane recovery and eliminating the need for the slurry.
- The project team demonstrated production of high-purity AlH_3 in gram quantities.
- The project team has produced a model for the electrochemical generation of AlH_3.
- The team succeeded in isolating AlH_3 and confirming purity.
- The results are encouraging in terms of an efficient closed cycle for "release/regeneration" using AlH_3.
- Alane is formed effectively using the electrochemical approach developed in the course of this project.
- Significant progress has been made in harvesting alane from an electrochemical cell and gram quantities of alane have been successfully formed. This is an important achievement.

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

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

- Close collaborations exist between SRNL and many of its Center partners. This has proven to be very beneficial for this project.
- The project team has made excellent interaction with BNL and University of Hawaii groups.
- The project team has collaborated with BNL, University of Hawaii, University of New Brunswick, and ANL.
- The project team has collaborated closely with alane researchers in the center.
- There is good coordination with ANL analysis.
- The project belongs to the Metal Hydride CoE. There is some collaboration and partnership with BNL (on the alane-TEDA formation issue) and also others contributors are mentioned; however, the extent of the coordination of these activities during this reporting period was not entirely clear.

Question 5: Approach to and relevance of proposed future research

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

- The future plans are sound and build on current experiences with attention to the determination and optimization of the process efficiency.
- The future plans are built on the results already obtained and no new initiatives are planned. The collaborations that have worked so well will continue.
- The PI should provide data that ANL will use to determine and optimize efficiency.
- The researchers should work with BNL and SNL to identify better separation solvents.

- The researchers should work with the University of Hawaii to explore new solvent(s) that promise higher efficiency.
- The PI should determine if there are other complex hydrides that can be regenerated in similar manner.
- The project team has a good plan for future work.

Strengths and weaknesses

Strengths
- The project team has a solid understanding of electrochemistry.
- The results are very encouraging (on a promising hydrogen storage material) for meeting the capacity targets of the program.
- The PI and his colleagues are well qualified to carry out this research. The close collaborations with CoE partners are working well. The project is well focused and has led to a method of producing gram quantities of alane.
- The emphasis is on a storage material that has a chance of meeting the DOE targets.
- This project seemingly had a very successful year.
- The objective of producing AlH_3 of reasonable purity in a moderately efficient manner was met.
- Collaborations clearly helped and should continue to help this project.
- The future plans are well thought out and sensible.

Weaknesses
- Scalability could be an issue and practicality and cost effectiveness of the process could be prohibitive for its application.
- This project is not likely to lead to an "on-board" method of regenerating alane, however there are no other projects that are close to achieving this goal
- Some electrochemical engineering is needed to optimize the cell design. Based on the pictures of the very simple cell embodiment used, it is clear that there is much room for improved electrochemical regeneration performance (e.g., improved current efficiency), product recovery, and dendrite abatement.

Specific recommendations and additions or deletions to the work scope

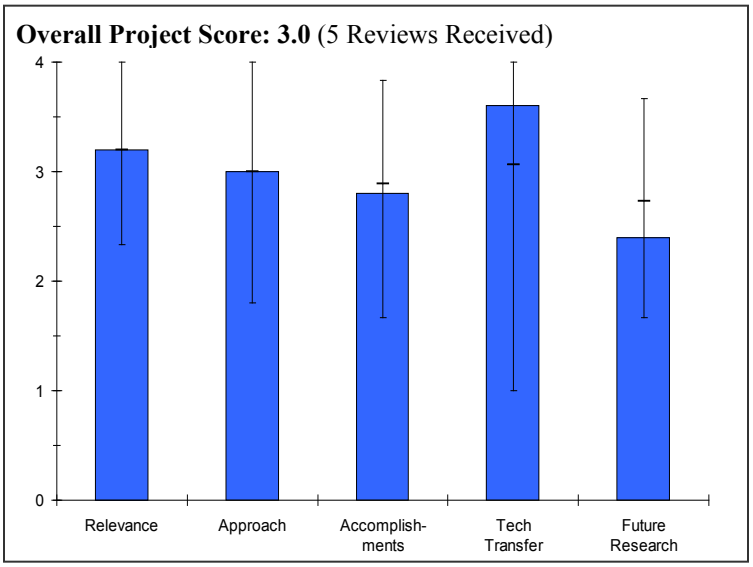
- The project team with its partners and with the support of the Engineering CoE should evaluate the lifecycle system costs and its potential for practical commercialization.
- A more practical electrochemical cell design (e.g., involving the implementation of concentric, rotating electrodes) might work nicely for this application.
- The project team should intensify the interactions with the alane regeneration experts.

Project # ST-07: Fundamental Studies of Advanced, High-Capacity Reversible Metal Hydrides

Craig M. Jensen; University of Hawaii
Sean McGrady; University of New Brunswick

Brief Summary of Project

The objectives of this project are to 1) develop new materials with the 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, 2) determine the mechanism of action of dopants for the kinetic enhancement of the dehydrogenation and re-hydrogenation of complex hydrides, and 3) 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 project addresses hydrogen storage system gravimetric and volumetric targets and barriers to meeting those targets.
- The PI seemed to be working on several aspects at the same time, all of which align with the Hydrogen Program.
- Hydrogen discharge/recharge rates and storage system thermal management issues are addressed in a substantive manner.
- Some aspects of the project contribute to an improved understanding of hydrogen chemisorption and physisorption.
- The project has partial relevance to DOE on-board storage goals. It does focus on weight, kinetics, and process efficiency.
- Work is relevant to DOE RD&D objectives.
- Project does not focus adequately on volume, cost, and H_2 purity which relate to the fuel cell needs.
- This project is clearly relevant.

Question 2: Approach to performing the research and development

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

- The general approach is effective to address the barriers.
- The approach is to develop new classes of reversible complexes that have the potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets.
- The project team tries to pursue too many directions at the same time and thus stretches themselves too thin.
- Systems of current interest include:
  - Al and Mg nano-confined carbon aerogels.
  - Borohydrides that can be reversibly dehydrogenated at low-temperatures.
  - Unconventional solvents for the hydrogenation of Al to AlH_3 and/or LiH/Al to $LiAlH_4$ at moderate pressures.
- The approach is scientifically interesting, but somewhat unfocused because it deals with three rather distinct efforts.

- The science is not always clearly extrapolated to technological (engineering) potential for a practical vehicular system, refueling modes, and spent product regeneration. Some engineering implications are perhaps easy to see, but the PI needs to more clearly state them.
- In some cases, it is not obvious how the scaffolding work is distinct from similar efforts within the CoE.

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

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

- For three projects with total funding of approximately $400K, the project team is making reasonable progress in developing the basic understanding of high-capacity, reversible metal hydrides.
- The project team has made progress with nanoconfined Mg in carbon aerogels:
  - High (9-16 wt%) MgH_2 loadings of carbon aerogel without host degradation were obtained using an organo-metallic method. Higher MgH_2 loadings were obtained with materials that have larger pore sizes.
  - Nanoconfinement of MgH_2 was found to improve kinetics (by a factor of 5 over the previous best result) but did not appear to effect the dehydrogenation of MgH_2.
- Progress with anionic borohydrides.
  - Full hydrogenation of MgB_2 to $Mg(BH_4)_2$ was achieved in the presence of a catalyst at pressures as low as 120 atm.
  - NMR spectroscopy confirmed that the product of the hydrogenation is $Mg(BH_4)_2$.
- Progress was shown with hydrogenation in non-conventional solvents.
  - Fully charged, Ti-doped $LiAlH_4$ was obtained in major yields from the direct hydrogenation of Ti-doped LiH/Al in liquefied dimethyl ether (DME) at room temperature in 100 bar of Me_2O/H_2.
  - Well-To-Tank (WTT) efficiency analysis of a $LiAlH_4$-based hydrogen system utilizing liquid DME as a rehydrogenation medium showed that the system approaches the 60% target value.
- The number of positive results is significant.
- It is not clear that the nanoconfined MgH_2 (in aerogels) can meet the systems targets.
- The best loadings are 17-23% MgH_2 and thermodynamics have not been significantly improved. In response to the question, the PI stated that MgH_2 insertion in C-aerogel was preliminary model work and the solution work will move on to materials with more hope of meeting DOE needs.
- The catalyzed synthesis of $Mg(BH_4)_2$ from MgB_2 and transition metal (TM) borides seems promising, but the present pressures and temperatures (900 atm and 500°C) seem daunting . The PI's hope of achieving milder conditions may be too optimistic. Like the BNL AlH_3 work, the use of solvents such as DME to synthesize $LiAlH_4$ seems promising. It sounds as if this has to be an off-board regeneration process if it is going to meet the 3 minute refueling goal.
- It is disappointing not to see a few fundamental calculations carrying this materials synthesis and property work toward the many DOE system targets. Some simple calculations would have been appreciated. By doing a little "back-of-an-envelope" calculations, it seems that nothing reported herein has much intermediate-term chance of overcoming the present DOE barriers.
- The presentation was inconsistent regarding the reversibility of $Mg(BH_4)_2$. Slide 20 states that reversibility is at 120 atm, but does not state the temperature, while slide 11 suggests reversibility at 950 bar and 400°C.
- Bu_2Mg is hardly the most efficient reagent. Cp_2Mg or t-Bu_2Mg may be considered as potential precursors for MgH_2.
- The formation of $MgB_{12}H_{12}$ during continuous operation of $Mg(BH_4)_2$ is not addressed. The question if $Mg(BH_4)_2$ behaves differently from $Ca(BH_4)_2$ is also not addressed.
- The role of the Ti catalyst in Li-Al-Ti-H system was not addressed effectively and does not seem to be well understood.
- The direct synthesis of $LiAlH_4$ in polar solvents has already been reported in the past and DME is a known process.

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

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

- There is good collaboration with other partners.

- This project's collaborations are indeed extensive, however how each contributed was not obvious in the presentation, but it is clear that collaboration did occur.
- The list of collaborators includes California Institute of Technology, HRL Laboratories, National Institute of Advanced Industrial Science and Technology, PNNL, University of Rome, University of Geneva, Institute for Energy Technology (Norway), Jet Propulsion Laboratory, UOP, KEK (High Energy Accelerator Research Organization), Tohuku University, University of Illinois, SNL, NIST, and the University of New Brunswick.
- The University of Hawaii work involves many good collaborations. It is an excellent example of collaborations within the Hydrogen Program.
- There is a lot of good collaboration.

Question 5: Approach to and relevance of proposed future research

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

- Interesting basic research is planned; however, it does not offer a way of meeting the DOE targets within a reasonable period of time.
- Given that the upcoming year will be the last year of the program, the plan should focus on a few specifically defined objectives. The current plan has too many tasks to perform in one year.
- Future work on nanoconfined Mg in carbon aerogels includes:
  - Determine dehydrogenation and rehydrogenation kinetics of aerogels loaded with both MgH_2 and Ti catalyst.
  - Prepare nanoconfined MgH_2 from the hydrogenation of dimethyl magnesium intercalated aerogels as a means of increasing loadings.
  - Determine pressure-composition-temperature (PCT) isotherms to elucidate the effect of nano-confinement on the dehydrogenation of MgH_2.
- Future work on anionic borohydrides includes:
  - Explore variations in reaction conditions to improve yield from low-pressure hydrogenation of MgB_2 to $Mg(BH_4)_2$.
  - Continue the studies of the catalyzed and un-catalyzed hydrogenation of MgB_2 to elucidate the mechanism and possibly learn how to improve the kinetics.
- Future work on hydrogenation in nonconventional solvents include:
  - Maximize the extended cycling capacity of Ti-doped $LiAlH_4$ through variation of the dopant concentration and recharging conditions in liquid dimethyl ether.
  - Continue exploration of methods to improve the levels of hydrogenation of alane using alternative supercritical fluids (SCFs) and a variety of initiators/catalysts.
  - Explore SCF synthesis of $Mg(AlH_4)_2$.
  - Proceed with further evaluations of WTT efficiency of the DME/$LiAlH_4$ system in collaboration with ANL.
- Future work proposed on anionic borohydrides and hydrogenenation in nonconventional solvents is worthwhile.
- There are not plans to focus on overcoming the many system property barriers.
- The scope should be narrowed from the past year to address fewer key areas in greater detail.

Strengths and weaknesses

Strengths
- There is good collaboration with various DOE and non-DOE research groups including international collaborations.
- There is good collaboration with other CoE partners.
- The PI and his co-workers seem to have good instincts about how to improve things. In the past they have tended to stay focused on systems with a reasonable chance of meeting DOE hydrogen storage targets.
- The collaborations are extensive and seemingly effective.
- Stepping away from the supercritical CO_2 effort was a good decision.
- Good, innovative chemistry.
- Excellent collaborations.

Weaknesses

- The group tries to pursue too many directions at the same time, thus being unfocused and skipping essential details.
- There are too many research areas that are not related in the project.
- Some of the approaches are not well explained.
- The project may be going in too many directions with the available funding and possibly limited time.
- While the results from the work on aerogels are interesting, it appears that the dilution factor makes the hydrogen storage targets unachievable. The presenter referred to it as a "model approach," but it seems to have little chance of meeting the targets.
- The connection to on-board system end points and associated DOE barriers is poor.

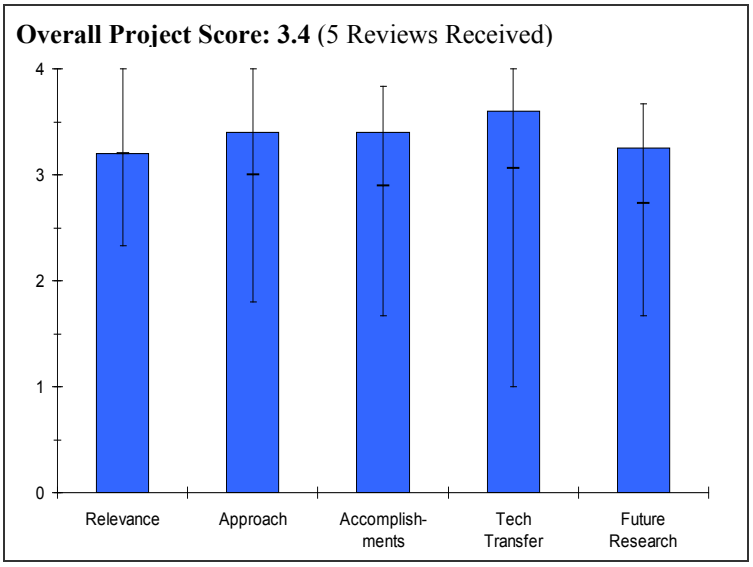
Specific recommendations and additions or deletions to the work scope

- The PI should reduce the number of research topics/directions.
- The project should focus on directions with the highest potential for meeting DOE targets.
- More attention to the science behind the many informative research accomplishments and fewer sidebars about factors outside the control of the PI would help the project to end on time and produce a better appreciation of the significance of the results.
- The PI should end all work on nanoconfined MgH_2 in carbon aerogels and move to better materials with more potential.
- Given the poor results to date, it is suggested that PI and University of New Brunswick partner terminate further work on rehydriding Al in SCFs. The approaches in the BNL and SRNL projects seem much more promising from technical and cost angles.
- The project team should begin cost projections and systems target calculations.

Project # ST-08: First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems
J. Karl Johnson and David S. Sholl; University of Pittsburgh/Georgia Institute of Technology

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 FY 2009-2010 are to 1) complete reaction screening, including multistep and metastable reactions and new additions to the database; 2) finalize work on thermodynamics of multiple, gas-phase species; 3) include thermodynamics of amorphous and crystalline closo-borane structures such as $MgB_{12}H_{12}$ and related materials in the screening of candidate reactions; and 4) finish work on mixed metal hydrides.



Question 1: Relevance to overall DOE objectives

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

- Material modeling has become an important tool in the development of storage materials, both in guiding experimentalists toward promising materials and in understanding the behavior of complex material interactions.
- This project addresses issues/barriers associated with meeting DOE's hydrogen storage system gravimetric and volumetric targets, as well as factors affecting charging/discharging rates (e.g., kinetics).
- Theory is a powerful tool for screening candidate materials, but needs to tie-in with experimental work.
- This project addresses the lack of understanding of hydrogen physisorption and chemisorption.
- Overall this project is highly relevant.

Question 2: Approach to performing the research and development

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

- The PIs have been leaders in developing techniques for modeling complex material behavior using first principles calculations. Entropy is not included in the energy calculation, without this it will not give the information necessary to tell if a phase is stable or not.
- The project team uses first principles density functional theory (DFT) to compute structures and energies of solid phases and gaseous species.
- The project team uses phonon density of states calculations for determinations of finite temperature thermodynamics.
- Free energy minimization methods are employed for screening mixtures suitable for promising reactions.
- Surface energy calculations are used to assess the influence of nanoscale structures on the thermodynamics.
- The project now includes the application of first principles molecular dynamics to generate and study amorphous phases.
- The project team employs transition state theory to characterize surface reactions and diffusion mechanisms.
- It is suggested that the project team downplay the effort on amporphous phase calculations. The energy differences between these systems and their crystalline counterparts will be small and there will likewise be a small impact on reaction energetics.

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

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

- The project team has made good progress.
- The project team has made sizeable additions of thermodynamic data to key databases used by the Hydrogen Storage Program.
- Computational methods were used to generate and characterize 200 amorphous structures (100 atom assemblies).
- The project team computed diffusion barriers for charged defects and showed evidence that diffusion can be controlled by doping.
- Free energy calculations now include multiple gas phase species.
- New mixed metal borohydrides were characterized.
- Now that the kinetics calculations have been performed for MgH_2 (a baseline system), it would be good to see this effort extended to materials of current interest.
- It is nice to see the thermodynamic models include the formation of gas phase species. This will be a big help in improving the predictive accuracy of these methods.
- A clear description of what structures have been added to the metals hydrides database is needed.

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

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

- The project team has shown good collaborations.
- The project team collaborates broadly throughout the Metal Hydride CoE program. Collaborating institutions that benefit from working with the Pittsburgh group include California Institute of Technology, HRL Laboratories, University of Hawaii, Jet Propulsion Laboratory, University of Missouri, NIST, SNL, Stanford University, University of Illinois at Urbana-Champaign, and University of Utah.
- There is coordination of theory work within the Metal Hydride CoE through the theory working group.
- The PIs continue to have close collaboration with others and are responsive to input from experimentalists.

Question 5: Approach to and relevance of proposed future research

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

- Proposed future work included:
  - Carry out analysis of multi-step reactions and submit paper for publication.
  - Finish calculations for updated database reactions and carry out screening.
  - Analyze the thermodynamics and structure of amorphous $MB_{12}H_{12}$ systems for M=Ca and Mg.
  - Examine diffusion through void spaces in metal hydrides, as prompted by experimental observations.
  - Implement fast reaction screening with multiple gas phase species for as many cases as possible.
- The listed approach for proposed future research was too vague to be meaningful.

Strengths and weaknesses

Strengths

- This project is good for screening candidate materials.
- The PI is knowledgeable and enthusiastic. This is a force in the theory community working on hydrogen storage issues.
- Good choices have been made regarding computational methods and research thrusts.
- This project provides a lot of useful data to the Hydrogen Storage Program community.
- The PI is clearly responsive to prior reviewer comments and recommendations.
- There is strong coupling of experiment and theory.
- This is a strong collaborative effort.

Weaknesses

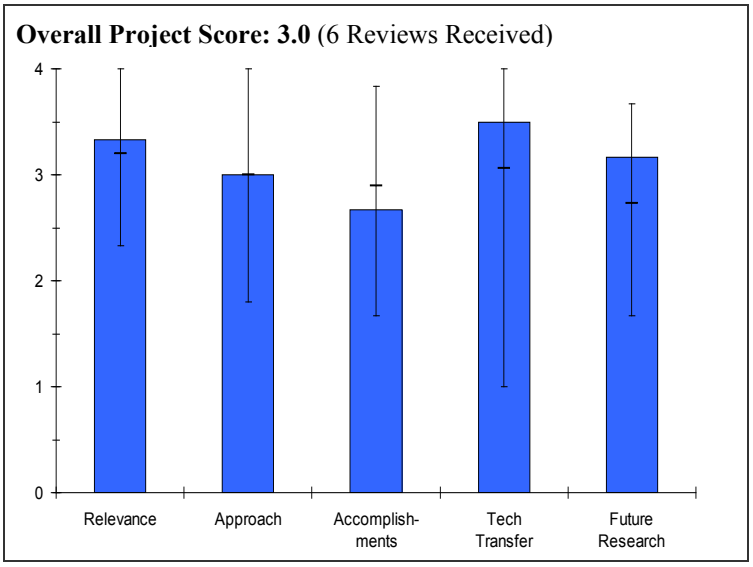
- Inclusion of entropy into energy calculation is lacking.
- Some aspects of the work on amorphous materials calculations need shoring up. A determination should be made of what happens as one varies the number of atoms. These types of calculations definitely need some form of experimental corroboration.
- There have been a relatively small number of publications.

Specific recommendations and additions or deletions to the work scope

- The project team should continue the good work.
- The project team should tighten up their work on amorphous phases. The results are interesting, but they need to be validated.

Project # ST-09: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage
Ping Liu and John Vajo; HRL Laboratories, LLC

Brief Summary of Project



The overall objective of the Metal Hydride CoE is to research, develop, and validate reversible onboard 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% and 45g 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 charge/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: Relevance to overall DOE objectives

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

- The development and demonstration of a safe and cost-effective light-metal hydride material system is critical to the Hydrogen Program.
- Lower dehydrogenation temperatures of $LiBH_4/MgH_2$ were achieved in scaffolds, but cycling properties still need to be improved. The search for new borides containing light transition metals for H_2 storage purposes is a valuable objective, but a major breakthrough in that field is uncertain.
- The PIs investigated the $LiBH_4/MgH_2$ destabilized system, and looked into how nanostructured carbon scaffolds affect the thermal dynamic property of the system.
- The scaffold approach has hydrogen capacity penalties inherent to it.

Question 2: Approach to performing the research and development

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

- The general approach is novel and effective.
- Examining a new system in addition to the $LiBH_4$-MgH_2 system is a good approach, given the lack of success in $LiBH_4$-MgH_2.
- The use of scaffolds is turning out to be more difficult than expected, but it still warrants further study.
- The project team uses a good approach: it is fairly well integrated with other efforts and contributes to overcoming some barriers.
- The overall approaches are appropriate; however the project team needs to design experiments to understand how the carbon scaffolds change before and after hydrogenation, after storage material is incorporated and even after cycling. Structural, volume, and composition change could reveal fundamental processes that govern the hydrogenation performance. This is important to the performance as well as the final loading.

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

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

- Lower dehydrogenation temperatures of $LiBH_4/MgH_2$ were achieved in a scaffold, but cycling properties need to be improved.
- Given the fact that the funding level was the same in 2008 and 2009, this year's progress is less impressive compared to last year.
- There is no explanation for the mechanism of reaction between $LiBH_4$ and MgH_2 in carbon aerogel.
- The investigated materials exhibit relatively poor cycling behavior.
- The $LiBH_4$-Mg_2NiH_4 system has desorption temperatures that are still too high.
- The $LiBH_4$-MgH_2 system in the carbon aerogel exhibits capacity problems with cycling.

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

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

- Collaboration appears to be very good in terms of key interactions with LLNL on carbon aerogels and University of Hawai'i on incorporation techniques for hydrides into aerogels.
- Good collaboration within the CoE.
- Professor Jensen of the University of Hawai'i seems to be making a solid contribution to this work.
- Collaborations are appropriate.

Question 5: Approach to and relevance of proposed future research

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

- This project is 80% complete, so the future work needs to be well focused.
- The search for new borides containing light transition metals for hydrogen storage seems to be a valuable objective, but the possibility of a major breakthrough is uncertain.
- It would be helpful to understand why the scaffold helps the hydrogenation performance. There are many parameters that play important roles such as scaffold structure, the filling of the storage materials, the structure and mechanical changes during the hydrogenation process, the real diffusion length, etc. A possible physical-chemical model on the hydrogenation and dehydrogenation process should be proposed.

Strengths and weaknesses

Strengths
- Work is focused on new destabilized systems and nanoporous scaffolds and is therefore likely to yield new valuable insight into thermodynamics and kinetics of hydrogen storage materials
- A novel technical approach and the outcomes can be utilized by other partners.
- Good collaboration with other partners.
- A variety of experimental techniques are utilized in research.
- The destabilization approach is generally a good one.

Weaknesses
- There is a lack of strategic planning in the experimental design. There is too much effort on optimizing $LiBH_4/MgH_2$ in scaffolds.
- Mechanisms of reported transformations remain unclear.
- There is no evidence that pure hydrogen is released.
- Gas analysis would be a useful tool to utilize.
- It appears that the destabilization approach does not work well for the $LiBH_4$-MgH_2 system.
- Incorporation of an aerogel framework to accelerate kinetics possesses a hydrogen capacity penalty.
- It may be difficult to overcome barriers for practical applications.

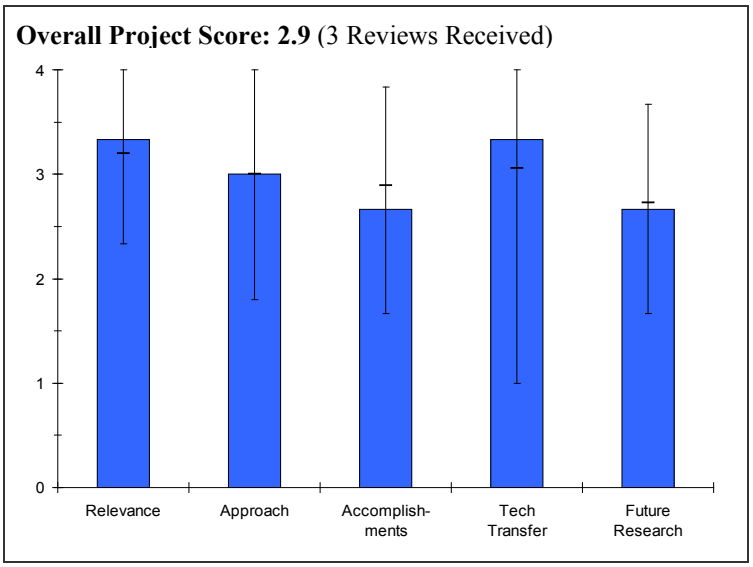
Specific recommendations and additions or deletions to the work scope

- With the time remaining for this project, it is suggested that the PIs drop the "search for other ternary systems with high capacity and low reaction temperatures" in their future work plan and allocate the available resources to achieve a more fundamental understanding of the current system.
- In the time left, this project should probably focus on characterizing and understanding the $LiBH_4$-MgH_2-carbon-aerogel and $LiBH_4$-Mg_2NiH_4 systems as completely as possible in order to provide guidance for future hydrogen storage materials that might adopt this approach with better success.
- It seems that the $LiBH_4/MgH_2$ system cannot meet the targeted goal, therefore another potential system should be examined. Further fundamental understanding of the role the scaffolds is needed.
- If possible, there should be a theoretical estimation of similar systems.

Project # ST-10: Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

X. Tang, D. Mosher, S. Opalka, X. Tang, T. Vanderspurt, B. Laube, and R. Brown; United Technologies Research Center
E. Rönnebro and T. Boyle; Sandia National Laboratories
F.-J. Wu and J. Strickler; Albemarle Corporation

Brief Summary of Project



The first objective of this project is to design and synthesize hydride/nano-framework combinations to improve reversible capacity, desorption temperature, and cyclic life. The second objective is to build upon successes previously demonstrated in the community and extend to a wider range of doped, functionalized and catalyzed framework chemistries in order to 1) advance the understanding of behavior modification by nanoframeworks, 2) obtain/maintain nanoscale phase domain, 3) tune hydride/framework interactions to decrease desorption temperature for highly stable compounds, stabilize high capacity compounds (resulting in ligand elimination) and influence desorption product formation, and 4) activate H_2 dissociation on highly dispersed catalytic sites.

Question 1: Relevance to overall DOE objectives

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

- The concept of using frameworks to reduce the hydrogenation/dehydrogenation temperatures for high capacity reversible metal hydrides is relevant, provided that the hydrogen capacity penalties associated with the framework are not prohibitive.
- Work on calcium borohydride does not appear to be the most straightforward way to support the goals and objectives, but is likely to yield valuable insight into basic research issues such as hydride/nanoframework interactions.

Question 2: Approach to performing the research and development

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

- Both carbon and oxide framework materials are being examined, the metal hydride materials being studied are relevant and the materials modeling work is supportive.
- The project is well designed and well integrated with other efforts, but it may contribute only indirectly to overcoming technical barriers.
- The PIs combined both theoretical work and experimental results, which is very good. Questions: For the molecular modeling, both the host and the guest are in an open space (i.e., not confined to a nanosized pore). Would that affect the calculation results? Especially when compared to the experimental results?

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

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

- The project has made significant progress towards objectives and some barriers (e.g., high loading of borohydrides in silica gel).
- The team made very good progress.
- The project does not appear to have produced any significant positive results.

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

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

- Good collaborations in attempting to try various routes to obtain a positive result.
- Collaborations exist and partners have contributed fairly well to the project.

Question 5: Approach to and relevance of proposed future research

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

- The proposed work on calcium borohydride does not appear to be the most straightforward way to support goals and objectives but is likely to yield valuable insight into basic research issues such as hydride/nanoframework interactions.
- There are three questions that should be addressed in the proposed future research:
    1. How would the filling of the metal hydride affect the hydrogenation property in the nanopore framework?
    2. Does the volume change of the metal hydride that occurs during hydrogenation and dehydrogenation have an effect on the property?
    3. Why would the doped framework, rather than a catalyst-decorated inner surface of the framework, give better results?
- There does not seem to be a clear path forward to achieve positive results.

Strengths and weaknesses

Strengths
- The project combines computational and experimental methods to design hydride-nanoframework composites.
- This project did not exhibit any strengths.

Weaknesses
- The modeling work is secondary to the experimental achievement of positive results.
- The project concentrates on a system (calcium borohydride) that has been down selected by other groups.

Specific recommendations and additions or deletions to the work scope

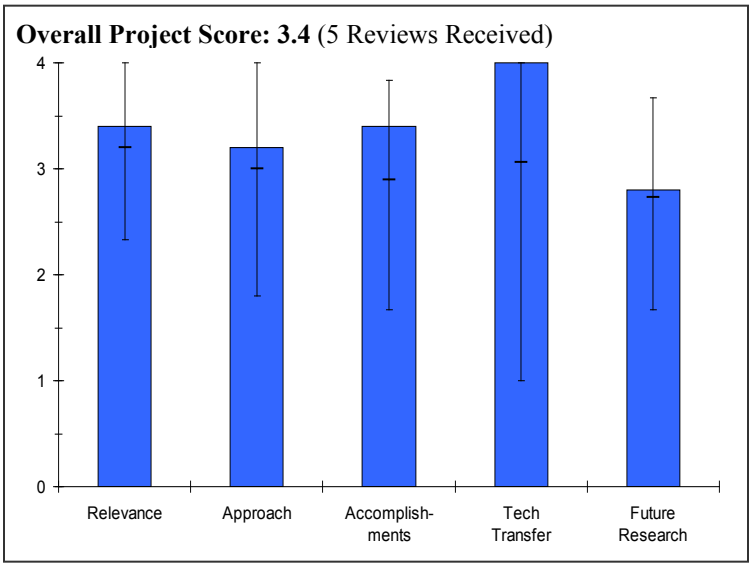
- A no-go decision should be made for this project.

Project # ST-11: Neutron Characterization and Calphad in Support of the Metal Hydride Center of Excellence

Terrence J. Udovic and Ursula R. Kattner; National Institute of Standards and Technology

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 CoE-developed materials and storage systems using state-of-the-art neutron methods and Calphad and 2) help speed the development and optimization of storage materials that can meet the 2010 DOE system target of 6 wt% and 45 g/L capacities. Objectives are to 1) characterize structures, compositions, hydrogen dynamics, and absorption-site interaction potentials for candidate storage materials and 2) provide Calphad calculations of phase relationships of potentially promising hydrides.



Question 1: Relevance to overall DOE objectives

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

- The nature of the results, particularly those from neutron experiments, is unique to the program in that the information generated cannot be obtained (or easily obtained) by other available methods.
- NIST boasts a high performance neutron scattering facility and its scientists in charge of research are among the best worldwide, at least from a European perspective. The facility and its scientists are critical assets for the Hydrogen Program, in particular for the Metal Hydride CoE, and this project fully supports DOE RD&D objectives. A reduction of DOE RD&D funding for hydrogen research would annihilate years of successful buildup of R&D knowledge and endanger the competitiveness of U.S. industry in the long run.
- Neutron characterization is the best tool for the Hydrogen Program.
- Neutron characterization is important to support the development of hydrogen storage materials.
- This project addresses issues that relate to hydrogen storage system gravimetric and volumetric targets and barriers to reaching those targets.
- The results provide new understanding of hydrogen physisorption and chemisorption phenomena.

Question 2: Approach to performing the research and development

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

- The Neutron and Calphad methods are both effective at addressing the technical barriers and the project is well designed.
- The PI should get a better picture of the overall approach to the direction of research than just characterizing the materials.
- Neutron methods are used to elucidate hydrogen diffusion mechanisms and determine the following:
  - Elemental compositions of materials;
  - Location of hydrogen atoms in storage materials; and
  - Resolve crystal structures of materials and the nature of bonding of absorbed hydrogen on surfaces and in bulk structures.

- Application of Calphad methods contributes to the development of a thermodynamic database from the available literature and from first principles calculations, including the incorporation of database information into an overall temperature-pressure-composition framework for multicomponent metal-hydrogen systems.
- The very nature of the work performed (neutron scattering on a great variety of new hydrogen storage materials for various research groups) contributes to a sharp focusing on technical barriers.

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

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

- Progress towards objectives is truly outstanding. The location and dynamics of hydrogen atoms have been successfully studied for a great variety of new hydrogen storage materials, including the $M_XB_{12}H_{12}$ intermediate, and a very useful diagnosis of a practical hydrogen storage bed has been performed by neutron imaging.
- The neutron imaging of hydrogen-storage beds is new this year.
- There needs to be more directed progress to see a clear path.
- Structures of $Li_2B_{12}H_{12}$, $Na_2B_{12}H_{12}$, and $CaB_{12}H_{12}$ were solved by a combination of X-ray diffraction (XRD), neutron vibrational spectroscopy (NVS), and density functional theory (DFT) calculations.
- It was found that only partially filling a 13 nm carbon aerogel with $LiBH_4$ increases the fraction that exhibits non-bulk-like BH_4-reorientation dynamics. Results indicate preferential filling of smaller pores and/or surface film formation.
- Neutron imaging techniques, employed to provide in-situ, real-time diagnostics of practical hydrogen-storage beds, illustrated how the use of deuterium instead of hydrogen enables the imaging of thicker beds.
- A Calphad database for H-Li-Mg-Ca-B-Si-N with thermodynamic descriptions of the constituent subsystems is being developed from literature data for the binary solution phases and intermediate compounds and from first principles calculations.
- The project team used the modified Neumann-Kopp rule for rapid prediction of the heat capacities of complex metal hydrides.
- It was found that confinement of $Li_3BN_2H_8$ in nanoporous carbon materials renders it partially reversible.
- NVS and prompt-gamma activation analysis (PGAA) indicated non-trivial amounts of residual hydrogen in carbon aerogels.

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

This project was rated **4.0** for technology transfer and collaboration.

- This project exhibited very good and close collaboration with CoE partners.
- A regular meeting with collaborators is fruitful to streamline the direction of research.
- This program provides unique neutron-based experimental data that can only be measured in a select few places. The collaborators that have received these data include California Institute of Technology (Caltech), General Motors, HRL Laboratories, Jet Propulsion Laboratory (JPL), LLNL, University of Maryland, University of Michigan, University of Missouri-Columbia, Ohio State University, University of Pennsylvania, SNL, and Stanford University.
- The Calphad work is done in collaboration with Georgia Institute of Technology, University of Illinois, University of Missouri-St. Louis, University of Pittsburgh, and SNL.
- NIST works in a coordinated manner with the Metal Hydride CoE and the Hydrogen Sorption CoE lead laboratories.
- Due to the very nature of its work (neutron scattering studies in collaboration with other research groups) the project is well integrated with other research efforts.

Question 5: Approach to and relevance of proposed future research

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

- The plans are built on past progress and sound effective. Proposed future work includes: to
  - Continue structural and spectroscopic characterizations of dodecahydro-closo-dodecaborates ($M_XB_{12}H_{12}$) (with SNL, Caltech, University of Maryland, University of Missouri-St. Louis, and Ohio State University);
  - Continue rotational dynamics investigations of nanoscaffolded borohydrides (with HRL, LLNL, Michigan State University, Caltech);
  - Continue Mg thin-film characterizations using neutron reflectometry (with Stanford University);
  - Perform neutron scattering characterizations of new materials in conjunction with the needs of the other partners, including borohydrides and nanoscaffolded materials of interest;
  - Continue feasibility studies using neutron imaging to probe hydrogen distribution and transport in storage beds for candidate materials (with JPL, University of Maryland);
  - Develop Calphad description of the Ca-B-H and Mg-B-H systems including the $Ca(BH_4)_2$ and $Mg(BH_4)_2$ compounds (with MHCoE Theory Group); and
  - Continue to expand Calphad database (evaluate literature for data, identify data needs and systems with Metal Hydride CoE partners for future database development).
- Future work should address issues listed in the *Project Weaknesses* section below.
- The investigations planned for the future have been built on past progress and are well focused on barriers, and the systems for future research are well chosen. However, an unexpected need for studying new systems may arise at short notice and should be accounted for in the planning.
- Future work was not proposed.

Strengths and weaknesses

Strengths
- Neutron characterization is the most critical tool for the Hydrogen Program.
- Neutron characterization is important.
- The project provides unique capabilities that employ neutron-based measurement methods.
- The project also provides experienced access to a useful database (Calphad) and also contributes to the building of that database.
- The results have a broad impact on the progress of the hydrogen storage CoEs.
- The work is skillfully done.
- This is excellent work.
- There are numerous collaborations.
- There has been a large amount of presentations and publications.
- This project provides the most basic and complete information on the structure and dynamics of solid hydrogen storage materials.

Weaknesses
- There is a lack of novelty.
- Close collaboration with a sample provider is lacking.
- There is concern about the attitude with respect to future plans. The PI left an impression that NIST is opening itself up to being treated like a job shop within the Hydrogen Storage Program. See the statement: "Perform neutron scattering characterizations of new materials in conjunction with the needs of.....partners..." This is okay, but threads of continuity (leading to focused pieces of research) should run through the work plan. With limited time and resources, the emphasis should be on the storage system materials with the best chance of meeting the DOE targets.
- The Calphad calculations do not appear to have reached their full potential yet.

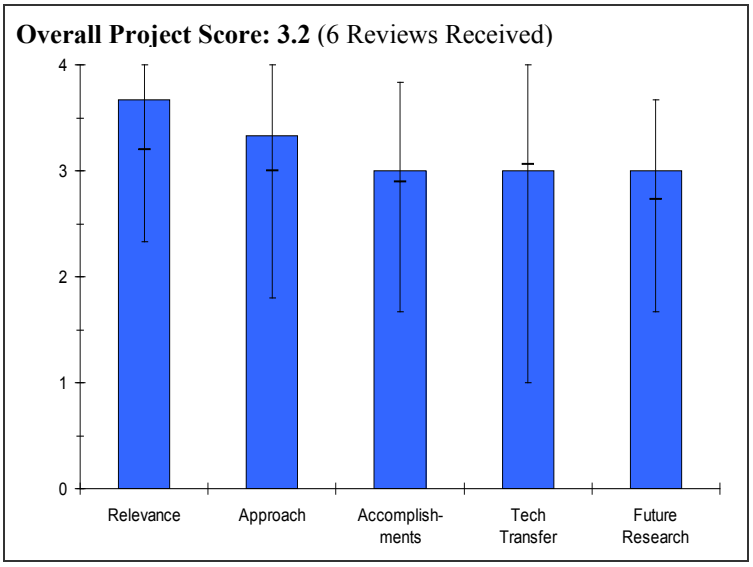
Specific recommendations and additions or deletions to the work scope

- The remaining work should be organized in such a manner so that the project is focused on specific science issues for hydrogen storage.

Project # ST-12: Analyses of Hydrogen Storage Materials and On-Board Systems
Stephen Lasher, Kurtis McKenney, Jayanti Sinha, and Paul Chin; TIAX LLC

Brief Summary of Project

The overall objective of this project is to help guide DOE and developers toward promising R&D and commercialization pathways by evaluating the status of the various on-board hydrogen storage technologies on a consistent basis. The on-board assessment objective is to evaluate or develop system-level designs to estimate weight, volume, and bottom-up factory cost for the on-board storage system. The off-board assessment objective is to evaluate or develop designs and cost inputs to estimate refueling cost and well-to-tank energy use and greenhouse gas (GHG) emissions for the fuel chain.



Question 1: Relevance to overall DOE objectives

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

- The economic analysis of various storage option is a vital and critical element in determining the path forward.
- The project is highly relevant and critical to the Hydrogen Program.
- These types of cost estimations are necessary.
- On-board storage is one of the two or three most critical areas of R&D necessary for hydrogen fuel cell vehicles to be successful. This project analyses the well-to-whells (WTW) costs and performance of potential on-board storage technologies and compares the results to the DOE targets. This is essential to screening out storage technologies that cannot achieve the targets and highlight the critical areas for R&D for promising storage technologies.
- The presentation was clear and focused, and solid improvements were shown over the years. The analyses are clearly relevant to DOE objectives on various pathways for storage in vehicles.
- Good balance of on-board versus off-board (regeneration) system costs and barriers.

Question 2: Approach to performing the research and development

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

- The approach includes bottom-up design and cost estimation, use of the H2A Production and Delivery tools as appropriate, seeking information and input from a broad rangeof stakeholders and experts, as well as a thorough a WTW approach to costs. The work being done is excellent.
- The approach is consistent and well established, albeit requiring considerable feedback from the PIs and thus the need to decouple the cognitive biases.
- The media and storage tank assumptions are clearly stated.
- TIAX, LLC is collaborating directly with ANL who performs the WTW energy efficiency and GHG analysis for the storage technologies. Between TIAX and ANL, a complete analysis of WTW costs, energy efficiency, and GHG emissions can be obtained.
- TIAX and ANL presentations should be integrated into one or each should show the total WTW results including costs, energy efficiency, and GHG emissions in a summary slide.

- It is not clear if the H2A Delivery Components and Carier Components models being used are up-to-date with the latest H2A Delivery efforts. It is not clear if these component model tabs are being properly used and pulled together for a particular delivery scenario.
- Solid; however the projections to high-volume (500,000 vehicles per year) are not credible without transparent comparisons to *current* costs.
- It should be made clear up front that assumptions regarding liquid carriers are based primarily on Air Products and Chemicals, Inc. (APCI) inputs. Are there other investigators or end-users interested in this approach to storage? The use of the n-ethylcarbazole systems is not feasible due to toxicity and will not be a long-term storage choice. N-ethylcarbazole serves as a stand in material while the reactor is developed in this project and other material carriers are developed in other parts of the program.

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

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

- The project is on target with the set objectives and deliverables.
- Given that this is the last year of the program, most of the on-board and off-board assessments are complete.
- Ammonia borane on-board analysis could have been a higher priority than LCH_2 given the effort and focus at the Chemical Hydrogen CoE, however automanufactuers have shown more .interest in LCH_2.
- Good progress in terms of completing the analysis of the liquid carrier technology, and updates of compressed hydrogen gas technology.
- Too much time and effort was spent on fine tuning the compressed gas technology analysis.
- Considering the FY 2008 budget, more analyses of different storage technologies could have been achieved.
- New DOE storage targets should be used for comparisons.
- Solid year-after-year improvement and presentations are now crisper. While the effort is primarily modeling, there must be simultaneously some "qualitative" assessment or ranking of such alternatives relative to practicality (beyond cost).
- Excellent breakdown of materials versus equipment costs, but when one has glaring sensitivity to one material (e.g., Pd for the carrier system) should there not be an attempt to project Pd demands under a 500,000 units/year scenario? Are we exchanging one vulnerability for another (beyond Pt)?
- Why the high losses for the carrier material and what are the costs of environmental impact of such losses?
- It is suprising that the ownership impact variations are so minimal among the carrier, Compressed H_2, and liquid H_2 options. What is the conclusion if this analysis is correct and how do we rank these for applicability (based on geography)?

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

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

- There is excellent collaboration with ANL, the Storage CoEs, and key hydrogen storage tank vendors which together cover a large portion of expertise in storage technology and analysis.
- Naturally, this project has to develop a working relationship with the PIs and also coordinate efforts with ANL system analysis.
- It is stated that TIAX interacted with the FreedomCAR Technology Teams, but only the Delivery Technology Team meeting is mentioned specifically. More interaction with the auto original equipment manufacturers (OEM) and energy companies could be helpful.
- There has been good collaboration with Air Products and Chemicals on carrier materials, but where are the cross-checks with other industrial gas companies? This should be done to ensure due diligence.

Question 5: Approach to and relevance of proposed future research

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

- The future plan is detailed, constructive and will add additional important results as well as detailed report documentation of results to date.

- Given that the project is almost completed, it is not clear when all the reports will be available to partners and general public.
- DOE is directing TIAX on what storage technologies to analyse. A thorough WTW analysis of a potential on-board "sorption" technology that operates at a variety of temperatures and pressures (-100°C to room temperature) and charged with cold H_2 gas (-150° to -50°C) would be very beneficial to the HFCIT Program. This would include looking at different sorption characteristics, including those achieved to date and potential ones. This is a very promising storage technology and would give DOE a clear picture of what sorption characteristics and other parameters are needed for this approach to meet DOE targets.
- Not clear what the final recommendations would be to the Engineering CoE for storage.
- There needs to be a more definitive chart for recommendations or very clear, focused suggestions for the discrimination of the different approaches.

Strengths and weaknesses

Strengths
- Consistency and experience are the two strengths.
- The cost analysis is one of the most critical aspects in evaluating the feasibility of hydrogen-based transportation system.
- Cost analysis is necessary to identify technology viability.
- On-board storage is one of the two or three most critical areas of R&D for hydrogen fuel cell vehicles to be successful. This project analyses the WTW costs and performance of potential on-board storage technologies and compares the results to the DOE targets. This is essential for screening out storage technologies that cannot achieve the targets and highlight the critical areas for R&D for promising storage technologies.
- The approach being taken includes bottom-up design and cost estimation, use of the H2A Production and Delivery tools as appropriate, seeking information and input from a broad range of stakeholders and experts, as well as a thorough a WTW approach to costs. The work being done is excellent.
- TIAX is collaborating directly with ANL who performs the WTW energy efficiency and GHG analysis for the storage technologies. Between TIAX and ANL, a complete analysis of WTW costs, energy efficiency, and GHG emissions can be obtained.
- The future plan is detailed, constructive, and will add additional important results as well as detailed report documentation of results to date.
- Different hydrogen storage technologies have been evaluated.
- Very comprehensive, detailed approach in attempt to settle on recommendations for action; however there is not clear pathforward in the end.

Weaknesses
- Lack of secondary analysis of the results and their implications. There needs to be further assessments of the bottlenecks in cost reduction. In short, is this pathway ever going to result in a decrease in cost? If so, what should happen and what is the likelihood of it happening?
- There is limited collaboration between this project and other projects in hydrogen storage and delivery team.
- The communication seems to be primarily with telecons. Face-to-face workshops would be helpful to ensure mutual understanding.
- It would be better if the TIAX and ANL presentations were integrated into one or if each showed the total WTW results including costs, energy efficiency, and GHG emissions in a summary slide.
- Considering the FY 2008 budget, more analyses of different storage technologies could have been achieved.
- It is stated that TIAX interacted with the FreedomCAR Technology Teams, but only the Delivery Technology Team meeting is mentioned specifically. More interaction with the OEMs and energy companies could be helpful.
- DOE is directing TIAX on what storage technologies to analyse. A thorough WTW analysis of a potential on-board "sorption" technology that operates at a variety of temperatures and pressures (-100°C to Room Temperature) and is charged with cold H_2 gas (-150° to -50°C) would be very beneficial to the HFCIT Program. This would include looking at different sorption characteristics, including those achieved to date and potential ones. This is a very promising storage technology that would give DOE a clear picture of what sorption characteristics and other parameters are needed for this approach to meet DOE targets.
- What is the best approach given the work, thus far?
- What key analyses are needed to break the logjam of viable options?

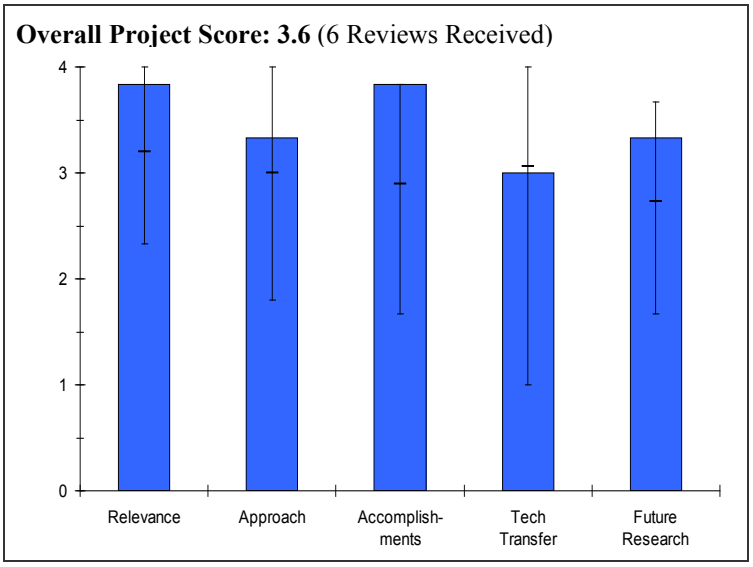
Specific recommendations and additions or deletions to the work scope

- While it may be a little out of scope, it is useful to start looking at the core issue(s) of each technology being analyzed. The objective should be to determine the major bottleneck of each technology and under what conditions they will be able to solve problems.
- Analysis should cover materials focused on within the DOE program, such as the the on-board storage material AlH_3 and its off-board regeneration.
- A thorough WTW analysis of a potential on-board "sorption" technology that operates at -100°C to Room Temperature at different temperatures and pressures and charged with cold H_2 gas (-150° to -50°C) at different temperatures, would be very beneficial to the HFCIT Program. This would include looking at different sorption characteristics including those achieved to date and potential characteristics. This is a very promising storage technology and would give DOE a clear picture of what sorption characteristics and other parameters are needed for this approach to meet DOE targets.
- More focus should be placed on key issues uncovered by the analysis and specific recommendations going forward.

Project # ST-13: System Level Analysis of Hydrogen Storage Options
R.K. Ahluwalia, T.Q. Hua, J-K Peng, and R. Kumar; Argonne National Laboratory

Brief Summary of Project

The objectives of this project are to 1) perform independent systems analysis for the DOE, 2) provide input for go/no-go decisions, 3) provide results to CoEs for assessment of performance targets and goals, 4) model and analyze various developmental hydrogen storage systems, and 5) identify interface issues and opportunities and data needs for technology development. ANL will develop thermodynamic and kinetic models of processes in cryogenic, complex metal hydride, carbon, and chemical hydrogen storage systems. Additionally, improvements needed in material properties and system configurations necessary to achieve hydrogen storage targets will be assessed.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.8** for its relevance to DOE objectives.

- This is a critical project to the overall Storage Program. It has consistently provided valuable information on the overall storage system requirements.
- On-board storage is one of the two or three most critical areas of R&D needed for hydrogen fuel cell vehicles to be successful. This project designs and analyzes the performance of potential on-board storage technologies and compares the results to the DOE targets. It is also responsible for well-to-wheel (WTW) energy efficiency and greenhouse gas (GHG) emissions of on-board storage technologies. These analyses along with WTW cost analyses done by TIAX are essential to screening out storage technologies that cannot achieve the targets and highlight the critical areas for R&D for promising storage technologies.
- This work is well balanced and has clear objectives.
- This is a highly relevant project for providing system-level analysis of hydrogen storage options for materials developed in the CoEs and independent projects.
- This is one of the *core* projects that make the DOE Hydrogen Storage Program such a well-run ship

Question 2: Approach to performing the research and development

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

- The approach is technically sound, albeit somewhat optimistic. In this case, the built-in optimism is required for the current approach.
- ANL does its own on-board storage system design, modeling, and analysis and is quite skilled at this. In some cases, it could be more efficient to work with vendors and/or original equipment manufacturers (OEM) or others to obtain guidance and/or designs of certain components rather than always developing their own designs and models from scratch.
- The PI needs to be clearer about which DOE storage targets they are comparing to on any given slide. It would be best to always use the new DOE storage targets.
- Moving forward, it is unclear what the roles and responsibilities of ANL will be versus those of the new Engineering CoE (in terms of designing and evaluating on-board storage systems for various storage

technologies). The WTW analyses assume hydrogen is made from natural gas. This may not be the best choice as a baseline for production. It has relatively large GHG emissions, and it is intended as a means for hydrogen production only in a distributed manner at refueling stations and only during a transition period.
- The flow is appropriate and systematic including incorporation of alanes, metal organic frameworks (MOF), and ammonia borane (AB). The connection to science-based understanding is appropriate, but the options may be too broad or too comprehensive. Meaning, if budgets are being trimmed, are there options that are closer to reality for transfer to the Engineering CoE for execution?
- The project is well designed and addresses important technical barriers for different groups of materials with potential for meeting the DOE targets.
- The approach is thorough.
- It is suggested that the PI exert more effort to highlight important aspects of the analysis. It is easy for important data to be lost among other less relevant information.

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

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

- The project team has delivered on all the assignments.
- ANL has made a great deal of progress over the past year and has done some excellent storage system design and performance analysis. This includes alane slurry system performance and well-to-tank (WTT) efficiency, MOF system design and performance with liquid-N_2 cooling, WTT efficiency for amino-borane systems with two regeneration schemes, and WTT efficiency of lithium allanate with a new regeneration scheme.
- The value of the work being done by ANL and TIAX on storage systems analysis would be much clearer if the last two graphical slides in the ANL back-up slides were put into their presentation. Other summaries of WTW cost, energy efficiency, GHG emissions, and performance for various storage technologies that have been analyzed would be very beneficial to the stakeholders at the Annual Merit Review.
- Solid accomplishments were seen in each of the areas, but there is no clear resolution or indication as to which are the closest to practicality. For example, are MOFs truly viable (at this stage of development) or is an ammonia borane system safe enough for the general public?
- This year's presentation (focused on MOFs and ammonia borane) must be put into the larger context of previous conclusions and suggestions.
- What stands out for transfer to the Engineering CoE?
- It was noted that the PI was flexible enough to include and perform an analysis on a very recent material from University of New Brunswick/University of Hawaii (i.e. a method for regenerating $LiAlH_4$). This task has been focused upon in the past without finding a satisfying solution, but now there is more promise.
- The 5.9 wt% estimate for 350 bar is much higher than what is seen in any existing 350 bar tank.
- Important analyses of AB regeneration and cryogenic MOF tanks were provided.

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

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

- There is strong collaboration with TIAX, the Storage Systems Analysis Group, and the Storage CoEs. Together, these cover a large portion of expertise in storage technology and analysis.
- It is stated that ANL interacted with the FreedomCAR Technical Teams but there is nothing specific about this in the presentation. Much more industrial company interaction with the auto OEMs, energy companies, vendors, etc. would be very helpful.
- Some collaborations were mentioned but not fully fleshed out during the presentation. In some cases, roles could be implied, but for others (e.g., FreedomCAR) they were unclear; these roles needed to be explained.
- It is not clear if there are any interactions with the Hydrogen Sorption CoE. This project builds on communicating with materials researchers; thus being update on new findings is crucial. It is also important that the results from this project are promptly provided to the experimentalists. A good discussion forum is the materials CoEs and communications could be facilitated by attending meetings with them.

Question 5: Approach to and relevance of proposed future research

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

- The future plan is detailed, constructive, and will add additional important results. The choice of storage technologies to be analyzed is well thought out.
- It would be better to make it clear that the ANL work is part of the overall Storage Systems Analysis Group and that the net result of the total effort will include the all important WTW cost, energy efficiency, GHG emissions as well as performance characteristics of the storage technologies that will be analyzed.
- Not very clear or definitive.
- Materials from different groups are being pursued, however, within the Metal Hydride CoE, there is much research focusing on borohydrides and amides, besides alane and the alanates. Are there any plans on assessing these materials? This would be useful in helping guide the materials scientists on what materials to continue developing.
- Would like to see AB analysis updated based on the new hydrazine pathway.

Strengths and weaknesses

Strengths
- Strengths include consistency, experience, a strong technical approach, and careful analysis.
- On-board storage is one of the two or three most critical areas of R&D for hydrogen fuel cell vehicles to be successful. This project designs and analyses the performance of potential on-board storage technologies and compares the results to the DOE targets. It is also responsible for WTW energy efficiency and GHG emissions of on-board storage technologies. These analyses, along with WTW cost analyses, are essential for screening out storage technologies that cannot achieve the targets and highlighting the critical R&D areas for promising storage technologies.
- ANL has made a great deal of progress over the past year and has done some excellent storage system design and performance analysis.
- There is strong collaboration with TIAX, the Storage Systems Analysis Group, and the Storage CoEs, together these cover a large portion of expertise in storage technology and analysis.
- The future plan is detailed, constructive, and will add additional important results. The choice of storage technologies to be analyzed is well thought out.
- The project team has been strong in describing work on MOFs and ammonia borane.
- The strength of this project is the feedback provided from the system analysis of different materials to the experimentalists, which is important to better understanding the potential of the materials of interest as well as improvements necessary to meet the DOE targets.

Weaknesses
- Moving forward, it is unclear what the roles and responsibilities of ANL will be versus those of the new Engineering CoE (in terms of designing and evaluating on-board storage systems for various storage technologies).
- It is stated that TIAX interacted with the FreedomCAR Tech Teams, but there is nothing specific about this in the presentation. Much more industrial company interaction between the automobile OEMs, energy companies, vendors, etc. would be very helpful.
- It would be better if it was clear that the ANL work is part of the overall Storage Systems Analysis Group and that the net result of the total effort would include the all important WTW cost, energy efficiency, GHG emissions, as well as performance characteristics of the storage technologies that will be analyzed. ANL presentations should include summary slides of the total analysis of WTW cost, energy efficiency, GHG emissions as well as performance characteristics of the storage technologies that will be analyzed.
- One of the barriers (Barrier B: system cost) is not addressed in the presentation for any of the systems.
- Recent work is not cross-referenced well with earlier work and conclusions.

Specific recommendations and additions or deletions to the work scope

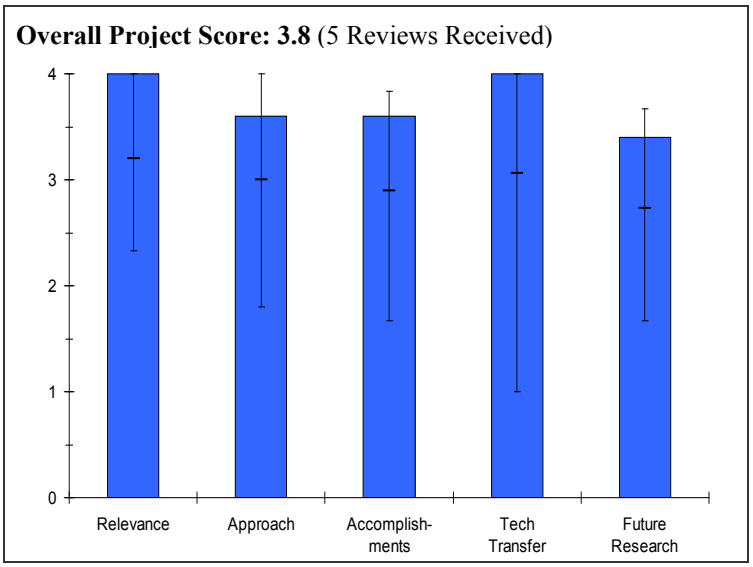
- This project has been a critical element of the storage research. In view of the new engineering center and the potential duplication of effort, it is highly recommended to keep this project and preserve the institutional memory and experience.
- The project team should find a way to better connect their work with past presentations and future work, and should strive to develop more definitive recommendations.
- The project team should consider including other groups of materials that are currently focused on within the community.

Project # ST-15: 2009 Overview - DOE Chemical Hydrogen Storage Center of Excellence
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.]

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 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 **4.0** for its approach to R&D and CoE management.

- The CoE has been one the most coordinated teams.
- The CoE directly attacks the primary barriers to success for this method of storage. Recycling is a key challenge and they have highest focus there. Design is a challenge, and they have resources there. The use of theory to guide experiments is essential in areas of focus where data does not exist. Also, the center is looking at business-related questions that should be answered up front, which is important. For example, is there enough boron in the world?
- Overall, the CoE is very well focused on achieving a material that will meet the DOE targets.
- The CoE strategy considers engineering aspects as well as material properties (e.g., emphasis on liquid systems and Rohm and Haas engineering and analyses).
- This CoE is obviously well managed, communicates well internally, and is unusually well focused on virtually all DOE targets and technical barriers.
- There is excellent support between modeling and experimental efforts.
- The center is very well managed.
- There is good communication and interaction between CoE participants.
- There is good coordination between PIs on specific topic areas.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated 3.6 on its accomplishments and progress.

- The overall productivity of this CoE is high.
- Progress has been excellent on all three fronts: ammonia borane (AB) decomposition kinetics and thermochemistry, new materials, and regeneration of AB-based materials.

- There are several meaningful progress items, plus help for Metal Hydride CoE. Kinetics is improved in high capacity material. While new processes are good and give the center a better chance to find a regeneration scheme, the raw number of things tried is not progress. However, the reduction in the number of steps reported by the center clearly is progress. Improved efficiency is good progress, too. Also, down-selecting effectively to focus on winning strategies, which is an administrative progress in my view, is still a good way to meet targets that have not yet been attained, but that may be met with continued funding.
- The down-selection process was logical with good quantitative and qualitative criteria.
- Metal aminoborides are offering interesting new potentials.
- Important progress was achieved on improvements in the regeneration process for AB.
- The engineering cost and energy efficiency analysis of AB processing is a significant achievement.
- The \$7-8/kg H_2 regeneration cost calculations are promising relative to DOE cost targets.
- The simplified AB regeneration approach is promising. The wider issue facing this process is the infrastructure and total cycle energy efficiency.
- In terms of on-board properties, AB is close to, or can meet, some of the DOE target values simultaneously: wt. density, vol. density, operating temperature, and kinetics.
- Compared to the other CoEs, this effort seems to be technically closest to achieving a practical on-board system, given that off-board regeneration is acceptable.
- The CoE continues to make significant progress on the development of a high capacity chemical hydrogen storage material.
- Improvement continued in the properties of various forms of AB.
- The team has continued to explore other materials as well.

Question 3: Proposed future research approach and relevance

This project was rated **3.6** based on future plans.

- Given the past results, the proposed future work is logical and reasonable.
- Proposed future work builds on achievements to date and shifts focus toward identifying properties and issues relevant to engineering issues.
- The CoE has good plan but it was presented more or less as, “We will figure out what is needed and do it.” The regeneration plan is right: there is a need to lower steps and global energy input to system. The center should work with ANL on what needs to be done on engineering support and address it. If history is a guide, good work will be done, but it could be better planned in this single area.
- All of this planned work cannot be completed by the March 2010 end of the CoE.

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

This project was rated **4.0** for collaboration and communication within the CoE.

- This CoE has always had close coordination internally, as well as externally.
- There is a clear mechanism for formal communication, but it is also clear that the partners talk "offline" a lot. Collaboration is frequent and effective. Virtually every program references a theory group project. Most of the engineering is attached to a material person or two to help inform and improve it. Personnel exchanges are key to accomplishing these goals.
- Organization and communications are models of what a CoE should be.
- Contributions to the new Engineering CoE will be very valuable.
- As mentioned earlier, there is excellent communication and coordination within the CoE, resulting in true synergism.
- The modeling support of experimental efforts is noteworthy.

Question 5: Collaborations/Technology Transfer Outside the CoE

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

- Collaboration is frequent and effective. Continue to help Metal Hydride CoE. Worked with New Energy and Industrial Technology Development Organization (NEDO) in workshop. Also, DOE partners (e.g., TIAX and ANL), are part of the International Partnership of the Hydrogen Economy exchanges and linked to the Engineering CoE as they are required to be.
- Outside collaborations are reasonably extensive and good.
- Collaborations with ANL, TIAX, and the Storage Systems Analysis Working Group (SSWAG) are especially useful.
- I would have liked to see some comments as to how useful, in fact, the international collaborations (e.g., LANL/AIST and IPHE) have been.
- Interactions with the other CoEs have not proved to be fruitful; however, this may not be due to the CoE's efforts, but rather related to differences in expertise, approach, or focus.

Strengths and weaknesses

Strengths
- There is outstanding team coordination and approach to the development of chemical hydrogen storage materials. The results from the CoE are outstanding as well.
- The CoE exhibits strong technical competency.
- There is an excellent spectrum of R&D relative to DOE needs and targets.
- The CoE effectively down-selected materials.
- The CoE is focusing on high capacity material.
- There is a good mix of theory and experimentation.
- Overall, the CoE is well managed.
- Coordination and communication are excellent.
- The CoE maintains close collaboration internally and externally.
- The people are great.
- Organization and communications are also top notch.

Weaknesses
- The chemical (off-board regeneration) hydrogen storage is arguably the largest departure from the existing transportation energy economic model. While this is not (and should not be) the focus of the CoE, it has to be addressed technically, if at all.
- There is a tough challenge to face regarding energy efficiency.
- There is uncertainty regarding the funding level or whether there will be funding at all.
- None.
- None.

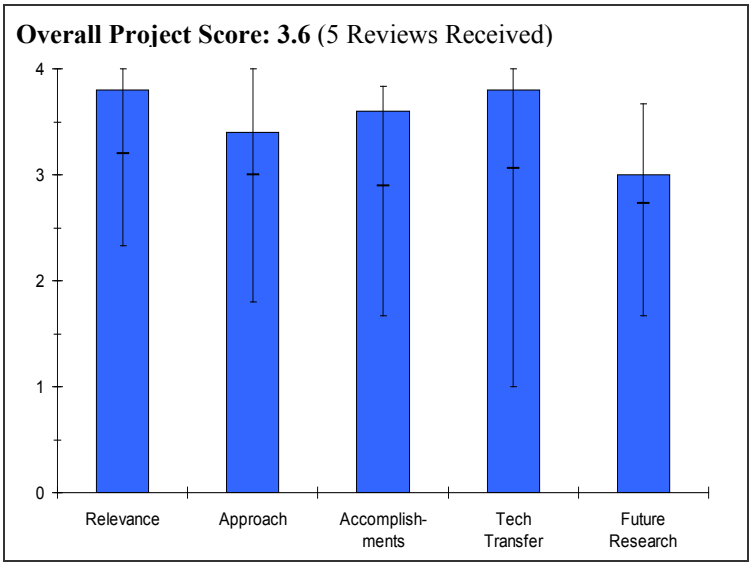
Specific recommendations and additions or deletions to the work scope

- It would be useful to consider forecourt models for the chemical hydrogen storage materials.
- Find budget to continue this work after the CoE charter is complete.
- Keep them aligned to old targets (as they intend), because they can do it. Allow them to maintain focus on regeneration.
- None.
- None in these closing days.
- Strongly consider renewal of CoE.

Project # ST-16: Amineborane-Based Chemical Hydrogen Storage
Larry Sneddon; University of Pennsylvania

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 DOE targets and 2) develop high conversion off-board methods for chemical hydride regeneration. In collaboration with CoE 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. The University of Pennsylvania 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 **3.8** for its relevance to DOE objectives.

- Work on high-capacity liquid systems that release H_2 below 100°C can significantly improve the ability to meet targets and commercial viability for the transportation sector.
- The project is aligned with Hydrogen Program objectives and addresses key issues for one of the more promising hydrogen storage options.
- This project is closely aligned with the DOE objectives stated in the multi-year RD&D plan. The ammonia borane (AB) system has considerable potential as a high-capacity hydrogen storage material. The strong emphasis of this project is on novel methods for enhancing hydrogen release and for improving the efficiency of spent fuel regeneration in support DOE objectives. Further, it complements related activities within the Hydrogen Sorption CoE.
- This project is highly relevant. It has the potential for the development of high hydrogen gravimetric and volumetric hydrogen storage capacities and rapid release rates.
- The project aspects are generally well aligned with DOE goals and objectives for vehicular storage systems. Weight, volume, release rates, and practical regeneration of storage material are nicely addressed.
- Cost is not significantly addressed. At this rather advanced stage of the project, not to mention the strong partnership with Rohm and Haas, it would seem that preliminary costs would begin to be addressed.
- Hydrogen purity targets are not adequately addressed – at least not in this presentation.

Question 2: Approach to performing the research and development

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

- A multi-faceted approach employing the use of ionic liquids, proton sponge additives, and metal catalysts is resulting in significant improvements in hydrogen release rates. Although the halide-based approach to regeneration is intriguing and appears to relatively straightforward and scalable, the efficiency of the spent fuel digestion step remains a serious challenge.
- The ionic liquid approach is excellent because liquids rather than solids are preferred for vehicular applications. Because of the high capacity of ammonia borane, the weight penalty associated with the ionic liquid still leads to materials with high capacities.

- The project team is thoroughly and effectively looking at three approaches for fast release of H_2 from AB: ionic liquids, chemical promotion and metal catalysts.
- Practical off-board regeneration of AB is effectively studied from both theoretical and confirming experimental chemical perspectives.
- Considering the project is in its final stages, the PI should consider making down-selects from the three approaches to concentrate on one. If no down-select is possible at this time, the PI should establish down-select criteria to help direct the work and avoid diluting his efforts.
- Work is focused on addressing key issues for the AB systems including optimizing capacity, hydrogen release kinetics, and regeneration of AB.
- The use of ionic liquids and catalysts to increase H_2 release rates is promising.
- The project team has looked at dehydrogenated AB product without IL or catalyst present. It was unclear whether this was material dehydrogenated from AB/IL or without IL. It has been suggested that the products are different. Dehydrogenated product with IL and/or catalyst present should be investigated because regeneration chemistry may be affected (positively or negatively) since they are believed to affect degree of cyclization and dehydrogenation mechanism. Initial cost studies of the regeneration scheme have identified separations as a major cost factor. It is not clear if catalysts and ionic liquids need to be separated from dehydrogenated AB for regeneration. If they do, what is separation technique, and how is it expected to affect cost of regeneration? Rhodium and ruthenium catalysts would likely need to be reclaimed during regeneration cycle also.

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

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

- Progress toward the goals has been very good on all three fronts. Much new and good data has been generated during the last year.
- Impressive increases in H_2 release rate have been accomplished using ionic liquids and catalysts. A system which releases 2 equivalents of H_2 in 9 min at 110°C has been demonstrated. A system has been demonstrated with >11 wt% H_2, 0.089 kg·H_2/L (material); this exceeds DOE system targets significantly, suggesting system targets may be reached.
- Good progress is being made on parametric studies designed to improve release rates using different combinations and amounts of ionic liquid additives, proton sponge compounds, and metal catalysts at different temperatures. Although some questions about the temperature-additive-concentration behavior remain unanswered, an improved overall understanding of the factors that control hydrogen release from AB is emerging from this work.
- It was mentioned that AB-20% ionic liquid system is a solid, whereas the AB-50% ionic liquid system is a liquid. The overall characteristics of the hydrogen release kinetics would be expected to be significantly different for those two cases. It is unclear why dramatically different trends in the H_2 release characteristics are not observed experimentally.
- Significant progress has been made in reducing the amount of ionic liquid required for good hydrogen capacities and reasonable release rates.
- It seems that the recent material weight, volume, and discharge rates are close to being successfully extrapolated to DOE system targets. It would have been nice to see a little of that in the presentation.
- There are many seemingly promising AB decomposition approaches demonstrated. Which will be the most promising from a cost point of view?
- Less promising results are apparent in the area of spent fuel conversion. It is not apparent what aspects of the regeneration mechanism are limiting the efficiency of spent fuel digestion in the halide-based regeneration process.
- The super-acid regeneration approach appears to have run into a significant problem with the low yield of BX_3.
- Regeneration of AB work demonstrated BX_3 reduction. Digestion work less successful.
- Great progress on rate and equivalence continues. At this time, the PI should consider performing a rate vs. capacity comparison to determine the optimum level. Perhaps this work could be coordinated with the Engineering CoE on a system-level analysis.

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

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

- Collaboration with other CoE members is apparent.
- Extensive interactions and collaborations with other participants in the Chemical Hydride CoE (especially with PNNL and Rohm and Haas) are evident. This contributes greatly to the overall success of project and the CoE in general.
- There are very strong collaborations between the University of Pennsylvania, PNNL, and Rohm and Haas.
- Collaborations are excellent.

Question 5: Approach to and relevance of proposed future research

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

- The project is nearing completion; it is highly recommended that the PI establish some down-select criteria.
- The focus for future work on this particular project appears to be mostly on optimizing H_2 release. Need to make sure that those working on regeneration schemes include the effects of catalysts, IL, and other additions to the system in their regeneration work.
- Speaker mentioned the need to do work to try to maintain dehydrogenated AB product in the liquid phase. That work would be very beneficial. For this project, focus can be on optimizing H_2 release if the CoE as a whole is more focused on regeneration, which is still the major hurdle for these systems.
- The approach(es) for achieving efficient hydrogen release at acceptable temperatures have been largely validated in the last two years. A solid plan is in place to develop a comprehensive understanding of the dependence of hydrogen release rate on additive type, concentration, and sorption temperature. A critical remaining hurdle to the overall success of this project is improvement in the efficiency of the spent fuel digestion to BX_3. Based upon the information provided in the presentation, the cause of the low efficiency remains an outstanding question. A sharply focused effort on understanding the rate-limiting steps should be major part of the future plan in order to develop a coherent experimental for improving the efficiency.
- The future work is directed at all of the key remaining issues.
- Plans generally aim at continued work on all the decomposition approaches. Is it time to down-select the least promising one or two approaches?
- Down-selection will require some cost and engineering considerations of the competing processes, especially decomposition.

Strengths and weaknesses

Strengths

- The PI and his colleagues constitute a very strong research team, and they are addressing the challenging issues that underlie the development of ammonia borane using novel and scalable approaches. Use of ionic liquid additives and proton sponge materials for enhancing release rates and reducing foaming are especially interesting and important.
- Use of the AB liquid phase system is highly desirable. In addition to obvious practical benefits of on-board vehicle application, it allows combinations and concentrations of reactants and additives to be readily evaluated at different temperatures.
- Use of ionic liquids should help reduce volatility of undesirable compounds and could lead to a scalable process.
- Materials being investigated have high H_2 storage capacities and good release rates at appropriate temperatures.
- Good collaboration with other CoE members.
- An understanding of the reaction chemistry is being developed.
- The PI and project approach are excellent. The PI's record of achieving significant results is also excellent.
- Excellent, innovative chemistry.

Weaknesses

- The PI should make every effort to keep desorption temperatures under 100°C. Continuous 120°C operation is unlikely in the near- to mid-term for fuel cell systems.

- Over the last two years, a clear pathway to improving the efficiency of spent fuel digestion and conversion to BX_3 has not emerged. Future plans for dealing with this critical issue are not developed particularly well.
- The regeneration approach appears to have run into a roadblock.
- At this stage, the project is a bit far from cost and practical engineering considerations. Other than the positive system implications of weight, volume and kinetics, how close are these materials to other system targets regarding cost, H_2 purity, transfer of spent product/regeneration/refilling scenarios, control considerations, etc.?
- There is potential weakness due to the complexity of the reactor system that will be required to control the reaction.

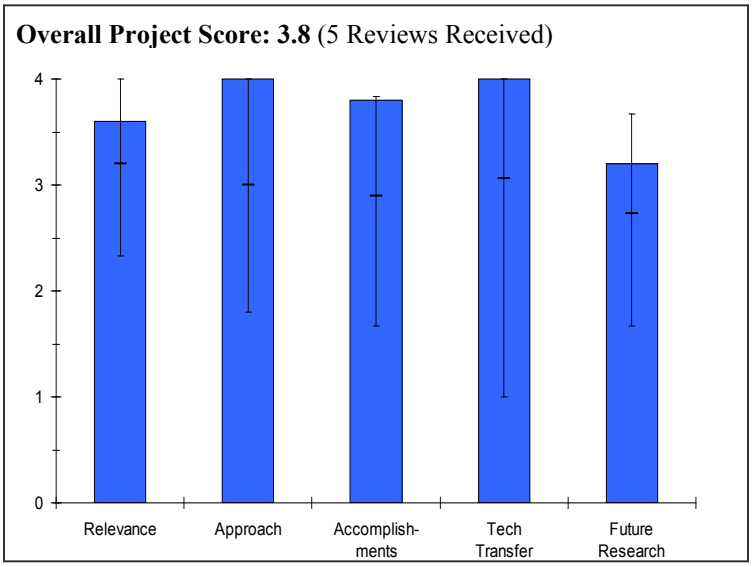
Specific recommendations and additions or deletions to the work scope

- Future work should look a little more at composition of the gas phase during H_2 release experiments in order to determine what routes avoid or minimize potentially problematic species like ammonia and borazine. Work to retain products in liquid phase for removal would be very valuable.
- Given the fact that the project is nearly complete (<20% funding remains), it is highly unlikely that all of the proposed future work on hydrogen release and spent fuel regeneration can be completed. A focused effort on the most critical issues is needed so that sufficient information is available to support a meaningful down-select of the processes and materials being investigated here.
- Since this project is 80% complete, perhaps it should focus its remaining efforts of non-precious metal catalysis for improving hydrogen generation and on alternative methods of producing BX_3.
- Given the impending time limit, the PI should focus on the best one or two decomposition approaches.
- The PI should continue to look at digestion schemes that avoid formation of B-O bonds.
- Use preliminary cost and impurity studies to aid the down-selection process.
- Begin the rough, conceptual chemical engineering design of an on-board system in relation to the required regeneration processes.
- The PI should work with the Engineering CoE to establish a rate vs. capacity comparison. As the rate of the reaction increases, the potential complexity and mass/volume of the "balance of plant" could decrease, thus saving weight (i.e., less buffer tanks, reactor volume, etc.) However, if the rate increase comes at the cost of a material weight decrease, a tipping point may occur where a further increase in rate may lead to a heavier overall system.

Project # ST-17: Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

Roshan Shrestha, Ben Davis, Himashinie Diyabalanage, Anthony Burrell, Neil Henson, Michael Inbody, Kevin John, Troy Semelsberger, Frances Stephens, John Gordon, Kevin Ott, Andy Sutton, and Koyel Bhattacharyya; Los Alamos National Laboratory

Brief Summary of Project



The objectives for this project are to 1) develop and demonstrate heterogeneous catalysts and continuous flow reactor operation for hydrogen release, 2) develop liquid ammonia borane (AB) fuels and increase rate and extent of hydrogen release, 3) identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release, 4) demonstrate all chemical steps and conduct engineering assessment for energy efficient AB regeneration process (high yields, rates and energy efficiency, integrate steps when possible), 5) develop materials and processes to minimize gas phase impurities and demonstrate adequate purity of hydrogen stream, and 6) provide materials chemistry support for the Pennsylvania State University work on electrochemical conversion of B-O to B-H.

Question 1: Relevance to overall DOE objectives

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

- Aminoborane materials are potentially very important towards achieving the DOE objectives.
- The project is well aligned with key problems of AB regeneration, hydrogen gas impurities, low system penalty in use, and the need for better materials. Also, the overall goal of chemical hydrogen storage is aligned with meeting the needs of the vehicle H_2 system.
- Chemical hydrogen storage approaches have the potential to achieve high hydrogen storage gravimetric and volumetric capacities with rapid hydrogen release rates, in a liquid form that is amenable for vehicular applications.
- This project is unusually relevant to almost all of the DOE on-board targets and perceived barriers.
- The work covers multiple aspects, relating to both engineering and materials, of the use of AB as a hydrogen storage material.

Question 2: Approach to performing the research and development

This project was rated **4.0** on its approach.

- LANL, as the CoE lead for chemical hydrogen storage materials, is working on all necessary fronts to make AB materials achieve targets (e.g., catalysis, hydrogen gas impurity reduction, AB regeneration). They are coordinating heavily with all the necessary partners and experts.
- The effort is rather highly funded, but correspondingly covers many useful technical areas. Looking at M-substituted AB, liquid AB forms, heterogeneous catalysis, and thermodynamic control are all well-placed directions.
- A simplified "single pot" AB regeneration process is the ultimate goal for realizing commercial AB use.
- The materials examined are appropriate; the work to reduce energy intensity and number of steps is spot on; and the catalyst work is also aimed squarely at kinetic and H_2 purity challenges. Science guided by a combination of theory and engineering is the appropriate approach.

- Science guided by theory and engineering is the best approach for the DOE portfolio.
- The approach is targeted at all the key issues.
- The approach covers both on-board H_2 release and AB regeneration, both very important.
- The effort is unusually well focused at the ultimate application (e.g., engineering, cost, impurity) factors.
- The effort on regeneration is very logical and thorough.
- This is a good approach covering new materials exploration and development, as well as specific aspects of AB.
- The focus on targets is maintained when exploring new materials and their properties.

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

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

- The project team has made many significant accomplishments.
- The project was well presented, and it is obvious that much excellent progress has been made on many fronts.
- The catalysts shown reduce impurity production and raise rate.
- Important contributions were made toward individual process steps in AB regeneration.
- Development of a 1- or 2-step regeneration process for AB is an important development.
- The project team had the guts to scrap a working regeneration system and come up with one that avoided high-energy mass movement and reduced total steps to gain efficiency.
- The project team managed to find a simpler and more efficient regeneration method even when it had a process that worked before.
- Important contributions were made toward cost analysis of AB regeneration.
- There are interesting differences in kinetics and thermodynamics as a function of metal substitution.
- The project team managed to reduce the exothermic nature of the reaction (a necessary step towards simplified systems). The results varied significantly, and the PI needs to continue efforts to understand why. The PI should be coordinating with the Engineering CoE to determine the optimal exothermicity of the system.
- What effect on material density is incurred by the addition of salts to the AB in order to reduce the thermodynamics?
- KAB material gives sub-100°C one-step release, which is very nice. It would be better if a similar, lighter material could be crafted based on what was learned here.
- The project team has made significant progress toward characterizing and understanding impurity release from AB.
- Catalysts seem to be a key variable in reducing impurity emissions from decomposing AB; however, can the impurity levels ever be reduced to the levels required for fuel cells or will an on-board purifier always be required?
- There are so many promising results that down-selection of the best possibilities will be difficult.
- The project team found promising alternatives to Pt for heterogeneous catalysts.
- The project team examined a number of AB liquid alternatives in terms of impurity release.

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

This project was rated **4.0** for technology transfer and collaboration.

- The collaborations with Rohm and Haas, ANL, TIAX, etc., are nicely getting to the bottom of cost, practical reactor designs, and practical regeneration processes. These are impressive group efforts.
- Outstanding − the project team works with everyone in the CoE and many outside too. The team got significant value from ANL collaboration. The IPHE partnership may answer some key questions, and it is nice to see that initially politically driven activity bear technical fruit.
- Collaborations are excellent and are targeted at key issues.
- There are many excellent collaborations within the Chemical Hydrogen Storage CoE and outside.
- The project team is working with all the relevant material partners. The team should now coordinate with the Engineering CoE to understand the system.
- The planned connection to the new Engineering CoE will be very valuable.
- Work includes effective collaborations and interactions with others inside and also outside of the CoE.

Question 5: Approach to and relevance of proposed future research

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

- The project is near completion.
- This project should work with Engineering CoE to both address system-related requirements of materials and begin transferring knowledge to the Engineering CoE.
- Future plans are in right areas (i.e., AB regeneration, enough engineering to guide mechanism selection, and storage stability). Future plans seem well conceived, though details are scant.
- The future work is comprehensive and targeted at the key issues.
- In general, the plans listed are logical and needed.
- Given only 20% remaining in the project duration and funding, it is hard to see that so much can be done.
- Some near-term down-selection is needed.
- Proposed focus on the new AB regeneration process should be an important contribution to the development of an effective storage material.

Strengths and weaknesses

Strengths
- This is a very well-coordinated effort aimed at almost all the DOE targets and barriers.
- This is a strong team.
- The project team has good approaches.
- Connections have helped the team make progress.
- High capacity material to develop.
- The project team is organized.
- The project team has made the hard choices.
- There is a potential for high hydrogen gravimetric/volumetric capacities and rapid hydrogen release rates.
- Aminoborane-based materials are targeted for a liquid form, which is more amenable for vehicular applications.
- Ultimate thinking is practical and realistic.

Weaknesses
- The barrier to meet on AB regeneration efficiency and yield at the same time is high.
- The funding is uncertain.
- The cost of regeneration is the key issue going forward.
- None.

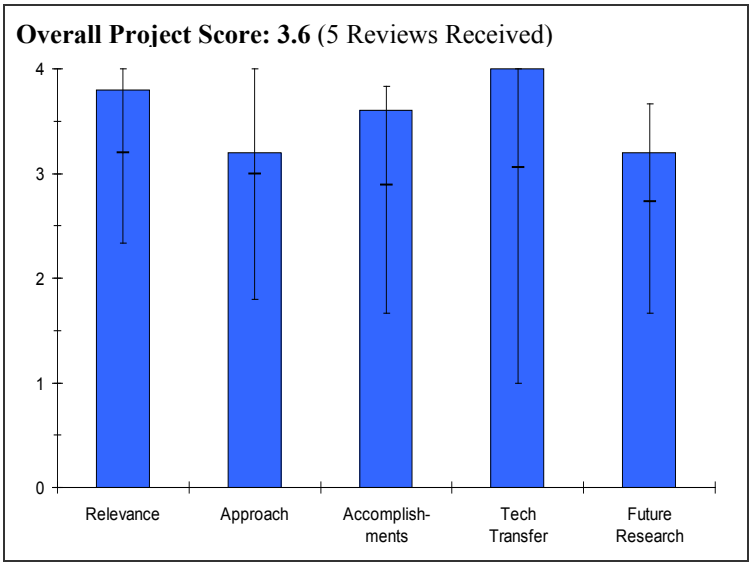
Specific recommendations and additions or deletions to the work scope

- Keep these guys working in 2010, and try to fund them afterwards.
- None.
- Other than careful down-selections and focus for the project duration, no real changes are recommended.

Project # ST-18: PNNL Progress as Part of the Chemical Hydrogen Storage Center of Excellence
Tom Autrey; Pacific Northwest National Laboratory

Brief Summary of Project

The 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 DOE targets and 2) develop high efficiency off-board methods for chemical hydride regeneration. PNNL'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 **3.8** for its relevance to DOE objectives.

- The project addresses the DOE objectives, targets, and barriers very well.
- This work is highly relevant to the development of high capacity hydrogen storage materials.
- Regeneration of, and low temperature and high purity hydrogen carriers are good foci. These materials are likely to bear fruit, and are thus good choices.
- Ammonia Borane (AB)-based materials have the best combination of hydrogen gravimetric/volumetric capacities and rapid hydrogen release rates.

Question 2: Approach to performing the research and development

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

- The approach is very well balanced to include experimental work, theoretical modeling to support the experimental work, and engineering activities.
- The project is very well focused on developing high capacity materials for hydrogen storage.
- The project team is using the right tools and studying suitable hydrogen storage materials (AB variants), guided by internal and external theory.
- The approach is heavier on experimental than theoretical. This is appropriate given the complexity of the chemical systems.
  This is a relatively large effort, by DOE standards, and generally addresses many important subjects both in the H_2 generation and storage material regeneration directions.
- The project focuses somewhat more on fundamental mechanisms and reaction pathways than the LANL effort. Also, the AB regeneration approach is apparently somewhat different from that of LANL's and UPenn's. As such, the PNNL work seems to be generally complimentary to that of the other CoE partners.
- It is not completely clear how the metal amino borane (e.g., $LiNH_2BH_3$) differs from the large effort in this by LANL. Is there some duplication?

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

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

- A wealth of new and positive data has been generated in the last year.
- Stabilizing AHBH in solution is important step.
- An approach was developed to mitigate foaming during pure AB hydrogen release.

- Antifoaming agents are a big step, though much of it previously reported.
- Clever process to activate the hydrogen so it will react more easily with spent fuel.
- Tuning the BOX species being regenerated is important, and the further tuning most likely lowers energy requirements.
- The PNNL regeneration approach seems to be approaching a final state (i.e., beginning cost and engineering modeling [with ANL, Rohm and Haas, etc.]). It will be interesting to soon make the final comparison with the somewhat different LANL (Pennsylvania) regeneration approach.
- Many significant accomplishments have been made. The room-temperature-stable ammonium borohydride is very interesting.
- Progress has been made in morphology control (antifoaming), thermodynamic manipulation, decomposition kinetics quantification, and impurity control.
- The relatively new work on NH_4BH_4 (ABH_2) is to be highly praised. It will be difficult to safely apply, but offers some fantastic vehicular possibilities in terms of weight and volume.
- The project team made important contributions to understanding impurity release from AB variations.
- The work has expanded to investigate M-NH_2-BH_3 materials.
- The project team developed capability to make lab-scale amounts of AB for use in its experimental studies.
- The project team completed a number of kinetic studies on materials and improved release properties in some cases.
- The project team developed a way to improve stability of NH_4BH_4 at room temperature.
- Work to determine hydride transfer reactions for various metal hydrides was continued.

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

This project was rated **4.0** for technology transfer and collaboration.

- Good communication and collaboration inside and out of the CoE to achieve value in the work. Examples include University of Alabama, etc. collaboration on theory for cost and efficiency and work with the International Partnership for the Hydrogen Economy (IPHE) and others.
- PNNL is covering solid aminoborane, while LANL is covering aminoborane in liquid form.
- There are many good collaborations, which are generally well explained.
- Other than mentioning the area of M-substituted AB, the exact nature of the IPHE collaboration is not well documented. At this stage, what can be said about the synergism of the IPHE effort and its likely benefit to the United States and DOE? Is there potentially more benefit coming out of the International Energy Agency collaborations?
- There have been effective collaborations with CoE participants and with other researchers.
- There have been a broad number of partnerships.

Question 5: Approach to and relevance of proposed future research

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

- Future work covers all of the key areas.
- The proposed future work seems like a logical and reasonable extension of the past work and results. Batch reactor work is appropriate as is cost analysis.
- Impurity reduction is appropriate.
- AB Regeneration plan is appropriate.
- It seems very unlikely all this work can be reasonably completed by March 2010 – the project's end.

Strengths and weaknesses

Strengths

- Strengths of this project include:
  - A strong team.
  - The right material.

- Strong method.
- Excellent benefit from collaboration.
- High hydrogen gravimetric and volumetric capacities.
- Rapid hydrogen release rates.
- Excellent understanding of what is needed for the chemistry of AB decomposition and regeneration.

Weaknesses

- Weaknesses of this project include:
  - Funding at risk.
  - Solids handling for vehicular applications.
  - Efficiency and cost of AB regeneration.
  - None.

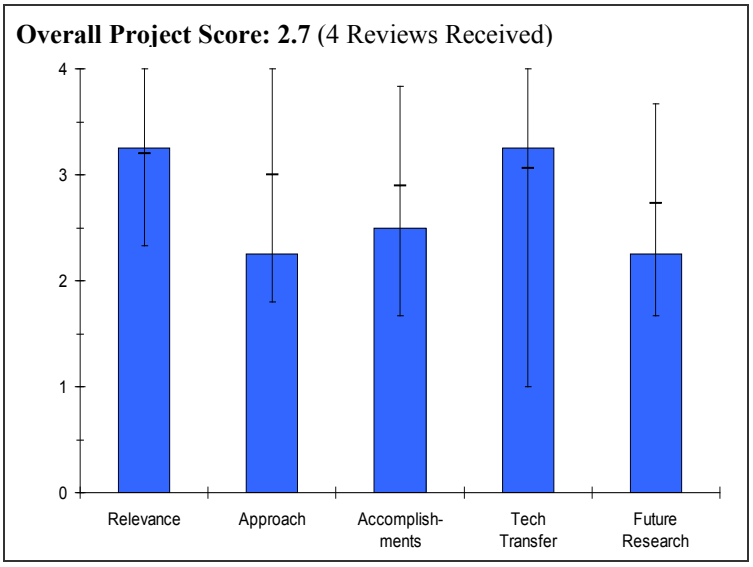
Specific recommendations and additions or deletions to the work scope

- The project team would benefit from the same engineering guidance LANL uses at this point. The team may be planning to do that sort of review, but this was not clear.
- The project team should follow up on NH_4BH_4 stability work because of the high capacity, but should eliminate the use of the NH_3 stabilizer as they see fit.
- Phase 2 (if it is justified and funded) should be completely consolidated with LANL. Two parallel efforts cannot be afforded. Down-selections will have to be applied.

Project # ST-19: Main Group Element and Organic Chemistry for Hydrogen Storage and Activation
Anthony J. Arduengo and David A. Dixon; University of Alabama

Brief Summary of Project

The objectives of this project are to 1) develop promising approaches to chemical hydrogen storage for current and future DOE targets using computational chemistry and synthetic organic/inorganic chemistry and 2) provide computational chemistry support (i.e., thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE CoE 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 **3.3** for its relevance to DOE objectives.

- This project fully supports DOE program objectives. The computational approaches are yielding results on thermodynamic properties, hydrogen release, spent fuel regeneration pathways, and discovery of new compounds with improved sorption characteristics. Those results are vital to the overall success of the Chemical Hydride CoE, and the work is directly relevant to DOE RD&D objectives for hydrogen storage.
- The project aims to develop new approaches for meeting DOE targets for H_2 storage using computational chemistry; it is well aligned with the DOE objectives.
- The PI's efforts seem to be valued by the experimental members of the CoE.
- This project couples strongly with many activities in the Chemical Hydrogen Storage CoE, and is helpful in understanding experimental results. However, the overarching goals of this effort are not entirely clear. What exactly are they looking for? The results seem somewhat scattered and not focused on a specific goal.

Question 2: Approach to performing the research and development

This project was rated **2.3** on its approach.

- A comprehensive computational effort comprising multiple approaches is being used to predict thermodynamic properties and reaction pathways for candidate chemical hydrogen storage systems. Experimental validation of these predictions is made both within the project and through extensive collaborations with CoE partners. The molecular orbital and density functional theory approaches are powerful adjuncts to the experimental efforts in the CoE, and they are being used to determine thermodynamic properties and to identify new compounds with improved sorption properties.
- Kinetics issues have received less attention in the project. Accurate predictions of reaction rates, identification of transition states, and elucidation of elementary steps in reaction mechanisms remain important challenges.
- The PI has expertise in quantum chemistry calculations, and it shows in the choice of problems that are included in the project. The calculations are restricted to liquids and gas phase molecules, but there is no work on solids; this is an obvious shortcoming of the approach and scope of research.

- The project uses an "enumerative" approach to calculating thermodynamics of all imaginable reactions (>500); a more systematic approach to identifying desired reactions with targeted thermodynamics would be preferable to what is currently a computational "trial-and-error" technique.
- Overall, a large number of molecules are being considered, and the project seems a bit unfocused.
- Relevance of gas phase calculations to real solid-state materials has not been established. This comment was made previous Reviews but has not yet been addressed.
- For the amidoborane work, the PI is starting with the molecular state, and says that this will help them when they move to the solid state. However, for several years, this PI has been saying that they will move to solid-state calculations, but it never seems to happen. In this case, how will they obtain the crystal structures for the metal amidoboranes? When they have them, how will they do the quantum chemistry calculations? (The methods used by this PI are only applicable to molecules and clusters, but not solids.) There are a lot of literature of solid-state calculations in these and related (e.g., complex hydride) systems for consideration.

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

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

- A significant database on the thermodynamics of hydrogen release and regeneration from candidate compounds has been generated. This is very useful for guiding experimental work both within this project and by CoE partners. A large number of potentially useful systems are being explored in this project. This is a useful and important complement to the sharply focused efforts on ammonia borane (AB) being conducted elsewhere within the CoE.
- Although new systems are being investigated, there are several important outstanding issues concerning the efficient regeneration of ammonia borane that are also being addressed. The work on this project is providing information that will undoubtedly be important overcoming existing obstacles to efficient conversion of spent reactants.
- It would be helpful if more information could be provided concerning the predictive accuracy and reliability of the kinetics calculations. The project has amassed a large amount of data on reaction kinetics and thermodynamics. However, there does not seem to be many breakthroughs in materials, regeneration reactions or theoretical methods that show promise for making significant progress towards meeting the DOE goals.
- Not clear that the experimental portion of this project is really producing useful results. They had a no-go on the main experimental chemistry they were pursuing, but it's not clear what they are doing now or whether they are making progress. For a program in its fourth year, this is quite disappointing. The budget is just far too large to justify the results obtained.

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

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

- The collaborations have been extensive, especially with experimentalists within the Chemical Hydrogen Storage CoE are evident.
- The computational effort in this project is fully integrated with other projects in the CoE, and the collaborations are yielding positive results.
- The project has a very well-developed collaborative network. This is an area of strength.
- Collaboration seems to be a strong suit of this project.
- There is a good connection between the computational effort and the CoE and other partners. The connections between the experimental efforts and other collaborators are less clear.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- Reliable thermodynamics predictions for "thousands of compounds" have been made in this project.
- Given the existence of that vast database, it is not entirely clear why additional predictions are needed. On the other hand, if new work is warranted, it would be helpful to understand what rationale is being employed to identify and explore other systems.
- What approaches will be used to predict kinetics of the key steps in the regeneration process? How is the reliability of model predictions for hydrogen release kinetics and rates of selected steps in the regeneration process being established?
- The very broad scope of the proposed future work is inconsistent with the time and funding available for the project. A thoughtful examination of the most critical remaining issues is needed, and the future work should be prioritized to reflect those considerations.
- The project will continue using the same methods as previously; there does not seem to be a clear path to success that could improve future accomplishments.
- Many (eight) routes listed in future work slide, with limited remaining time in the CoE, suggest focusing efforts on a smaller number of avenues for study.
- Far too much future work is proposed given that only one year of funding remains. The work needs to be prioritized, and it is unclear which work is the most important and which work will not be completed.

Strengths and weaknesses

Strengths
- The computational work on this project is a critical element of the overall technical effort within the Chemical Hydrogen Storage CoE. Valuable information concerning reaction thermodynamics and the identification of improved storage compounds has been generated in the project.
- The PI and his colleagues are highly qualified to conduct this project. The computational approaches they have employed and the results that have been obtained thus far have greatly aided the search for improved candidate storage systems.
- The project team has shown expert use of computational chemistry tools to study gas phase molecules and liquids. The collaborative network has been well developed. The project team has accumulated a large amount of computational chemistry results for molecular reactions.

Weaknesses
- There are many directions being pursued in this project. It is not clear which barrier or problem is considered to be the most challenging and should therefore receive the most attention. At this point in the overall technical effort, it would seem that a more focused effort on only a few critical issues is needed.
- This project needs a stronger focus. It would benefit from developing systematic computational framework for finding new, attractive reactions. There are no realistic plans to extend calculations to solid phases.

Specific recommendations and additions or deletions to the work scope

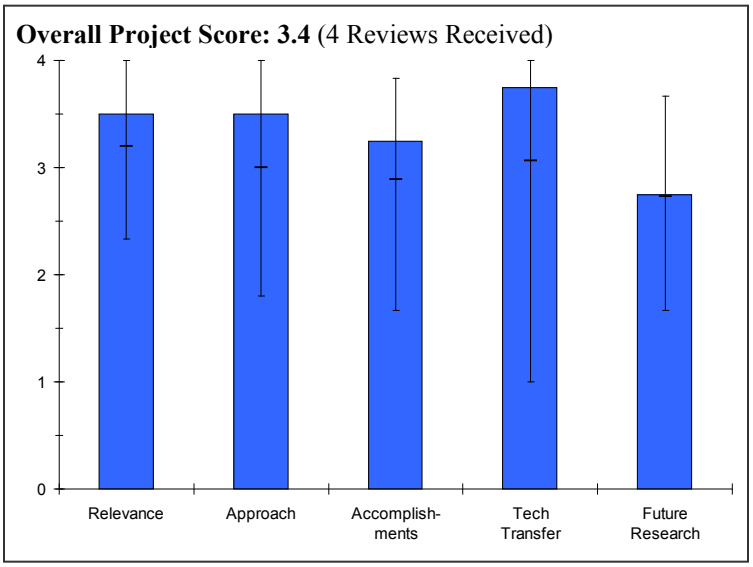
- Improving the efficiency of spent fuel conversion is the most critical remaining issue facing the Chemical Hydrogen Storage CoE. Recommend a sharply focused computational effort in close collaboration with experimentalists to address the regeneration issue.
- The experimental effort of this project does not seem to be producing useful results. It appears as though it could be deleted from the project scope without significantly affecting the overall project goals.

Project # ST-20: Low-Cost Precursors to Novel Hydrogen Storage Materials

S. Linehan, N. Allen, R. Butterick, A. Chin, L. Klawiter, F. Lipiecki, S. Nadeau, and S. November; Rohm and Haas Company

Brief Summary of Project

The overall objectives for this project are to 1) develop and advance novel hydrogen storage materials that meet the DOE 2010 targets and with the potential to meet 2015 targets, 2) leverage expertise and experience across the CoE, and 3) support the DOE Chemical H_2 Storage Systems Analysis Sub-Group. The Phase 2 goal is to identify cost- and energy-efficient pathways to "first fill" and regeneration for ammonia borane (AB) and other borane materials, define and evaluate novel chemistries, and process for producing chemical hydrides.



Question 1: Relevance to overall DOE objectives

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

- The project is quite relevant to the DOE storage mission. Low-cost precursors to $NaBH_4$ are necessary not only for the chemical center but can also have application for the metal hydride center.
- The work has high relevancy and is consistent with the overall CoE direction.
- The project addresses the critical issue of cost for first fill and cost for AB regeneration of one of the most promising hydrogen storage options.
- Reducing the cost of $NaBH_4$ is crucial to reducing the cost of ammonia borane for chemical hydrogen storage.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- The project team is very well focused on the key issues in its approach.
- The approach is working along three paths: 1) cost analysis for regeneration of AB, 2) a first fill AB process analysis, and 3) low-cost $NaBH_4$ for the first fill. The approach is good in that several different strategies are being investigated. The low-cost $NaBH_4$ process work is looking at different routes for converting B-O bonds to BH bonds.
- Considerable expertise and knowledge in the area including commercial application and scale.
- The project is focused on costs of producing $NaBH_4$ cheaply for first fill and AB regeneration. A company with extensive experience in chemicals market should provide a reliable cost estimate with good credibility.

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

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

- Reactive milling and solution-based systems for reduction are progressing well. Estimates of more than an order of magnitude reduction in $NaBH_4$ cost leads to substantial savings in first-fill cost.
- Separations have been identified as being responsible for a huge portion of costs for regeneration. In the LANL AB regeneration route, areas for significant cost savings have been identified.
- First fill and regeneration costs of amido borane have been estimated with a high degree of confidence.

- The project is 80% complete and a decision between borohydride production via a chemical route versus a carbothermal route has not been made. Similarly, a replacement for tin in the chemical route has not been found. Remaining effort should be directed toward one route so that there are time and resources left for a meaningful contribution from this project. The time remaining on this project is relatively short; it is difficult to see that all the process development work will be far enough along to provide a comfort level that the process(s) is feasible.

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

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

- As part of the overall structure of the CoE, this work is well integrated with the rest of the program. Understanding that the scopes may change quickly, it would have been useful to look at the two-step regeneration process.
- Collaboration within the CoE appears to be working well. There is collaboration with TIAX on cost analysis; TIAX well established in the Hydrogen Program for cost estimates.
- Excellent collaborations are taking place.
- There has been excellent collaboration within the Chemical Hydrogen Storage CoE. The Rohm and Haas work is well integrated within the center.

Question 5: Approach to and relevance of proposed future research

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

- Proposed down-selection between carbothermal and metal reduction is appropriate. Plans to investigate cost of AB first fill using alternative routes (PNNL and Shore schemes) are appropriate.
- Future work is directed at the key issues.
- Is the plan to repeat the same process for the two-step AB process?
- The project is scheduled to end in March 2010 and may end prematurely depending on available funding. The future work plan should include some down-selection points.

Strengths and weaknesses

Strengths
- Dow Chemical's experience is a strength.
- The project team has an excellent strategy and approach for manufacturing cost estimates.
- It is good to investigate multiple routes to lower-cost precursors. Analysis tools appear to be effective in guiding the work. Rohm and Haas brings industrial process development expertise to the team.

Weaknesses
- None.
- Little data has been shown on the carbothermal route. In fact, earlier work at INL cannot be reproduced. It is not clear how much longer this path should be continued if the results are poor. Suggest that this path have a near-term go/no-go decision point.
- Process efficiency for either route is low. Projections appear to point to routes with higher efficiency, but this has not been demonstrated.

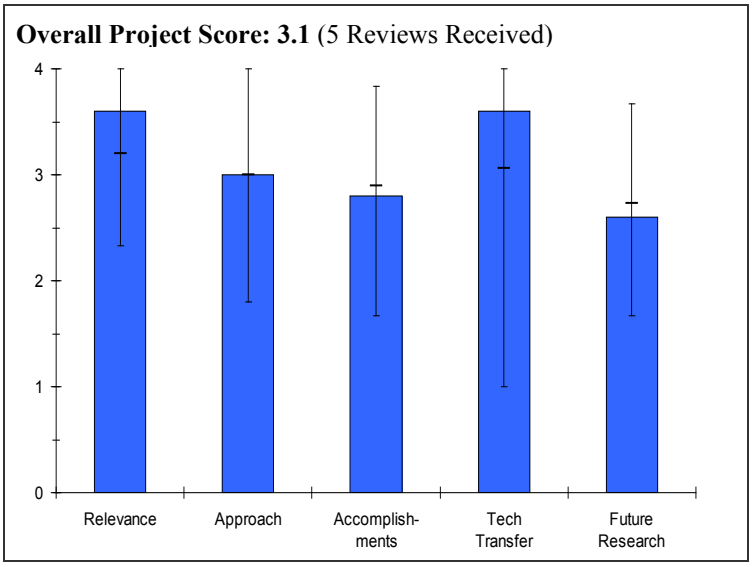
Specific recommendations and additions or deletions to the work scope

- It would be useful to also consider the business model implication for this technology. The PIs have considerable knowledge in the commercialization. One of the weaknesses of this route is the question of competitive distinctions among the manufacturers if there are to be multiple providers of AB. It is not clear how this market functions aside from being a monopoly. If so, is this a feasible approach? Why should there be additional effort or resources devoted to this route? (Granted the proposed technology has many more immediate challenges.)
- Perhaps the carbothermal approach for $NaBH_4$ production should be discontinued, since the initial results have not been promising.

Project # ST-21: Ammonia Borane Regeneration and Market Analysis of Hydrogen Storage Materials
David Schubert, Jonathan Owen, Duane Wilson, and Larry Harrower; U.S. Borax

Brief Summary of Project

The objectives of this project are to 1) meet the need to maximize efficiency of off-board regeneration of ammonia borane (AB) fuel and 2) provide an understanding of global supplies of boron ore resources required for hydrogen storage. This project will 1) find recyclable thermodynamically favorable intermediates, 2) collaborate with PNNL and other CoE partners to maximize efficiency of AB regeneration, 3) tune chemistry of borate esters as hydride acceptors in PNNL's AB regeneration cycle, 4) develop a better understanding of global supplies of boron ore resources required for hydrogen storage, and 5) develop a resource model applicable to other materials of interest for hydrogen storage (e.g., lithium and magnesium).



Question 1: Relevance to overall DOE objectives

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

- The project is quite relevant to the objectives of the Chemical Hydrogen Storage CoE, which is focusing on ammonia borane as the storage material with the most promise. A sufficient source of boron is necessary if this fuel will be a large-scale substitute for gasoline.
- Study of borate resources important in establishing long-term feasibility of chemical hydrogen storage with ammonia boranes as well as several borohydride systems proposed in the Metal Hydride CoE for large vehicle fleets.
- AB Regeneration is currently the major hurdle for materials being investigated in the Chemical Hydrogen Storage CoE.
- The issues/barriers addressed in this project include hydrogen storage system cost, efficiency, AB regeneration, and system life cycle assessment (i.e., availability of boron and other constituent elements).
- The FY 2009 focus was on maximizing efficiency of off-board regeneration of AB fuel and on determining the size of present day, known, global borate resources.
- The viability of boron sources is critical to the AB chemical hydrogen storage approach. It is also important for a number of metal hydrides.

Question 2: Approach to performing the research and development

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

- The project team is looking at borate esters for AB regeneration based on guidance by theory at PNNL. Borate esters are being prepared guided by theory, with experiments feeding back to help validate theory.
- The model for Boron reserves is less conservative than that of the U.S. Geological Survey, and likely more realistic. Estimating future boron demands is a good approach, but has considerable uncertainty.
- The project team is using alcohols for digestion of spent ammonia borane to produce borate ester intermediates.
- Properties of aryl borate esters have been tuned to yield thermodynamically favorable AB regeneration intermediates and validating computations. (The overall approach focuses on tuning the chemistry of the critical digestion and reduction steps of the AB regeneration process.)

- Established global reserve estimates through review and analysis of publicly available information sources to quantify borate resources.
- The assumption of 15% hydrogen storage in ammonia borane used for boron demand may be a bit on the optimistic side.
- U.S. Borax (USB) most likely is the best source of information regarding world borax reserves. They have a good understanding of the global economics of the boron industry. They are looking at boron resources in the context of other competing economic uses of the ore.
- They are also looking at synthesizing several aryl borate esters that may lead to thermodynamically favorable regeneration intermediates that the CoE can use to validate computations for the AB regeneration process with metal hydrides.

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

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

- This is a new project. The project team has had a good start on obtaining significant results.
- The project is still in early stages.
- Several borate esters have been prepared for AB regeneration testing by PNNL.
- U.S. Borax is proceeding with the synthesis of a large set of borate esters of several types to be supplied to PNNL for experimental validation of theory/basis for proposed AB regeneration process. U.S. Borax has begun sending borate esters to PNNL for testing.
- Several esters have been synthesized and provided to PNNL to validate some of the reaction steps in AB regeneration.
- The project is new. Borate reserves work indicates there are sufficient borate resources in the United States to meet U.S. demand for H_2 storage in the U.S. vehicle fleet in 2050.
- First order estimation of U.S. and global borate reserves has been completed by U.S. Borax. In this analysis, account is taken of consumption by competing applications through initial fill timeframe for the first fleet of fuel cell vehicles (FCV). A key finding is that present day known U.S. borate resources are sufficient for projected U.S. FCVs and competing boron needs through 2050.
- The initial assessment of boron resources indicates that there are sufficient supplies of boron to accommodate the widespread introduction of FCVs, as well as meet the current demand for boron-containing chemicals.

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

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

- Collaboration with PNNL is apparent and appears to be working well.
- The project claims to be highly collaborative and is. The collaborators are PNNL, LANL, and Rohm and Hass. There is a clear role for each member institution.
- This seems to be an effort that is being taken very seriously by the Chemical Hydrogen Storage CoE.
- This project team appears to have excellent collaborations with PNNL, LANL, and Rohm and Haas.
- Collaboration is excellent within the Chemical Hydrogen Storage CoE.

Question 5: Approach to and relevance of proposed future research

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

- The future work covers the appropriate bases.
- The project team plans to:
  - Synthesize a larger set of borate esters of several chemical types for AB regeneration studies at PNNL.
  - Perform spent fuel digestion studies.
  - Participate in AB regeneration cycle validation in collaboration with PNNL.
  - Provide analytical support, safety analyses, and other required consultation.
  - Further refine boron global reserve data.

  - Analyze important questions regarding industry impacts of hydrogen storage technologies and market parameters, including impacts on competing uses and impacts on borate prices.
- Ramping up production to meet first fill requirements could result in excess capacity as spent AB will likely be recycled back to AB.
- It is not clear how the new acetate development will help the overall project.
- The project team could provide more details on future work.

Strengths and weaknesses

Strengths
- U.S. Borax represents a knowledgeable partner for AB regeneration process development and borate resource assessment.
- U.S. Borax's cost share is a relatively large fraction of the total budget.
- Close collaboration appears to exist between U.S. Borax, Rohm and Haas, PNNL, and also LANL.
- The project team is working with the major U.S. supplier of boron.
- U.S. Borax brings extensive knowledge of the boron industry to bear on the production and regeneration of ammonia borane. They are a good addition to the center team.

Weaknesses
- There are no obvious weaknesses.
- None.
- Market projections would be more comprehensive if worldwide demand for boron were estimated assuming FCVs are widely adopted throughout the rest of the world and not only in the United States.

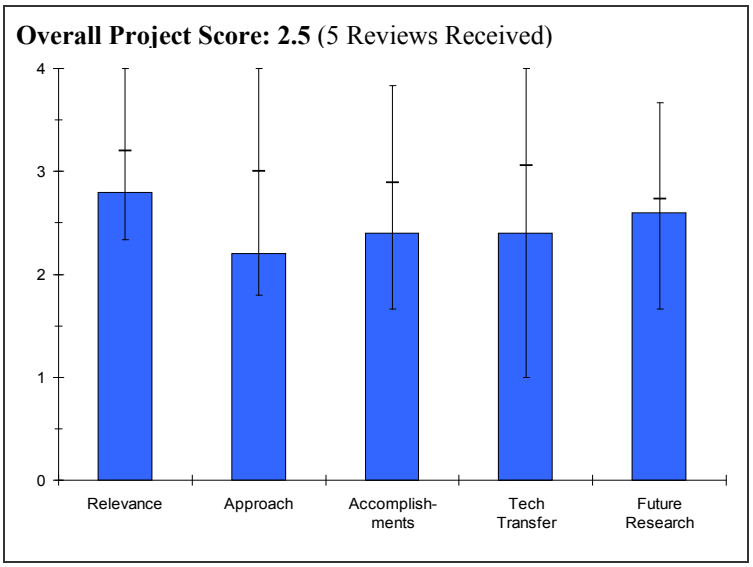
Specific recommendations and additions or deletions to the work scope

- It seems from the funding numbers presented by U.S. Borax that the project was perhaps slightly under-funded by DOE in FY 2009. This project needs to receive the full amount of the requested budget. As that budget is understood, DOE is putting up $300K total and U.S. Borax is putting up ca. $350K.
- Perhaps there should be a little more emphasis on helping to reduce the cost of AB regeneration.

Project # ST-22: Overview of the DOE Hydrogen Sorption Center of Excellence
Anne C. Dillon and Lin J. Simpson; 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.]

Brief Summary of Project



The overall goals of the DOE Hydrogen Sorption CoE are to 1) discover and develop high capacity sorbent materials that can operate near ambient temperatures and at moderate pressure and be efficiently and quickly charged on board with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure and 2) overcome barriers to 2010 DOE system goals and identify pathways to meet 2015 goals. Objectives are to 1) develop materials which utilize mechanisms that bind hydrogen with an optimal energy for near room temperature operation (15-20 kJ/mol·H_2); 2) rapidly correlate capacity, structural, and energetic information to reduce time between discovery, assessment, and down-select; 3) integrate experiment and theory seamlessly in both "feedback" (explanation) and "feed-forward" (discovery) modes; 4) devise facile synthetic routes using low-cost approaches; and 5) create a nimble, flexible yet structured, teaming environment to accelerate discovery, evaluation, and selection of promising development directions.

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

This project earned a score of **2.8** for its approach to R&D and CoE management.

- A broad-based R&D effort is being conducted by the Hydrogen Sorption CoE. The CoE is managed well, and the use of research clusters is a useful approach for subdividing the comprehensive technical effort and avoiding duplication. Close attention is being paid to down-select criteria, and that is providing a straightforward, efficient way to focus the technical work within the Center.
- There is a good balance between universities, national labs, and industry, as well as between computational and experimental efforts within the CoE.
- The research cluster (RC) approach for organizing project topics is appropriate and efficient and the CoE resources (i.e., task mix) are well balanced. Moreover, the specific topic breakdown by sorption mechanism is productive for fostering collaboration by grouping projects that tend to have common synthesis, characterization, and motivation.
- The complementary "clusters" research approach is good in general. However, there is a real need for close coordination among all the clusters.
- The technical barriers appear to be hard to overcome based on the current progress. The CoE relied too much on theoretical estimation rather than using it in a supportive role.
- The approach seeks to develop materials that operate from "100K to 350K with no significant thermal management issues to efficiency [to] meet DOE targets." Given the recent energy efficiency analysis of liquid nitrogen (LN_2) cooling of a cryogenic storage medium by Argonne (ANL) (for metal organic framework [MOF]-177), is the CoE going to focus on reducing this relatively large energy input? Similarly, if the intention is to raise the temperature in the storage bed in order to access lower pressure (below the 3 bar min. delivery pressure), how would this mode of operation (P & T swing) compare with an isothermal mode of operation (e.g. only P swing) from efficiency and dormancy perspectives?

- It is nice to see focus on volumetric capacity (e.g., Argonne (ANL) volumetric capacity, gravimetric capacity, material density plot). The gravimetric versus volumetric capacity plots in future accomplishments slides are very insightful for demonstrating progress. However, are these volumetric capacity values based on single crystal materials densities or based on that for powders, tablets, etc.?
- It is not clear what metrics and decision-making tools are used to down-select various research directions.
- The director says that sorbents meet 13 of 16 targets, but this is somewhat irrelevant. First of all, the most important 3 targets are the ones that are not met and secondly, the targets must all be met *simultaneously*.
- It was stated that there are viable paths to achieve the "ultimate" targets (all of them). However, the issue of volumetric densities is still a real concern. There should be serious attention paid to this issue. What is the highest (measured – not inferred) volumetric density ever shown for a sorbent material?
- Far too much emphasis seems to be placed on highly speculative predictions coming from theory. The theoretical calculations predict nanostructures which are predicted to store H_2 with more favorable binding energies. But more often than not, these predictions involve things that seem to be impossible to synthesize.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **2.2** on its accomplishments and progress.

- New results on boron-substituted materials (notably porous BC_3), high specific surface area (SSA) MOFs, and new materials containing metal centers capable of multiple H_2 binding at higher energies are promising. A focused effort among multiple CoE partners on understanding spillover effects and competing processes, as well as on increasing hydrogen uptake rates is yielding valuable information.
- A great deal of progress is clear in the area of "optimized binding sites". This work seems to be diverse (with no apparent overlap), novel, and promising.
- Overall, results on substituted MOFs and covalent organic frameworks (COF) for cryoadsorption tanks and high SSA BC_3 appear to be most promising for meeting DOE targets.
- One of the approaches stated by the CoE is that optimized pore sizes can greatly improve volumetric capacities and therefore can help meet DOE targets. However, it seems like each of the CoE partners are defining their own optimized size without a common understanding.
- There is still no baseline checking and confirmation of the reported measurement results from last year.
- Last year spillover was a key topic (Southwest Research Institute and University of Michigan results) so the CoE decided to refocus its efforts and resources on spillover. This year spillover is not a strong role. The CoE did well in checking the data reproducibility, but it is left with progress based on theory estimations that does not warrant a real material.
- Good progress has been made by all clusters on improving volumetric and gravimetric capacity, especially for cryo-adsorption applications. In contrast, high capacity storage at temperatures compatible with fuel cell operation remains problematic for all approaches, and at this late stage in the project, poor reproducibility in spillover studies is a serious issue.
- Given the length of time and resources that have been devoted to spillover, it is imperative to resolve reproducibility issues and achieve consistency of experimental results across CoE partners.
- The "closed loop" between theory and experiment is great to see in this CoE, which previously seemed to lack such a connection. In this area what is the "ideal" % boron content and SSA determined from computation and how does that compare with current experimental values? What methods have been identified for bridging this gap?
- In the area of spillover it should be of high(est) priority to demonstrate robust reproducible results across the Sorption CoE (i.e., akin to a round-robin testing). It is imagined to be very difficult to validate theory, down-select or discontinue materials, and/or have confidence in individual results if synthesis and measurements are not currently capable of being reproduced by different researchers.
- The accomplishments are not very strong. Much of the highlighted accomplishments either has to do with spillover materials (where the results are not very compelling and clouded by issues of irreproducibility and inconsistency) or theoretical or idealized models of sorbent materials. This CoE was largely founded on ideas of the theorists in this field, and unfortunately, the experimental efforts simply have not been able to verify a large number of these theoretical calculations. So, the number and impact of accomplishments having to do with real, measured materials of high capacity is quite limited.

Question 3: Proposed future research approach and relevance

This project was rated **2.4** based on future plans.

- The future work plan is well formulated and addresses the critical issues identified in the RCs.
- Good use is being made of down-select criteria to focus the technical effort in the future.
- Go/no-go criteria were detailed and RC-specific. However, given the limited remaining timeframe of the current Sorption CoE and the initiation of the Engineering CoE, it might be more instructive to have more stringent criteria or a additional categorizing of down-selected materials (e.g., priority level 1, 2, 3, etc.). If there are already 40 materials (with more anticipated), that may be too much information to sort through for the Engineering CoE.
- There has been too much effort on spillover materials without a fundamental understanding.
- The creation of the down-selection criteria and road map is very important at this stage. Real measurements at the higher temperature in the down-selection criteria would be necessary.
- The majority of the focus should be on reproducing/understanding spillover results given the amount of resources being devoted to this topic.

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

This project was rated **2.4** for collaboration and communication within the CoE.

- The management approach adopted by the CoE is facilitating good communication among the participants. Theory and experimental studies are well integrated. This is essential for addressing the serious technical challenges (e.g. temperature, binding energy, capacity) faced by the Hydrogen Sorption CoE.
- It is clear that there is a great deal of collaboration and coordination both within and between the CoE projects.
- There should be a concerted effort (e.g., round-robin testing) with regard to spillover validation.
- The CoE seems to be reasonably coordinated.
- There has been insufficient communication within the CoE.

Question 5: Collaborations/Technology Transfer Outside the CoE

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

- Collaborations with other CoEs (e.g., aerogel work with Metal Hydride CoE) and with other institutions are in place and are yielding positive results.
- The excellent publication and presentation record is validating the broadly based technical contributions being made by participants in the CoE and is an effective means of disseminating results to the scientific community.
- One area of suggested improvement is to strengthen communication and collaboration with independent researchers (e.g., Long & Yaghi) where there is logical overlap and expertise that could aid, for example, with sample/synthetic reproducibility for spillover in MOFs.
- There has been insufficient communications with other CoE partners.

Strengths and weaknesses

Strengths
- The approach to develop structures with a high number of sites with enhanced enthalpies of adsorption and optimized pore sizes can greatly improve the materials properties for on-board application.
- A highly qualified and well-managed research team is conducting first-rate R&D work that is focused on DOE objectives. Good communication and collaboration is facilitating progress across all research clusters.
- This is a strong, capable team and leadership.
- Resources have been appropriately dispersed.

Weaknesses
- There have been insufficient communications with other CoE partners.
- There is still no baseline checking and confirmation of the reported measurement.

- The CoE relied too much on theoretical predictions based on non-existent materials to design the sorption material. So far synthesis of these materials has been very difficult or even not impossible (i.e., down-selected NREL's metal-decorated C60). However, the CoE continues to follow the same track with current materials (i.e., boron-carbon [BC] systems synthesis with different approaches, yet the theory has not been validated).
- A straightforward statement or exposition of the critical issues faced by the CoE and whether those issues can be addressed in a timely and successful way is needed. Although there is a great deal of useful information being generated within the CoE, potential problems and "show-stoppers" need to be highlighted and a straightforward and transparent plan for addressing the problems should be provided.

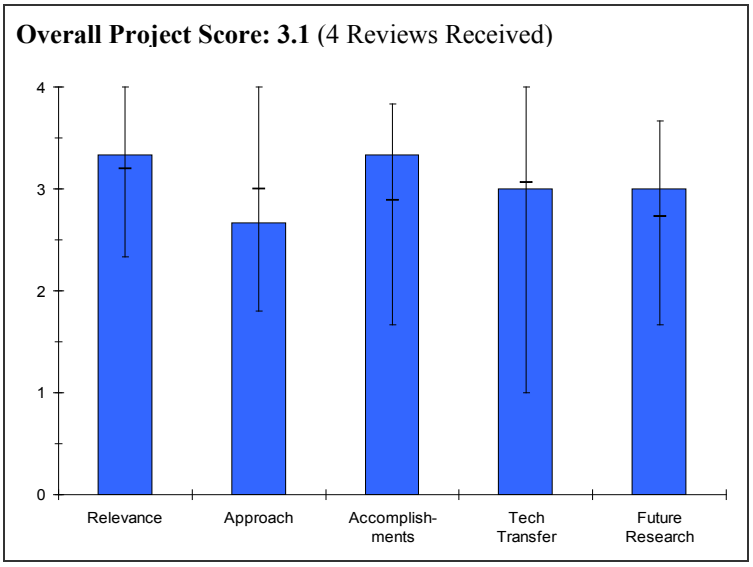
Specific recommendations and additions or deletions to the work scope

- The center should refocus and reduce the number of materials systems based on the down-selection criteria provided. The results for the down-selection have to be based on the experimental results, not the theoretical estimation.
- The key advantage of sorption over other H_2 storage systems is the fast release and sorption of H_2, therefore spillover of H_2 proves to be at a huge disadvantage and its deletion is subsequently recommended.
- Lack of reproducibility in the spillover studies at different Hydrogen Sorption CoE laboratories is an important issue. A strongly focused effort is recommended in order to understand the origins of the reproducibility problem so that a down-select decision on spillover materials can be made in a timely way.

Project # ST-23: A Biomimetic Approach to Metal-Organic Frameworks with High H_2 Uptake
Hong-Cai (Joe) Zhou; Texas A&M University

Brief Summary of Project

The objective of this project is to design, synthesis and characterize MOFs with active metal centers aligned in porous channels and accessible by hydrogen molecules. Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity to hydrogen. These MOFs can help to reach DOE 2010 goals, and ultimately the 2015 hydrogen storage goal.



Question 1: Relevance to overall DOE objectives

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

- If MOF materials can be developed with significant hydrogen storage capacities at room temperature it will have a large impact.
- The project's aim at better uptake and retention at room temperature is a very well-aligned goal. Use of biomimetic concepts would be novel and diversify the portfolio, but they are not at all evident in this project.
- Further exploration of high surface area materials with enhanced physisorption binding potential is an important and viable approach toward meeting the DOE targets. In particular, MOFs offer vast opportunities to chemically engineer a broad range of physisorption binding mechanisms while maintaining accessible surface area. This project is currently focused on surveying a wide variety of open metal sites with which dihydrogen's polarization can be affected to a significant degree.

Question 2: Approach to performing the research and development

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

- The PIs approach is generally good, if not outstanding, but heavily weighted on much empiricism. While a healthy amount of experimental sorption measurements is refreshing, progress may be accelerated by augmenting the experimental work with more theoretical calculations than have been undertaken at this point in time. In particular, the effects of entatic metal centers on the polarizability and binding energy of dihydrogen deserves further attention as a means of screening potential metal-center candidates and developing trends based upon electronic structure. Such calculations are tenable by various levels of theory and could be applied to exploring open metal sites.
- The team's approach of utilizing open metal sites, interpenetration, and optimal pore size is certainly not new and seems to be following in the footsteps of University of California, Berkeley; University of California, Los Angeles; and several groups in Europe. The actions are suitable, but there is a need to try to plan experiments that will show something new.
- Of the MOF approaches of catenation, mesocavities, and open metal sites, only the open metal sites have the potential to increase hydrogen binding energies, and hence, room temperature adsorption.

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

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

- The CoE metal centers appear promising.
- The team made several new linkers and associated MOFs. Many have low capacity but a few are good, *if confirmed*. (7%. These results would be more powerful four years ago when things like the effect of interpenetration and pore volume versus area were hot topics.)
- The 7,200 m^2/g specific area by Bruner–Emmett–Teller surface area analysis method (BET) measurements would be a very good accomplishment, but it is called into question by both theory and H_2 capacity.
- Overall accomplishments are outstanding given the time-frame. It would have been helpful, however, to learn more details about PCN-103, which yielded exceptionally large surface area.

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

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

- There was a partnership with Air Products, but there did not appear to be well connected. They listed several "partners," but there was no evidence that they worked together.
- Collaborative efforts to explore spillover effects might be expanded to other organizations in addition to the University of Michigan.

Question 5: Approach to and relevance of proposed future research

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

- The project team is seeking H_2 capacity of 7,200 m^2/g material and validating the BET.
- The plans seem better than current work, which is good.
- The future plan makes no mention of further characterizing of PCN-103. Given its incredibly large surface area and potential for dihydrogen binding, it would seem this should be a notable priority for the ensuing year.
- Emphasis should be placed on exploring the metal center avenues.

Strengths and weaknesses

Strengths
- The project team seems to have found its special area and should have a chance to make good progress.
- The project has a library of many ligands with which to work.
- The project team is addressing a promising pathway toward achieving significant gains in physisorption binding energies, while addressing gravimetric capacity via exceptionally high surface area.
- The project team is using new innovative MOF approaches to improving hydrogen storage.

Weaknesses
- The project does not at this point make effective-enough use of theoretical predictions, which would otherwise help select the most promising systems for experimental measurements.
- Volumetric hydrogen capacities are on the low side.
- The project team has been catching up to leaders, but seems to have done so.

Specific recommendations and additions or deletions to the work scope

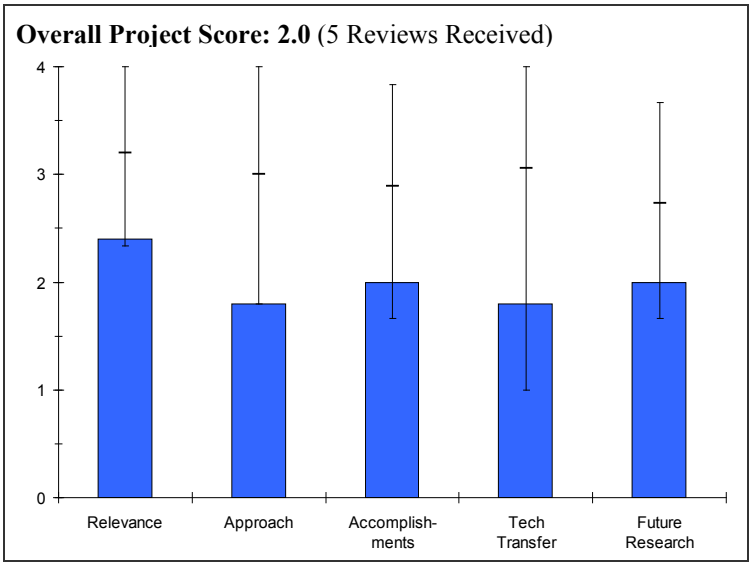
- The project team should test the 7,200 m^2/g material in H_2 as soon as possible; if the result is good, the team should have it reproduced as soon as possible.
- If not already in the scope of work for the ensuing year, further characterization of PCN-103 should be a priority.
- Through additional computations, the project scope could begin to establish trends on the polarizability or binding energy of dihydrogen to entatic metal centers versus the metal type. Such trends could be used to make appropriate selections of the entatic metal for synthesis of the MOF, thus accelerating progress in experimental verification.
- Evaluations of the stability of the MOFs produced would be useful.

Project # ST-24: Hydrogen Storage by Spillover

Anthony J. Lachawiec, Jr., Lifeng Wang, Yuhe Wang, and Ralph T. Yang; University of Michigan

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 new 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) because of the enormous potential of carbon for hydrogen storage by spillover as to be explained, 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 **2.4** for its relevance to DOE objectives.

- The project is addressing H_2 storage, which is important for future fuel cell vehicles.
- The project focuses on materials that have recurring problems with reproducibility.
- The concept is relevant to DOE goals and objectives.
- The project team is trying to achieve higher uptake in sorbents at room temperature due to spillover. It is not at all clear whether this technique is really going to produce anything useful in terms of a storage technology.

Question 2: Approach to performing the research and development

This project was rated **1.8** on its approach.

- Systems with high platinum group metals (PGM) loadings being investigated may be of academic interest but are not practical. They will not come close to meeting the cost targets, even if they meet the loading targets. The storage system cost target of \$67/kg · H_2 means less than 2 grams of Pt can be used per kilogram H_2 stored at current prices. For storing H_2 at 5 wt%, the system weight is 20 kg/kg · H_2. This means Pt loading cannot be higher than 2 g/20,000 g or 0.01 wt%. They are investigating systems with 10 wt% Pt loading, 3 orders of magnitude higher Pt loading than would be acceptable than if they reach 5 wt% H_2 storage (which they haven't achieved). They need to focus on non-precious metal dopants for spillover and look at systems with higher initial H_2 storage capacity (MOFs). Spillover in MOFs is likely to be different than spillover on C due to the differences in binding between the metal center and the C or MOF.
- Spillover appears to lead to C-H binding at least judging from the hydrogenation/dehydrogenation rates vs. other sorbents. This coupled with the demonstrated low wt% places spill over in a weaker position vs. the other sorption materials researched.
- The project only uses sorption measurements. This is a very serious weakness, since sorption data alone is not enough to understand the microstructure of the materials and to reach convincing conclusions about the hydrogen adsorption and diffusion mechanisms. Reproducibility of the measurements is suspect in the absence of more information on the properties of the materials used.

- The approach should include objectives toward understanding spillover mechanism in the context of hydrogen storage in order to make research amenable to logical, rational targeting of materials. In its current form, it seems to be more or less a trial-and-error search of materials for which spillover is observed.
- These experimental efforts should be complimentary to analogous computational efforts for cross-validation.
- The spillover approach generated a lot of interest several years ago, but has more recently repeatedly become problematic due to problems of irreproducibility and inconsistent results. Unfortunately, this makes all of the results from a project like this (even the seemingly promising ones) somewhat suspect.

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

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

- Work looking at increasing charging rates with co-doping has shown positive results.
- The effect of surface area was determined to be a key factor last year and it still remains a challenge judging from the low surface area spillover systems reported so far on carbon.
- Pt and Pd are known to be perfect for hydrogen dissociation, addition of transition metal halides is not well justified given they reduce the wt% storage unless they are replacing the noble metal catalysts.
- This project has obtained some interesting results on adsorption in the presence of linkers and activation barrier for hydrogen diffusion. However, there is not enough to decide on the validity of the conclusions due to lack of supporting microscopic measurements and microstructural characterization (e.g., TEM, Raman, and NMR).
- In regard to using gas adsorbate molecules as bridges (e.g., co-adsorption of CH_4 and H_2), it is not understood how this will be able to be implemented in practice for fuel cell application. In particular, will not the CH_4 and H_2 simultaneously be desorbed from the sorbent, and if so, this will have serious implications for fuel cell operation. The current SAE J2719 fuel purity standards do not allow greater than 2 ppm (C1 basis) for hydrocarbons. Currently 50 ppm CH_4 is being explored as a bridge which exceeds these limits. In the current form, it is unclear how this research topic is practical.
- While the back-up slides indicate that this research program focuses on exploration of both MOFs and carbons for spillover, the vast majority of the last year's research appears to be devoted only to carbons. Given that MOFs (in particular IRMOF8) remains the project's top performer, it is unclear why this topic has been seemingly abandoned. Previously cited sample "synthesis reproducibility issues" are something that should be easily overcome given that other research groups/companies are capable of producing such materials.
- All results shown are for ~1-1.5 wt% at room temperature and ~100 bar. There were no high capacity results shown and no discussion or mention of volumetric capacities (presumably because they are extremely low).
- The project team found some results that dosing with CH_4 could produce an enhanced spillover effect (within a certain range of CH_4 pressures).
- The project team found enhanced spillover in graphite due to oxidation. Even so, one would need to obtain a very high surface area material to make these results useful, and it is not clear that there is a path towards achieving this.
- The project team catalyzed spillover with metal catalysts and attributed the enhanced rates to a lower binding energy upon metal doping, but the increased rates were in *both* directions (desorption and absorption), and it is difficult to understand how a decreased binding energy could increase the rate of absorption.

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

This project was rated **1.8** for technology transfer and collaboration.

- Collaboration with NREL for testing is visible.
- Beyond the collaborators listing on the overview slide, it was not obvious what the extent and role of these collaborations are in the research program. Although other research projects in the Sorption CoE are actively investigating spillover, both in terms of experimental validation and theoretical investigations, the integration of these important activities into this project was absent. Going forward, it is essential that this project coordinate with the other activities in the CoE devoted to spillover.
- There are seemingly very few collaborations. It appears as though the program is largely isolated, which is unproductive from DOE's standpoint, since one of the main drawbacks of this idea is the lack of consensus, reproducibility, and reliability in the results.
- There seems to be no collaboration with other projects.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.0** for proposed future work.

- Future work should look at realistic loading levels and non-precious metal dopants. The project team plans to look at MOFs and continue work on kinetics of spillover, which is good.
- Illustration of surface area enhancement is strongly recommended
- Measurement of charge/discharge rates for oxidized systems and comparison with other systems are necessary.
- Approach to and relevance of proposed future research was not discussed in the presentation and/or slides. Assuming that the project will continue "as is," it suffers from the lack of characterization measurements.
- The project team should focus on reproducibility of synthesis and measurements within this project as well as validation by other groups (e.g., round robin testing).
- The project team should focus on achieving an experimental understanding of spillover mechanism to avoid continuation of trial-and-error testing of diverse sorbent material. That is, the team should strive to understand why one MOF works better than another (i.e., derive structure-property relationships).
- The project team should continue to actively investigate MOFs since they are the top performers.
- Much of the promise of the graphite oxide depends on the ability to create high surface area samples. However, the plans for how to achieve this are not very convincing.

Strengths and weaknesses

Strengths
- The team has performed studies of kinetics of spillover and attempted to increase rate of H_2 uptake.
- A unique, novel approach has been used and has shown promise.

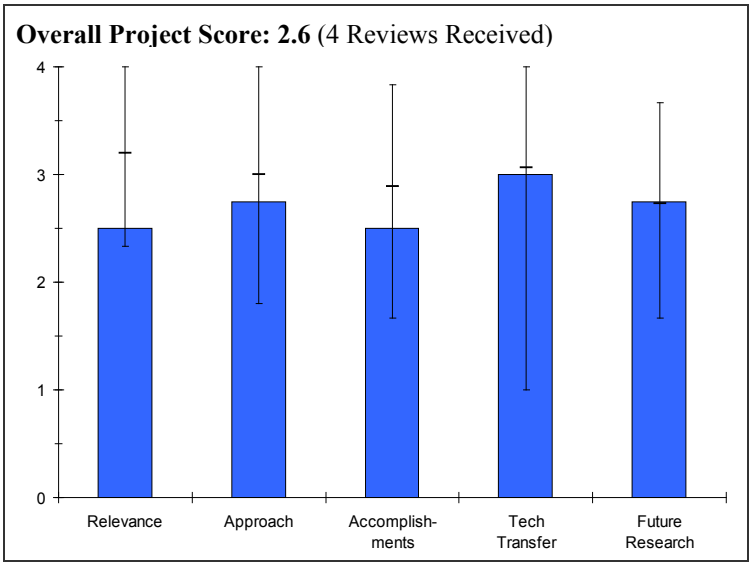
Weaknesses
- The project team has focused on precious group metals at high loadings.
- Low wt% H_2 combined with the slow charge rates is a weakness.
- The addition of catalysts impact the storage capacity.
- Utilization of expensive noble metal catalysts to allow for the spillover could be an issue.
- The project needs characterization of the materials and probes of hydrogen dynamics (collaborations with other projects could help, if they existed). Measurements in this area often suffer from irreproducibility. Many of the considered materials and catalysts are too expensive.
- There has been a misdirection of efforts (which should be focused on reproducibility of measurements across CoE partners as well as striving for an understanding of the spillover mechanism).
- The project should focus on why only certain materials are amenable to spillover.

Specific recommendations and additions or deletions to the work scope

No recommendations were received for this project.

Project # ST-25: Optimization of Nano-Carbon Materials for Hydrogen Sorption
Boris I. Yakobson and Robert H. Hauge; Rice University

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 recommendations for the synthetic goals (e.g., pore/channel size, metal enhancement routes). The 2008-2009 objectives include to 1) identify the obstacles (thermodynamics and kinetics) for the spillover for suggesting the materials design 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; 3) explore doping as a anchor to metal/metal cluster, role of bridges and dopants on the threshold of spillover; 4) synthesize metal-and electronegative-group-(F, BF_3) enhanced VANTA (vertically aligned nanotube arrays, contrast to fibers) for H_2 adsorption; 5) assess the effect of impurities and environment on the spillover; and 6) study the conditioning of graphitic substrates, by adding O, B, and organic molecules.

Question 1: Relevance to overall DOE objectives

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

- The use of theory to reduce mass and volume and increase the capacities of sorption materials is correct, and the method is good. The centerpiece of the group, targeting spillover, is well chosen.
- This project supports the DOE RD&D objectives. The strong emphasis on computational analysis and modeling of porous sorption media, catalytic spillover effects, and metallocarborane-based MOFs supports experimental efforts within the Hydrogen Sorption CoE.
- The project considers materials that can hardly be synthesized (e.g., H_2-filled carbon nanocages) or are thermodynamically unstable at ambient conditions (metallacarborane MOFs).
- Spillover simulations seem to be the most relevant part of this project.

Question 2: Approach to performing the research and development

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

- The pairing of theory and experiments is a good approach and the theory platform is suited to doing the work. The use of bookending potentials is also good.
- Experiments seem well chosen.
- The multi-task modeling and computation effort focus on storage properties of nanoporous materials, diffusion barriers, and H-binding energies in presence dopants in catalytic spillover systems and hydrogen sorption energies in metallacarboranes and MOFs. The approach is well formulated and is providing information that helps to guide experimental efforts within the Hydrogen Sorption CoE.
- At this stage in the project, the computational studies on storage capacity in nanoporous foams and the experimental effort on storage in vertically aligned carbon nanotubes appear to be much less likely to overcome the technical barriers for high capacity storage than the work on spillover and metallacarboranes.

- The project team uses a combination of first principles and classical potential approaches to study the thermodynamics of hydrogen physisorption. This is appropriate for studying hydrogen-material interactions theoretically, but not enough to suggest new realistic storage materials.

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

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

- The results on spillover, especially computations of binding energies in the key states and evaluation of anchors for metal clusters are particularly noteworthy contributions and support related theory and experimental efforts within the Hydrogen Sorption CoE.
- The project team seems to have found a great surface – super acid, but seems to be off when compared to measurements. The validity of the experiments is unclear. Likewise, the Ni work seems in contrast to the results which have never been shown to work.
- The majority of the work on this project focuses on simulations of hydrogen binding energy and storage capacity in nanoporous materials and analysis of spillover mechanisms. Although this information is valuable, at this late stage in the project, experimental validation is needed.
- Metal aggregation remains a serious problem for the spillover process in weakly bound metal-carbon systems. A clear plan for addressing this issue is not readily apparent from this presentation. An estimate of the spillover efficiency with cluster size would be useful. Likewise, a more detailed investigation into the problem of slow hydrogen uptake rates in spillover systems is needed.
- Although from a materials science perspective the carbon foam work (including quantum corrections to the foam capacity) is intriguing, it is not evident why subtle changes in foam pore size distribution can produce significant changes in hydrogen storage capacity. Comparisons with other carbon systems containing micropores (e.g., activated carbon) would be useful.
- The experimental results on the vertically aligned nanotubes appear is less promising. Advantages of vertically aligned nanotube arrays (VANTAs) over simple activated carbon for enhanced storage by addition of electro-negative groups are not obvious.
- Numerical results for many cases of hydrogen-material interactions have been obtained. Unfortunately, it is not clear how these results can lead to better understanding of the fundamentals and/or to improved hydrogen storage materials.
- Not as impressive as last year's, which was very good.

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

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

- The project team is well connected to other teams in the CoE. The team is helping other teams and being helped by them, so there is value. Examples include the teams at University of Michigan, Rice University, NREL, and Air Products.
- Good collaborations between this project and other CoE partners, especially in areas of hydrogen capacity testing (California Institute of Technology [Caltech]) and comparison with experimental results on spillover (University of Michigan) are evident.
- It is not clear that the technical effort on this project is integrated adequately into the overall work within the CoE. There are numerous activities within the CoE on spillover (both computational work and experimental work) and on substituted MOFs. A stronger connection between this project and those efforts would be helpful.
- There is a long list of collaborations; some of them are productive (e.g., with Caltech on aligned nanotube arrays).

Question 5: Approach to and relevance of proposed future research

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

- Future plans are well oriented to address problems within the CoE.
- Unfortunately, the project team is not solving the discrepancy in experiments.

- The future work builds upon the current technical effort and addresses the important issues that have been identified. A missing aspect seems to be a candid assessment of key technical barriers and how they will be addressed during the remainder of the effort. It is critical to identify those obstacles, determine their severity, and then focus on finding solutions.
- The plans are to continue along the same lines as done previously. There needs to be sharpening of the focus to study phenomena outside of the present scope (e.g., thermodynamic stability of the proposed materials).

Strengths and weaknesses

Strengths
- The project team was able to explain the spillover work.
- The project is well aligned to experimental teams' greatest needs.
- This is a strong research team that is highly qualified to conduct leading-edge work on hydrogen storage in substituted nanophase carbon materials.
- This broad-based computational effort supports experimental work in the Hydrogen Sorption CoE.
- The project has added some understanding to the energetics of the so-called spillover effect.

Weaknesses
- The project team might benefit from association with other theory groups in other CoEs.
- It is not clear that a continued emphasis on porous foams and VANTAs is appropriate. Although the materials have interesting physical properties, high storage capacity for hydrogen appears to less promising than in other materials.
- Several materials being considered are unrealistic (e.g., nanocages) and there are too few comparisons with experimental data; which currently not even on a qualitative level.

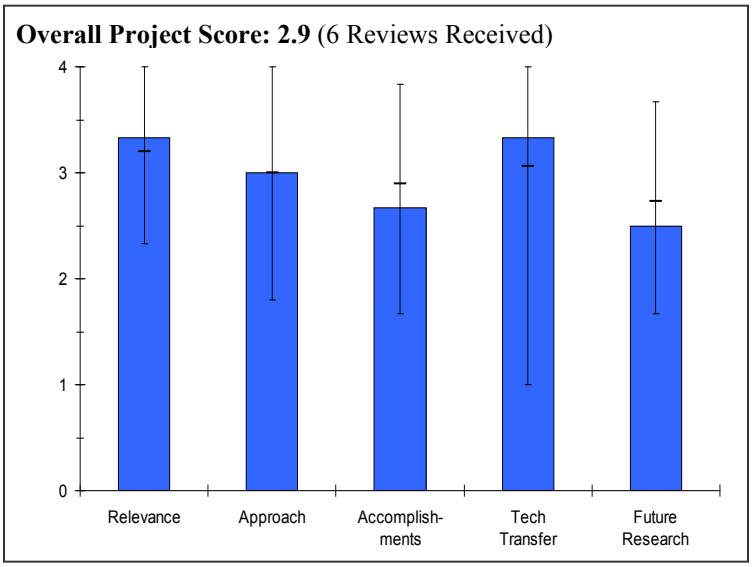
Specific recommendations and additions or deletions to the work scope

- It is important for this project to identify and focus sharply on the critical technical barriers that remain.
- Simply continuing work on several on-going tasks will undoubtedly produce some useful results, but could give insufficient emphasis to the key technical obstacles.
- A heart-to-heart on theory with the team at Air Products (especially on the work from last year on spillover limitations where hydrogen was on both sides of the graphene) would still go a long way; however, to have value the CoE lead would need to first elucidate both team's concerns about the other's work in private and then mediate the exchange.
- There needs to be a stronger focus on materials that work in the lab and are well characterized and quantitative comparison to experimental data needs to be added.

Project # ST-26: NREL Research as Part of the Hydrogen Sorption Center of Excellence

L.J. Simpson , A.C. Dillon, J.L. Blackburn, J. Bult, C.J. Curtis, M. Davis, T. Elko-Hansen, C. Engtrakul, T. Gennett, A. Groves, , A. Herwadkar, K.M. Jones, Y-H. Kim, K.J. O'Neill, P.A. Parilla, J.D. Rocha, E. Whitney, and Y. Zhao; National Renewable Energy Laboratory
M.J. Heben; University of Toledo
S.B. Zhang; Rensselaer Polytechnic Institute

Brief Summary of Project



NREL's research in the Hydrogen Sorption CoE is targeted at addressing key technical barriers in DOE's Hydrogen Storage Program: 1) efficiency - it is clear that the highest efficiency storage system will be achieved with a sorbent material that operates reversibly on board with a hydrogen binding energy in the range of 15 to 20 kJ/mol (room temperature operation); 2) refueling time - the fastest on-board refueling time will be found for a sorption system when the materials are not limited by heat transfer processes; 3) weight and volume - when the sorption material has an optimized binding energy and thermal conductivity, non-sorbing system hardware can be kept to a minimum, capacities of the system will then be approximated by the capacities of the materials; and 4) cost - closing the gap between the idealized sorption materials that have been predicted and the synthesis of actual materials using low-cost source materials and synthesis processes.

Question 1: Relevance to overall DOE objectives

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

- The project is well aligned with DOE objectives and is providing good leadership for the overall Hydrogen Sorption CoE effort. The overall relevance of the project has been enhanced in 2009 by the greater emphasis on sorption materials capable of higher capacity storage at near-ambient temperature.
- These materials have a chance to meet all goals and exceed compressed gas. The challenges they have targeted (i.e., mass, volume, and cost) are the keys.
- This project covers virtually all aspects of hydrogen storage by sorption methods for on-board fuel cells, including system cost, gravimetric and volumetric H_2 storage targets, reversibility, refueling time, and efficiency.
- This is a centerpiece project within the Hydrogen Sorption CoE.
- Project's focus on enhancing dihydrogen binding energies in novel, high-surface area chemistries and elucidating sorption/spillover mechanisms is clearly essential to the technical goals of the hydrogen program.
- Generally well aligned with DOE goals, with a few projects focusing on more basic energy science concepts rather than applied research.

Question 2: Approach to performing the research and development

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

- Near-ambient work is a big enabler and a good thing to research.
- The low temperature work by doping is good.
- Indicate 5 minute fill of 82% capacity with new catalyst.

- This project conducts high-quality research that seeks pathways to increasing the H_2 binding energy, the number density of binding sites, and the number of H_2 molecules per binding site. The project also seeks to achieve near ambient temperature regeneration.
- NREL leads and assures coordination of activities within the Hydrogen Sorption CoE. In this role, NREL evaluates progress across the entire Hydrogen Sorption CoE in terms of demonstrated achievements versus the entire set of DOE hydrogen storage system targets.
- Project effort now places more emphasis on low-cost materials and viability of synthetic routes than in previous years. This approach to materials discovery should continue for both the experimental and theoretical efforts. However, theoretical predictions appear to be outpacing experimental verification, which can be expected. Synthesis and characterization of theoretically promising candidates need to be undertaken expeditiously in collaboration with other groups (including groups outside the center).
- A welcome shift in emphasis in 2009 away from more exotic materials (e.g., OM-fullerenes, Ca-C60 compounds, Co-intercalation) toward more experimentally accessible systems that have a better prospects for hydrogen storage at acceptable temperatures.
- A new approach using chemical vapor deposition (CVD)/templating has provided a pathway for evaluating physisorption, dihydrogen binding, and spillover using a well-controlled process.
- Important focus on materials capable of multiple H_2 storage via Kubas interactions. This is a potentially useful approach to increasing storage capacity. Likewise, work on CA-COFs is a promising new research direction.
- Continuing effort on spillover is directly supporting related efforts in the CoE. Work on improving rate of hydrogen uptake and on understanding lack of reproducibility in spillover results is especially important.

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

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

- The project team continued to develop novel, scalable synthetic processes for adequate storing of hydrogen on high surface area materials.
- Calculations show that the modeling formalism can predict what is seen in Si systems with Ti catalyst.
- Boron-doped carbon lattice increases H_2 binding temperature.
- Calculation says COF with Ca would be stable and hold around 5.6% at modest temperature.
- There is possible insight on the batch-to-batch, lab-to-lab problems with spillover.
- The project team demonstrated that B substitution in C increases H_2 capacity and binding energy.
- The project team validated initial, theoretical prediction that single, metal atoms dispersed and stably supported on a matrix are able to reversibly hold more than two H_2.
- The project team identified new inexpensive materials that make use of unique properties of Ca via viable synthetic routes.
- The project team continued to make advances in the understanding and application of spillover, including the development of a new catalyst processing method that improved spillover capacity and charging rates.
- The project team identified potential issues that produce irreversibility and cause irreproducible hydrogen sorption measurements.
- The project team continued to improve the measurement capabilities to provide more accurate determination of H_2 storage characteristics.
- The team continues to produce an impressive amount of work along diverse paths, perhaps too diverse in some instances. It is not clear why the project team is, in some instances, spending effort on the analytical validation of material performance for other groups when that time could be utilized on verifying the hydrogen uptake in novel materials predicted from theory. Analytical validation should be directed to the DOE-designated storage testing laboratory (Southwest Research Institute [SwRI]).
- The improved spillover catalyst processing is showing some promise for enhancing capacity and uptake rate. Results on elucidation of mechanisms that affect hydrogen diffusion during spillover is improving understanding of this potentially important process. However, it is not clear how this information is being used to guide experimental work. Have differences between NREL and University of Michigan results been reconciled? The lack of reproducibility remains a serious issue.
- The new CVD/templating work is providing a well-controlled platform for studies on physisorption, enhanced H-binding, and spillover. Is the CVD templating process scalable?

- The work on high specific surface area (SSA) BC_3 and Ca-COFs (covalent organic frameworks) is especially intriguing. Materials synthesis appears to be comparatively straightforward, and both material systems show considerable potential for high capacity hydrogen storage.
- The accomplishments are not very strong. Much of the highlighted accomplishments either have to do with (1) spillover materials, where the results are not very compelling and clouded by issues of irreproducibility and inconsistency or (2) theoretical or idealized models of sorbent materials. This CoE was largely founded on ideas of the theorists in this field and unfortunately the experimental efforts simply have not been able to verify a large number of these theoretical calculations. So, the number and impact of accomplishments having to do with real, measured materials of high capacity is quite limited.
- The Ca doping prediction is quite suspect, since CaH_2 is such a strongly bound phase. It seems quite likely that this system would simply form the CaH_2 phase upon repeated cycling. The binding energy of CaH_2 is larger than the binding energy quoted for Ca to the COF, thus making this a very real possibility.
- It is disappointing to see that not much progress has been made on the reproducibility or characterization of spillover.

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

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

- The project team has connected with many other groups, lead other groups well, and provided international leadership in this area for years.
- The project team has collaborated with institutions within the Hydrogen Sorption CoE include Rice University, Air Products, Duke, California Institute of Technology, LLNL, NIST, ORNL, Pennsylvania State University, University of Michigan, University of Missouri, University of North Carolina, Texas A&M, ANL, and University of Chicago.
- NREL has done an admirable job of spearheading and coordinating research throughout the Hydrogen Sorption CoE.
- This project has extensive collaborations both with the Hydrogen Sorption CoE and with external research groups that are facilitating more rapid progress. Impressive publication and presentation record is resulting in efficient dissemination of research results.
- The CoE teams seem to work together reasonably well.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.5** for proposed future work.

- The project team's close-out plan is suitable and wise to have.
- The project team has good plans; the Ca work will be very instructive.
- The team's plans focus on spillover sorption, which is right.
- The down-select on material is good.
- A down-select is recommended on theory approaches to those that can predict, not just tune, results to reproduce data in hand.
- Develop and optimize H_2 storage materials; prepare for program culmination:
    - Optimize templating processes used to synthesize high surface area materials.
    - Create stable coordinated unsaturated metal centers with higher site density that exhibit substantial hydrogen storage using inexpensive materials.
    - Perform experiments to identify surface/material processing strategies that increase spillover capacity and sorption rates; determine H_2 state on receptor; investigate site poisoning.
    - Accelerate theoretical efforts to design viable H_2 storage materials and synthetic routes thereto.
    - Complete down-selection process for all materials and assist CoE with go/no-go decisions based on material/system potentials.
    - Scale up synthesis of most promising materials for round-robin verification of samples.
    - Provide materials/systems recommendations; determine viability of high surface area materials to meet DOE 2010, 2015, and "ultimate" hydrogen storage system targets.

- Future plans/recommendations appear to be overly ambitious given that many of the theoretically promising candidate materials have not yet been synthesized.
- Solid plan for building upon recent results on templating, modifying surface properties to enhance spillover capacity and rates, and testing new materials is in place. However, the presentation provides very little information concerning a candid assessment of specific technical obstacles and barriers and the status of the project with respect to overcoming those barriers. Instead, general statements about how results in each of the areas are providing a "development path to meet DOE goals" are given.
- Without a more compelling assessment of critical problem areas (especially at this stage in the project), it is difficult to adequately evaluate whether the plan effectively meets the program needs.

Strengths and weaknesses

Strengths
- This is a highly qualified, multidisciplinary research team. The NREL team has shown ability to effectively make "midcourse corrections," which enhance technical efforts in areas that are most promising.
- There has been excellent collaboration between theory and experiment. Results are paying off in areas of multiple H_2 binding, enhanced spillover rates, and materials discovery (e.g., high SSA BC_3 and COFs).
- There are mixed strengths on this team.
- The cost target could be met, that is not a trivial thing to do!
- The project team has made a broad attack on the problem (e.g., room temperature, low temperature, theory, experiment, Kubas, spillover).
- The project was well represented and well presented by the PI.
- The project team has made strong collaborations with other Hydrogen Sorption CoE partners are starting to bear fruit.
- Reconsideration of the storage system targets by DOE (to define more realistic values) gives hydrogen sorption a much better chance of meeting the targets in a timely manner.
- Diverse pathways and mechanistic issues are being addressed.

Weaknesses
- This project has no significant weaknesses.
- It is troubling that the predictions are never verified, but the new ones are always assumed to be correct.
- The volume is troubling, but new goals will be more possible.
- Synthesis and characterization of theoretically promising candidates need to be undertaken expeditiously in collaboration with other groups (including groups outside the center). More active collaboration with the DOE-designated storage testing lab (SwRI) to share the burden of verifying theoretical predictions needs to be included.
- The lack of a straightforward assessment of the severity and scope of the remaining technical barriers, as well as a statement concerning the extent to which the R&D in the remainder of the project will be able to effectively deal with those obstacles, are weaknesses.

Specific recommendations and additions or deletions to the work scope

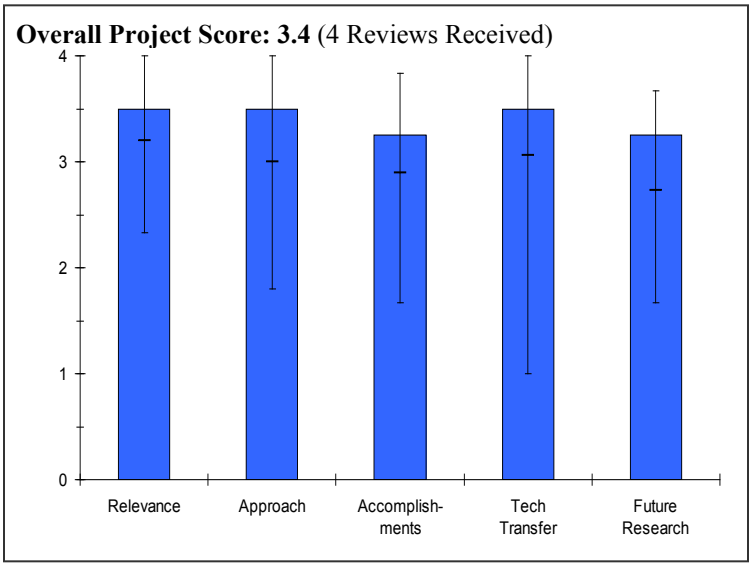
- The project team needs to do everything possible to make the COF with Ca and find out if the theory works predicatively, or only can be tuned, to match known results. It is absolutely essential that they are funded enough to do this.
- It seems essential to obtain a clear elucidation (theoretical and experimental) of the best way to optimize spillover and how much can be gained from its application under conditions that meet all the DOE hydrogen storage targets.
- In the current light of the "revised" DOE storage targets, NREL should put more emphasis on the many storage system targets that hydrogen sorption methods can seemingly meet, particularly in respect to the other two storage options (metal hydrides and chemicals).
- Any activities aimed at validating material performance that is beyond the phase of pure research should be directed to the DOE-designated hydrogen testing laboratory (SwRI).
- A sharply focused effort is recommended on improving rates and storage reproducibility in spillover materials and on synthesis and testing of Ca-COFs.

Project # ST-27: Hydrogen Storage through Nanostructured Polymeric Materials

Di-Jia Liu, Shengwen Yuan, Brian Dorney, Scott Kirklin, Suhas Niyogi, Shengqian Ma, Ricky Regalbuto, and Peter Zapol; Argonne National Laboratory
Jiangbin Xia, Zhou Wang, and Luping Yu; University of Chicago

Brief Summary of Project

The objectives of this project are to 1) design, synthesize, and evaluate nanostructured polymeric materials 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 (SSA) and porosity can be controlled at the molecular level. Polymer-hydrogen 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 **3.5** for its relevance to DOE objectives.

- The project is relevant to the storage goals.
- The design and synthesis of nanostructured polymeric materials as new hydrogen storage adsorbents is critical to Hydrogen Program.
- The present project, which aligns with the hydrogen program objectives, is concerned with developing novel porous organic materials and their use for hydrogen storage applications.
- The most novel area of this work is the formation of metallo-organic porous polymers. There appears to be analogies here with the MOF work, but unlike the MOFs, this is an amorphous system. The approach means that there is a high degree of control of the chemistry and it will be interesting to see what the effect of this is on the hydrogen characteristics. This system therefore has the potential to tailor the chemistry for higher isosteric heats of adsorption.
- It should be mentioned that the reviewer missed the oral presentation due to an injury.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- The approach well combined theory calculation, experimental design, H_2 uptake measurement, and fundamental understanding.
- Very interesting approach, any estimate on other objectives (kinetics and prices, for instance)?
- It is not clear from the PI presentation and answers to the questions how the H_2 gravimetric uptake will be increased toward the DOE target at higher temperatures and moderate pressures. In addition, the reported isosteric heats of sorption are low to moderate, far from the needed ~15kJ/mol. The lower heats of sorption suggest that it will be difficult using the present materials which possess narrow pores to access elevated isosteric heats.
- Independent verification should be sought from CoE partners for the hydrogen isotherms, as these have an uncharacteristic shape. If this proves to be true, then the PI should look to investigate with partners who can

investigate the phenomenon (e.g., neutron work to investigate any swelling effect or other potential sorption mechanisms).
- A potential flaw in the metal-loaded polymer strategy is that if the metal centers are not coordinatively unsaturated, then any enhanced interaction of the materials with H_2 is likely to be low. The PI should think about ways to activate the metal centers.
- Further understanding is needed on the porosity and diffusion of H_2 within these materials.

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

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

- Given that this is a new area, this project really made excellent progress in a short time frame.
- Interesting that compression does not affect specific surface (in contrast with activated carbons where densification invariably lowers it).
- The present group has synthesized a series of porous organic polymers that can adsorb higher amount of H_2 at 77 K and high pressures.
- They also showed the ability to control the pore size of the obtained porous polymers.
- The group initiated collaboration with the University of North Carolina (UNC) to study H_2 uptake using nuclear magnetic resonance (NMR) at higher pressures. The recently obtained results from this collaboration are encouraging.
- Nevertheless, it is not clear what will be the rational to be pursued to improve the H_2 uptake and isosteric heat adsorption toward better materials that can answer the DOE target at higher temperatures and moderate pressures.
- Significant progress has been made on synthesis and characterization of the polymers. Given that the metal-loaded polymers are the most likely candidates to give hydrogen properties closer to the DOE targets, it was disappointing that more had not been undertaken. The PI showed that this would be the focus for the next 12 months, and this reviewer hopes that this remains the case.

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

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

- Close collaboration not only with the center partners, but also with other parties in the field.
- There seems to be good integration with other teams.
- The new collaboration with the NMR group at UNC is very important to the future success of the proposed research.
- There was a good level of collaboration, but further collaborations to verify uptake measurements and to probe the characteristics of the materials would benefit the project.

Question 5: Approach to and relevance of proposed future research

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

- Hopefully this very interesting adsorption approach will continue.
- Good plans for coming year and focus on addressing the barriers.
- The polymer synthesis and hydrogen interactions with the samples have been investigated. The focus for the future work is on metal loaded polymers. A clear strategy for the synthesis was given, and the design and selection of metal centers will be developing through the next 12 months.
- The incorporation of new potential sites into the available pores is very critical to the success of the present project and may indeed lead to higher isosteric heats of sorption. It is recommended that such a proposed approach be pursued. It is also recommended that the choice of guest molecules to be incorporated into the voids of the porous polymer be based on the input of the computational team on the project.

Strengths and weaknesses

Strengths

- Relative invariance of specific surface after densification.
- Is it easier to include metal dopants in the structures with respect to AC or other adsorbents?
- It is a novel approach.
- Addresses the material's engineering properties at very early stage.
- The team has access to a large library of porous organic polymers. They also showed that the organic functionalities, as well as pore sizes, can be tuned with ease.
- Such modularity offers the potential to design the desired porous polymers suitable for H_2 storage with the help of the computational component.
- Strengths for this project are the novel materials being investigated. There is a lot of transferable knowledge and expertise from the CoE partners that will benefit the project. The PI has the necessary expertise to undertake a logical and in-depth investigation of these interesting materials.

Weaknesses

- It is not clear how the present project will lead to a material that will answer the DOE target for H_2 storage at higher temperatures and moderate pressures. It is not obvious from the presented data that incorporation of extra sites into the pores will lead to higher uptakes.
- The achieved storage densities are still below MOFs and activated carbons.
- This is not a major weakness, but greater collaboration will strengthen the project and aid refining the direction of the project.

Specific recommendations and additions or deletions to the work scope

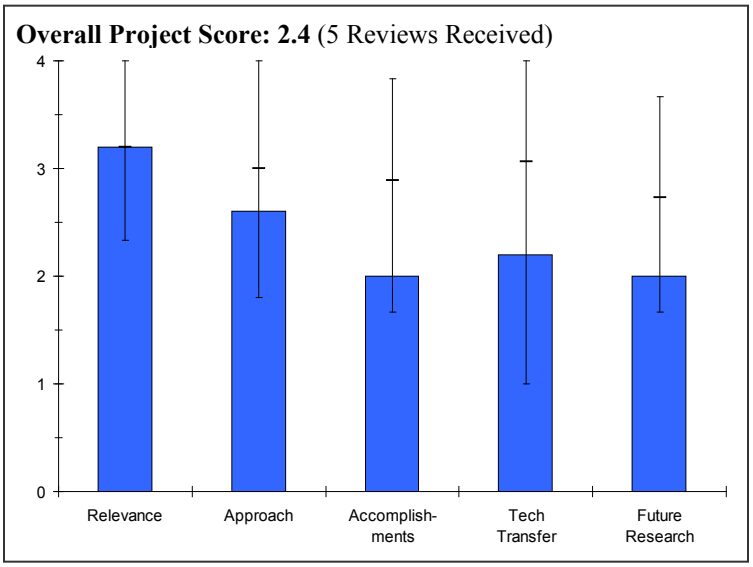
- The specific surfaces obtained so far seem somewhat low compared to MOFs and some activated carbons. Is it possible to increase it, or is there some limit to below 2,000 m^2/g? It would be interesting to see if the uptake scales with specific surface area.

Project # ST-28: Discovery of Materials with a Practical Heat of H_2 Adsorption

Alan Cooper, Hansong Cheng, Wade Bailey, Xianwei Sha, Garret Lau, John Zielinski, and Guido Pez; Air Products and Chemicals, Inc.

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 DOE 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 **3.2** for its relevance to DOE objectives.

- Materials with a practical heat of hydrogen adsorption are critical to the success of Hydrogen Program.
- Good relevance and hopeful signs from theory on the BC_3-related compounds, but disappointing results for graphite intercalation compounds (GIC).
- The project generally supports the objectives of the Hydrogen Storage Program.
- The project team focused on increased binding energy in sorbents and did not seem to address issue of volumetric capacity, which is two one of their main weaknesses.

Question 2: Approach to performing the research and development

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

- Use of modeling as a guide for synthetic targets appears to be promising.
- Although the approaches pursued in this project (H-adsorption on F-intercalated graphite and H-spillover in BC_3) are fairly high-risk, they are novel and broaden the overall scope of the Hydrogen Sorption CoE. There is a good mix of computational work (molecular dynamics [MD] simulations and energy path calculations related to spillover on BC_3) and experimental work (H adsorption in F-intercalated graphite).
- The computational techniques employed here are not adequate for the complex systems. Can they be used as a guide?
- Worth trying!
- Good idea, but limited approach.
- The approach appears ad hoc. For example, why was a graphite system chosen when the Center has many high surface area materials? How did F-/BF_4-GIC become a candidate? There are several experimental projects within the Carbon Center that could have used a basis for experimental approach. Was that considered?

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

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

- Concluding that fluoride materials are not practical H_2 storage materials is very useful information for other partners.
- Do the results of the first part of the work indicate that the approach was inadequate? What are the implications and critical analysis?
- In view of the conflicting experimental results, what does the spillover work simulation show?
- The GIC compounds exhibit lower adsorption density than traditional materials (AX-21, for instance). There is a definite problem with the specific surface of these materials, however, no measurable beneficial effect of BF_4-intercalants for AX-21.
- At what temperature and pressure is the calculated hydrogen intake for bulk BC_3?
- The isosteric heats of adsorption seem high compared to the achieved storage densities.
- The results obtained in 2009 are not consistent with the funding level for the project. There has been only very limited progress in 2009 on improved hydrogen adsorption in F(-)- and BF_4(-)-intercalated graphite. In 2008 nitrogen-doping of the graphite host was suggested as a strategy to increase the heat of adsorption. However, follow-up work employing this approach was met with only very limited success. Likewise, only minor progress on increasing the overall surface area is evident.
- Although the work on chemisorbed hydrogen on BC_3 sheets is showing more progress, the stability of the hydrogen-BC_3 bond at high loadings is problematic with respect to reversibility and cycling (the investigators have chosen not to pursue this experimentally). The pathway to overcoming this problem is not clear (i.e., is there evidence to support the notion that inclusion of other heteroatoms will modify chemisorption energies?).
- The F work had largely negative results, the B doping work does not look promising because of the very large chemisorptive binding energies and very little has been accomplished yet in terms of actual enhanced sorption measurements.

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

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

- Good team integration.
- The project does not seem to use or benefit from the considerable amount of work and experience that the Hydrogen Sorption Center of Excellence has been collected over the past few years.
- There are limited collaborations within the Hydrogen Sorption CoE and with external investigators on the two major materials systems being investigated in this project. Although there are numerous partners within the Hydrogen Sorption CoE working on spillover mechanisms, it is not obvious that this project is well-integrated with those efforts.
- Not clear how close the collaborations really are and whether a significant exchange of ideas is occurring.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.0** for proposed future work.

- Although not successful, the team did make a reasonable effort in completing the tasks.
- The proposed work is a straightforward extension of the on-going spillover work on BC_3. However, at this stage of the project, a more definitive statement of future work is needed in some of the project areas (i.e., "develop strategies for increasing surface area of BC_X materials" and "develop a systematic model of B content and H_2 adsorption enthalpy ..." are far too general and vague for a project that is more than 90% complete).
- There is a weak connection between the results and the future plan. A critical analysis of the results would be helpful especially with respect to approach and veracity of the techniques employed.
- The boron-containing compounds are worth exploring, although there has not been an experimental realization offering significant improvement towards DOE storage density targets in using spillover strategies as of yet.
- The B doping work seems to be a dead end given the large binding energies. It's not clear why this is being pursued.

Strengths and weaknesses

Strengths
- Project leverages extensive capabilities at Air Products in materials science and chemistry. The PI and his team are well qualified to conduct this work.
- Interesting approach from a fundamental point of view.
- Use of modeling as a guide for synthetic targets appears to yield promising approaches.

Weaknesses
- The project needs to identify the right types of material to study at the early stage. The down-select criteria for the approach should also be identified.
- The project is nearing completion, but future plans suggest an ongoing effort without a clear delineation of the outstanding technical barriers and obstacles. It seems unlikely that given the very general statements regarding proposed future work and with limited progress achieved in 2009 that a breakthrough on the BC_3/BC_X systems will be forthcoming.
- Overall, given the significant level of funding, the payoff from this project is low.

Specific recommendations and additions or deletions to the work scope

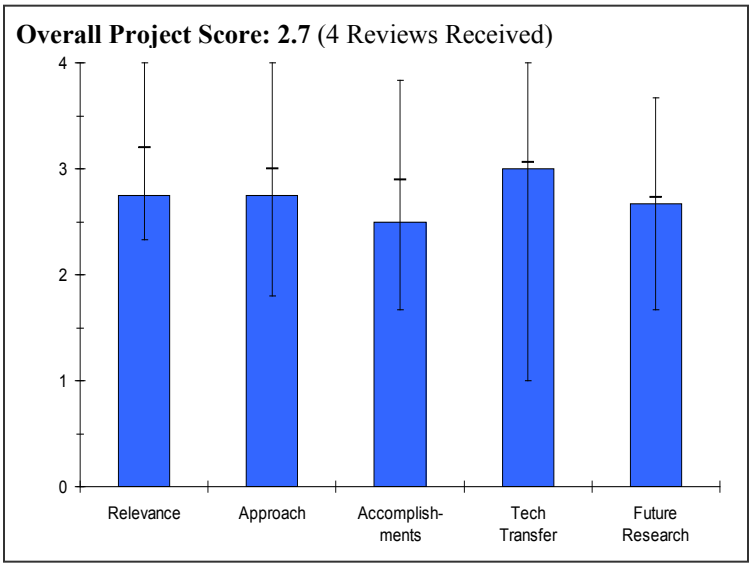
- Based on the approach and the results, it is recommended to rework the work scope and rationalize the first part of the project. The spillover work will also require some reconsideration in view of the question raised.
- With the limited time left for this project, the team should limit their effort in further exploring higher surface area BC_X materials.
- A very focused effort on the most promising aspect of the BC_3 spillover study is recommended. Dilution of the effort through inclusion of subordinate tasks would be counterproductive to the technical effort in the remainder of this project.

Project # ST-29: Optimizing the Binding Energy of Hydrogen on Nanostructured Carbon Materials through Structure Control and Chemical Doping

Jie Liu, Anmiao Wang, and Tom McNicholas; Duke University

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 DOE 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.

- Project attempts to address the need to optimize interactions between physisorption materials and hydrogen to increase binding energy. This is consistent with the DOE objectives.
- Relevant to DOE goals and objectives; however, unclear if this approach will ultimately be capable of achieving the short- or long-term targets.
- The project is investigating a range of microporous carbons (MPC) made from polyether ether ether ketone (PEEK). The rationale behind the project is to make small pores to increase the isosteric heat of adsorption. It is, however, unlikely that this alone will lead to significant room temperature uptake capacities.

Question 2: Approach to performing the research and development

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

- While the idea of modifying a high-temperature thermoplastic, such as PEEK, is intriguing from the perspective of future scale-up, the premise of the project plan does not seem to hold much promise. In particular, the essential premise is to make PEEK behave like a highly active, porous carbon through high-temperature treatment. This seems uneconomical since there are already activated carbons that outperform the converted PEEK product.
- Multifaceted approach toward achieving enhanced binding via control of pore size and incorporation of dopants.
- While these are both relevant approaches, it is not clear what the ultimate (ideal) materials characteristics are and why. In particular, pore diameters of <1 nm are targeted for the PEEK materials; however, it is not clear what binding energy is ultimately feasible if this goal is reached and whether the center's 15 to 25 kJ/mol H_2 binding is possible. For the boron substitution, it should be specified what the desired content of boron is and why.
- The group is relying on partners for porosity measurements and >2 bar hydrogen isotherms. The uncertainty about the values for the materials is a significant weakness in the project, which is not the fault of the investigators but sounds to be a problem in the CoE partners being overwhelmed with samples. This is slowing down the project, and the CoE should look into ways that it can service the characterization needs of its members.

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

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

- Nuclear magnetic resonance (NMR) analysis appears to be very useful and diagnostic for determination of micro- and macropore content. This capability is being fully utilized for efficient screening and characterization of materials.
- The conclusion that steam heat treatment of PEEK samples is more effective than that for carbon dioxide (stemming from preservation of microporosity) suggests promise and approaches the properties of state-of-the-art activated carbon but with potential for improved volumetric capacity. Given this important dependence between heat treatment gas and resulting structure/properties, it makes sense to perform a more systematic investigation of heat treatment gas size/composition and resulting PEEK pore structure.
- Survey of many materials with complete property summary. Nevertheless, materials capacities are still uncompetitive with other sorbents. Thus, it is unclear if this method is ultimately capable of reaching other state-of-the-art sorbents.
- A range of materials were made and higher isosteric heats of adsorption were measured. However, there is currently uncertainty that these very narrow pores can store the hydrogen as efficiently and what the high pressure capacities will be.
- As indicated from the results presented, it is evident that any manipulation of the PEEK processing conditions still only yields surface areas and gravimetric capacities that are comparable to an already commercially available activated carbon (AX-21). The statement that "PEEK-MPCs have significant H_2 storage capabilities compared to other pure carbon materials" is not supported by the data. PEEK-MPC is comparable to AX-21, with each yielding ~3 wt% at 2 bar and 77 K. Given that there are no gains in surface area, it is not likely that Pd-doped MPC will yield any major gains above current spillover materials (such as the Pd- or Pt-doped AX-21).

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

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

- Collaborations with NREL and University of North Carolina appear established and clear. Although in responses to reviewer's comment, it was pointed out that this work is quite different than that at University of Penn (also looking at boron doping). Nevertheless, at a minimum it is logical and reasonable to coordinate and communicate results between these two projects.
- The PI had little faith in the porosity analysis that its partners supplied. This needs to be addressed to improve the quality of the project. If there is a characterization capacity issue, then the CoE needs to address this (either by expanding capacity or prioritizing resources).

Question 5: Approach to and relevance of proposed future research

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

- Project needs to include in future work, room temperature sorption measurements on the highest surface-area PEEK-MPCs.
- Broader, systematic investigation of heat treatment gas size/composition and resulting PEEK pore structure.
- Gain an understanding of the theoretical potential for capacity and hydrogen binding energy for this approach.
- Higher pressure measurements to continue to understand comparison of PEEK materials with other carbon-based sorbents.
- Investigating B-doped carbons is a valid line of approach. This reviewer was unconvinced at the suggestion to investigate spillover enhanced hydrogen storage, especially as Ralph Yang predicted a maximum capacity of 2 wt%. Modeling work for B-doped carbons shows much greater likelihood of leading to enhanced uptakes, and the PEEK synthesis gives a versatile route to forming such materials with higher porosities and surface area.

Strengths and weaknesses

Strengths
- Project started with an intriguing idea based upon long-range potential for scale-up.
- Range of microporous carbons made.

Weaknesses
- Project has not devoted enough effort to characterizing PEEK-MPC materials in sufficient detail. What is the resultant state of carbon hybridization (Raman analysis)? What are the phase-change properties of the material (differential scanning calorimetry [DSC] measurements)? What is the room temperature hydrogen uptake? Are there other high-temperature thermoplastics that would give more favorable results?
- The characterization and high pressure H_2 isotherms are needed to assess the usefulness of these materials.

Specific recommendations and additions or deletions to the work scope

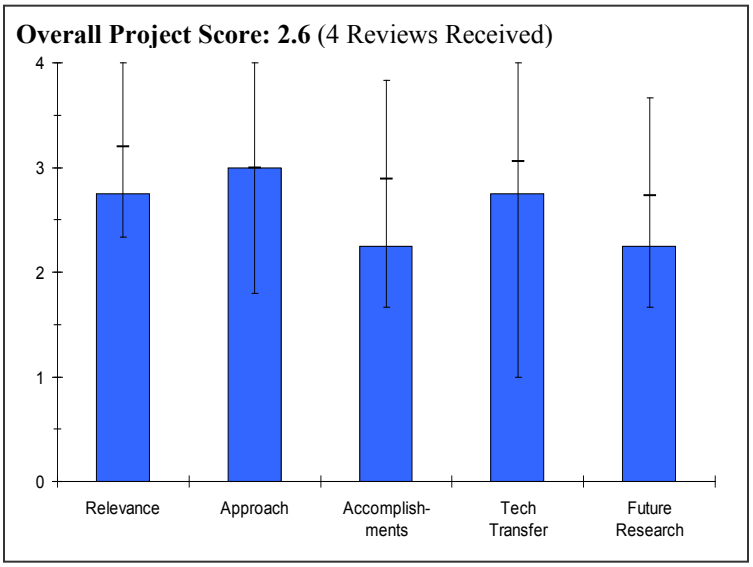
- Recommend abandoning PEEK-MPC materials. However, complete work to measure possible spillover effects.
- Suggest that PI focuses on doped carbons rather than investigating spillover catalysts.

Project # ST-30: Nanoengineered Graphene Scaffolds with Alternating Metal-Carbon Layers for H_2 Uptake at Ambient Temperatures

Carter Kittrell and James Tour; Rice University

Brief Summary of Project

The primary objective is to design and produce carbon-metal media and/or mobile nanoparticle catalyst in a graphene slit-pore scaffold to 1) achieve more than 9 wt% uptake of hydrogen, 2) be capable of exceeding 80 g/L volumetric uptake of dihydrogen at near ambient temperatures, and 3) simultaneously meet all major DOE 2015 targets and other desirable traits. This will be accomplished with fibers spun from a graphene slit-pore nanoengineered scaffold or with mobile catalyst particles to convert graphene to hydrogen-saturated graphane.



Question 1: Relevance to overall DOE objectives

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

- This project is well suited to the program's objectives and is one of the few open metal sites on carbon substrate projects with much hope of keeping those sites open over time. As such, this project could truly address mass and volume goals.
- The project is focused on the development of a specific material concept for hydrogen storage and attempts to meet the DOE targets.
- It is not really clear what the overall direction and goals are for this project. The synthesis effort seems good, but is not clearly connected to the DOE goals for storage. There are many statements are made about the H_2 storage properties of these materials, but essentially no data is shown.

Question 2: Approach to performing the research and development

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

- The approach is good and logically organized and has a good hope of functional success, if the technical steps can be achieved. It includes both science and engineering steps so the product, if successful, will have a better possibility of scale up. Some of the steps are less likely to be done well (e.g., properly spacing graphite at all points will be much harder than separating nanotubes).
- Enhanced binding of H_2 and utilizing spun graphene instead of single-walled nanotubes (SWNT) is a very good approach.
- Mobile Pd catalyst intercalation as "H_2 capture" might not work as expected since the catalyst would agglomerate and loose its small size and mobility.
- The advantages to using nanotubes for some measurements and for synthesis are not clear. Why study these materials when there is so much room for advancement on the graphene materials?
- The project team uses a unique approach of intercalating alternate layers of metal with graphene.

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

This project was rated **2.3** based on accomplishments.

- The project team made tubes of graphene and expanded them without lithium.
- There are four new data points on uptake chart.
- The concept of dynamic multilayer adsorption was proposed last year, but it is applied using SWNT. It is important to illustrate the synthetic viability and proof-of-concept using the graphene.
- Developed process for making metal intercalated graphene ribbons and measured enhanced H uptake compared to carbon.
- So far, it appears all of the measurements were made at 77 K. Room temperature behavior, that is, enhanced binding properties, have not yet been shown.
- Synthesis accomplishments are noteworthy, but it is not clear how this impacts the DOE storage goals and the CoE.
- The project team made less progress than expected relative to what was listed in last year's poster; in fact, many of the figures are the same.

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

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

- Good collaboration with NREL. There were other partnerships listed, but it was not clear what interactions/collaborations are active or whether they are productive. However, the level of collaboration is probably adequate since the PIs appear to be progressing well.
- The project team certainly talks to others, but there does not seem to be evidence of meaningful exchanges lately or value from the C & C.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- The project team seems focused on the right steps to make progress.
- There is not a whole lot of detail, but that is normal at the AMR.
- Few actual tasks are planned, but they will be difficult so that is fine.
- Mobile Pd catalyst intercalation as "H_2 capture" might not be feasible given that the catalyst would agglomerate and loose its small size and mobility.
- Focus on illustrating the graphene functionalization and metal intercalation to illustrate the concept viability.
- There was no discussion of future work.

Strengths and weaknesses

Strengths
- Working to reduce costs of material.
- Very good experience with CNT systems.

Weaknesses
- It was not very clear that there is actual progress toward goals; the capacity is too low and was unchanged over the years. It is the same pictures and concepts each year and not much advancement.
- Graphene metal intercalation and functionalization concepts illustration.

Specific recommendations and additions or deletions to the work scope

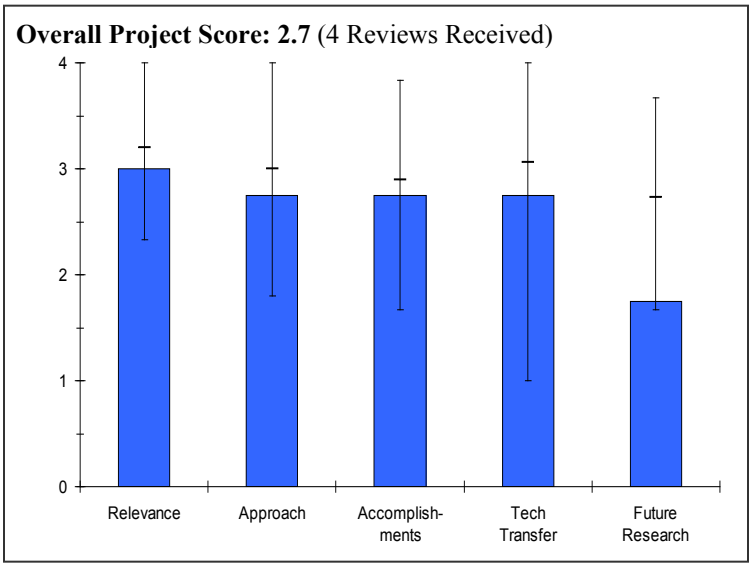
- The project team really needs to get a full-pressure pressure-concentration-temperature (PCT) done because the 2-bar capacity (i.e., tank has no usable H_2) may also be the high-pressure capacity given how much above the Chahine rule the 2-bar data is.
- Propose to focus on graphene dynamic multilayer work.

Project # ST-32: A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part I

Jean M.J. Fréchet, Martin Head-Gordon, Jeffrey R. Long, Thomas J. Richardson, and Samuel S. Mao; University of California, Berkeley

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 **3.0** for its relevance to DOE objectives.

- The project is exploring a subset of novel materials and processes with potentially useful hydrogen storage properties. The project contains elements that are unique within the overall DOE Hydrogen Storage Program, and, for the most part, the project is well-aligned with Hydrogen Program goals.
- Relevance to Hydrogen Program goals is adequate. The project investigates a number of interesting nanostructured framework materials (e.g., hypercrosslinked polymers, metal organic frameworks [MOF]) based on a synergistic approach that includes theoretical modeling and materials design aspects.
- Highly relevant project which fully supports DOE research objectives.

Question 2: Approach to performing the research and development

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

- The development and testing of hypercrosslinked polymers and other nanoporous polymeric materials as hydrogen storage media is an intriguing and worthwhile approach.
- The approach is well designed, combines modeling and characterization, but needs to focus further on the most interesting and promising systems for the last phase of the project.
- On the basis of the overall program topic listing, the breadth of this project is extensive and spans basic science and applied research.
- A simply stated R&D approach that includes the rationale and criteria that drives the selection of compounds would be helpful. For example, a wide range of materials, from hypercrosslinked polymers to substituted MOFS, to paddlewheel frameworks, and to several other metal-substituted porous coordination solids is being explored. What criteria are driving the selection of those particular compounds?
- While the general approach for this project was not provided and remains unclear, one can infer that it has evolved into a multifaceted strategy toward realizing increased binding energies in sorbents (e.g., polymers, MOFs).
- The additional task related to destabilization of metal hydrides (i.e., partial substitution of MgH_2 with Mn, Fe, etc.) has already been exhaustively studied. It is unclear what is new beyond the dearth of previous work.
- Not clear what the purpose is of the destabilized work on MgH_2. Work on alloying of this hydride has been ongoing for decades, and it is not clear what the present project will do to overcome the obstacles for this material that no one else has been able to overcome.

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

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

- Good progress is being made on characterizing the hydrogen sorption properties in hypercrosslinked polymers and other porous coordination solids. These are novel materials for hydrogen storage, and understanding their sorption behavior directly complements the work in other EERE projects (especially efforts in the Hydrogen Sorption CoE).
- The results from calculation of substituent effects are interesting and may provide a predictive capability for compound selection. Have any of those predictions been experimentally validated?
- Very impressive results on high-capacity gravimetric and volumetric storage in MOF-5 at 77 K.
- The destabilization work on the enhanced utilization and improved cycling capacity of MgH_2 in the presence of a MgF_2 additive is an important new contribution.
- A number of promising and original systems have been identified. This includes the Mn-BTT, $M3(BTC)_2$, and Zn-BTT structures, as well as the addition of MgF_2 in MgH_2 that offers the possibility for enhanced desorption amounts despite added weight. Interesting new knowledge is generated by the project in that respect.
- Hydrogen storage in hypercrosslinked polymers has promise but appears to be relatively slow moving.
- Beryllium analog of MOF-177 is a good synthetic achievement. Based on low-pressure measurements, higher pressure uptake looks promising. However, obvious concerns regarding the potential toxicity of material would have to eventually be considered/addressed.
- Nice library of frameworks possessing open-metal sites. Should be aware of potential overlap with Texas A&M University and University of California, Los Angeles, who both have projects in the same area.
- The concept of using Cr (m) (or other metal) functionalized linkers was presented in the 2008 AMR. What progress is being made in regard to synthesis and experimentation?
- Despite a large amount of data, the overall results are quite disappointing in terms of the actual sorption measurements.

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

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

- Some collaboration is reported, especially with industry.
- A great deal of independent, non-EERE collaborations appears to be established; however, it is not clear that there are ongoing, regular communications between other independent projects and/or the Sorption CoE. Strengthening of such communications is highly recommended.
- Although internal collaborations (within University of California, Berkeley) are occurring, collaborations with other institutions are not readily apparent. Extensive efforts on porous coordination solids and MOFs, as well as on destabilized systems are ongoing in other Office of Energy Efficiency and Renewable Energy (EERE) projects. Collaborations and interactions with those groups (especially the CoEs) would be beneficial.

Question 5: Approach to and relevance of proposed future research

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

- Future plans are not clearly described. Only limited information concerning future work is provided in a few of the results slides. Likewise, there is very little mention of the remaining technical barriers that must be addressed. A more detailed research plan that focuses on the remaining obstacles is needed.
- Future work suggested interesting elements (e.g., Zn-BTT structures and the addition of MgF_2 in MgH_2), but the investigators need to focus to those that are most promising as the project end approaches fast.
- Beyond a few indirect comments at the bottom of the slides, no clear discussion of future work was given.
- Future plans were not described.

Strengths and weaknesses

Strengths
- Well-qualified team exploring hydrogen-surface interactions in novel porous coordination materials. The project is generating results that will be important in understanding the details of hydrogen adsorption in nanoporous media.
- Very high expertise on the topics studied.
- Interesting innovative ideas on a number of framework materials and metal hydrides.

Weaknesses
- Only limited information concerning the overall approach is provided. Rationale for selection of specific chemical systems and compounds is missing and virtually no information is given about remaining obstacles and future plans for overcoming them.
- There is a lack of focus on promising aspects.

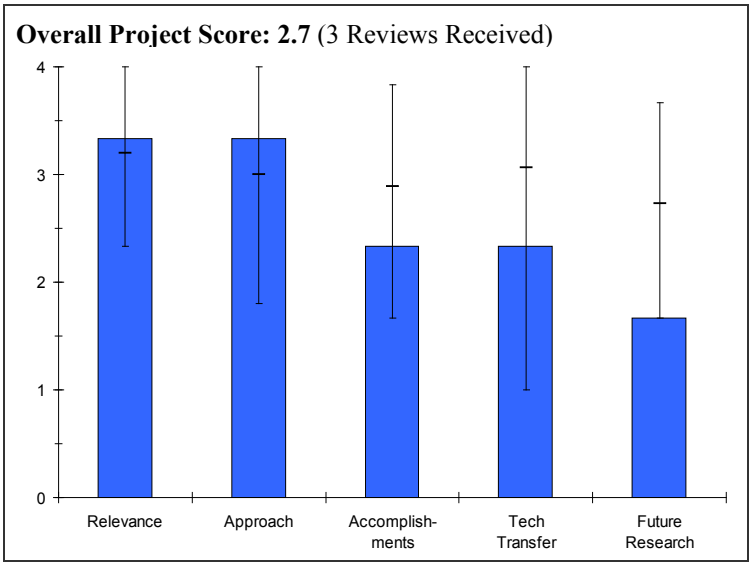
Specific recommendations and additions or deletions to the work scope

- A large number of chemical systems are currently being explored. In the remainder of the project it will be important to focus on the most promising set of materials. The priority should be established by the most critical technical barrier(s) and the investigation of materials that are capable of most effectively meeting those challenges.
- Project finishes soon and the only suggestion would be to focus on the promising aspects of the work.

Project # ST-33: Hydrogen Storage in Metal-Organic Frameworks
Chris Doonan and Omar M. Yaghi; University of California, Los Angeles

Brief Summary of Project

The objectives of this project are to 1) research the relationship between metal organic framework (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 **3.3** for its relevance to DOE objectives.

- The project has a high relevance to the DOE R&D objectives. The capabilities and expertise of this project are among the best in the sorbent area, one of the primary classes of hydrogen storage materials.
- This project is well aligned with goals of mass- and volume-efficient storage.

Question 2: Approach to performing the research and development

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

- The approach of increasing the hydrogen storage of MOFs at room temperature by improved binding energy demonstrates a correct focus on the key challenge associated with such materials. This project appears to be actively developing and testing numerous strategies (e.g., metal and linker modification and impregnation) in this regard.
- The approach is reasonable.
- Attempting to increase binding energy with new corners and metal sites.
- Replace ligands or atoms on attached groups with active metal, in addition to simply decorating on rings.
- No specific slide on approach was used in this presentation. Coordination with theory was poor, and no apparent feedback to theory was employed.

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

This project was rated **2.3** based on accomplishments.

- The project has not actually realized significant progress in improved binding energy via the numerous outlined approaches, but it is clear that quite a bit of research and testing has been done. Although progress was not demonstrated, the focus and development on the most challenging area for this class of materials is technically significant.
- Every sample that was made showed performance that was worse than already published data. If the PI had presented some rationale, it would have been of some value. Instead, the investigators have put all of their effort into metal additions that do not have a likely chance of producing a material of technological value.

- Slide 5 shows volumetric data, but this is for a theoretical single crystal of material. Are the investigators proposing that this is what will be employed? If they want to discuss volumetric density, they need to indicate a real material packing density as a function of the theoretical crystal density.
- Made many new systems, but headway was minimal. Still, the techniques are good (leaving aside use of Pd and Sc as major mass components of material).
- Even though all this work was done with DOE funding, it seemed to overlap with much outside work that has been presented elsewhere.
- I doubt that the fourth route, making structures with very large pores, is likely to meet the volumetric requirements, even with metal groups. The PI should show how that would work first.

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

This project was rated **2.3** for technology transfer and collaboration.

- The presentation did not highlight the role of the partners within this project. The collaboration with BASF is beneficial for an industry-scale perspective.
- While one might infer that showing computational results from collaborators suggests that collaboration is taking place, it has never been clear that theoretical structures with high delta H can be synthesized. There has not been an example of a material that has been modeled and synthesized that is of relevance to this program.
- Largely independent work, perhaps because the PI is seen as a leader. Still, leaders can help the whole portfolio by collaborating with other teams.
- They have partners, but only Goddard group seemed to be relevant to the DOE work.

Question 5: Approach to and relevance of proposed future research

This project was rated **1.7** for proposed future work.

- The future work information was limited and could be expanded to provide confidence in the progress and plans for the next steps.
- Plans were scant and vague. They have done interesting work in the past though, so one hopes this will continue.
- No “Future Work” slide was included.

Strengths and weaknesses

Strengths
- This group makes a lot of material.
- World leading team.
- Capable of making the measurements and exotic compounds well.

Weaknesses
- This group makes a lot of material, but appears to do so as an end in itself.
- Somewhat unfocused.
- Not clear that DOE gets full value, much of this work is presented in other forums also and seems to sell the same work to several funders.

Specific recommendations and additions or deletions to the work scope

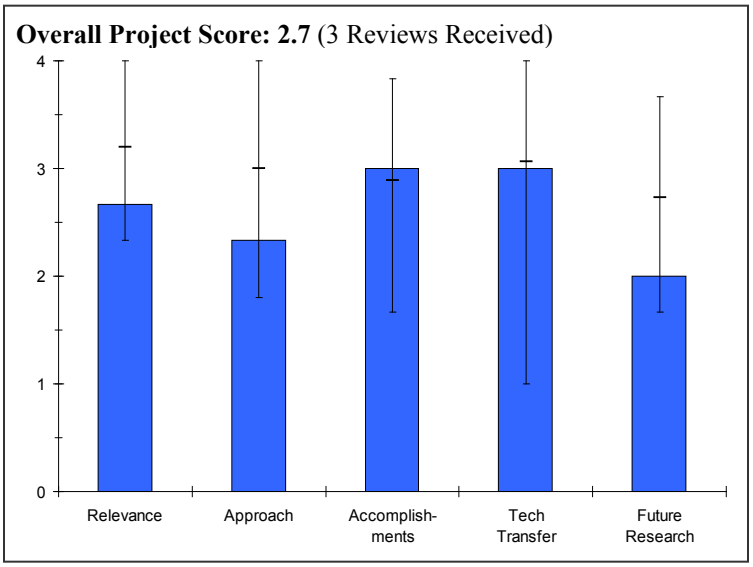
- More closely monitor what work is being done for DOE and discuss future plans to verify that plans are suitable.

Project # ST-34: Compact (L)H_2 Storage with Extended Dormancy in Cryogenic Pressure Vessels

Gene Berry, Salvador Aceves, Francisco Espinosa, Tim Ross, Vernon Switzer, Ray Smith, and Andrew Weisberg; Lawrence Livermore National Laboratory

Brief Summary of Project

Cryogenic pressure vessels offer technical potential to exceed 2010 hydrogen storage goals and approach the 2015 goals. The project objectives are to build systems exceeding 2010 volume/weight targets in collaboration with industrial partners and to understand the fundamental potential of both system and H_2 behavior. Approaches include to 1) fabricate third generation cryotank storing >45 kg H_2/m^3 system, 2) achieve more than 1 week of dormancy, 3) understand dormancy impacts of para-ortho conversion, 4) investigate composite vessel impacts on vacuum quality, 5) demonstrate adequate cycle life (cryogenic shock, high pressure), 6) perform cryogenic vessel development and burst testing, and 7) explore superliquid H_2.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.7** for its relevance to DOE objectives.

- Adequate and convenient on-board hydrogen storage is one of the key challenges to fuel cell vehicle commercialization. This project is developing one option to meeting DOE targets.
- Vessel design is a required research activity for meeting the DOE objectives. The optimal pressure and temperature operating regime must be investigated with the effects of sub-ambient temperature systems in concert with pressure fully understood.
- The project supports enhancing the gravimetric and volumetric capacity, however, the storage temperatures are still very low.

Question 2: Approach to performing the research and development

This project was rated **2.3** on its approach.

- The project is building on past experience to achieve extended dormancy, verify cycle life, and continue cryogenic vessel development.
- Biggest issue is the excessive size of the tank. The density can be made to look artificially good since bigger systems tend to have better densities. A 225l tank is 2 to 3 times larger than the tank required for the FreedomCAR targets. Unfortunately, the storage density of this tank system will decrease significantly as the tank size decreases. This type of system is best suited for large commercial and transport vehicles that have high fuel requirements and relatively low dormancy events.
- The utilization of high-pressure tanks with cryogenic H_2 practicality could be an issue (i.e., liquefaction cost, unknown tank component integrity).

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

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

- PI continues to refine and understand the limits of the technology.
- They have refined vessel and structural designs to reduce weight, reduce heat in-leakage, and improve vacuum jacket reliability.
- They are working closely with an automobile original equipment manufacturer (OEM) (but outside of this project) to address some real-world issues.
- The third generation showed improvement over the previous generation.

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

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

- Choosing BMW as an automotive partner will help the PI to understand vehicle requirements and costs.
- They are working with an automotive OEM and a composite tank manufacturer.
- New collaborations started, however, recommend strong collaboration with ANL and TIAX to conduct well-to-wheel analysis.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.0** for proposed future work.

- This project needs to address the infrastructure and fueling interface issues.
- The energy required for fueling is prohibitive.
- The interface is complicated/undefined, and not likely applicable for the whole fleet.
- This technology needs to find a compromise on temperature and pressure to make it more compatible with standard pressurized fills (5,000 psi).
- PI should investigate the use of storage materials in the system that either increase dormancy or reduce the fill cooling energy requirements (endothermic materials) to make the system feasible on an energy basis.
- The planned future work is described in rather generic terms and lacks specificity. It is difficult to evaluate the merits of the planned work.

Strengths and weaknesses

Strengths
- This system is achieving real world results.
- This project has been an evolutionary one, where each improvement builds on previous developments.
- They are validating concepts and designs with in-vehicle installation and testing.
- Engineering system capabilities.

Weaknesses
- Choosing BMW as an automotive partner will help the PI to understand vehicle requirements and costs. However, BMW's business case tends to favor high-end (expensive), large, and powerful cars. This model could favor larger tanks, but may not align with the entire range of the U.S. fleet mix that the FreedomCAR targets wish to address. One must question the viability of a technology that requires a completely different filling infrastructure from other methods if it is only applicable for quarter of the U.S. fleet.
- The PI has not provided sufficient information (as in past) regarding the charging interface and energy requirements for tank fill. There are many fill scenarios that could make this system more or less applicable to the targets. They need to narrow in on the optimal fill protocols and temperature/pressure specifications.
- There were no weaknesses identified.
- Focus on gravimetric and volumetric capacity and oversight of liquefaction costs.
- There needs to be a well-to-wheel cost analysis.

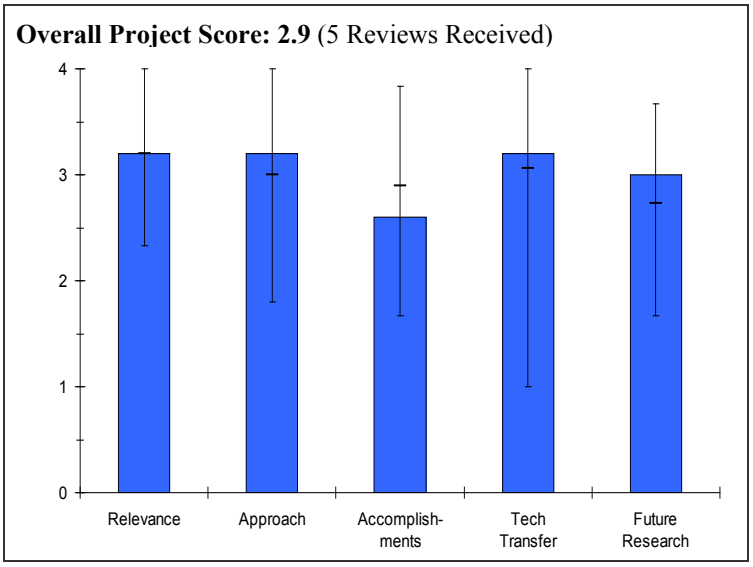
Specific recommendations and additions or deletions to the work scope

- The project should identify and address institutional issues such as 1) public perception and acceptance of liquefied hydrogen as an automotive fuel and 2) the evolution of safety standards and relaxation of U.S. Department of Transportation (DOT)-type constraints.

Project # STP-01: Lifecycle Verification of Polymeric Storage Liners
Barton Smith and Lawrence Anovitz; Oak Ridge National Laboratory

Brief Summary of Project

The overall objective of the project is to verify durability of polymer liners in high-pressure storage tanks. The approach will include 1) subject polymer specimens to extreme temperature cycling while pressurized with hydrogen, 2) measure hydrogen permeation at prescribed intervals to assess the ability of the liner materials to maintain the required hydrogen barrier capability, and 3) test protocol derived from SAE J2579, Technical Information Report for Fuel Cell and Other Hydrogen Vehicles (January 2008).



Question 1: Relevance to overall DOE objectives

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

- It is important to verify the lifetime of tank liner materials, and it is especially important to determine lifetime under cycling conditions.
- The durability of hydrogen storage tank liners is almost as important as the durability of fuel cell systems.
- It is important to understand the failure modes of tank liners and the influence of ambient and operational parameters on the failure mechanisms for the liner materials.
- Definitely pertinent and relevant given that polymeric liners are now being used.
- The work is relevant to the hydrogen program goals and objectives.
- The overall objectives of the project, and how it fits into the gaseous and liquid storage effort, was not discussed or illustrated. This should be communicated in the future.

Question 2: Approach to performing the research and development

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

- The size of the liner test specimens is too small to be representative of total liner area. Larger specimen sizes should be considered.
- They are exposing 1-cm-diameter samples of tank liner polymers and subjecting them to extreme temperature (-40 to +125°C) and pressure (6,250 to 12,500 psia) cycles. The specimens are then tested for hydrogen permeation.
- They are using standardized test protocols as recommended in SAE reports.
- Additional details on how permeation measurements will be carried out should have been discussed (i.e., what is actually contained in SAE J2579).
- Even though project has NOT delivered results yet (based on experimental difficulties around seals), the approach is truly innovative and "out-of-the-box" in working at constant pressure while executing thermal cycles. Normal recommendations: pressure cycle at different temperatures.
- Project is also limited in scope, but the presenter was truly excellent.
- Project leverages previous work.

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

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

- They have built and put into service an automated pressure and temperature cycling system, and they have begun testing polymer samples with it.
- They have successfully addressed issues of leak-tight specimen mounting at low temperatures and high pressures.
- This project is a new start and, hence, little or no data has been generated thus far. However, good progress on set-up of experimental apparatus.
- Project has shown great understanding of the issues.
- My contention is that we should move to aromatic polymers (e.g., aromatic amides or imides) because they are better materials than high density polyethylene (HPDE) in barrier properties.
- Progress appears to be slow, and the project is behind schedule. After almost a year, the May 2009 milestone is only 50% complete.
- I only rated it fair because of stage of progress: no definitive results because of experimental difficulties in sealing.

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

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

- Collaborations are with tank suppliers and are appropriate.
- They are collaborating with industrial developers of hydrogen storage tanks and polymer liner materials.
- The project team is working with the key players in the industry.
- The project team is partnering with leading organizations in application space.

Question 5: Approach to and relevance of proposed future research

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

- The project team will conduct hydrogen permeation tests at 1,500 and 5,500 cycles at 6,250 psia and then begin testing at 12,500 psia.
- If the project is continued into the next year, they will test alternative tank liner materials.
- The approach is clear and to the point.
- The project needs to be accelerated. Tank liner durability needs to be verified as soon as possible.

Strengths and weaknesses

Strengths
- Good laboratory facilities, personnel, and external collaborators.
- This project addresses the pressing need to acquire cyclic permeation data on candidate barrier materials for hydrogen storage systems.
- Innovative approach of thermal cycling at constant pressure versus pressure cycling at constant temperature.

Weaknesses
- No weaknesses identified.
- No weakness noted.
- Test specimen size needs to be increased.
- Progress needs to be accelerated.
- Experimental problems in analysis of permeation properties.

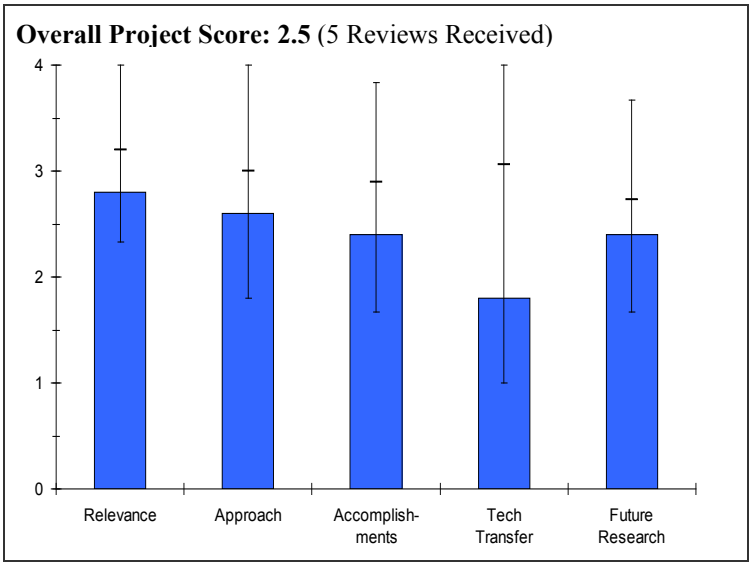
Specific recommendations and additions or deletions to the work scope

- Execute the test plan and future work as proposed.
- Include more discussion on the experimental details of standard test methods employed so that an assessment can be made about their relevance to polymeric materials.
- Continue to correct sealing problem so that experiments can be ran.
- Move to aromatic polymers because of their improved barrier properties.

Project # STP-02: Electron-Charged Hydrogen Storage Materials
Chinbay Q. Fan; Gas Technology Institute

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 2008 were to 1) combine internal electron-charge (doping) and external charge to increase hydrogen storage capacities and 2) investigate performance optimization and prototype container systems. Objectives for 2009 are to 1) reselect the best hydrogen storage materials for charge modifications and 2) explore carbon-based materials, such as AX-21 and other high surface carbon using polymer as a precursor, metal-modified carbon, and ammonia-borane.



Question 1: Relevance to overall DOE objectives

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

- The project addresses the hydrogen storage targets related to cost, storage capacity, refueling rate, and durability.
- This project offers a unique approach that needs to be fully explored for its potential to assist on-board hydrogen storage.
- Shows promise for higher capacities.
- Fits the objective of kinetics, but capacity and operating temperature are probably more important focus in sorption.
- In the big picture, this is relatively low impact.
- This project is researching the usefulness of external and internal (doping) electron-charges to increase hydrogen storage capacity and hydrogen desorption kinetics. It was initiated in 2005. Results to date are not at all promising in terms of having the major positive impact on hydrogen storage materials required to meet the DOE targets. The cost of this approach would seem to be quite high. It does not appear to be a very useful project to the DOE Hydrogen Program.

Question 2: Approach to performing the research and development

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

- The project has taken the approach of modifying the electron charge distribution structure to increase the hydrogen uptake and sorption kinetics.
- Good exploration of effect of electric fields, both internal and external, on the adsorption of carbons and hydrogen release and reabsorption in ammonia-borane.
- Interesting approach. Should get independent confirmation of results and have a clearer theoretical explanation of the results. It would be useful to know what metals were used for materials modification; the metals cost may make the system too expensive.
- The project is stated to be only 55% complete, but is 80% of the way through its time schedule (began in 2005 and ends in 2010).

- There are well-planned milestones and go/no-go decisions, yet it is not at all clear that the September 2008 milestones were met.
- Task 6, due to be completed by July, 30 2009, calls for scale-up to an 11-liter tank for fueling. The project seems nowhere ready for this and has not demonstrated significantly improved useful performance of a storage system based on the project's approach.
- The project is primarily focused on increasing wt% hydrogen adsorbed, with some work also being done on adsorption/desorption kinetics. There is no attention being paid to the DOE volumetric target for the system or target cost considerations.
- The project has recently shifted its focus from increasing the wt% of carbons to trying to increase the rate of desorption of aminoborane. Aminoborane is being studied by the Chemical Hydride CoE. It is not clear why this project is looking at it or how electrostatic charging would increase its rate of desorption, though it appears to be having that effect to some degree.
- The approach is fine, but also appears pretty Edisonian. There is not much understanding of the mechanism or what is happening at the surface.

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

This project was rated **2.4** based on accomplishments.

- The effect was demonstrated and is interesting, however the design appears difficult to scale. There is no assessment of what the data mean in terms of impact to a system design, operating conditions, and so on.
- The technique has shown some encouraging results for AX-21 at room temperature, but the improvement is small at cryogenic temperatures needed for adequate storage capacities. The project has now shifted focus to boron nitride material.
- Significant increases in capacity at low pressures. Analysis is needed to find the "sweet spot" for optimum storage.
- There has been some good science and experiments done. There has been some positive impacts of electrostatic charging on carbons and aminoborane in terms of improving hydrogen wt% stored and increasing the desorption rates respectively. However, the results are very modest and fall far short of DOE targets.
- Interesting effects of electric polarization; however, capacities are low in most cases. Understanding and overcoming capacity limitations will be vital going forward. Some characterization efforts were delayed by slow sample turnaround by others.

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

This project was rated **1.8** for technology transfer and collaboration.

- The project is collaborating with State University of New York (SUNY)-Syracuse. The arrangements with a Japanese manufacturer and University of Houston were also mentioned.
- Work with SUNY is good, but need to get independent confirmation of results and analysis of ultimate system capacity and cost. Should work with OEM or tank manufacturer to understand how system might be manufactured and implemented.
- There is no evidence of collaboration except for obtaining some storage material candidates from SUNY. Collaboration with the Japanese charge control agent (CCA) manufacturer; ATMI, Inc.; and the University of Houston is mentioned but it is not clear what this "collaboration" entailed. There is no collaboration with any of the DOE CoEs or the many other universities and organizations in the hydrogen storage arena.
- Some collaboration indicated with SUNY-Syracuse, ATMI, University of Houston, and a Japanese manufacturer.
- This appears to be an independent effort.

Question 5: Approach to and relevance of proposed future research

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

- The project proposes to continue the boron nitride work and scaling up to an 11-liter tank.

- The 11-liter prototype is good step; however, before it is built, investigators should get independent confirmation of results and analysis of ultimate system capacity and cost.
- The future work plan is reasonable, but the lack of significant progress of this approach to hydrogen storage makes one question the value of this effort.
- It was unclear if this would continue. In terms of overall impact to the sorption cause, this appears lower priority with respect to other activities within the Hydrogen Program.
- It would be interesting to address the following question: What happens if the material, say metal modified AX-21, starts filling in the absence of an electric field, and then the field is increased in situ (i.e., referring to Slide 9) to 2,000 KPa in the absence of field, and then slowly increase the field to +100 V)? How does the hydrogen capacity respond?

Strengths and weaknesses

Strengths
- Knowledgeable and experienced PI.
- Adequate facilities.
- Some initial success with capacity improvement of metal-modified AX-21 at room temperature and enhanced desorption kinetics of boron nitride material.
- Novel approach.
- Demonstration that applied electric fields and/or polarized materials appear to influence hydrogen storage characteristics, in particular kinetics, of adsorption materials and ammonia-borane. Unique approach to augmenting hydrogen storage. Partial re-hydrogenation of ammonia-borane.

Weaknesses
- Lack of theory.
- Initial results are not very positive.
- Need to know if increases in H_2 capacity seen so far are really enough to make a difference in a final system. There is no clear vision of whether the increases in capacity are enough to enable materials.
- This project is researching the usefulness of external and internal (doping) electron-charges to increase hydrogen storage capacity and hydrogen desorption kinetics. It was initiated in 2005. Results to date are not at all promising in terms of having the major positive impact on hydrogen storage materials required to meet the DOE targets. The cost of this approach would seem to be quite high. It does not appear to be a very useful project to the DOE Hydrogen Program.
- It is not at all clear that the milestones that were due in September 2008 have been met.
- The project is primarily focused on increasing wt% hydrogen adsorbed, with some work also being done on adsorption/desorption kinetics. There is no attention being paid to the DOE volumetric target for the system or target cost considerations.
- There is no evidence of collaboration except for obtaining some storage material candidates from SUNY. Collaboration with Japanese CCA Manufacturer, ATMI, and the University of Houston is mentioned, but it is not clear what this "collaboration" entailed. There is no collaboration with any of the DOE CoEs or the many other universities and organizations in the hydrogen storage arena.
- Not clear whether high capacities can be achieved or maintained with this approach. System cost will be increased by additional hardware, however this might be mitigated by augmented control available through applied fields (i.e., another real-time knob to turn in controlling system behavior). Some lack of familiarity with the hydrogen storage literature.

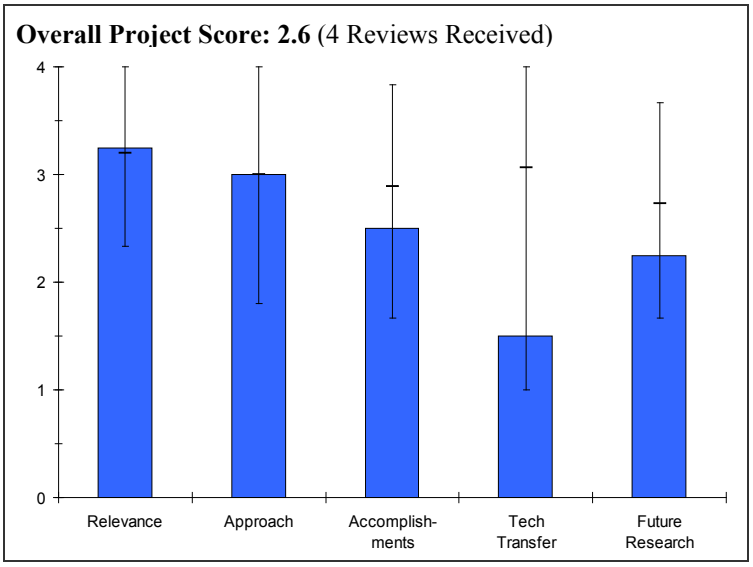
Specific recommendations and additions or deletions to the work scope

- This project is still in an exploratory stage. It appears premature to initiate the proposed scale-up effort.
- Techno-economic system analysis. Cost estimates for material and tank.
- This project should be terminated.

Project # STP-03: Polymer-Based Activated Carbon Nanostructures for H_2 Storage
Dr. Israel Cabasso; State University of New York

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 the potential to meet DOE 2010 system-level targets.



Question 1: Relevance to overall DOE objectives

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

- Increasing surface area and getting into an appropriate pore structure is really driving the entire adsorption area at the moment. This is consistent with that goal.
- Overall the concept is well within the Carbon Center activities even though this is an independent project.
- Project aligns generally well with DOE hydrogen research objectives.

Question 2: Approach to performing the research and development

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

- Approach is clear and comprehensive, containing all necessary elements for a productive research program (i.e., synthesis, processing, and testing capabilities). It was good to see focus shifting toward strategies which could increase binding energy (for ambient temperature storage).
- The reviewer understands the approach but does not seem to have a clear understanding of the data. If there is in fact a substantial increase in the temperature at which these materials operate, then there should be a substantial change in the heat of adsorption. This was not demonstrated in the poster. Although significant capacity was claimed at -25°C, the data was not shown. Why? This is the most important result.
- The approach is well within the norm.
- There does appear to be potential overlap with Duke concerning polyether ether ketone (PEEK) materials, which both research groups are actively investigating.

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

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

- It is evident that a large number of materials have been prepared and tested. Moreover, the corresponding property correlations that have been insightful for establishing trends in behavior.
- A good number of samples were tested, but the results need to be independently validated. This data will be highly controversial until another laboratory can validate the claims.
- It is imperative to have the higher adsorption temperature samples tested independently (for example, at Southwest Research Institute [SwRI]).
- While the goals of this effort make sense, a lot of data is presented in tabular form, for 77 K H_2 uptake. These numbers do not make much sense. I have never seen data from carbons that exceeded ~5.5 wt% but some of the carbons reported on page 12 have values above 6.5 wt%. At least part of the problem is that the investigators have not made a distinction between mass and wt%. The isotherms on page 14 do not appear to be characteristic

of a predominantly microporous carbon. I would have expected isotherms to appear more "Langmuir" with a maximum between 20 and 40 bar. At 60 bar, the H_2 adsorption data continues to rise. Because there is no discussion of how the data were obtained, it is impossible to judge the accuracy of what is presented. The data on page 19 indicating 8 wt% H_2 release at dry ice temperatures is incorrect. Given that this is a solvated carbon, and given no mass spec data, other organic groups being released. The adsorption enthalpies for these materials make an 8 wt% release impossible.

- The PIs have been able to make high surface area substrate with impregnating compounds to increase the adsorption energy. Some results indicate a possible effect on adsorption/desorption temperature. While the implications are significant and noteworthy, the results are not clear.
- The PIs state that some samples could adsorb at ~ −50°C but no data is shown. The highest TPD data is at ~ −120°C.
- The table of materials is very informative and is a testament to the breadth of work. When reporting volumetric densities in this table, it is helpful to provide what material density form this is in respect to. That is, are these based on single crystal, loose powder, or tableted densities?
- The performance of the Melem-Carbon blends appear promising, however, it is interesting that with only a 14 kJ/mol·H_2 binding energy room temperature uptake is possible. This seems at odds with thermodynamics given the temperature and pressure ranges.
- For the "solvated"-carbon alloy work, what is the identity of the "solvent"? And, is the solvent volatile under the measurement conditions? That is, has it been ensured that only hydrogen is being released?

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

This project was rated **1.5** for technology transfer and collaboration.

- It the response to reviewer's comments section, the collaborations are mentioned. However, it would be helpful in the future to integrate these efforts into the presentation because, in the current form, it is not clear the extent or value of these interactions.
- This appears to be an independent effort. Collaboration is needed to validate results.
- All the hydrogen measurements appear to be done by one company, Gas Technology Institute (GTI). There seem to be errors in the way that data is measured or processed, resulting in the work that been rendered virtually valueless.
- Further collaboration with other team(s), especially the SwRI measurement group or Carbon Centers, could be very valuable to the project. It is important for PIs to do their best and utmost to share samples and further validate their results.
- Communication with between the State University of New York (SUNY) and Duke University is recommended in the area of PEEK materials which both groups are actively working on.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- This project was ending. Validation would be worthwhile.
- This work needs to be done in collaboration with someone who can report the uptake data accurately, otherwise the correlation between synthesis and uptake properties have no meaning.
- See comments in Recommendations.
- The focus on exploring methods to increase hydrogen binding energies is appropriate and valuable. More detailed analysis of the preliminary compositions (i.e., Melem or solvated carbons) which could involve residual gas analyzer (RGA) would also be beneficial.

Strengths and weaknesses

Strengths

- Philosophically, the correct approach in designing sorbents.

Weaknesses

- Inaccurate uptake measurements.
- Need better measurement techniques through utilization of existing project and collaboration with appropriate teams within the program.

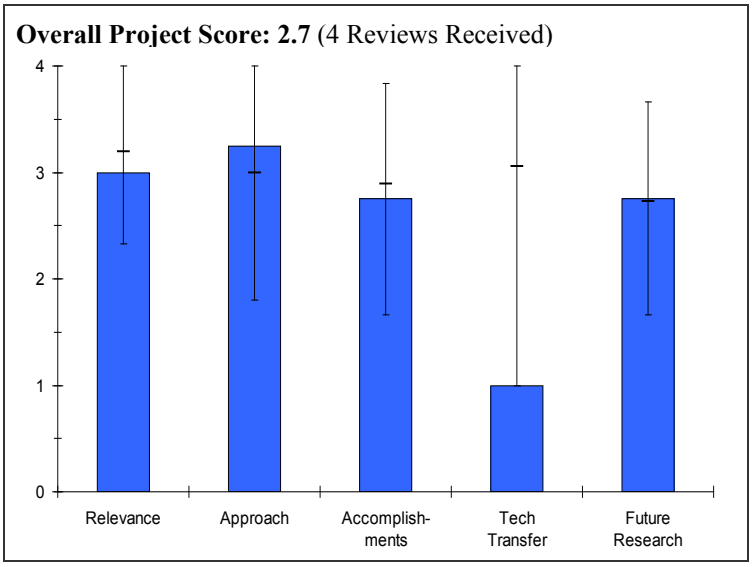
Specific recommendations and additions or deletions to the work scope

- It is important to independently test and verify the veracity of the high-temperature adsorption materials stated by the PIs. Further support for this project should be contingent upon verifications of the aforementioned claims.

Project # STP-04: Low-Cost High-Efficiency High-Pressure H_2 Storage
Carter Liu; Quantum Fuel Systems Technologies Worldwide Inc.

Brief Summary of Project

The overall objective of this project is to improve the cost and weight efficiency of Type IV compressed H_2 storage vessels to approach the 2010 DOE targets by reducing raw material costs through material development and design and manufacturing parameter modifications. The project is split into the following tasks: 1) plastic liner development, 2) metal fitting development, and 3) optimization of carbon fiber composite usage.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- Development of low-cost, high-efficiency tanks for compressed hydrogen storage is directly relevant to DOE Hydrogen Program objectives.
- High-pressure tanks are the only viable option for storage of hydrogen on board vehicles at the present time. Even though tanks cannot meet the DOE ultimate targets for weight and volume, they have the potential to meet the 2010 targets and are in virtually every fuel cell vehicle on the road today.
- Cost-effective tank development is a crucial piece towards achieving the DOE objectives. However, this project looks to be an engineering exercise instead of a high-risk research project that could result in a disruptive technology to current Type IV tanks construction methods.
- PI was not present; review is based on read of presentation only.

Question 2: Approach to performing the research and development

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

- PIs and Quantum have considerable experience in designing and manufacturing carbon fiber composite tanks for high pressure gas storage.
- Good approach to address cost and weight by focusing on liner development, metal fitting, and optimization of carbon fiber composite.
- Quantum is investigating various options to reduce the weight and cost of 700 bar tanks to meet the DOE targets.
- PI is proposing incremental improvements to an existing technology that will not meet the DOE objectives.

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

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

- Considering that this is a new project (Start Date: July 2008), good progress has been made.
- There does not appear to be a great deal of progress in the project to date. Most of the presentation concerns future work.
- PI did not demonstrate any results from the blow molding trials. This process is not new – INERGY in collaboration with Lincoln composites have already evaluated several different materials with blow molding processes.

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

This project was rated **1.0** for technology transfer and collaboration.

- They should be partnering with fitting companies (e.g., Parker, Swagelok) for boss development and plastic blow molding experts for their liner work. No partners have been indicated.
- No external collaboration or partners as yet.
- There are no partners associated with the Quantum effort.

Question 5: Approach to and relevance of proposed future research

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

- Proposed future work is well planned to reduce material cost by more than 50% and weight by about 15%.
- The 50/50 cost share is appropriate for an engineering exercise.
- Almost all of the presentation related to future work. The approach is good, but there are limited results.
- Future work will lead to incremental gains and will not result in the significant improvements in cost, weight, etc. required to meet the DOE goals.

Strengths and weaknesses

Strengths
- Significant experience in designing high-pressure tanks for hydrogen gas storage.

Weaknesses
- Lack of external collaborations.

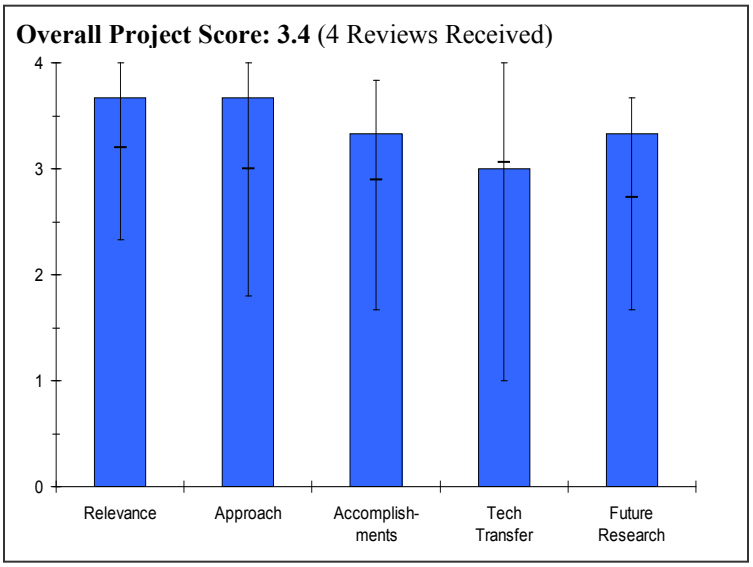
Specific recommendations and additions or deletions to the work scope

- No specific recommendations were given.

Project # STP-17: Solutions for Chemical Hydrogen Storage: Hydrogenation/Dehydrogenation of B-N Bonds
Karen Goldberg, Mike Heinekey, Tony St. John, Brandon Dietrich, Travis Hebden, and Steve Matthews; University of Washington

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 DOE 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 **3.7** for its relevance to DOE objectives.

- This research team is developing new catalyst materials for the ammonia borane desorption reaction. The catalysts being developed are Ru-based and Co-based. The team established the performance level of the costly Ru-based metallorganic catalyst and is working on lower-cost Co-based metallorganic catalysts. In their earlier work, they have stabilized the highly exothermic ammonia borane desorption reaction by mixing with an endothermic hydride. This is a very nice strategy.
- This project is of great importance for the Chemical Hydrogen Storage CoE's work on B-N materials and how to improve H-discharge rates by exploring catalysts, as well as screening for new materials.
- Project objectives primarily centered on catalyst design for ammonia borane (AB)-based dehydrogenation. Effective strategies for demonstrating improved kinetics in hydride-based storage reactions (e.g., via catalyst identification) remains a key area of focus toward reaching the DOE goals.

Question 2: Approach to performing the research and development

This project was rated **3.7** on its approach.

- The major technical barrier being addressed is to improve the desorption kinetics in ammonia borane through catalysis.
- The team is combining theory/computational work with experimental work in catalyst design. This is always a very effective platform in new materials development.
- The project is well designed, but it wasn't clear if there was a systematic search for new materials and catalysts? This procedure could have been better clarified.
- Efforts surrounding investigation of organometallic catalysts for AB dehydrogenation add value to Chemical Hydrogen Storage CoE. This approach provides for catalyst optimization (activity and stability) by exploring various metal-ligand combinations.
- The large scope of catalyst metal-ligand candidates should attempt to be narrowed by understanding the identity and role of intermediate AB species. In doing so, the catalyst structure could be more rationally designed to favorably interact with intermediates. This year's work appears to begin to focus on this task (i.e., using electrospray ionization mass spectrometry [ESI-MS]).
- Tasks related to exploring endothermic (and potentially on-board reversible) C-B-N compounds are interesting and leverages theory to guide experiments.

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

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

- The group has used experience with the performance of Ru-based catalysts to move on to Co-based catalysts (a less expensive and more readily available starting material).
- Within the Co-based catalysts, the team has tested an assortment of at least four different organic functional groups attached to Co. The outcome of those tests is a potential catalyst, which the team will pursue for future studies.
- The team did not directly address go/no-go decisions in their project planning matrix. However, it was clear from their presentation and planned future direction that performance measures for the Co-based catalysts were considered. Additionally, the development of catalysts for the ammonia borane system is at such an early stage (for all researchers in this field), that a clear measure during development is that some catalysts simply do not work. With that said, it would still be a useful activity if the authors were to "spell out" performance measures for acceptable catalysts.
- It was not clear what other catalysts, or how many catalysts, had been tried.
- Progress toward the identification of products/intermediates via ESI-MS techniques is clear and should prove very valuable for catalyst design. However, it was unclear how the identification of these product oligomers is linking to subsequent selections of catalyst metal/ligand combinations (i.e., still appears to be trial-and-error based)? Many of the catalysts shown here seem the same as last year (e.g., with Co).
- Work on C-B-N heterocycles also appears relatively slow moving. No data on these compounds, which were proposed last year, were provided. What is the desorption/decomposition profile for these molecules?

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

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

- The University of Washington team is working collaboratively with the University of Oregon, University of Alabama, PNNL, and LANL. This represents a good mixture of universities and national laboratories contributing to the effort. Each group has a well defined project goal: the University of Oregon is working on catalyst development, the University of Alabama is working on thermodynamic predictions, PNNL on gas phase chromatography, and LANL building comparable catalysts with differences in the organic functional groups (relative to the University of Washington's catalysts).
- The poster did not highlight contributions/comparisons/collaborative work with the LANL catalysts. Only after discussing the project did the PI mention the role of LANL in alternative catalyst development. Perhaps the collaboration with LANL is not developing as firmly as with the other collaborative efforts.
- The team has appropriate collaborations, but it perhaps needed to get help from another institute on the synthesis of catalysts to increase the outcome.
- Clear collaboration with University of Alabama for computational data on C-B-N compounds, as well as University of Oregon for synthesis and testing, is apparent.
- Further coordination of research and data with PNNL in the area of determining AB intermediates is encouraged and should be helpful for rationale design of catalysts.

Question 5: Approach to and relevance of proposed future research

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

- The proposed future work is building on their past experience and steady progress is expected on the identified tasks in support for the Chemical Hydrogen Storage CoE and towards meeting the DOE technical barriers.
- Proposed work is logical extension of current work. More focus on HOW ligand and metal selections for future catalysts will be made (on what basis?) is important for determining ultimate efficiency of this project (e.g., trial-and-error vs. rationale design).

- The team did not directly address go/no-go decisions in their project planning matrix. However, it was clear from their presentation and planned future direction that performance measures for the Co-based catalysts were considered.

Strengths and weaknesses

Strengths
- This project represents a very good mixture of synthesis, experimental testing, characterization, and computation-guided work relevant to metal organic catalyst development for a promising hydrogen storage material system.
- Focuses on crucial issues for improving materials that has potential to meet the DOE targets.

Weaknesses
- The collaborative with LANL seems to be lagging behind the development of collaborative efforts with PNNL, the University of Oregon, and the University of Alabama.
- The team did not directly address go/no-go decisions in their project planning matrix. The team should develop performance targets and assess catalysts according to those performance targets.

Specific recommendations and additions or deletions to the work scope

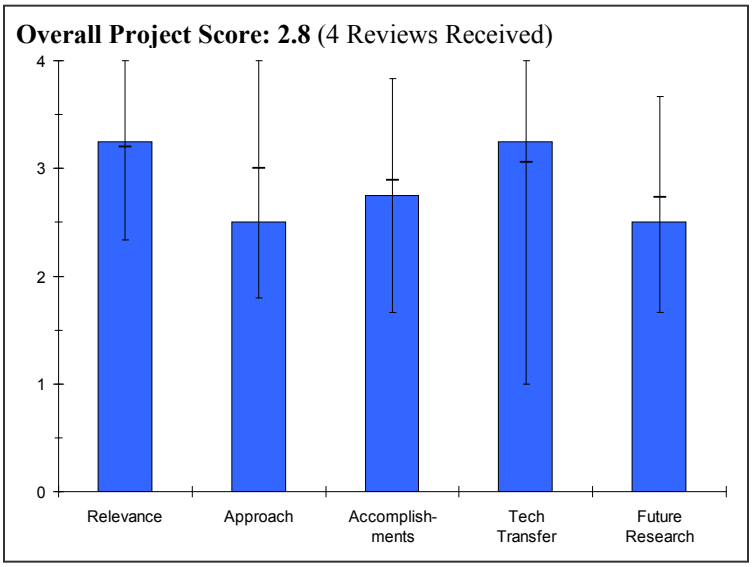
- The idea of adding an endothermic hydride to stabilize the ammonia borane (exothermic system), and to remove some of the excess heat associated with H_2 desorption from ammonia borane, is an excellent one.
- The researchers may also consider other endothermic hydrides, such as borohydrides or other complex metal hydrides.
- A more quantitative assessment of the heat released (per gram of ammonia borane) and heat taken in (per gram of endothermic hydride) would be a good addition to this work.

Project # STP-18: Chemical Hydrogen Storage Using Ultra-High Surface Area Main Group Materials & The Development of Efficient Amine-Borane Regeneration Cycles

Philip P. Power and Susan M. Kauzlarich; University of California, Davis

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 borane 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 AB with light element hydride nanoparticles.



Question 1: Relevance to overall DOE objectives

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

- Efficient regeneration of spent ammonia borane is a primary area of focus in the Chemical Hydrogen Storage CoE and aligns with the DOE RD&D objectives.
- This is an interesting project.
- Chemical hydrogen materials are one of the primary routes to meeting the hydrogen storage challenge. And, regeneration of candidate materials is considered to be one of the major issues facing the identification of viable chemical hydrogen materials.
- Project is relevant to one of the regeneration schemes of ammonia borane, as being investigated by the Chemical Hydrogen Storage CoE.
- The work on regeneration of AB, assuming formic acid and metal hydrides are available commercially, does not constitute a closed-cycle regeneration pathway.

Question 2: Approach to performing the research and development

This project was rated **2.5** on its approach.

- The approach is reasonable, systematic, and appropriate.
- The light element hydride nanoparticles work is interesting.
- Tasks related to augmenting hydrogen release properties of AB are relevant. However, the effort here (involving addition of nanoparticles) appears somewhat redundant and at the expense of focusing on the primary regeneration project.
- Approach on AB regeneration by the formate system with the use of formic acid will not likely lead to a viable scheme.
- Creation of a simple, efficient chemical regeneration cycle for ammonia borane remains a critical area of research in the Chemical Hydrogen Storage CoE. The approach of this project (involving main group formates) is complimentary to the larger regeneration effort in the CoE.
- Good progress. Rigorous plan with go/no-go decisions; good turn around.

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

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

- Progress to date is reasonable. The down-select of candidate systems is an important step in the overall chemical hydrogen process. This project has effectively eliminated systems that are not viable and has moved on to the more viable approaches.
- Light element hydride nanomaterials eliminate foam problem associated with H_2 release.
- Effects of nanoparticles on kinetics and elimination of foam are not well understood.
- No results on impurities (i.e., borazine NH_3, diborane), a very important issue.
- What is the ratio of nano-BN to AB? The ratio directly affects the H_2 material capacity
- For the task related to addition of nano-BN to AB, the amounts of BN being explored seem much more than typically employed (e.g., 4:1 BN:AB) if the intent is to use BN as "catalytic" product seeds. This large amount of "dead weight" BN also suggests a drastic decrease in capacity. What is the effect of adding much smaller amounts (e.g., 1 to 5 wt%) of BN?
- Limited meaningful progress on regeneration of AB.
- In the area of AB regeneration, progress is apparent with respect to synthesis, testing, and down-selection of appropriate tin formates. Additionally, "down-selected" reactions are beginning to be optimized by substituting undesirable reactants/products (e.g., NaCl).

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

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

- Extensive collaborations with other partners in the Chemical Hydrogen Storage CoE have greatly benefitted this project.
- Good collaboration with CoE partners.
- Need better coordination with the CoE regarding approach of work, such as those involving formic acid in regeneration pathways.
- Coordination for the regeneration efforts (e.g., with PNNL and LANL) appear to be in place. Additional collaborations are encouraged to routinely estimate regen efficiency, which can aid in the direction of current and future regen reactions/pathways.
- Given the numerous other strategies that are currently being pursued in the Chemical Hydrogen Storage CoE for augmenting hydrogen release from AB, this relatively narrow scope of adding nano-BN might fit better at PNNL where the testing is already occurring.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.5** for proposed future work.

- Future plans for this project are sound and reasonable and will support joint CoE efforts.
- Proposed work on preparation of meso-BN to optimize hydrogen release is sound.
- While kinetics is very important, the issue of impurities can be problematic. Need to quantify the release of impurities.
- Future work on AB regeneration that does not involve formic acid is in the right direction.
- The proposed future work suggests that the metal formate regeneration approach will be abandoned, being replaced with hydrogenolysis. Is there a reason for terminating the formate-based route?
- If BN nanoparticle work is to be continued, suggest significant reductions in the amount of additive (e.g., to catalytic levels). It is recommended that this work be completed as a lower priority to that for regeneration.

Strengths and weaknesses

Strengths
- Rigorous plan with go/no-go decisions, good turn around.
- Strong technical approach.
- Collaborations with other CoE partners.
- Significant experience in experimental work on synthesizing nanomaterials.

Weaknesses
- More detailed discussion of efficiency and scale-up would be nice.
- Absence of data on the release of impurities from AB with nanoparticle additives.
- Pursuit of formic acid route toward regeneration of AB is fruitless.

Specific recommendations and additions or deletions to the work scope

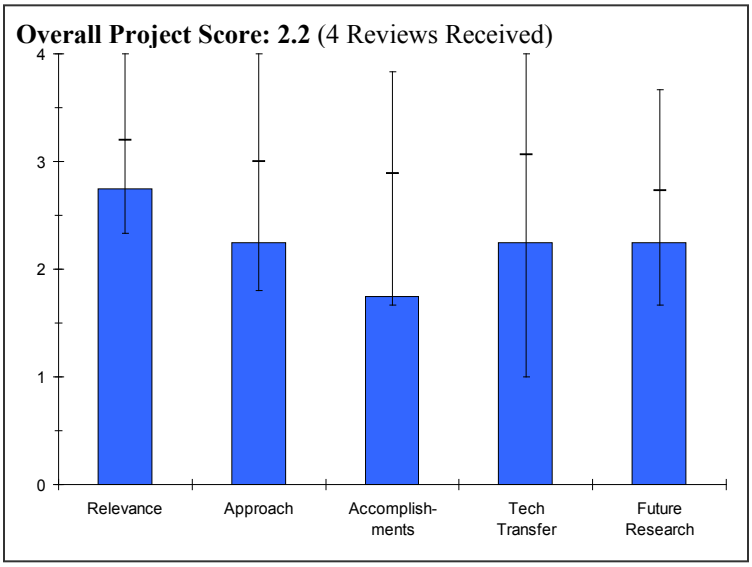
- Work on formate route with formic acid should be discontinued because it is no longer considered an acceptable approach for regeneration of AB spent fuel.

Project # STP-19: Electrochemical Hydrogen Storage Systems

Dr. Digby Macdonald, Justin Tokash, Jason McLafferty, Dr. Amr Saleh, and Dr. Rezwana Sharna; Pennsylvania State University
Dr. George Engelhardt; OLI Systems

Brief Summary of Project

The objectives of the project are to 1) demonstrate an electrochemical route to the conversion of spent ammonia borane (AB) (lower hydride) back to AB fuel (higher hydride) to meet DOE 2010 regeneration process goals, 2) explore the feasibility of electrochemical regeneration of organotin hydrides for use as a reagent in the regeneration of AB, and 3) develop a general model of electrochemical impedance spectroscopy to study coupled reaction mechanisms and utilize the model to extract kinetic parameters from experimental data.



Question 1: Relevance to overall DOE objectives

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

- Looking at a major roadblock for ammonia-borane systems − AB regeneration.
- Electrochemical regeneration of spent fuels being investigated in this project differs markedly from the chemical regeneration approaches in the Chemical Hydrogen Storage CoE. This generally broadens the scope of the spent fuel conversion effort. Since the development of an efficient method for regenerating spent fuels is a linchpin issue for chemical hydride technologies, this project is a useful and potentially valuable complement to the more conventional methods.
- Project is supportive of regeneration efforts for ammonia borane.

Question 2: Approach to performing the research and development

This project was rated **2.3** on its approach.

- The use of EIS for analysis of reaction mechanisms is an important component of the overall approach. The electrochemical reactions investigated here are complex and strongly coupled. The use of EIS for elucidating mechanisms and key reaction steps will be vital to developing an understanding of the reaction sequences.
- Addresses regenerating spent ammonia borane, the major roadblock for ammonia-borane systems.
- Electrochemical reduction has some potential advantages.
- Utility of electrochemical impedance spectroscopy (EIS) model has not been demonstrated.
- The fundamental basis for pursuing this approach has not been stated in a compelling way.
- Although the electrochemical regeneration approach is novel and potentially useful, a more detailed description of predicted energy balance(s) and efficiency, as well as a comparison of those predictions with results from more conventional methods, would greatly help to motivate the present approach.
- The project has made a significant effort to reconfigure itself, given the fact that the electrochemical approach for the direct regeneration of ammonia borane was unsuccessful.

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

This project was rated **1.8** based on accomplishments.

- Interesting results have been obtained on hydrogenation using the Devanathan cell.
- Experiments with Devanathan-Stachurski cell showed low conversion of simple test material (styrene to ethylbenzene - 17% in 6 days). Tests not yet performed with material of interest.
- Metal hydride electrodes for R_3SnH regeneration have not been successful.
- EIS model development is completed, and validation with ferrocyanide is underway. Model has not yet been able to provide impact on systems of interest.
- Progress has been slow and results limited for a project that started in 2005. Electrochemistry of these systems may be more complicated and not provide simpler routes to regeneration than chemical methods.
- Only limited experimental results are provided on electrochemical regeneration of ammonia borane and on solution-based generation of inorganic hydrides using the new Davanathan-Stachurski cell. At this stage of the project (>70% complete), it is expected that a stronger proof of feasibility and a more extensive base of supporting data would be available. Likewise, the EIS model has only been validated using a comparatively straightforward (single-electron) reaction in ferricyanide. Although the extension to the more complex reactions involved in AB regeneration is non-trivial, it should be viewed as a crucial part of the project.
- No information is provided concerning the important issue of overall efficiency. Without experimental data (or at least predictions from modeling studies) it is impossible to assess the efficacy and utility of the electrochemical regeneration work.
- It is not clear how the developed model will help develop practical AB regeneration strategies.

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

This project was rated **2.3** for technology transfer and collaboration.

- Good collaboration in attempting to find a role for the electrochemistry approach in the regeneration of ammonia borane.
- Collaborations with other CoE members are present, but they do not seem to be productive.
- Although there are collaborations with PNNL and LANL (the two lead organizations in the Chemical Hydrogen Storage CoE) are listed, it is not readily apparent what roles those organizations are playing or what specific contributions they are making to this project. The project would benefit greatly from a closer collaboration with those organizations, especially in the area of benchmarking the electrochemical regeneration results with results obtained from other methods in the Center. Likewise, beyond a purely advisory function, it is not clear what role Rohm and Haas is playing in the project.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- The proposed future work is reasonable, given the fact that the project is in its final stages.
- Plans for R_3SnH regeneration appear to focus on developing analytical techniques to characterize products. This should not be the focus.
- Plans to demonstrate electrochemical transformation of ammonia borane are vague.
- The most important remaining technical obstacles are not clearly identified. A clear and detailed statement of technical barriers is needed to provide a proper context by which to assess the future work.
- The future work statement is very general; it does not inspire a great deal of confidence in the ability to understand and test the electrochemical regeneration concept described here.

Strengths and weaknesses

Strengths
- Good collaboration with other center members.
- Development of an understanding of the reaction chemistry.

- The EIS analysis capability is an especially valuable component of this project. The use of this tool can hopefully guide the experimental work by providing a better understanding of the complex reaction steps involved in the electrochemical processes being explored here.
- Excellent electrochemistry expertise.

Weaknesses

- Too much work on model systems (i.e., styrene-ethyl benzene and ferrocyanide) versus work with systems of interest (e.g., ammonia borane, R_3SnH).
- An identification of the critical technical barriers and a sharply focused effort that addresses those barriers is needed. The project is nearly complete; without a focused effort, it is unlikely that a meaningful conclusion concerning the utility of the electrochemical approach will result from this work.
- The electrochemistry approach does not present that much utility for ammonia borane regeneration.

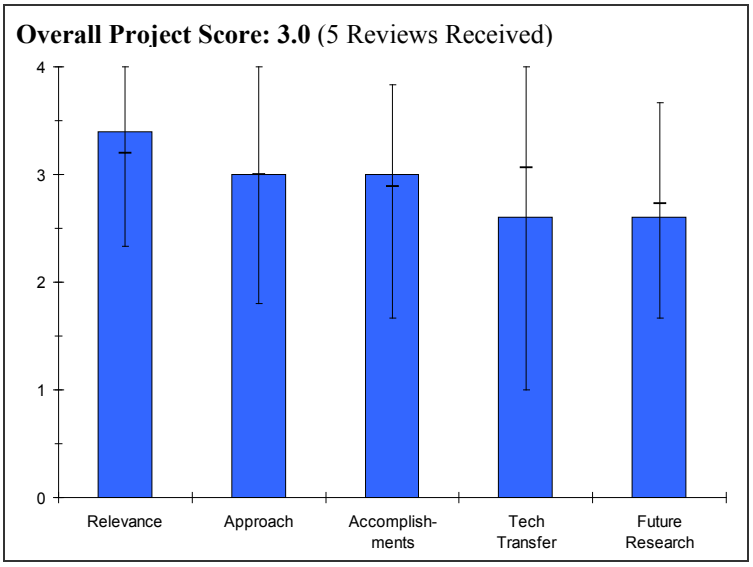
Specific recommendations and additions or deletions to the work scope

Rapid validation of the EIS model for complex reaction systems is needed. A parallel, very focused effort on AB regeneration is critical. Recommend less effort on the organotin system.

Project # STP-20: Chemical Hydrogen Storage Using Aluminum Ammonia-Borane Complexes
Satish S. Jalisatgi, Jianguo Wu, and M. Frederick Hawthorne; University of Missouri - Columbia

Brief Summary of Project

The objectives of this project are to 1) evaluate aluminum amidoborane derivatives as hydrogen storage candidates that can achieve DOE targets; 2) in collaboration with CoE partners, develop efficient thermal dehydrogenation methods for hydrogen release from aluminum amidoborane derivatives; and 3) in collaboration with CoE partners, determine a suitable route for the regeneration of the spent material.



Question 1: Relevance to overall DOE objectives

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

- The project is quite relevant to the DOE Hydrogen Program objectives. Aluminum aminoborane complexes and their derivatives have high hydrogen capacity that can meet the DOE targets.
- This project is making important contributions to the total effort of the Chemical Hydrogen Storage CoE by studying viable candidate materials.
- Project goals and targets are aligned with H_2 Storage Sub-program targets.
- $Al(NH_2BH_3)_3$ and other systems being investigated have a high enough material storage capacity that they may be able to meet targets. They are looking to influence reaction rates and improve hydrogenation with Al addition.
- The issues/barriers addressed by this project include the following:
  - Hydrogen storage system gravimetric and volumetric targets.
  - Flow rate.
  - Overall energy efficiency.
  - System cost.
  - Regeneration process.

Question 2: Approach to performing the research and development

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

- The approach is technically sound and logical. It is consistent with the joint directions of the Chemical Hydrogen Storage CoE.
- The approach to look at Al-(ammonia borane [AB)] compounds to try to influence rates of hydrogen release and uptake has merit. The Al should alter chemistry some, but not drastically from B. Previous work showing regeneration of AlH_3 suggests that this approach may lead to easier or direct regeneration. They have addressed hydrogen release issues, but need to increase focus/work looking at regeneration, which is still the major barrier for this class of materials. They have not addressed the effect of Al on regeneration.
- Evaluate aluminum amidoborane derivatives as hydrogen storage candidates that can achieve DOE targets.
- In collaboration with CoE partners, develop efficient dehydrogenation methods for hydrogen release from aluminum amidoborane derivatives.
- In collaboration with CoE partners, determine a suitable route for the regeneration of the spent material.
- The approach centers on the basis that Al-AB complexes will have lower enthalpy on dehydrogenation than AB. The poster does not present evidence that this is indeed true.

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

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

- Good progress continues to be made in this project. Project milestones have been accomplished on the established project schedule.
- Have made $Al(AB)_3$ and $LiAl(AB)_4$ and have demonstrated reduced H_2 release temperature for $Al(AB)_3$.
- Synthesized $Al(AB)_3$, $LiAl(AB)_4$ complexes, and their ammonia adducts in good yields.
- Preliminary dehydrogenation studies indicate Al-AB complexes release hydrogen at 60°C, lower than AB alone. They currently release 8+ wt% H_2 at <190°C.
- Thermogravimetric analysis-mass spectrometer (TGA-MS) studies show that the ammonia adduct forms of Al-AB complexes tend to release ammonia. (These forms need to be avoided.)
- Two key milestones were met.
- Several Al-AB complexes have been synthesized and characterized. Al-$(AB)_3$ starts to release hydrogen at around 60°C, lower than AB alone. Li $Al(AB)_3$ starts to release hydrogen at around 175°C. NH_3 Al-$(AB)_3$ releases ammonia when heated. Preliminary differential scanning calorimetry (DSC) analysis indicates that the hydrogen release is exothermic.

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

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

- Extensive collaborations have occurred during the course of this research with other partners in the CoE.
- Collaboration appears to be good across the CoE. Direct collaboration with LANL and PNNL is evidence.
- DOE Chemical Hydrogen Storage CoE (LANL, PNNL).
- Should University of Missouri, Columbia (UMC) have broader collaborations in the Chemical Hydrogen Storage CoE?
- Collaboration not evident in this project. Not clear what collaborators provided to this project. Collaborators listed as working on regeneration efforts, but no regeneration efforts were discussed.

Question 5: Approach to and relevance of proposed future research

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

- Plans for future work in this project are logical and complete and will ensure the timely completion of the proposed research program.
- Continue the analysis of hydrogen release from new materials.
- Determine long-term stability of new materials.
- Establish hydrogen release kinetics for new materials.
- Determine solid state structures.
- The proposed future work continues and builds upon the success of the current work. There ought to be some emphasis on understanding how clean the release is. Stability of the material needs to be established. In what form is the spent fuel?
- Future work plans do not focus on the major issue for these materials, which is regeneration. Future work needs to look at regeneration and the effect of Al on regeneration of amino-borane type materials.

Strengths and weaknesses

Strengths

- Strong technical research activities.
- A systematic approach is being taken to address the research objectives of the project that is consistent with the overall objectives of the Chemical Hydrogen Storage CoE.
- The primary mentor of the group at University of Missouri, Columbia (Professor Fred Hawthorne) has world-class experience in the synthesis chemistry required for success in meeting program objectives.

- The resources at LANL and PNNL help this project move forward in an orderly fashion.
- Directly related to the CoE objectives.

Weaknesses

- The project team needs more work in the regeneration area.
- The proposed future work was very generally stated. It needs more specificity (approach details) and more depth (e.g., which new materials and why).
- It seems that UMC does the synthesis work while LANL and PNNL do much of the characterization work. It's not clear how much work is being done for $350K/year.
- It is not clear how involved Professor Hawthorne is in the detailed planning and execution of the project.
- Not much time left in the CoE lifetime to establish this work, if the material is viable and can be regenerated.

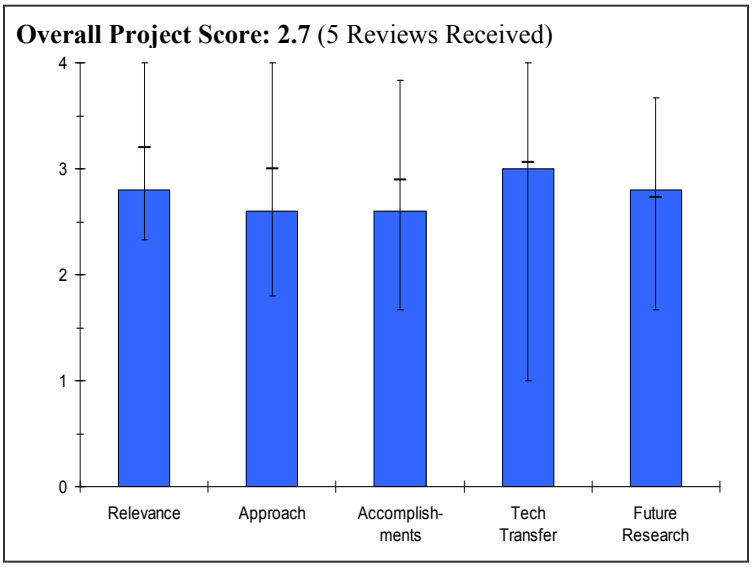
Specific recommendations and additions or deletions to the work scope

- The Chemical Hydrogen Storage CoE needs to evaluate whether the general types of materials under study at UMC have a chance of providing a leading candidate for on-board storage compared to the other promising material types under study in the CoE. Aluminum seems too heavy an element to be a viable hydrogen storage material when one takes account of the fact that, for any aluminum amidoborane, one cannot remove all of the hydrogen and expect to be able to perform a cost-effective regeneration. So, the question is "Can aluminum amidoboranes achieve upwards of 11 wt% H_2 (a likely material gravimetric target that permits meeting system targets) and also pass the acceptable regeneration litmus test?"

Project # STP-21: Novel Metal Perhydrides for Hydrogen Storage

Jiann-Yang Hwang, Shangzhao Shi, Steve Hackney, Douglas Swenson, and Yunhang Hu; Michigan Technological University

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 objectives over the past year were to 1) study the H_2 adsorption behavior of material systems having charged species in the material structure, 2) design and develop material systems capable of auto-charging under H_2 pressure, 3) study the H_2 adsorption behavior of materials systems capable of auto-charging under H_2 pressure, 4) design and develop devices for directly measuring H_2 sorption in an electric field, and 5) study the H_2 adsorption behavior of materials systems charged by applied electric potentials.

Question 1: Relevance to overall DOE objectives

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

- Project aligns with the Hydrogen Program and DOE RD&D objectives.
- This project is the original attempt to solving this problem.
- The project addresses appropriate barriers for hydrogen storage.
- This project includes trying to improve room temperature hydrogen storage capacities.
- I did not receive a clear understanding that the work, if successful, would lead to progress against the Hydrogen Program goals and objectives.

Question 2: Approach to performing the research and development

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

- The approach is effective, but has some room for improvement.
- The research is focused towards the program goals.
- The approach appears to be solid.
- Systems with applied potentials of 2 kV to generate charged species are impractical, and at these potentials, it is unclear if any increase in adsorption observed is not due to non-reversible reactions. What would be the cost to apply this large potential across the storage media, and what effect would this have on system efficiency? Also, Pt doping will likely increase the cost of the storage material beyond the allowable cost. Need to check reversibility of H_2 adsorption and determine that gas desorbing is all H_2 (i.e., not H_2O, a hydrocarbon, or other species). Integration/collaboration with other CoE should allow for adsorption/desorption measurements to be made on these materials.
- The basic physics behind the approaches being pursued for introducing extra hydrogen into materials is not clear.

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

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

- There are too many unknowns.
- The existence of (H+)x clusters remains to be proven.
- Mechanism of hydrogen absorption is still poorly understood.
- Good progress (experimental), interesting results, good indication that the phenomena enhances adsorption.
- Materials with the required H_2 adsorption capacity have not been identified. Small improvements are noted for "charged" materials over the baseline materials used. It seems that for any appreciable amount of adsorption, the increases in adsorption seen for materials with charge generating materials (CGM) are relatively small (~ 10% increase from carbon without CGM). Could this be due to sample-to-sample variation or small changes in surface area upon adding CGM? In NiO, CGM enhancement is a larger percentage, but overall adsorption is much smaller (<0.2%, more than an order of magnitude less). Similarly for Pt/C with an applied potential, it is more difficult to measure these small amounts accurately. Depending on level of doping or potential, other changes are likely to be occurring which can affect adsorption, including just the presence of a metal atom on the surface (spillover effect vs. a charge effect).
- The claimed "charge enhancement" for vermiculite may not be related to charge at all, but just to increasing the free volume by removing water with increased temperature. While the Bruner−Emmett−Teller surface area analysis method (BET) area did not increase with increasing treatment temperature, it is clear that water molecules take up space and are most likely interacting with some of the interior surfaces. Removing these should free more surface sites where H_2 could adsorb.
- Only marginal increases in absolute room temperature hydrogen storage capacities were obtained, but there were significant relative increases.
- Progress appears to be made, but again, it is hard to understand from the materials available how this will lead to significant progress against the program goals and objectives.

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

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

- There has been adequate collaboration.
- The specific role of the partners could be more explicitly highlighted in the presentation.
- Collaborations with other universities, companies, and a national laboratory are in place. Collaborations on measurements (reversible adsorption/desorption) would be beneficial.
- Collaborative activities appear limited.
- A diverse team has been established.

Question 5: Approach to and relevance of proposed future research

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

- Plans to look at materials with higher intrinsic storage capacity are appropriate. Plans to utilize the ORNL neutron facility to try to look at materials and the uptake mechanism should move the work towards improved understanding.
- The future work makes sense, but is not quite clear how it will be accomplished.
- Why does the effect vanish as a function of pressure?
- Temperature dependence studies could help determine heat of adsorption?
- Reversibility?
- This should really be "Not Applicable," since this project is essentially over.

Strengths and weaknesses

Strengths
- Good collaboration.
- Clear understanding of challenges
- Some indications that the approach works at low pressure.
- None.

Weaknesses
- Conclusions are not always supported by facts.
- Adsorption measurements methodology should be discussed.
- Measurements have not shown reversible adsorption/desorption. Charge effects observed have been fairly small.
- Approaches adopted are vague in their scientific justification.

Specific recommendations and additions or deletions to the work scope

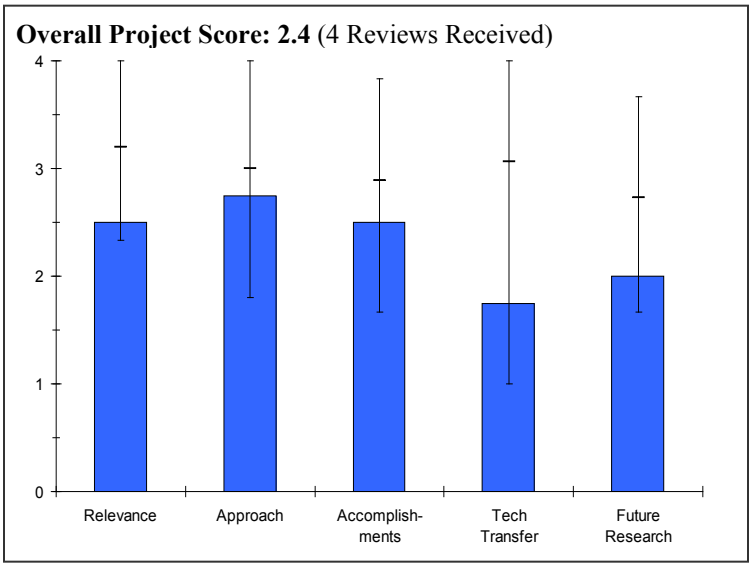
- Continue the project. Make go/no-go decision at the next AMR meeting.
- None.

Project # STP-22: Purdue Hydrogen Systems Laboratory

J. Gore, A.P. Gagare, S. Basu, A. Brockman, M. Diwan, A. Al-Kukhun, H.T. Hwang, Y. Zheng, P.V. Ramachandran, and A. Varma; Purdue University

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 the 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 **2.5** for its relevance to DOE objectives.

- AB recycling is well aligned with program goals in that it supports use of one of the few materials that can meet goals. Slurry work is interesting in that it may allow for liquid filling which will be easily accepted by the public, but the claimed density is not especially at the system around 4% . Additionally, it is not suitable to cold weather use as it becomes very viscous below 0°C and freezes around 0°F. The hydrolysis work is poorly aligned because, energetically, it is unreasonable to recycle efficiently.
- Project goals align with DOE R&D objectives.
- This project is focused on the development of ammonia borane as a hydrogen storage material.
- The project addresses hydrogen storage system gravimetric and volumetric targets.
- It also addresses the development of by-product/spent material removal and regeneration processes.
- The project is well aligned with the RD&D objectives, but it appears that there is overlap with efforts in the Chemical Hydrogen Storage CoE.

Question 2: Approach to performing the research and development

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

- AB approach is good in that it is new and may work. The energy pathway seems less optimal, but it is not bad.
- The slurry at the level of water contemplated seems unlikely to be fluid at low temperature as a reactant, and will be a solid in the product state. The use of the water to make H_2 will leave a solid. There will almost certainly be a need for more water in real systems, which will reduce the capacity to perhaps 2% or so.
- The approach to hydrolysis is well conceived and has the advantage of working at fuel cell exit temperature so heat is "free."
- Rheological measurements are useful for systems design.
- Calculations suggest regeneration of borates or $B(OH)_3$ is too energy intensive due to the stability of the B-O bonds. The authors try to get around this using triflate ligands. It is not clear what happens to the Me_3SiOTf in this recycle scheme. It appears the project will have an even larger problem with forming a Si-O bond than with

the B-O bond. The project must reduce the Si-O bond now or Et_3SiH becomes a consumable reagent driving up cycle costs. Most likely, having to reduce this stable Si-O bond will drive down energy efficiency for the cycle when its recycle or manufacture of Et_3SiH from starting materials is included.

- Approach to AB recycling:
  - Spent fuel, ammonium borate converted to boron tris(triflate) or boron tris(trifluoroacetate), which provides molecules with weaker B-O bond.
  - Further reduction of boron tris(triflate) or boron tris (trifluoroacetate) in the presence of triethyl amine, followed by the displacement of the amine -using ammonia, leading to efficient ammonia borane regeneration.
- Approach to dehydrogenation of AB Slurry:
  - Enhance the AB powder, water, and catalyst mixing process using ultrasonic mixing and high shear mixing to obtain high hydrogen yields near stoichiometric.
  - Characterize transportability of AB slurries and associated hydrolysis by-products by viscoelastic property measurements.
  - Use a reactor module to provide engineering studies of AB and other materials that have potentials for off-board recyclable chemical hydrogen storage.
- Approach to non-catalytic AB hydrothermolysis:
  - Perform isotopic experiments to understand reaction mechanism of H_2 release from aqueous AB solutions/slurries.
  - Investigate solubility of AB in water at temperatures in the range 25–70°C.
  - Study H_2 yield over a wide concentration range (5–50 wt% AB).
- Approach to characterization of reaction by-products:
  - Initiate development of a continuous-flow reactor for hydrogen release.
- The approach has potential when it comes to addressing technical barriers, but could be improved to make the Purdue approach more distinguished from other on-going efforts. Clarifications needed for how to improve the performance of the AB slurry.

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

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

- The program ends soon. It would have been nice to have seen more progress on the recycle chemistry at this point, but they may still finish on time. The utilization has made suitable progress in glassware and a bomb-like device, It would have been nice to have seen a larger scale demonstration in metal that showed the expected mass transport devices. Still, they are showing, at least in idealized conditions, what might be done and making good use of design to be more efficient.
- Have proposed an AB recycling scheme for hydrolysis of AB going through $B(OH)_3$ and demonstrated reduction of boron tris(triflate) to BH_3.
- It is not clear what happens to $Me_3Si(OTf)$ in this recycle scheme.
- Non-catalytic hydrothermolysis is interesting, but it is not clear what is happening. It appears to increase H_2 released/mol AB, especially at low AB concentrations; however, it is not clear that it increases the H_2 storage density on a wt% basis. UPenn obtained 7.2 wt% at 50% AB in IL at 120°C while this project obtained about the same for 50 wt% AB at 135°C. At 50% AB, is this project just doing thermolysis in water, in place of the ionic liquid? The potential for water soluble products in this system is attractive. If it need to be pressurized much, it is probably not practical.
- AB recycling:
  - Achieved reduction of B-OTf bond in dibutyl boron triflate followed by hydroboration of 1-octene.
  - The reduction of boron tris (triflalte) was achieved using diethyl silane.
- Dehydrogenation of AB slurries:
  - A 92% hydrogen yield in a (1:2) AB/water slurry hydrolysis test using ultrasonic mixing was observed; it provided a material based hydrogen storage capacity of 8.2 wt%.
- Investigation of non-catalytic AB hydrothermolysis:
  - AB solubility is ~ 50 wt% at 70°C; at >70°C, hydrogen generation is observed.
  - While varying AB concentration from 5 to 50 wt% (~135°C, 200 psia), the total hydrogen yield (H_2+HD) remained at around 2.5-2.75 equivalent per mole of AB.

  - Hydrogen yield varied linearly with AB concentration (for <50 wt% AB), with a maximum hydrogen yield of ~8 wt% as reported in slides. But at poster session, they reported >11 wt% recovery at 85°C. In addition to hydrogen, some NH3 formation is also observed.
- OK.

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

This project was rated **1.8** for technology transfer and collaboration.

- While they show General Motors (GM) as a partner, it turns out they are not a partner in this work. GM may have given some vehicle requirements, but that may have also done that in previous programs and not this one. They do not seem to be working with the Chemical Hydrogen Storage CoE very much at all even though there is a natural synergy.
- Collaboration with General Atomics and General Motors.
- Collaborators are General Motors (lab infrastructure) and General Atomics (AB synthesis)
- Seemingly, no direct collaboration with the Chemical Hydrogen Storage CoE or its member institutions.
- Seems like most work is done by Purdue University. There is a need for interacting with the Chemical Hydrogen Storage CoE to learn fundamental aspects of ammonia borane chemistry and to avoid overlap. The presentation did not indicate any ongoing communications with the CoE and the experts on ammonia borane.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.0** for proposed future work.

- The program is a little diffuse, trying to cover all aspects at a low level of intensity rather than making a major step in one area; that is OK, but perhaps less efficient use of DOE money. That said, each component seems well planned, with the recycle using surrogate systems to demonstrate the process and then refining reactants and conditions. The bomb reactor tests are also well designed, making good use of heat streams. A little hazier in the glass bomb demo, that seems to have ignored the fate of the products (i.e., how they will be moved from the reactor in solid form). They did nice mechanical tests, but did not have a convincing plan for dealing with the products.
- Include all parts of cycle in regeneration scheme (i.e., recycle of Me_3SiH or other reducing agents).
- Future work on AB recycling:
  - Calculation of bond energies for the proposed AB recycling is underway.
  - The conversion of ammonium borate or boric acid to boron tris(triflate) will be examined.
  - Optimization of the reduction of tris-acylborate to borane-ammonia.
- Future work on dehydrogenation of AB slurry:
  - Conduct AB slurry hydrolysis using a high shear mixing reactor.
  - Conduct catalytic AB hydrothermolysis below 85°C (joint effort).
  - Conduct AB ionic liquid slurry thermolysis tests.
  - Design, construct, and test an AB slurry dehydrogenation reactor module.
- Future work on non-catalytic AB hydrothermolysis:
  - Determine reaction mechanisms and yield of hydrogen generation from AB hydrothermolysis in aqueous solutions and slurries.
- Future work on quantification of reaction by-products:
  - Develop, test, and analyze continuous flow reactor setup.
- Seems to be potential for improvements, but the future plans need to be more specific regarding how to meet the DOE targets. What about trying other AB recycling paths?

Strengths and weaknesses

Strengths
- Strong team intellectually and good support from the university – the assistant dean helped present the work!
- High capacity material.
- Simple concept to execute (except for the recycle, which is complex).
- Potential for soluble products or well-behaved, pumpable slurries for reactants and spent products.

Weaknesses

- Huge energy efficiency barrier in recycle of borate.
- Moving solids is difficult in rectors; liquids would be better, but that option would destroy the mass efficiency.
- Not taking advantage of knowledge in the DOE system.
- Overcoming potential energy sink of borates formed from the hydrolysis.
- The project does not appear to be well connected to the Chemical Hydrogen Storage CoE.
- Hydrolysis of AB is not generally considered to be a promising route to hydrogen evolution from AB in terms of meeting DOE hydrogen storage system performance targets.
- No apparent teaming with other ongoing efforts on ammonia borane.

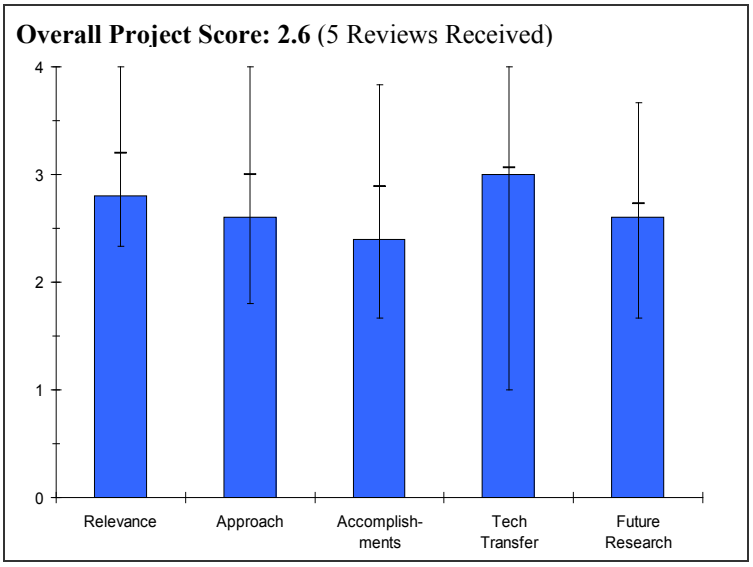
Specific recommendations and additions or deletions to the work scope

- Nearly complete; really too late for meaningful change.
- The extent to which this project is covering ground already plowed by the Chemical Hydrogen Storage CoE needs to be evaluated. Their results/accomplishments should be confirmed by another institution (e.g., the Chemical Hydrogen Storage CoE). The approach needs to be clarified to make sure that this project is distinguished from other ongoing efforts.

Project # STP-23: Hydrogen Storage Research
Lee Stefanakos and Sesha Srinivasan; University of South Florida

Brief Summary of Project

The overall objectives for this project are to 1) synthesize and characterize materials with high hydrogen storage potential; 2) discover new materials and processes; 3) perform catalytic doping, destabilization, and substitution strategies to improve the kinetics and reversibility of hydrides at low temperature; and 4) employ ab initio calculations to validate the experimental observations.



Question 1: Relevance to overall DOE objectives

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

- The project aligns with all HFCIT Program and DOE RD&D objectives.
- Project contains both theory and experimental components that are generally well aligned with Hydrogen Program objectives. Although there is significant overlap between this independent project and individual projects within the DOE Centers of Excellence (especially in area of complex hydrides), there is sufficient new work here to justify continuing support.
- Very good results and progress towards DOE goals.
- Overall, they are not moving the ball much; thought area is reasonably aimed. If the polymer work proves valid, this would need to be changed to "good."
- This project addresses the following hydrogen storage system technical targets:
  - Volumetric H_2 density, >45g H_2/L.
  - Gravimetric H_2 density, >6.0 wt.%.
  - Operating temperature, -30/50°C.
  - Delivery temperature of H_2, -40/80°C.
  - Cycle life, 1,000 cycles.
- Fast absorption/desorption rates.

Question 2: Approach to performing the research and development

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

- The project integrates synthesis, analysis, characterization, and computational studies of selected complex hydrides and polyaniline nanostructures. The PI and his colleagues have done a good job of making mid-course corrections during the project to focus on the most promising materials.
- The approach is effective but could be further improved.
- Sharp focus; promising results.
- The approach is alright. Not so well integrated with itself or others, but adequate. The work is in some regards a rehash of existing work with only small variation. For example, particle size is the repeat of the UOP work. This could have been good except that there was no control for other effects that might have gone along with particle size such as temperature reached in preparation, addition of unintended catalytic metal, and the other usual problems. The polymer work was again not sufficiently well planned for the experimenter to understand what they saw.
- Synthesis, characterization, and performance testing of (1) ternary and higher order borohydrides and (2) polyanaline nanostructures.

- Stabilization, nanocrystalllization, and nanomaterial doping are among the issues explored using crystal structure methods and thermodynamic stability calculations.
- A fairly detailed experimental process was used to arrive at the specific component concentrations and physical morphologies for the $LiBH_4/LiNH_2/MgH_2$ system. However, the conclusion that use of nanoscale MgH_2 results in dramatic improvements in hydrogen storage compared to earlier results obtained by investigators at Ford Motor Co. in a similar complex hydride system is questionable based upon the experimental data that were presented.

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

This project was rated **2.4** based on accomplishments.

- A lot of interesting and very useful results, both basic and applied.
- Synthesized multinary complex hydrides involving $LiNH_2$, $LiBH_4$, and MgH_2 using solid-state mechano-chemical process; prepared Li-Mg-B-N-H complexes showing efficient/reversible hydrogen storage capacity (>6 wt.% at 150-175°C). Independent validation of (pressure concentration temperature) PCT characteristics by Southwest Research Institute (SwRI) closely matched USF results and showed no evolution of ammonia or di-borane.
- Synthesized complex borohydrides, e.g., $LiMn(BH_4)_3$, by mechanical milling of $LiBH_4$ and $MnCl_2$. Accomplished reversibility of hydrogen sorption cycles in $LiMn(BH_4)_3$ by self catalyzing effect using Xmol% MgH_2.
- Studied the effect of nanomaterial doping and co-doping on the hydrogenation and dehydrogenation behavior of Li-Mg-B-N-H and Li-Mn-B-H.
- Established the structure of $Mn(BH_4)_2$ and calculated the thermodynamic stability by Density Functional Theory.
- Synthesized polyanaline nanostructures using chemical and electrospinning processes. Accomplished reversible hydrogen storage capacity of 3-10 wt.% from room temperature to 100°C.
- The results on the $LiNH_2/LiBH_4/MgH_2$ are intriguing. Previous work on this system (Ford Motor Co.) showed only modest gravimetric capacity (~3% at 200°C). The improved sorption behavior measured in the present work is attributed to the method of preparation and the suggested importance of nanoscale MgH_2. However, particle agglomeration/sintering upon repeated cycling occurs, and it's therefore difficult to understand how these results can be rationalized by invoking nanoscale effects. A very thorough examination of possible experimental artifacts in the PCT measurements is needed before conclusions can be drawn concerning significantly enhanced storage capacity at reduced temperatures in this multinary complex hydride.
- They have produced many results, and credit should be given for that accomplishment; however, the understanding is not good. For example, the assignment of delta particle size is simply a result of the fact they saw a rough correlation in five data points. With all the other variables in play it is hardly wise to assign a band of optimal size difference, especially with no theory as to why. Likewise, there was no indication of understanding of why the polyaniline (PANI) had higher reversible capacity at higher temperature, in contradiction to all other studies. Most difficult to accept was that in a series of runs, they saw a continuing loss of mass in pressure-composition isotherm (PCI) tests; however, when weighed, the sample had not lost mass. Clearly, this is a big problem and makes it impossible to accept an otherwise exciting result: room temperature and even high temperature storage of 8%.
- The stated sorption results on the nanophase PANI materials are extraordinary (6% gravimetric capacity at 125°C, multiple cycles). If correct, this is a breakthrough result. However, very unusual sorption behavior is evident, and the sorption data strongly suggest that experimental artifacts could be important (e.g., no threshold is observed in the H-uptake vs. pressure data). It is imperative that the PCT system is carefully calibrated using well-known standards to ensure that the PANI measurements are valid. Likewise, great care must be taken in the analysis of the PANI data to rule out any possible effects due to chemical reactions during testing. Finally, given the extraordinary nature of these results, it is crucial for the measurements to be validated by other laboratories.
- The reaction enthalpy (~78 kJ/mol) from the Van 't Hoff plot is totally inconsistent with the measured temperatures for hydrogen uptake and release (i.e., enthalpy much too high).
- The overall benefit of the computational work (density functional theory [DFT] calculations) seems to be limited. Although the calculations have some utility in establishing thermodynamic characteristics of selected

reactions (e.g., reactions involving $Mn(BH_4)_2$), it is not clear how those calculations are being used to guide the experimental work in this project.
- Validation of ab initio calculations? This is the weakest area.
- Both chemisorption and physisorption mechanisms are proposed to explain the PANI sorption data. However, a compelling argument concerning the mechanistic details and the relative contributions of these two processes to the overall sorption behavior has not been provided.

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

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

- Good degree of interactions between participants; nice slide on the structure of the collaboration.
- They use both industrial and lab partners to good advantage in getting catalysts and also in obtaining spectra that may illuminate the meaning in the data.
- Collaborations with:
  - QuantumSphere, Inc.
  - NIST
  - SWRI®
  - Nano-RAM Technologies, India
  - University of Hawaii
  - NNRC
- Seemingly, no direct collaboration or interaction with the Chemical Hydrogen Storage CoE.
- Many collaborations are listed (slide 42). These efforts are assisting the materials discovery and characterization in the overall University of South Florida program.

Question 5: Approach to and relevance of proposed future research

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

- Plans build on past progress and are designed to address existing challenges and barriers. There is some chance for discovering new materials.
- They have plans, and they are aligned with the goals. Again, they do not seem aimed at understanding the problems in the current work. For example there seemed to be no attempt to work out the odd mass conservation difficulty in the PANI work or any systematic approach to really understand if the particle size conclusion was supportable.
- Future work is clearly stated and represents a logical extension of the current effort. However, since the project is more than 85% complete, the plans seem to be unrealistic. It would have been helpful to establish some kind of priority for the future work based upon the most noteworthy remaining barriers (i.e., what are the most critical specific technical problems and what plans are in place to solve them?).
- Proposed future work includes:
  - Investigate hydrogen performance of nanoscale, dopant-enhanced complex multinary hydrides.
  - Investigate activation energy and mechanism of hydrogen release from nanoscale doped complex hydrides using Kissinger method.
  - Perform gas evolution analysis in-situ during cyclic hydrogen sorption measurements.
  - Establish the structure of $LiMn(BH_4)_3$ and calculate the thermodynamic stability by DFT.
  - Investigate the effects of nanomaterial additive on the dehydrogenation and reversible rehydrogenation characteristics of $LiMn(BH_4)_3$ by determining the cohesive energies and bond strength information.
  - Employ a mechanistic approach to enhance the hydrogen storage characteristics of polyaniline nanostructures by incorporating various materials (e.g., carbon nanotubes [CNT], fullerenes, SnO_2, and Ti) during chemical and electrospinning processes.
- Demonstrate and correlate the analysis results of DFT calculations with the experimental investigations carried out in previous tasks.

Strengths and weaknesses

Strengths
- A comprehensive project conducted by a well-qualified R&D team. Recent results on multinary complex hydrides and substituted PANI nanostructures are especially intriguing. Extensive collaborations are facilitating progress in the project.
- A very comprehensive research effort.
- Interesting results reported for synthesized polyaniline nanostructures.
- Earnestly want to advance the science.
- Well funded.

Weaknesses
- A straightforward assessment of technical obstacles and barriers and a careful validation of the experimental results are needed. Contributions from experimental artifacts appear to be important in the PCT data. These *must* be ruled out before meaningful conclusions can be drawn.
- The group can afford to narrow their focus.
- More validation of theory would be beneficial.
- The project seems more aimed at generation of data than understanding.
- The PI is insufficiently concerned with inconsistencies.
- It's not likely that a material with a significant amount of manganese in it will store upwards of 11 wt% H_2 and thereby meet the gravimetric "system" storage target for 2015.
- The poster is overloaded with details and secondary information. It is difficult to navigate through it without the presenter's assistance.
-

Specific recommendations and additions or deletions to the work scope

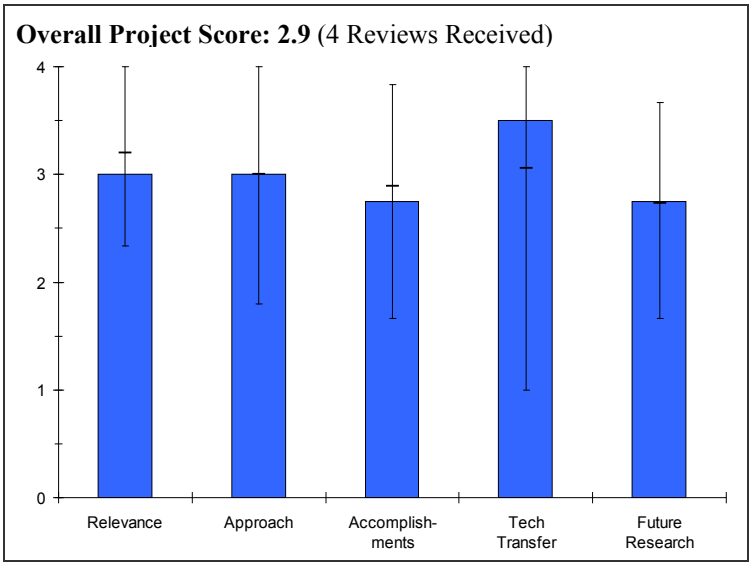
- This group would benefit from direct management (DOE may not accept that data, it clearly does not make sense) rather than just suggestion. They have data that is clearly flawed, and the programs are not as well planned as they would be if working with a more established group.
- Results obtained with the nanostructured polyanaline are interesting, but are also somewhat counter-intuitive. They need independent corroboration and/or vetting by the Chemical Hydrogen Storage CoE.
- Rather remarkable results for sorption behavior in the $LiBH_4/LiNH_2/MgH_2$ complex hydride and in the nanoporous PANI system have been presented. However, there are serious questions concerning the accuracy and reliability of the PCT measurements. It is imperative to investigate and eliminate any experimental artifacts, and it is strongly recommended that the results be validated by testing at other laboratories. This should be the principal focus in the remainder of this work.

Project # STP-25: Carbon Aerogels for Hydrogen Storage

T.F. Baumann, M.A. Worsley, and J.H. Satcher, Jr.; Lawrence Livermore National Laboratory

Brief Summary of Project

The objective of this project is the design of novel carbon aerogel (CA) materials that meet the DOE 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 **3.0** for its relevance to DOE objectives.

- The study of tailored aerogel materials for hydrogen storage is well aligned with the DOE HFCIT Program objectives and is directly relevant to the ongoing work of the Hydrogen Sorption CoE. There is good project focus on issues of weight, volume, temperature, and cost/scalability.
- Research on scaffolding materials to reduce enthalpy and thermodynamics of the storage materials is critical.
- Very high surface materials. Use as scaffolds has potential for high capacity.
- Use of CA to achieve 6 wt.% and 45 g/L targets. The latter will likely be the more difficult of the two, and so should have been paid more attention (project is almost complete). However, there doesn't appear to be compelling evidence that these scaffolds will actually improve hydrogen storage properties, so the relevance of this project is questionable.

Question 2: Approach to performing the research and development

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

- Interesting use of nanotubes in order to improve the thermal conductivity of the material and facilitate H_2 transport.
- The high surface area, the ability to tailor surface properties, and ease of synthesis make aerogels useful reaction platforms and active media for hydrogen storage. The major elements of the approach in 2009 include engineering of carbon aerogel-metal systems for enhancing spillover and development of porous scaffolds used as nanoscale hosts for simple and complex metal hydrides. The approaches are well formulated, and they address important thermodynamic and kinetic issues that are directly relevant to ongoing work in both the Hydrogen Sorption CoE and the Metal Hydrides CoE.
- Good efforts. Adding Pt may drive cost too high. Scaffolding for metal hydride particles is interesting combination. Some concern about aerogels with low thermal conductivity. May be difficult to heat hydrides for desorption and to remove heat on refueling.
- Cr_2O_3 and ZnO are of potential interest, but surface areas are low.
- Functionalized silica aerogels have potential, but are likely to be expensive.
- Trying to produce tailored CA for sorption. Not clear, even theoretically, how this can allow 6 wt.% and 45 g/L.
- Using aerogels as scaffolds for metal and complex hydrides.

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

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

- Progress seems to have slowed somewhat compared to previous years. Would like to see more results on the nanotube scaffolds − interesting approach. PI should keep cost of scaffolds in mind with this approach though.
- Solid progress is evident in several areas including synthesis of oxygen-containing aerogels serving as supports and (possibly) catalysts for enhanced spillover, hosts for organometallic complexes that can reversibly bind hydrogen, new sorbent materials (e.g., alpha-Cr_2O_3 aerogels), and improved nanostructured frameworks for metal-hydride reactants.
- The effort in 2009 was focused primarily on materials synthesis and processing.
- Although some preliminary results on hydrogen sorption behavior are available for the encapsulated metal hydride system (collaboration with Metal Hydride CoE) and on the chromia H_2 sorption media, hydrogen capacity data in most of the technical areas are not yet available.
- Although it is recognized that those results are being gathered by other collaborators, the fact that the project is nearly 90% complete underscores the need to obtain the results in a timely way.
- The work on spillover is thorough, and numerous approaches have been explored for improving spillover efficiency. However, rates of hydrogen uptake are prohibitively slow. Likewise, even though there has been some preliminary work on chromia aerogels as sorbent materials, the gravimetric capacity is limited. The most promising direction for this project seems to be the collaboration with the Metal Hydride CoE.
- The investigators used carbon aerogels as scaffold hosts for complex hydride reactants.
- Good work on tailoring pore space. Interesting initial results on $LiBH_4$ scaffolding. Investigators are moving away from unproductive approach of aerogels alone; this shows good stewardship and project management.
- Some success in fabricating novel scaffold materials. However, the hydrogen sorption data is mostly lacking. There does not appear to be much evidence that these scaffolds will actually improve hydrogen storage properties. Also, the spillover results are unclear in regard to their reproducibility for storage properties.

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

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

- The PI is working with all the relevant partners.
- Extensive and fruitful collaborations, mainly with several investigators within the Hydrogen Sorption CoE and researchers in the Metal Hydride CoE. These collaborators have accelerated progress and have provided a valuable expansion in the scope of this project.
- Good partners to complement LLNL capabilities.

Question 5: Approach to and relevance of proposed future research

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

- Please concentrate and continue efforts on nanotube (NT) scaffolds despite the initial setback. The intent is correct to improve heat conductivity and H_2 transport. The motivation is more important than the nanotube material itself. Not enough PIs are concentrating on this critical material property. Please continue this approach with other materials in case NTs do not work out.
- Proposed future work is clearly stated and addresses important technical barriers. However, the future work could be viewed as an entire research project in its own right. Given the fact that the project is 90% complete, a discriminating look at future plans must be made to select the areas that will provide the most impact in the remainder of the project. It is especially important to focus on acquiring hydrogen capacity data at elevated temperatures in the tailored materials already synthesized.
- Still pursuing many approaches. Need to move toward down-selection of most promising systems. Need to begin looking at possible engineering barriers to this approach, such as heat transfer mentioned above.
- A very large amount of future work is proposed, given that the project is essentially over.
- The budget for this project looks strange. Although it is a 5-year project, it appears as though 80% of the funding was obtained in the final two years of the project. Was that planned?

Strengths and weaknesses

Strengths

- PI is working on two important fields for metal hydrides, scaffolding for reducing thermodynamics and also facilitating heat and H_2 transfer within the material. These become big issues as large amounts of materials are packed into a system.
- The PI is an expert at synthesis and properties of nanostructured aerogel systems, and he is an important resource for the overall Hydrogen Storage Sub-Program. Robust collaborations are enhancing the relevance of the project within the Hydrogen Sorption CoE and Metal Hydride CoE.
- Good science. Well executed.

Weaknesses

- Too many approaches. PI should consider narrowing down or down-selecting approaches since the project is near completion.
- Storage at temperatures >77 K remains a serious challenge for these materials.

Specific recommendations and additions or deletions to the work scope

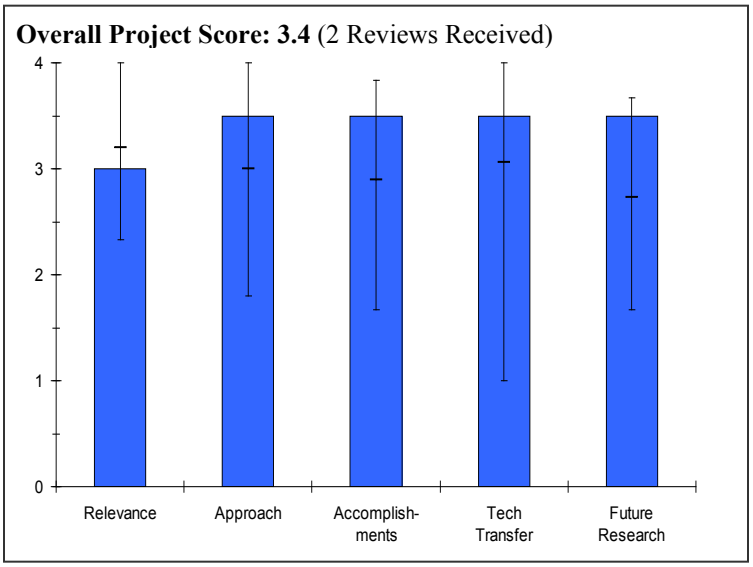
- The work on spillover seems to be open-ended at this point (especially with respect to the issue of slow uptake kinetics). No matter what results are obtained on the preliminary capacity measurements, there will be a large number of questions that cannot be addressed in the short time remaining in the project.
- Recommend that more attention be focused on the use of aerogels as nanoscale hosts for complex hydrides.
- Begin working with Engineering CoE to explore system configuration and possible issues.

Project # STP-26: Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

David B. Geohegan, Alex Puretzky, Mina Yoon, Chris Rouleau, Norbert Thonnaard, Matthew Garrett, Gerd Duscher, and Karren More; Oak Ridge National Laboratory

Brief Summary of Project

The overall objective of this project is to exploit the turnable 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 77 K, 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 approached for these materials.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- Coating carbon nanohorns with Ca is innovative, and it is valuable to see that any carbon can be uniformly coated by any metal without extensive clustering. Less clear whether sufficient capacity can be obtained, although somewhat idealized theory suggests that 8-10 wt% might be possible at 77 K.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- Processing is relatively simple, scalable to large quantities, and capable of placing Ca on the surface of carbon materials. Pelletization of materials has been demonstrated, which improves real world material handling.

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

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

- Methods developed to produce carbon nanohorns in quantity and to open interiors for sorption.
- Demonstration of deposition of a metal layer on carbon without clustering is an important advance.

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

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

- Strong collaboration with NIST, NREL, and University of North Carolina is indicated.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.5** for proposed future work.

- Proposed work on charged nanostructures is encouraged.

Strengths and weaknesses

Strengths

- Ability to synthesize Ca layers on carbon materials. Potentially easy to produce in large quantities. Some indications of stronger (i.e., higher temperature) binding, perhaps moving adsorption into the 150 K range.

Weaknesses

- Limited hydrogen capacities so far, even at 77 K; ultimate capacity may be limited. Unclear how to adjust binding energy. (Early results suggest that Ca may improve the binding energy, but opportunity to tune or further improve binding may not be there.)

Specific recommendations and additions or deletions to the work scope

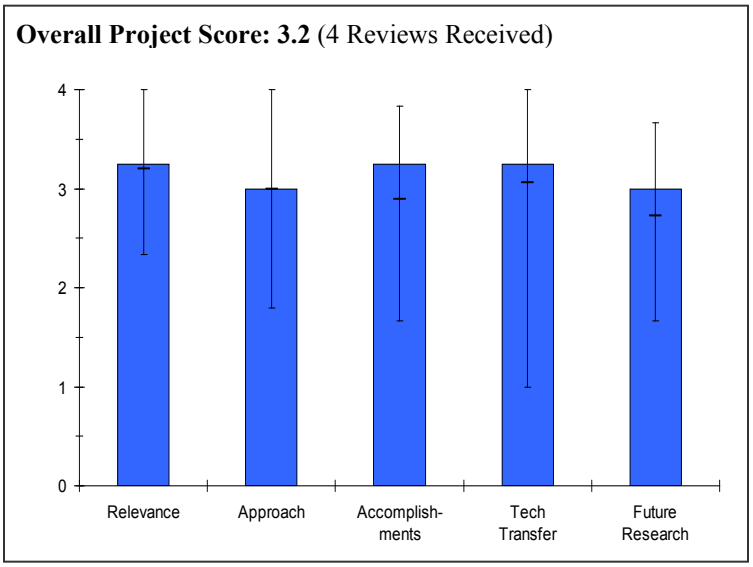
- None.

Project # STP-27: Enhanced Hydrogen Dipole Physisorption: Constant Isosteric Heats and Hydrogen Diffusion in Physisorbents

Channing Ahn, Justin Purewal, and Nick Stadie; California Institute of Technology

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 LLNL; 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 298 K 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 NIST.



Question 1: Relevance to overall DOE objectives

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

- The project is part of the Carbon Center and well aligned with the overall program objectives.
- The project, looking at critical issues of hydrogen sorption processes, is focused on hydrogen program goals and addresses key targets of RD&D objectives.
- The project is initially well focused on engineering or manipulating storage materials that evince binding energies adequate for room temperature storage. Project further explores systems that also yield nearly constant isosteric enthalpies with the view of improving the performance of engineered storage systems. These details are consistent with the Hydrogen Program objectives.
- Project adequately supports the Hydrogen Program goals. It tries to obtain enhanced dipole physisorption of hydrogen while also supporting other partners (e.g., by synthesizing metal-organic framework (MOF)-177 samples for neutron scattering studies).

Question 2: Approach to performing the research and development

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

- Good, systematic approach in identifying and evaluating relevant materials properties. It covers framework structures, aerogels, and microporous activated carbons; it also engages both theory and experiment
- The project's approach has become somewhat fragmented in focus. Materials of very different chemistries are being evaluated, from activated carbon to doped aerogels. This approach lacks focus from the central theme. Given the importance of the slit-pore studies for KC_{24} and CsC_{24} in intercalated graphites, focusing theoretical and experimental investigation on such systems would be prudent.
- The approach is in general effective and serves the project aims. There is some integration with other efforts (like the neutron scattering studies with NIST and the AX-21 fluorination with Rice University).

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

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

- Significant progress has been accomplished in line with the project objectives. The main achievement is the synthesis of layered enhanced physisorption structures with uniform high Δ H for adsorption and ability to retain 50% of 77 K capacity at 195 K and modest pressures. This also confirms the merit of high ΔH as a materials discovery goal for sorbent research. It was also demonstrated that diffusion kinetics of hydrogen in these systems are influenced by the extent of hydrogen loading with high loadings resulting in slower diffusion.
- Project accomplishments are excellent. In particular, the detailed, quasi-elastic neutron scattering studies on slit pores in intercalated graphite provide valuable insights into the diffusion and barrier properties of these materials. However, the MOF-177 effort seems to duplicate ongoing efforts within the CoE and from outside groups.
- The progress over the last year is fair. The work on alkali (K, Cs) intercalated carbons seems quite interesting. This is also valid for the fluorination efforts on AX-21, although only the first steps have been taken so far. Given that the project end is approaching, more focus on the really interesting parts of the work plan is needed to ensure fulfillment of major objectives.
- Finding materials with constant isosteric heats is desired (although not that important from an engineering viewpoint because these heats are rather small in physisorption). Connecting pore sizes with heat of adsorption could be better served if commercially available carbon molecular sieves with narrow pore sizes were used. It is suggested that the partners try that approach.
- It would have been more effective if high-temperature adsorption or desorption data were provided. Even a temperature programmed desorption (TPD) test would have been helpful.

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

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

- This project is well integrated within the sub-area of the research and appears to be in adequate interaction with the rest of the team. The only suggestion is for the project to make use of the full capabilities of the CoE and other projects to verify the claim on higher adsorption temperature materials.
- Substantial networking and collaborations with a good blend of expertise and access to facilities.
- There exists a sufficient degree of collaboration with other partners. Sample and data exchanges are in place to a certain extent (MOF-177 for NIST, fluorination of AX-21 for Rice University).

Question 5: Approach to and relevance of proposed future research

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

- Proposed work is sufficiently planned, builds upon present experience and expands current studies.
- Further work on chromia-doped aerogels and MOF or Material Institute Lavoisier (MIL) materials is inconsistent with the theme of the work already initiated on intercalated graphites. Perhaps the focus of the project should remain on the latter since other groups are already addressing the surface area and enthalpic properties of MOF and MIL materials.
- The proposed plans build on past progress, but they could be presented in a more detailed manner. It is important to focus on the more interesting aspects of the work as the project comes to its end.
- It is critical to test the samples and verify the claims.

Strengths and weaknesses

Strengths
- Lengthy experience and competence in the field. Good collaboration record; also, strong interactions within the CoE.
- Project addresses an exceedingly important aspect of materials engineering for physisorption uptake of hydrogen; namely, enhanced binding enthalpy, surface area, and constant enthalpy versus coverage.
- Very good expertise on physisorption.
- Work on intercalated carbons is very interesting. Also, fluorination work may prove useful.

Weaknesses

- No obvious weaknesses, but the field does remain challenging, taking into consideration the set hydrogen storage targets at mild conditions.
- The approach and materials base is fragmented and needs to be focused on the theme that is providing new information, such as the pore-slit intercalated graphites.
- Lack of focus on certain work plan aspects.

Specific recommendations and additions or deletions to the work scope

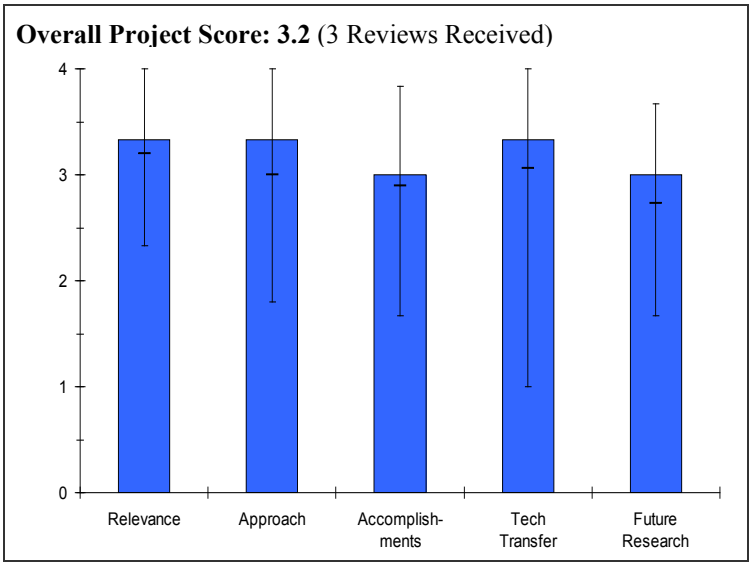
- A TPD or some other simple test would have been very useful for a quick test of the adsorbents.
- Place extra focus on getting a better understanding of the thermodynamic properties of these materials and on shedding light in the interrelations of pore size/distribution, enthalpies, temperature and pressure effects, and their influence on hydrogen uptake and release.
- Recommend concentrating effort on pore-slit studies based on graphitic structures in collaboration with Rice University.
- Work on AX-21 fluorination should proceed at a faster pace, given that the project end is approaching.

Project # STP-28: Characterization of Hydrogen Adsorption by NMR

Alfred Kleinhammes, B.J. Anderson, Qiang Chen, and Yue Wu; University of North Carolina

Brief Summary of Project

The overall objective of this project is to provide nuclear magnetic resonance (NMR) support to the DOE Hydrogen Sorption CoE team members in developing reversible adsorbent materials with the potential to meet DOE 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 **3.3** for its relevance to DOE objectives.

- This NMR tool will greatly support the DOE CoE team members in developing reversible H_2 storage materials.
- Relevance to DOE goals is sufficient. Project supports essentially other CoE members on a range of materials, providing useful input to several partners.
- This project is mainly a "support" for the activities of the Hydrogen Sorption CoE. So, the project itself will not focus on storage properties, but will support the other researchers in the CoE to ultimately achieve better storage properties.

Question 2: Approach to performing the research and development

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

- The approach of combining commercial NMR and a specialized setup allowing in-situ measurements of hydrogen loading in pressures from 0.001 to 100 atm and temperatures between 77 K and room temperature is one of the best.
- The project is particularly integrated with other efforts within the CoE. A range of materials (e.g., MOFs, carbon nanohorns, poly ether ether ketones [PEEK]) are included. However, as the project approaches its end, more focus on promising (or less understood, like spillover) systems should be exercised.
- The approach is quite straightforward: This project provides NMR support for the Hydrogen Sorption CoE.

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

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

- Good progress toward the objectives.
- Good progress has been demonstrated. Enhanced understanding on sorption mechanisms in systems like MOFs and nanohorns has been provided this year. The NMR technique has proven useful, as it may distinguish between different chemical environments for hydrogen and provide interesting information on bonding, diffusion, and other aspects. Issues that need further attention include the validation of the determined (porosymetry??) by NMR pore size distributions and the active investigation of spillover samples.
- Variety of different projects involving MOFs, carbon nanohorns, PEEK, and porous polymers. Some interesting new results regarding interpenetration and H_2 storage in MOFs.

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

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

- The close coordination with partners in other institutions is among the best within the CoE.
- I find the existing collaboration very appropriate. There seems to be extensive exchange of samples and data for a variety of materials and sorption aspects. Several members of the CoE profit from the project results.
- Good connection with many other groups. Due to the nature of a project like this, their ability to collaborate with other groups is essential. Good response to previous year's reviewer comments.

Question 5: Approach to and relevance of proposed future research

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

- The PI seems to have a good plan in carrying out the future based on past progress and learning.
- The future plans provided are clear and build on past progress. There are two issues that need to be taken in account:
    1. The NMR porosymetry should be further validated. It is mentioned that there will be, in the current year, correlation with results from CO_2 isotherms. This is appropriate and should be realized.
    2. More efforts should be made to include spillover samples in the investigations. This is mentioned in the "Collaborations," but not specifically addressed in the future plans. NMR may provide useful input to this poorly understood mechanism.
- Mainly a continuation of current activities, which seems appropriate for a project in its final year.

Strengths and weaknesses

Strengths
- The NMR tool developed in this project is a unique approach. It can really help the scientists to better understand the fundamental material properties and their relationship with the H_2 uptake.
- Good support to several CoE members on a range of materials.

Weaknesses
- The work is only limited within the CoE. The knowledge gained in this project can help other CoEs if there is a cross-center collaboration.
- NMR porosymetry needs further validation.
- Focus on promising and/or less understood systems, like spillover, should be applied.

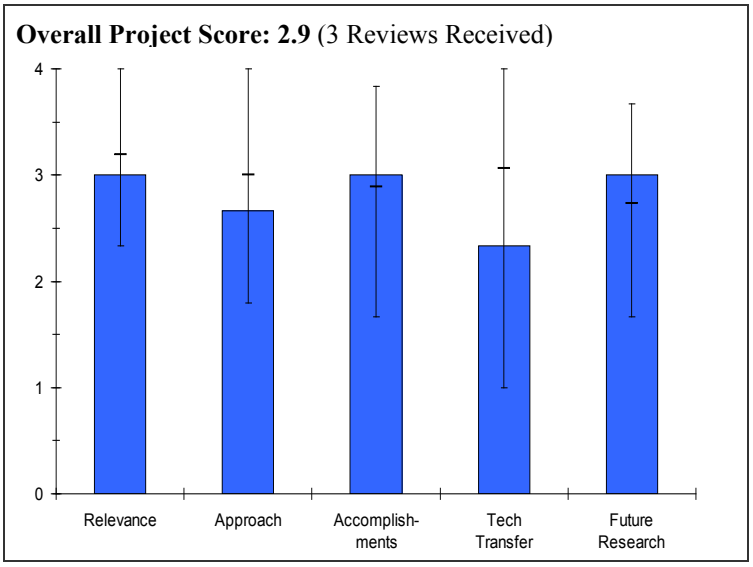
Specific recommendations and additions or deletions to the work scope

- Spillover studies should be added.

Project # STP-29: Advanced Boron and Metal Loaded High Porosity Carbons

T. C. Mike Chung, Vince Crespi, Peter Eklund, and Hank Foley; Pennsylvania State University

Brief Summary of Project



The primary objective of this project is to achieve the 6 wt% hydrogen storage goal by increasing binding energy (10-30 kJ/mol) and specific surface area (SSA) (>2,000 m^2/g). Boron (B) substitution in carbon (C) structures has the following advantages: lightness of B, enhancement of hydrogen interaction, no serious structural distortions, catalyzing carbonization, and stabilizing atomic metal. Activities for FY 2008 include 1) synthesizing the desirable B/C and metal (M)/B/C materials with B content of >10 mol%, M content of >3 mol%, and SSA of >2,000 m^2/g) and 2) studying the structure-property relationship. Activities for FY 2009 include 1) preparing BC_X materials with a combination of high B content (>15%), acidity, exposure, and surface area (SSA >2,000 m^2/g); 2) developing a well-defined B-framework with strong B acidity and high H_2 binding energy (>20 kJ/mol); and 3) studying the storage mechanism for spillover in M/C, M/BC_X materials M (e.g., Pt, Pd).

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- BC_3 and B-doped carbons have great potential to meet, or make a major step towards meeting, the DOE targets.
- This work is directly focused on developing an adsorption-based storage material with enhanced binding energy.
- Even with a 10-fold increase in surface area, it is hard to see how these materials will achieve high capacities.

Question 2: Approach to performing the research and development

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

- Good approach of using three different methods to make high surface area, B-doped carbon materials.
- This work has also investigated the use of dissociation catalysts and a number of nanosized metal clusters have been successfully deposited on the materials.
- Theoretical work from other groups has shown that BC_3 is expected to have a stronger interaction with dihydrogen. This group has successfully prepared a series of B-doped carbons with differing levels of B doping and surface areas. Higher isosteric heats of adsorption have been measured, but the storage capacities are modest because of low specific surface areas.
- Need to reassess the possibility that the current approach will lead to high capacities.

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

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

- Good progress achieved at well-dispersed metal particles on B-doped C surfaces and promising results shown for spillover effect on these materials.
- The project team has achieved very high B content in carbon structures.

- The project team has demonstrated increased hydrogen capacity in B-doped materials over pure carbon for equivalent surface area.
- The project team has measured increased heat of adsorption by B doping in carbon.
- Modeling results indicate promising result that metals are stabilized on B-doped C.
- The project has produced a range of novel BC_X materials. Characterization of their properties is ongoing, but significantly, the isosteric heat of adsorption has been shown to be enhanced. The challenges that remain, are to enhance the isosteric heat of adsorption further (>10 kJ mol-1) which might be achieved through higher B contents and/or the use of a dissociation catalyst. Unfortunately, the investigators have found that high B-content materials have low surface areas, which needs to be addressed (an area highlighted by the investigators).

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

This project was rated **2.3** for technology transfer and collaboration.

- There appears to be good collaboration within the group combining theoretical work and experimental. There seems to be less collaboration outside of this project. Given the number of groups investigating B-doped carbons, it would appear to be beneficial that all these groups coordinate their efforts to ensure they are not duplicating work elsewhere.
- Collaborations not specifically described in presentation.

Question 5: Approach to and relevance of proposed future research

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

- The group has identified the main barriers: improving heat of adsorption and increasing surface area, which is the focus for the next 12 months.

Strengths and weaknesses

Strengths
- Excellent progress in forming BC_X and examining the properties of these materials, not only for H surface adsorption, but also in terms of spillover and the effects of topological frustration.
- Appear to be a productive group and have led to greater understanding of the BC_X materials.

Weaknesses
- No major weaknesses, but greater collaboration within CoE will help with the exchange of ideas and reduce the likelihood of duplicating efforts.

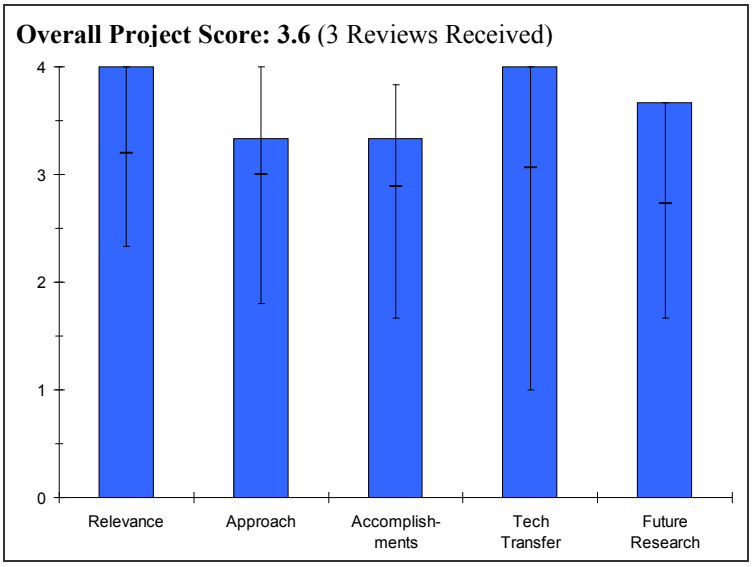
Specific recommendations and additions or deletions to the work scope

- The investigators have clear plans for future work, which is supported.

Project # STP-30: Best Practices for Characterizing Hydrogen Storage Properties of Materials
Karl Gross; H2 Technology Consulting LLC

Brief Summary of Project

The objective of this project is to prepare a reference document detailing the best practices and limitations in measuring hydrogen storage properties of materials. The document will be reviewed by experts in the field and will be made available to researchers at all levels in the DOE Hydrogen Storage Program. This project is being conducted to 1) reduce errors in measurements, 2) improve reporting and publication of results, 3) improve efficiency in measurements, 4) reduce the expenditure of efforts based on incorrect results, 5) reduce the need for extensive validation, and 5) increase the number of United States experts in this field.



Question 1: Relevance to overall DOE objectives

This project earned a score of **4.0** for its relevance to DOE objectives.

- This project is essential to the objectives of the HFCIT Program, and its final product will be an invaluable resource or reference guide that could be inducted into the standards organizations (i.e., ASTM International, International Organization for Standardization) as the basis for standards development in hydrogen storage measurements.
- The compiling of the "Best Practices Document" is a highly valuable effort. It is most important to have guidelines for researchers when performing reproducible experiments and this document aims at providing a reference on measuring comparable and accurate hydrogen storage properties.
- This project will be a huge benefit to the field. Kudos to DOE and to the PI for taking it on.

Question 2: Approach to performing the research and development

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

- This document aims at including all relevant properties, definitions, as well as role model experiments for performing accurate measurements of hydrogen storage properties. It is necessary for the document to engage both beginners and experienced researchers, which is the approach that the PI is taking.
- The project is aimed at developing recommended practices for the characterization of hydrogen storage materials for a broad audience. Presently, the approach comprises individual tasks that address topics on kinetics, capacity, thermodynamics, and cycle-life. A task devoted to instrumentation for each of the measurement techniques (e.g., volumetric, gravimetric, temperature-programmed desorption [TPD]) and other laboratory requirements, such as gas-source purity, should be included as a separate chapter of the final document.
- Considering that materials preparation plays such a key role in hydrogen storage experiments, there may be some logic in including a section focusing on (at least) ball milling and "activation" techniques.

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

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

- The project's technical accomplishments are progressing on schedule.
- During FY 2009, a new revision was compiled with requested chapters added, and the document is progressing well towards completion.

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

This project was rated **4.0** for technology transfer and collaboration.

- The PI is well connected with the hydrogen storage community, both within and outside the United States. New collaborations were initiated as needed to expand the document to cover more materials.
- It is nice to see many different experts involved in the effort.

Question 5: Approach to and relevance of proposed future research

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

- It is good to see that the interpretation and definition of "capacity" is being addressed individually for physisorption and chemisorption.
- There is no information on borohydrides, a group of materials currently of great interest for high-capacity, light-weight applications. These materials are fairly reversible, and thus challenging, for performing reproducible and accurate measurements. There needs to be a chapter included addressing these issues.

Strengths and weaknesses

Strengths
- The development of a long-needed general guide on hydrogen storage measurements for broad distribution. Contributors to this effort are known experts in the field.
- The “Best Practices” handbook is necessary for making sure that the hydrogen storage community is accurately measuring hydrogen storage properties in the same way in order to be able to compare them with the DOE targets, and thus show progress. It is also providing a reference for experimentalists with different levels of experiences, as well as theorists. Many recognized experts are involved in this project and providing feedback.

Weaknesses
- There were no weaknesses listed.

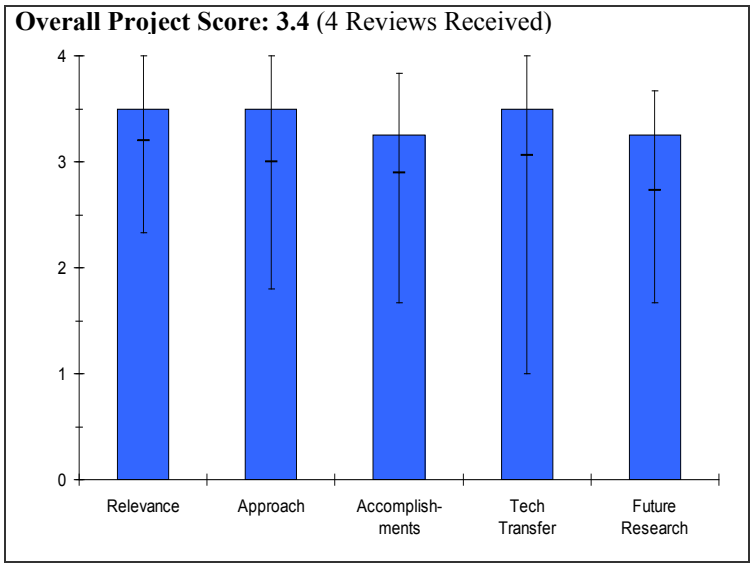
Specific recommendations and additions or deletions to the work scope

- A task devoted to instrumentation for each of the measurement techniques (e.g., volumetric, gravimetric, TPD) and other laboratory requirements, such as gas-source purity, should be included as a separate chapter of the final document.
- Add a chapter on borohydrides, and also expand the discussion of amide materials.

Project # STP-36: Reversible Hydrogen Storage Materials: Structure, Chemistry, and Electronic Structure
Ian Robertson and Duane Johnson; University of Illinois, Urbana-Champaign

Brief Summary of Project

The main objectives of the University of Illinois, Urbana-Champaign within the Metal Hydride CoE are to 1) advance the understanding of the microstructural and modeling characteristics of complex hydrides; 2) provide feedback and knowledge to partners within the Metal Hydrides CoE 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 **3.5** for its relevance to DOE objectives.

- The tools and plans for effectively using these tools are relevant to the DOE objectives in developing catalysts for metal hydride systems.
- This work examines various catalysts for the Metal Hydrides CoE using new characterization tools and computational approaches.
- Transmission electron microscopy (TEM) with holography, density functional theory (DFT), and scanning tunneling microscopy (STM) for in-situ hydriding are used.
- Data presented in the poster directly relate to three projects.
- Important microstructural support activity for the Metal Hydrides CoE.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- Three key and relevant technological challenges were worked on this year:
  - MOFs for catalysis
  - $Ca(BH_4)_2$ computational efforts to elucidate the structure of $CaB_{12}H_{12}$
  - $TiCl_3$-catalyzed AlH_3 structure and chemistry
- The investigators have used a combination of experimental and theoretical work to examine and model various materials with the aim of understanding the role of catalyst particles and morphology. The materials studied range from alane, to borohydrides, to MOFs, showing that their approach to the study of the hydrogen storage problem is quite general and likely to have an impact on progress toward satisfying the DOE objectives.
- Approach of combining the experiments and the theoretical finding is very good.
- Provides sophisticated microstructural analysis support to help answer selected key questions associated with advanced metal hydride development activities.

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

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

- The project has demonstrated the usefulness of their approach on quantifying the efficacy of ball milling and mixing for the dispersion of catalysts. The use of tomography in the analysis of catalysts is a very good approach. They have advanced the knowledge of the Ca-B-H system as to its reversibility and intermediate phases associated with dehydrogenation. Analysis of surface interactions with hydrogen has begun.
- Good progress.
- A significant amount of high-quality characterization work has been performed to support a number of programmatic issues.
- The research addressed understanding catalysis of metal hydrides and reversibility in borohydrides. In both cases, advances were made which point to fruitful directions for future work. However, there are some concerns about the interpretation of $TiCl_3$-catalyzed AlH_3 using TEM highlighted below.
    - In the case of understanding catalysts:
        - The research team used TEM to elucidate the location of $TiCl_3$ in AlH_3 (after addition by chemical means). The samples were provided by BNL. The outcome of that work is the discovery that the Ti was located everywhere in the sample (and not clustered as a titanium aluminide). From TEM (in which the beam transmits through the sample), it is still unclear whether the Ti is within the bulk or at the surface, however, the researchers defined the future direction for this work as an examination of surface layers of Ti over Al (then, hydride the system) in-situ within the STM. This future direction presumes surface distribution of Ti. This reviewer thinks that the future direction will yield fruitful results, but the researchers should also develop strategies for examining subsurface and bulk Ti.
        - Very nice work was presented showing that Ag could be inserted into the Angstrom-sized pores of the metal organic framework. The electron holography 3D images were impressive. The results of that study will provide collaborators an opportunity to use MOFs as regions for nanoconfinement and catalysis. These samples were provided by SNL to the researchers at the University of Illinois.
    - In the case of understanding reversibility:
        - The researchers used DFT to elucidate possible structures for $CaB_{12}H_{12}$, a nonreversible product phase occurring upon desorption from $Ca(BH_4)_2$. This is timely and useful work performed with collaborators at SNL.

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

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

- It is very good that this project includes collaborative research with other Metal Hydrides CoE and other critical DOE programs.
- The researchers are collaborating effectively with SNL (2 separate groups) and with BNL.
- This reviewer gives a “good” rather than “outstanding” rating to this performance category because there was no collaboration with other universities in the consortium. This reviewer urges the researchers to develop collaborations among universities. The tools used at the University of Illinois are advanced, and the project planning is superb. The educational benefits to working with the University of Illinois group are apparent, and this reviewer urges the team to seek out university partners.
- Visible collaboration with several members in the CoE.
- Collaborations both inside and outside the Metal Hydrides CoE.

Question 5: Approach to and relevance of proposed future research

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

- Each direction presented has a logical future direction associated with it.
- Again, this reviewer suggests examination of sub-surface and bulk Ti (because TEM is a transmission measurement and uniform distribution of Ti observed by this technique is not necessarily an indicator of uniform surface distribution of Ti).
- Good progress has been made, and much future work is planned. All of the areas planned are relevant to the DOE program and important directions to pursue. It seems, however, that some of the focus is on continuing rather than completing various areas of work.
- Project is 80% complete. Reasonable work plan for the remainder of the project.

Strengths and weaknesses

Strengths
- The collaboration between the University of Illinois and two national laboratories will provide tremendous opportunities to students working on this project to interact with researchers at national laboratories.
- The project combines computational and experimental work. Both aspects are very strong. However, these two modes of research were not used synergistically (i.e., TEM plus DFT to address a particular problem).
- The approach used is good and the materials relevant. Many good results are forthcoming.
- Characterization techniques/modeling combination.
- Excellent advanced microstructural characterization expertise and facilities.
- This project represents a number of strengths.

Weaknesses
- There appears to be a lack of collaboration with other universities.
- More of the tasks and future work should be specified so that completed milestones are apparent, rather than just continuing working on a material system. Also, one of the areas of future work is listed as "May explore...," and this seems to show that the direction of future work is not entirely clear to the researchers.
- None.

Specific recommendations and additions or deletions to the work scope

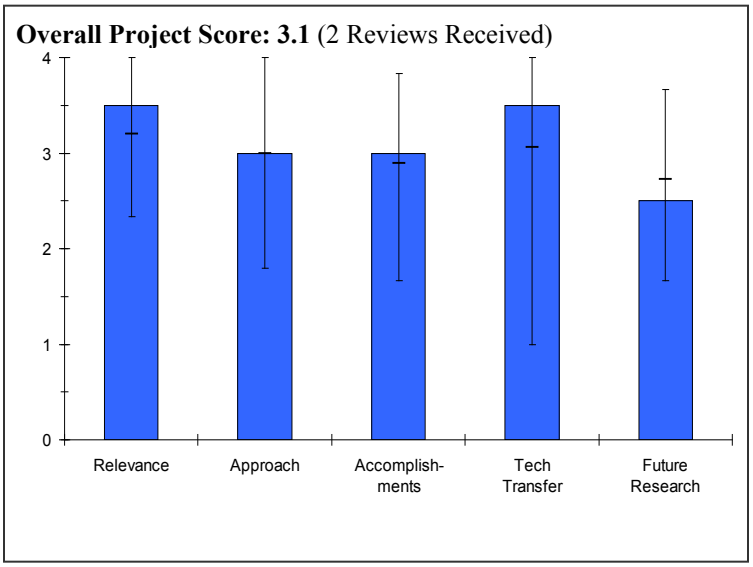
- In-situ STM examination of sub-surface and bulk Ti in AlH_3.
- Develop collaborations with other universities to balance out the team.
- Develop a program of student exchange so that University of Illinois students benefit from time at the national laboratory.
- Be more specific about tasks and accomplishments. Publish more of the completed work.
- Prioritization and focusing on compounds with high potential at the CoE is highly recommended

Project # STP-37: Metal Borohydrides, Ammines, and Aluminum Hydrides as Hydrogen Storage Materials

Gilbert M. Brown, Joachim H. Schneibel, Douglas A. Knight, Frederick V. Sloop, Jr., and Claudia Rawn; Oak Ridge National Laboratory

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, or the light alanates. Target materials and processes are 1) complex anionic materials (Metal Hydride CoE Project B); 2) amide/imide (M-N-H) systems (Metal Hydride CoE Project C); and 3) regeneration of alane (Metal Hydride CoE Project D). The ORNL 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 **3.3** for its relevance to DOE objectives.

- Project is targeting reversible high-hydrogen-capacity materials.
- Very broad area of research and not a realistic target for hydrogen storage.

Question 2: Approach to performing the research and development

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

- At this point in time, the project would benefit by focusing on the most promising avenue of its approach.
- The approach used in this project was not well thought out.

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

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

- The ammine aluminum borohydride results are very interesting. However, the reversibility of this system may not be possible.
- This work was not well focused.

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

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

- Good collaboration.
- Collaborations with the Metal Hydride CoE are good.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.0** for proposed future work.

- Concentrate on the most promising avenue.
- The proposed future work was unclear.

Strengths and weaknesses

Strengths
- Good knowledge for hydrogen storage.
- Excellent expertise and capabilities for working with reactive materials.

Weaknesses
- Diversified attempts.
- Project would benefit from more focus.

Specific recommendations and additions or deletions to the work scope

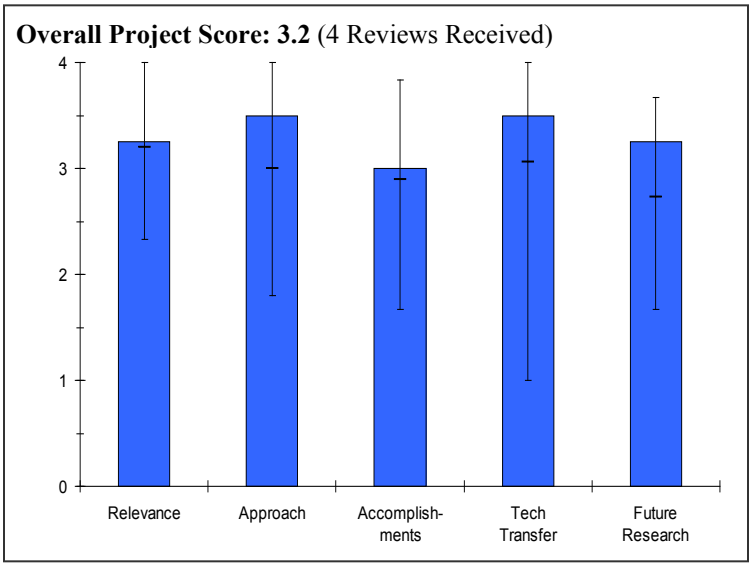
- None.

Project # STP-38: Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

Joseph W. Reiter, Jason A. Zan, and Robert C. Bowman; Jet Propulsion Laboratory
Son-Jong Hwang; Caltech

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 first Jet Propulsion Laboratory (JPL) objective is to 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 CoE 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 **3.3** for its relevance to DOE objectives.

- The development of advanced hydride systems for reversible on-board application is very critical to the overall Hydrogen Program.
- The project is very well aligned to the overall DOE objectives, addressing a number of key targets working under the umbrella of the Metal Hydride CoE.
- Nuclear magnetic resonance (NMR) provides a valuable tool for investigating reaction pathways and products. In some cases it can identify the presence of compounds in a sample that are not detectable by other characterization techniques such as X-ray diffraction and infrared spectroscopy. Identification of $[B_{12}H_{12}]^{2-}$ and similar species in borohydride decomposition products is particularly noteworthy.
- Project serves a key supporting role to the entire Metal Hydride CoE community by way of analysis and characterization. Such projects are key enablers toward gaining fundamental understanding of complex hydrogen storage reactions and thus are vital for CoE progress and meeting DOE R&D objectives.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- The multidisciplinary analysis and characterization combined with theoretical prediction is a good approach.
- Well founded, systematic approach, exploring possibilities within the Metal Hydride CoE and particularly getting the most out of the JPL team's high level expertise in the NMR field.
- Applies characterization tools, especially expertise in NMR, to establish reaction pathways and products. Understanding the reaction mechanisms is critical to finding ways to improve metal hydride storage materials.
- The diverse set of analysis and characterization capabilities is virtually unmatched in the Metal Hydride CoE. It is evident that these resources are being made available across the CoE for determination of reaction pathways (particularly for identification of reaction intermediates).
- State-of-the-art magic angle spinning (MAS)-NMR analyses are particularly invaluable for identification of non-crystalline product/intermediate phases which are very common in complex and chemical hydride systems.

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

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

- A satisfactory list of accomplishments. NMR once more proves to be a powerful tool for phase, type of bonding, and reaction pathways identification.
- Studies of the reaction mechanism in $Ca(BH_4)_2$ are valuable. $M(B_{12}H_{12})_n$ characterization and reactivity studies are useful to understanding formation of these intermediates during borohydride decomposition.
- The MAS-NMR work has proven to be very diagnostic in the experimental identification of the $B_{12}H_{12}$ intermediates. Given the recent computational work on reaction enthalpies for these species, it would be useful to experimentally corroborate these delta-H values.
- With regard to the prescience of water in the $Li_2B_{12}H_{12}$ experiments, it unclear what the origin of the water is and if it is possible to be mitigated. This water, that is observed for all $MB_{12}H_{12}$ systems, is likely prohibitive to facilitating low-temperature hydrogen release.
- Overall, the collaborative synthesis and in-depth characterization of various $MB_{12}H_{12}$ compositions is significant, high-profile work that is important for future development of complex anionic materials.
- The team made some progress in the past year. However, the progress is not proportional to the funding level compared to other team within the CoE.

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

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

- Strong collaboration within the Metal Hydride CoE, with other CoE's, and with outside collaborators. This is the "go-to" group for NMR within the CoE and one of the leading NMR groups in the field.
- This project relies on productive collaborations with CoE partners. It is clear that extensive coordination within the Metal Hydride CoE is in place, and PIs have been effectively leveraging JPL's/California Institute of Technology's capabilities.
- The team is fairly well coordinated with other partners within the CoE.
- Substantial, appropriate, and well-coordinated networking and collaborations with other institutions.
- Given that reactions based on chemical hydrides also commonly involve amorphous products, it would be a natural extension to examine these systems (e.g., ammonia borane [AB]) via collaboration.

Question 5: Approach to and relevance of proposed future research

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

- The future work is well planned. The team should shift more weight to the investigation of destabilization routes.
- Sound and targeted future planning which builds on recent progress and moving a step forward. Of particular interest is the work on the destabilization routes in the $MB_{12}H_{12}$ system and the use of NMR for investigating the N-enriched amide/imide systems.
- Builds on studies of intermediates to try to identify ways to mitigate or prevent formation of these intermediates, which interfere with reversibility. Studies of complex anionic materials and amide/imide systems will help elucidate reaction pathways in these systems as well.
- The proposed activity involving the collaborative examination of destabilized hydride systems embedded in scaffolds should be productive. Hopefully, an objective will be to gain an understanding of the interaction between the scaffold and metal hydride and impacts on kinetics (or thermodynamics).
- Continuation of work on the $MB_{12}H_{12}$ phases and M-B-N-H systems is also worthwhile.

Strengths and weaknesses

Strengths
- The tool developed in this project allows CoE partners to verify the reaction pathways predicted by the theory.
- Exploring NMR: a powerful tool and the PI and his co-workers have high caliber expertise in the field.

- NMR is a unique characterization tool which adds considerably to the study of reaction paths in hydrides, especially in cases where other characterization tools such as X-ray diffraction and infrared spectroscopy may be unrevealing.
- Highly valuable expertise in analysis and characterization that is being utilized.

Weaknesses
- No apparent weaknesses.
- Difficult to obtain $M(B_{12}H_{12})_n$ samples in pure form without hydration, in order to characterize pristine material.
- Lack of communication with other CoEs, especially with the ones that have similar knowledge in NMR tool.

Specific recommendations and additions or deletions to the work scope

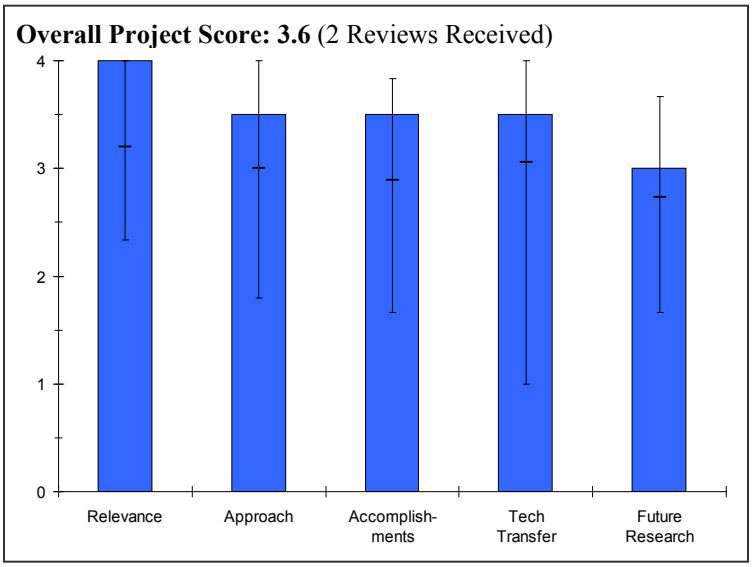
- Be ready to re-schedule resources and access to facilities in view of down-selections to account for possible new promising materials that may come up.

Project # STP-39: Effect of Trace Elements on Long-Term Cycling/Aging Properties and Thermodynamic Studies of Complex Hydrides for Hydrogen Storage

Dhanesh Chandra, Josh Lamb, Wen-Ming Chien, and Ivan Gantan; University of Nevada, Reno

Brief Summary of Project

The primary objective of the project is to determine the effects of gaseous trace impurities (e.g., O_2, CO, H_2O, CH_4) in hydrogen on long-term behavior of the complex hydrides/precursors by pressure cycling and/or thermal aging with impure hydrogen. Secondary related objectives are 1) vaporization behavior of hydrides and 2) crystal structure studies.



Question 1: Relevance to overall DOE objectives

This project earned a score of **4.0** for its relevance to DOE objectives.

- The project aligns with the Hydrogen Program and DOE RD&D objectives.
- Project nicely supports DOE objectives in practical engineering areas not covered very well by other projects.

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- Solid theoretical background and effective experimental approach.
- Project focuses on capacity (weight), cyclic durability (impurities) and kinetics (reaction pathways).
- The work is highly focused toward practical properties.
- The effort has focused mainly on the Li-N-H (Li nitride-imide-amide) system. This system is a logical choice for the time being, but does not necessarily have long-range, practical potential.

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

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

- The results are simultaneously excellent from both scientific and engineering points of view.
- Large amounts of practical data have been generated.
- PI has derived an excellent picture of the nitride-imide-amide reaction pathways via detailed Li-N-H ternary phase diagram determinations. An important new intermediate phase has been found.
- A more direct, quantitative tying of the results to the DOE goals might have been possible.
- A lot of interesting data. At the same time, some the key assumptions (e.g., Li_4N-H) need additional confirmation.

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

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

- Good industrial collaboration, but there is no direct industrial involvement in the project.
- There are many excellent national and international collaborations in place.
- This PI is an important contributor to the Metal Hydride CoE.

Question 5: Approach to and relevance of proposed future research

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

- Plans are reasonable, address major issues, and include necessary measures to overcome existing barriers.
- Future plans are good, but it is important to put more emphasis on new materials (i.e., beyond the Li-N-H system).

Strengths and weaknesses

Strengths
- Very good phase analysis results.
- Impressive international collaboration.
- A good, practical approach to hydrides from a material science point of view.

Weaknesses
- There should be more industrial involvement and collaboration.

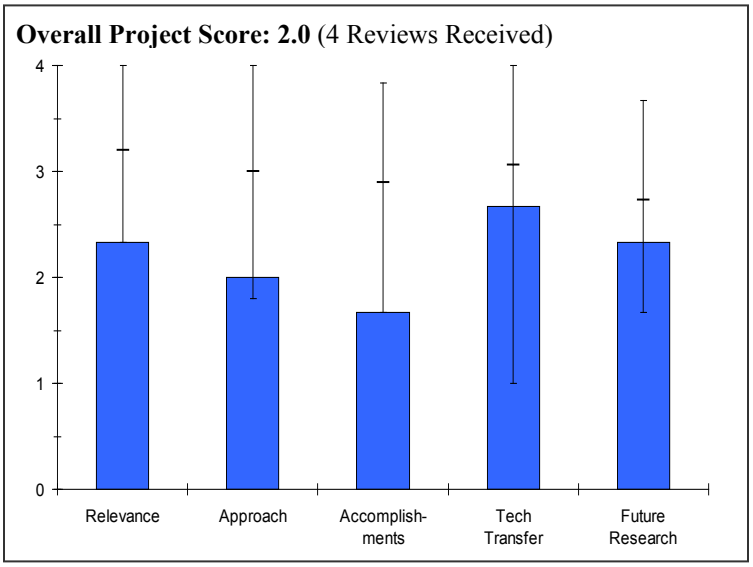
Specific recommendations and additions or deletions to the work scope

- Extend the project into related areas including materials chemistry (i.e., solid-state chemical transformations in ammonia-lithium-lithium hydride - nitrogen system[s]).
- Conduct more gaseous impurity cyclic studies on new candidate hydrides.

Project # STP-40: Amide and Combined Amide/Borohydride Investigations
J. Gray, L. Dinh, M. Bharaty, H. zur Loye and D. Anton; Savannah River National Laboratory

Brief Summary of Project

The objectives of this project are to 1) Collaborate with University of Utah group to perform complementary experiments to analyze the LiMgN system, 2) verify reversibility conditions of $TiCl_3$-doped LiMgN, 3) explore the effect of catalyst loading on both charge and discharge reaction pathways and kinetics, and 4) outline discharge and charge kinetics under various temperature and pressure conditions to prepare for hydrogen storage system design. The project will perform isothermal kinetic studies under well-defined, controlled reaction conditions to obtain the experimental data required to determine isothermal kinetics and characterize the proposed reaction for hydrogenation and dehydrogenation of LiMgN.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.3** for its relevance to DOE objectives.

- The research directions followed in this project are generally aligned with the program's objectives, support the DOE R&D plans, and target a number of barriers.

Question 2: Approach to performing the research and development

This project was rated **2.0** on its approach.

- Sensible, straightforward, targeted approach. The Li-Mg-N system study appears to be very well organized and followed up with engineering targets always in mind.
- Ball milling will not result in a high volume manufacturing process suitable for the automotive industry. Ball milling techniques with low yields and long milling times are only suitable for lab purposes. The PI should abandon this approach unless a clear alternative and commercially scalable synthesis process is identified.

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

This project was rated **1.7** based on accomplishments.

- Sound progress and satisfactory degree of achievement with respect to objectives and original planning.
- For what has been achieved over previous years, the charge and discharge temperatures are still far too high. The reversible storage capacity has not been improved significantly.

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

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

- PI is working with the appropriate partners.
- Not clear whether technology transfer and collaborations are more extended than with the few partners mentioned in the poster/presentation.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- The future plans are appropriate and justified by the results produced so far.
- All the proposed work has been conducted countless times (milling time vs. kinetics); the results are predictable. These materials have been heavily studied already. PI should investigate alternate, cost-effective and scalable synthesis techniques for these materials. Without this there is little commercial or research interest at this stage.

Strengths and weaknesses

Strengths
- Investigating the potential of a practical storage material.

Weaknesses
- It was not clear how the data obtained will affect the engineering tank design.
- It was not clear how the minimization of NH_3 by−products is tackled.

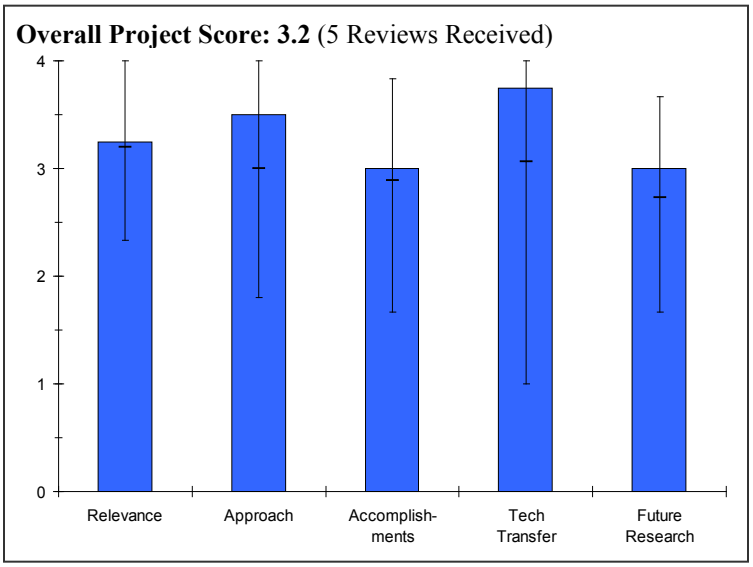
Specific recommendations and additions or deletions to the work scope

- The project team should stay well tuned to the progress within the Metal Hydride CoE, but also well linked to the Engineering CoE (e.g., for the issue of NH_3, breakthrough in trapping technologies or determination of maximum allowable levels).

Project # STP-41: Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

Channing Ahn, Sonjong Hwang, and David Abrecht; California Institute of Technology

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, which 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 (NMR), and transmission electron microscopy (TEM).

Question 1: Relevance to overall DOE objectives

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

- Systems with high overall hydrogen content have been considered.
- DOE goals in the areas of weight, refill kinetics, and reaction pathway understandings are adequately addressed.
- Relevance to HFCIT Program goals is adequate. The project investigates a number of nanophase materials while also offering support to other CoE partners (e.g., microstructural analysis of MgH_2 incorporated in aerogels).
- Destabilized systems offer one of the best routes to meeting the needs for high capacity and low cycling temperatures.
- Identification of phases and compounds formation based on the theoretical estimation results of promising systems is relevant to DOEs objectives.
- Some of the systems are too expensive to be commercialized (e.g., ScH_2).

Question 2: Approach to performing the research and development

This project was rated **3.5** on its approach.

- The work is well aligned with attempting to meet the DOE targets. A significant amount of support is also provided in characterizing materials from other labs, providing essential understanding of materials across a range of projects.
- Utilization of several characterization techniques is a very good approach. Also, looking at potential systems judging from density functional theory (DFT) calculations is reasonable.
- The California Institute of Technology group seems to have a range of skills (especially NMR) that is clearly helpful to the overall CoE.
- The overall approach contributes fairly well to the evaluation and enhanced understanding of the systems investigated. A better integration with other efforts in the CoE could have been attained though.
- The approach seems to be largely of a service and support nature to various partners and projects within the Metal Hydride CoE. This is fine, but makes it a bit difficult to judge the overall impact of this group.

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

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

- Quite a lot of interesting results have been obtained during the last year. Some are positive and some are negative, but all are important to developing necessary understandings.
- A number of accomplishments that offer useful data and input have been presented (e.g., on $MgB_{12}H_{12}$, Li-Sc-B-H, and Li-Ca-B-H systems). The $TiH_2 + LiBH_4$ system that was investigated (due to its interesting ΔH value) gave the results that might have been expected from the beginning.
- The data provided to other partners regarding the MgH_2 incorporation in aerogels are also useful.
- The systems investigated meet the DOE goals for capacity and in theory have cycling temperatures closer to the target range. Kinetics at these low temperatures is still an issue, but nanostructuring may help with this.
- The results are presented in a rather scientifically objective manner. There should have been clearer connections to practical implications for overcoming the DOE barriers.
- The alane:lithium borohydride system was not reported this year, is it no longer being pursued?
- Much remains unknown about the actual mechanisms of reactions under consideration.

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

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

- Visible collaboration with several CoE members.
- This effort has good collaborations within the CoE. It is a good example of a collaborative "service" partner within a CoE.
- Collaborating extensively across a range of projects, this is to be commended.
- A sufficient degree of collaboration with other CoE partners exists, although further improvements could be made in that respect.

Question 5: Approach to and relevance of proposed future research

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

- The proposed plans are a logical development upon this year's work.
- Future work continues to service CoE, as it should.
- Future plans should be given in a more detailed manner and focus on specific interesting aspects as the project end approaches. As they appear now, they seem diverse without appropriate prioritization (taking in account the limited time and funds available).

Strengths and weaknesses

Strengths

- Excellent characterization expertise and techniques capabilities (i.e., magic angle spinning (MAS)-NMR, Raman, TEM).
- High-hydrogen-content systems are being scrutinized.
- Good combination of techniques, including NMR.
- Group has excellent skills for complimenting the other CoE partners' capabilities.
- Good expertise of partner, wide range of available techniques.
- Characterization and insight into a range of storage materials. Extensive collaborations.

Weaknesses

- The implicit assumption that the only gaseous product of reactions is hydrogen needs to be verified for every transformation.
- The project is not really assessing the practical implications of the results very well. What do the scientific findings really mean relative to overcoming DOE barriers?
- Lack of focus on specific promising aspects.
- None.

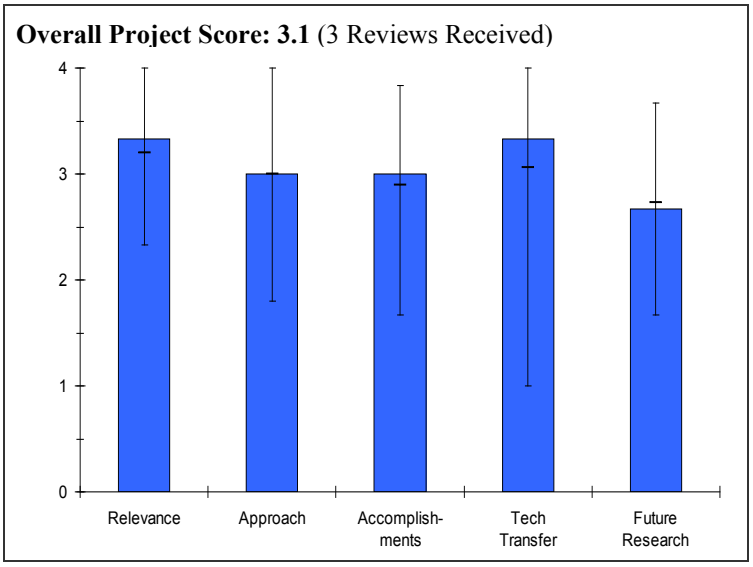
Specific recommendations and additions or deletions to the work scope

- Emphasis could be placed in the limited remaining time on scaffolding aspects.

Project # STP-42: Lightweight Borohydrides for Hydrogen Storage
J.-C. Zhao; Ohio State University

Brief Summary of Project

The overall objective for this project is to discover and develop a high-capacity, (>6 wt%) lightweight hydride capable of meeting or exceeding the 2010 DOE/FreedomCAR targets. Objectives for FY 2008 were to 1) study the desorption mechanism and explore ways to make the $Mg(BH_4)_2$ reversible, 2) explore new hydride materials, and 3) study an aluminoborane compound AlB_4H_{11} for suitability for hydrogen storage. Objectives for FY 2009 are to 1) study $Mg(BH_4)_2$, $Mg(B_3H_8)_2$, and $MgB_{12}H_{12}$and their amine complexes for hydrogen storage and 2) synthesize and characterize new boro-amine hydride materials.



Question 1: Relevance to overall DOE objectives

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

- This project is part of the Metal Hydride CoE and is aligned with the overall objective of the CoE and Hydrogen Program.
- The project aims at discovering and developing high-capacity, lightweight hydrides capable of meeting the DOE hydrogen storage targets for on-board vehicular applications. It is well aligned with the overall RD&D objectives.

Question 2: Approach to performing the research and development

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

- Well organized and focused using a systematic, clear approach for exploring two classes of materials: $Mg(BH_4)_2$ and aluminoborane compounds and their amine complexes. It also plans to use the mechanistic understanding it steadily gains on the complex desorption processes for developing a reversibility strategy for all borohydrides.
- The approach is well within the norm, albeit somewhat ineffective. Sometimes there are no good solutions to a thermodynamic problem. De-destabilization approach appears to have ad hoc success, at best, for complex hydrides. Having said that, this is a natural part of the scientific exploration and should not be considered as a criticism.

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

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

- The project has produced many results. The PIs have been very candid about the outcomes and have correctly decided to explore other alternatives.
- Significant progress has been accomplished in line with the project objectives. Highlights include the next steps for the understanding of the "nature" of the intermediate phase, the $MgB_{12}H_{12}$, which is very important for reversibility and forms during the decomposition of $Mg(BH_4)_2$. Despite literature claims, is not anhydrous.

Equally significant was the amine complexes work and the synthesis of $Li_2B_{12}H_{12}$, which will be encapsulated into aerogels.
- Nice work on aluminoborane compounds and attempts to isolate $B_{12}H1_2$ compounds.
- Little progress on ammoniated borohydrides this year.

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

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

- The project is part of the Metal Hydride center and appears to have adequate communication within the team.
- Exploring strong links established within the CoE and other institutions. Of particular added value is the establishment of the Metal Hydride CoE subgroup on borohydride-amine complexes led by the PI.

Question 5: Approach to and relevance of proposed future research

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

- Sound future plans that include further synthesis work, but also mechanistic studies and catalyst screening for improving the reversibility and exploring the potential of these material classes.
- It would have been more effective to define the other possible candidates to be examined.

Strengths and weaknesses

Strengths
- The project team has strong capabilities.
- The project team has valuable experience and competence in the field and strong collaborations.
- The project is rather exploratory: it looks for breakthroughs in reversibility of borohydrides (a strength, but also a weakness).

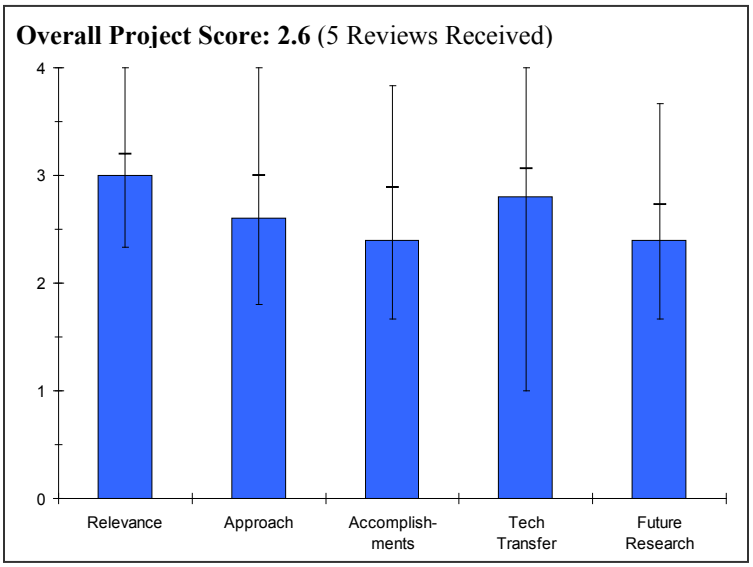
Weaknesses
- Difficult area of research.
- The project is rather exploratory: it looks for breakthroughs in reversibility of borohydrides (a strength but also a weakness).

Specific recommendations and additions or deletions to the work scope

- The PIs also need to review the work that has been completed by system analysis project (ANL) to help them narrow down the practical limits of a potential successful reversible metal hydride. Optimistically, there is enough data to suggest that a good candidate would have an enthalpy less than 30 kJ/mol-H2 and equilibrium temperatures below 120°C-150°C with absorption/desorption pressure of at least 5 atm. Before embarking on a new direction or materials, it is necessary (but not sufficient) to conduct an internal assessment of the potential success of a material.
- Recommendations are to intensify collaborative efforts, coordinate the research, and ensure transfer of knowledge within the Metal Hydrides CoE subgroup of borohydride-amine complexes.

Project # STP-43: Center for Hydrogen Storage Research at Delaware State University
Andrew Goudy; Delaware State University

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 2008 objectives were 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. The 2009 objective was to make a go/no-go decision. The team decided not to continue studies on ternary borohydride systems that contain amides. The team will continue to focus on other borohydride systems with reaction enthalpies predicted to be less than 50 kJ/mol·H_2.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.0** for its relevance to DOE objectives.

- The project aligns with the Hydrogen Program and DOE RD&D objectives.
- Designing or identifying new high-capacity materials for on-board hydrogen storage are a key element toward meeting DOE objectives for hydrogen storage. The mixed borohydride and destabilized materials presented in the 2009 AMR are members of a class of compounds that need to be explored because they could potentially offer sufficient capacity and reasonable thermodynamics. The kinetics measurements being performed as part of this work, using H_2 overpressure with a constant pressure driving force, have particular relevance to on-board storage. They map more directly to real storage systems than most kinetics measurements that either do not use constant pressure (e.g., PCT-type measurements) or are performed into an H_2-free atmosphere.
- The project is investigating high-capacity, complex hydrides and the use of either mixed metal cations or multi-component systems to achieve a destabilization of Group I and II borohydrides.
- The project is somewhat relevant to the DOE Metal Hydride CoE objectives, but it is not well integrated into that effort. The University of Delaware effort is not part of the Metal Hydride CoE.

Question 2: Approach to performing the research and development

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

- Work was reported on various compounds. The kinetics and cyclability of these systems are being investigated which compliments similar work to that coming out of Hawaii. The project appears to be well focused.
- Synthesis and measurement approaches are conventional, producing interesting mixed borohydride materials. Expanding expertise in mass spectrometry to examine composition of evolved gases is encouraged. Approach to kinetics measurements is on the mark.
- The limited number of characterization techniques is insufficient to elaborate on what is happening in the studied systems.
- The approach is effective but could be improved.
- Even though the presentation indicates that some collaboration is taking place, the work does not appear to be well guided or supported by theory. It appears to be Edisonian in nature, based on trial and error.

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

This project was rated **2.4** based on accomplishments.

- The group presented results on several interesting materials including the Li-Mn-B-H system.
- Interesting thermogravimetric analysis (TGA) results have been obtained on $AMn(BH_4)_3$ (A=Li, Na) systems, but more characterization is needed to determine the active phase(s) in the ball milled specimens. NMR might be a good adjunct to help determine phase composition for samples where X-ray diffraction (XRD) is not fully revealing.
- Some interesting effects have been noticed during the dehydrogenation of the mixed metal borohydrides. However, there is currently no theory to explain the effects. This needs to be investigated further and developing collaborations with other CoE members might help.
- A few reactions were studied and data was collected, but there appears to be no real understanding. The assumption that back pressure in the pressure-composition isotherm (PCI) may affect decompositions is unsupported.
- Not a lot was accomplished during the past year. Progress has been slow, perhaps additional effort is needed. Chemical analysis and composition of the dehydrogenation products is not presented. There is speculation that diborane may be an issue, but this was not confirmed. No evidence is presented that indicates reversibility for these materials. On a positive note, the number of publications and presentations has increased from 2008.

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

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

- Some collaboration with University of Pittsburgh, Georgia Institute of Technology, University of Delaware, and Air Liquide is indicated.
- Collaboration can be improved by adding an industrial partner.
- Collaborations with University of Pittsburgh and Georgia Institute of Technology are indicated, but there is little evidence of this in the presentation.
- The PI has made some collaborations, but for the future direction of the project, collaborations with some other key CoE members are recommended (e.g., Professor Jensen at University of Hawaii). This will also help develop added value to the work and avoid duplication of effort.

Question 5: Approach to and relevance of proposed future research

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

- Plans are reasonable, and goals look achievable.
- Focus is on developing further systems with lower than 50 kJ mol-1 dehydrogenation enthalpies, nanostructuring these types of materials, and investigating the kinetics and cyclability. All aspects are important to the design of a practical storage material.
- The proposed future work matches well with overcoming barriers, but is vague as to the candidate systems to be examined and the methods to be used. Also, given the size of the effort, it appears somewhat diffuse, covering a broad range including synthesis and characterization of unique new materials, thermodynamic measurements, kinetic measurements, cycling measurements, and nanotechnology additions to improve kinetics. Is it possible for the PI to successfully address all of these areas? The kinetics method proposed is very appropriate to materials for on-board storage.
- The planned future work is certainly necessary, but there is some doubt as to whether it can be accomplished in the remaining time given the slow progress to date. The work plan for the Mg-LiBH system is not evident. Since this system is still being investigated in the Metal Hydride CoE, additional kinetic and thermodynamic data would be welcome.
- It was difficult to evaluate the future plans because they were generic and it was unclear where this project is going.

Strengths and weaknesses

Strengths
- Realistic approach.
- An interesting set of research objects.
- Synthesis of mixed borohydrides; approach to kinetics measurements.
- Bringing more kinetic understanding of these types of systems.

Weaknesses
- The group may benefit from a better coordination with others working in the same field (the Li-Mn-B-H system has been studied by another group who also presented a poster at this meeting).
- Full characterization of samples needs greater emphasis to determine the active compounds in ball milled samples.
- Work plan is not well defined and progress has been slower than anticipated.
- Important to avoid duplication of work in other labs.

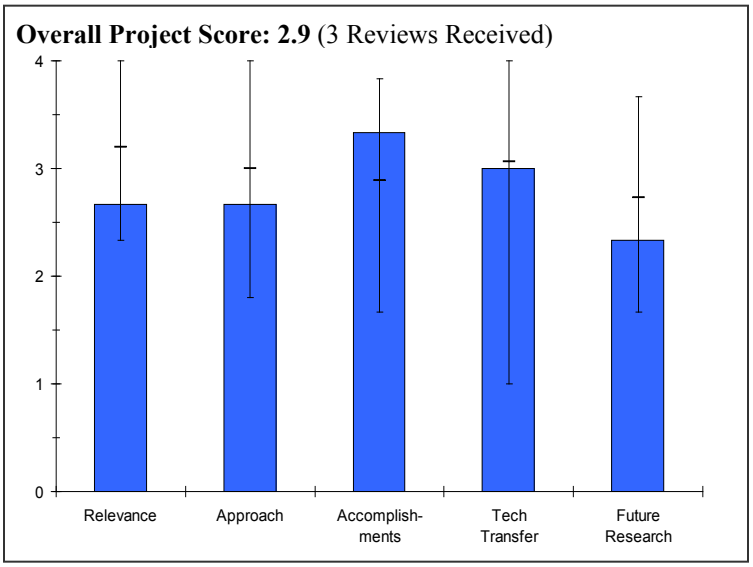
Specific recommendations and additions or deletions to the work scope

- Work going forward could be more focused on the synthesis/characterization work on mixed borohydrides and the kinetics studies using constant pressure driving force that have led to interesting results to date. Nuclear magnetic resonance, if available locally or collaboratively, could offer a good adjunct to XRD and infrared (IR) toward characterization of the compounds present in the prepared and decomposed mixed borohydride materials.
- The future work is sensible and supported, but the PI needs to think about developing some strategic collaborations. One important addition would be to investigate the phase changes during dehydrogenation and hydrogenation.
- The project needs to narrow its focus in order to bring the work to a conclusion with meaningful results (i.e., pick a material and determine adsorption and desorption kinetics and thermodynamics).

Project # STP-44: Solid-State Hydriding and Dehydriding of $LiBH_4$ + MgH_2 Enabled via Mechanical Activation and Nano-Engineering

Leon Shaw: University of Connecticut

Brief Summary of Project



This project is exploring fundamental mechanisms related to mechanical activation and nano-engineering necessary for improving kinetics of reversible hydrogen storage materials. This will be done by investigating the hydriding/dehydriding properties of $LiBH_4$+MgH_2 materials with different degrees of mechanical activation and nano-engineering; enhance the storage performance based on the understanding developed. The overall objectives of this project in FY 2009 are to (1) Further improve the solid-state hydriding/dehydriding properties of $LiBH_4$ + MgH_2 via ball milling at liquid nitrogen temperature with the addition of transition metals and milling additives such as boron nitride, (2) Investigate the hydriding and dehydriding reversibility of carbon aerogel confined $LiBH_4$ and increase its storage capacity, and (3) Demonstrate hydrogen uptake and release of $LiBH_4$ + MgH_2 systems with a storage capacity of ~ 10 wt% H_2 at 2000°C.

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 DOE Hydrogen Program goals. Work with the Mg-LiBH system is warranted because this material is still under consideration within the Metal Hydride CoE. Phenomenological studies on this material have some value. However, the project duplicates the effort within the Metal Hydrides CoE.
- Nothing unique was presented compared to 2008. Ball milling and nanoengineering have been attempted without sufficient reasoning.

Question 2: Approach to performing the research and development

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

- Gas analysis during decomposition could be helpful.
- Hydrogen uptake and release did not meet the milestone.
- The approach of incorporating nanoparticles into a support scaffold to prevent particle growth during cycling is similar to the effort in the Metal Hydrides CoE. However, there is no clear cut evidence that nanosizing particles improves the thermodynamics. Preparing material through extensive ball milling at liquid N_2 temperature does not appear to be a viable route to meet automotive quantities, even if this material can be successfully developed. Use of a catalyst may be necessary to increase reaction rates. A final dehydriding temperature of over 200°C is required to release all the hydrogen; this does not meet DOE targets. Doping with transition metals to improve kinetics seems to be more ad hoc than guided by theory.

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

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

- The PI has made a good attempt.
- A substantial amount of work was reported. A partial ion exchange model was developed to elucidate the hydriding/dehydriding mechanisms. Nuclear magnetic resonance (NMR) studies at PNNL have helped to elucidate the reaction mechanisms. Some success at incorporating the hydrides in the carbon aerogel was achieved, however there is no indication that the material is stable under cycling conditions.

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

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

- The collaborations were good.
- Good collaboration with PNNL and HRL Laboratories, LLC is evident. However, there does not appear to be good collaboration with the Metal Hydrides CoE. The PI did not offer a comparison with results reported by the Metal Hydrides CoE on similar materials.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.3** for proposed future work.

- No-go decision was made.
- The proposed future work plan is very ambitious if the project will end in December 2009 as stated in the presentation.

Strengths and weaknesses

Strengths
- Good group.
- Solid-state reaction was investigated very precisely.
- Good record of publications.

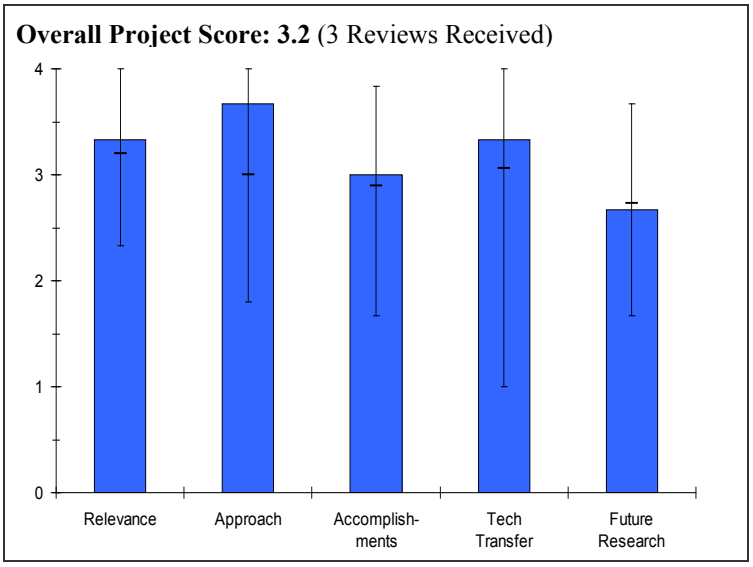
Weaknesses
- The project does not appear to be very well thought out.
- Strategy for selecting additives is not explained and is unclear.
- There is no clear path to reducing the end point dehydriding temperature.

Specific recommendations and additions or deletions to the work scope

- If the work is carried on, the PI should interact with HRL to decrease the risk of duplication of effort in the nanoconfinement activity.

Project # STP-45: Standardized Testing Program for Solid-State Hydrogen Storage Technologies
Michael Miller and Richard Page; Southwest Research Institute®

Brief Summary of Project



The overall objectives of this project are to 1) support DOE's Hydrogen Storage Program by operating an independent national-level laboratory aimed at assessing and validating the performance of novel and emerging solid-state hydrogen storage materials and full-scale systems; 2) conduct measurements using established protocols to derive performance metrics: capacity, kinetics, thermodynamics, and cycle life; 3) support parallel efforts underway within the international community, in Europe and Japan, to assess and validate the performance of related solid-state materials for hydrogen storage. Current objectives are to 1) provide an in-depth assessment and validation of hydrogen spillover in Pt/activated carbon (AC)-bridged metal-intercalated metal-organic framework (IRMOF)-8 and AX-21 compounds; 2) assess hydrogen adsorption and spillover phenomena in catalytically doped carbon foams; 3) evaluate the thermodynamic plausibility of hydrogen spillover in catalytically doped metal-organic frameworks; and 4) continue round-robin testing in collaboration with the European Union's hydrogen storage program (NESSHY).

Question 1: Relevance to overall DOE objectives

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

- This project is focused on establishing a standardized and robust testing procedure for hydrogen storage research. This is an extremely valuable element of the DOE program because reliable, reproducible results are essential for progress to be made in achieving DOE's goals and objectives.
- This effort indirectly supports DOE targets and plans, especially in the properties of weight, volume, thermodynamics, and cycle life.

Question 2: Approach to performing the research and development

This project was rated **3.7** on its approach.

- The basic philosophy of this project is to provide a national source of testing, verification, and other contributions. This is clearly important.
- The PIs have used care in choosing materials for their experiments and in preparing samples for testing. The current experimental assessment of hydrogen uptake seems to be limited to gravimetric methods. This is a very good start, but more should be done toward understanding spurious and irreproducible results. These have not only have appeared in the literature, but these researchers themselves have experienced it for the so-called "spillover effect" materials. Adding a separate, independent measurement, such as a Seiverts method, would be an excellent way to try to get internal consistency in their hydrogen uptake results. Very nice work on kinetics and cycle life of the Mg-Li-B-N-H materials.
- The work appears to be a mixture of DOE-directed efforts, international (DOE-supported) support, private jobs, and internal Southwest Research Institute (SwRI) work. It is not clear how these distinct activity bases operate, especially relative to setting time priorities and reimbursement to the testing center.

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

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

- These researchers have seen significant variability in their own results for spillover effect materials that they have measured (e.g., the metal-doped carbon foam) that remain unexplained. Is it the material or is the measurement in question? Because the validity of results for the spillover effect interpretation of otherwise unexplainable data is very controversial among the larger hydrogen storage scientific community, it would be better if this project focused more on being an unbiased assessment of that interpretation. This project needs to help to identify what results are accurate, what measurement techniques are required to really be accurate for this kind of study on these kinds of measurements, and how spurious data can arise.
- A number of diverse activities and results were shown, but it was not made clear how these results bring us closer to meeting DOE system targets.
- Except for one slide on Pd/polyaniline, all of the DOE directed results are on Li-Mg-B-N-H (from University of South Florida [USF]). What is the basis of the extensive work on this material? The results do not seem impressive, for example, relative to simple catalyzed MgH_2. How do these conclusions relate to DOE needs?
- The NESSHY work on PdHg/carbon foams has been useful, if apparently in a negative (poor reproducibility, H_2O) sense. At last year's AMR, the presenter stated that no H_2O was desorbed on this poster.

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

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

- This project has a very good collaborative research portfolio.
- Shows H_2O dominates over H_2 desorption. The major change and its technological implications are confusing. Does the NESSHY foam now have little practical potential as a storage medium for high-purity H_2?
- While it is beneficial for privately-funded, related work to be included in DOE merit review presentations, especially when carried out on DOE contributed equipment, potential intellectual property conflicts must be considered and avoided.
- The standardization and round-robin testing should have important worldwide effects in reducing error. Has this happened to a significant degree?
- A number of collaborations are listed; however, except for NESSHY, few details and results are given. Are these collaborations generally resulting in synergy and benefit for DOE's investments in the testing center?

Question 5: Approach to and relevance of proposed future research

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

- The proposed future work is fully directed toward achieving the stated goal of developing a standardized testing procedure for such materials as the spillover effect samples.
- Only seven samples are planned for future work.
- Only one sample is scheduled for completion in June 2009.
- Project completion date is 2011, but there is no clear description of future work.
- Future work planned is only the present sample backlog. What is the justification for accepting these particular samples versus the DOE barriers?

Strengths and weaknesses

Strengths

- Standardized testing procedures are essential to good research on hydrogen storage materials, and this project is all about that.
- The concept of having a national testing lab is, in principle, sound and valuable to DOE and the entire storage materials community.

Weaknesses

- It seems that there is too much bias toward acceptance of questionable results (e.g., spillover effect) that give hard-to-understand data. This leads to expectations that the results will be (or should be) verified. When there is variation of a factor of 4 in hydrogen uptake, the presumption is that the sample is to blame rather than questioning if the interpretation of the uptake data is correct. Could there not be something other than hydrogen uptake going on in these materials that could give the results? The project needs to give much more attention to the robustness and accuracy of the experiment and its interpretation before assuming the mechanism of spillover can be applied.
- It is not clear the results so far have improved the general, national, and worldwide accuracy of testing.
- There seem to be a number of independent activities being pursued without clear justifications.

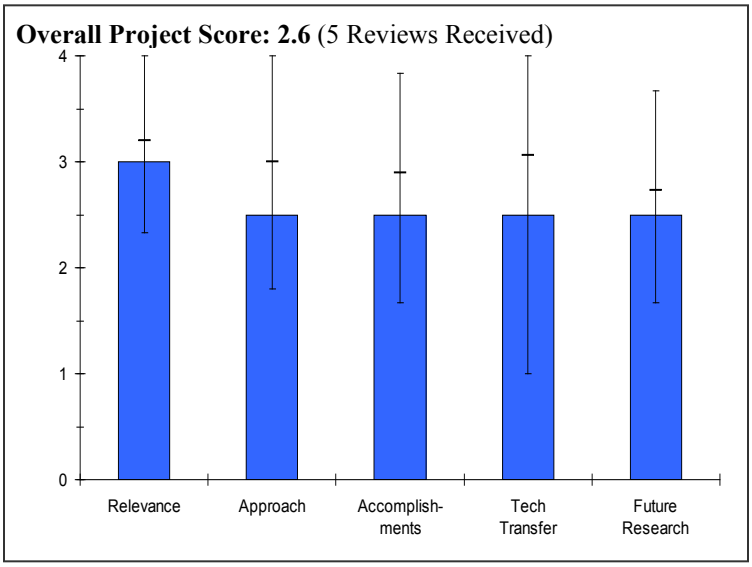
Specific recommendations and additions or deletions to the work scope

- Add more confirmation that hydrogen is really being taken up by the sample in the way assumed (i.e., spillover) via gravimetric and other methods. Explain why the conditioning is necessary for the Pd-doped polyaniline (PANI), and why the initial uptake of hydrogen is so rapid with pressure. Does this really have anything to do with the PANI, or is it merely due to Pd?
- A better mechanism is needed to decide on the value of taking on a new material. It is unclear what that mechanism should be.

Project # STP-46: An Integrated Approach of Hydrogen Storage in Complex Hydrides of Transitional Elements

Abhijit Bhattacharyya, Tansel Karabacak, Ganesh Kannarpady, Fatih Cansizoglu, Anindya Ghosh, Dustin Emanis and Mike Wolverton; University of Arkansas at Little Rock

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 a 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, 2) 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 **3.0** for its relevance to DOE objectives.

- This work is very well aligned with the goals and objectives of the DOE Hydrogen Program.
- Most project aspects are aligned with DOE RD&D objectives.
- The calcium borohydride work is the most relevant to the overall DOE objectives. The Ti in polymers has theoretical work in the literature predicting high capacities, but no researcher has managed to stabilize isolated Ti atoms in such materials. The least relevant work was the magnesium nanoblades as magnesium hydride has already been deselected by the MHCoE.
- There are gaps in the consideration of volume and cost.
- This project is not very well focused.

Question 2: Approach to performing the research and development

This project was rated **2.5** on its approach.

- This project focused on the possibility of synthesizing density functional theory (DFT)-predicted metal-decorated materials, synthesis and reversibility of Ca-B-H material, and the use of conventional metal hydride as an additive to complex hydrides. These approaches address, to a significant degree, the identified barriers of understanding physisorption/chemisorption, kinetics, and durability of hydrogen storage materials.
- This project is a mixture of various activities in macro- and nanomaterials.
- As shown by presenters' references to prior work, most of the materials being studied are also being studied elsewhere. It is not at all clear what is different in this work.

- There appears to be a lack of awareness between this project team and work going on in the MHCoE. Lack of communication with the MHCoE has meant the work has not progressed as well as it might have:
  - The group has struggled to synthesize calcium borohydride and would benefit from advice from the MHCoE into the conditions for this.
  - Ball milling Ti clusters with polymer will not achieve atomically dispersed Ti through the polymer matrix. This is the wrong type of synthetic approach.
  - The Mg nanoblades have dimensions too large for any size-induced affects on the dehydrogenation thermodynamics.
- This work was not very well thought out.

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

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

- Very good work on Ca-based complex hydrides and the nanostructured glancing angle deposition (GLAD) materials, especially with the quartz crystal microbalance (QCM). However the work also demonstrated how a faulty valve can give an apparent positive result for hydrogen uptake where none occurs and that the DFT-predicted metal-decorated materials are, once again, not possible to synthesize in the laboratory.
- Presenters are to be praised for the frank admission that all experimental work on metal-decorated polymers has been completely negative. Likewise for the admission that earlier finite storage results were a result of experimental errors.
- Development of the QCM technique may be useful.
- A new synthesis method for $Ca(BH_4)_2$ may have been developed from $NaBH_4$. However, here is the best example of ignoring cost considerations. A process for the chemical synthesis of Ca borohydride from expensive $NaBH_4$ seems highly questionable.
- The bulk characterization of $LaNi_5$ is especially perplexing. The results are exactly the same as shown by many early investigators of $LaNi_5$. Is this a learning process using an old reference material?
- Development of the GLAD technique may have some synthesis value. Will it ever be a potential low-cost mass production technique?
- Work on GLAD nanobladed Mg is interesting, but offers no real advantages over many other Mg efforts for meeting DOE goals. Catalyzed and composite micro- and nano-Mg have shown similar (and even better) H_2 absorption improvements. Without major improvements in desorption thermodynamics (e.g., 1 bar desorption plateau pressure at <100°C), significant H_2 will have to be burned for the necessary 300°C desorption enthalpy, making it impossible to reach DOE system goals.
- There are some interesting ideas which the group may wish to pursue for destabilized calcium borohydride systems. Unfortunately, this work has been hampered by the inability to synthesize this borohydride.
- The group proved that ball milling Ti clusters with various polymers did not produce materials with any interesting hydrogen storage properties.
- The magnesium nanoblades were shown to have fast hydrogenation kinetics at low temperatures. However, the thermodynamics of the system has not been addressed; hence, the work is of low impact. N.B.: 30 nm dimensions will not lead to a change in the thermodynamic properties.
- The progress has not been good.
- Progress towards the DOE objectives has been very limited.

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

This project was rated **2.5** for technology transfer and collaboration.

- Good collaborations.
- A few collaborations listed, but not described in any detail.
- The investigators seem to have little interaction with other hydrogen storage research groups. The exchange of ideas is essential if researchers are to avoid falling into the same traps as others. The work here would be greatly enhanced if the group integrates more with the MHCoE. The MHCoE should be encouraged to offer some guidance to these investigators (if this has not already happened).

Question 5: Approach to and relevance of proposed future research

This project was rated **2.5** for proposed future work.

- Efforts should be focused more on the areas that are more relevant to the DOE objectives. The calcium borohydride work would appear to be the most fruitful area for investigation. The investigators have down-selected the Ti-polymer materials, which seems sensible. There was no clear idea for how the nanoblade work was going to translate to other more relevant materials. This would appear to be a weaker line of investigation, and it is recommended that the magnesium hydride nanoblade work be stopped. If this nanoblade technology can be translated to other more relevant hydrogen storage materials, then this would be of interest.
- The proposal for future work was vague.
- This reviewer is glad to see that there are apparently no further plans to work on DFT-predicted metal-decorated materials in this project. It seems that this area of modeling work was an attempt to somehow legitimize the early work on hydrogen uptake by carbon nanotubes that turned out to be only metal impurity particles that do the absorbing of hydrogen. The idea that somehow those metal particles or atoms can decorate carbon structures, remain stable, and absorb hydrogen has not been convincingly demonstrated experimentally, and consequently, is not based in reality. It seems that the "spillover" effect is another example of this. It is past the time to move on to materials that have a better chance of being real and practical hydrogen storage materials.
- The proposed future work is not very innovative or new. There is a low potential for meeting any DOE goals. Most work planned has already is repeating work already completed in various places around the world.

Strengths and weaknesses

Strengths
- Enthusiastic to get results.
- Very interesting synthesis and characterization methods using GLAD and QCM.
- The strengths in this project were limited.
- Some interesting new ideas being proposed for the calcium borohydride system backed up by an enthusiastic thrust for discovery.

Weaknesses
- Not good background to follow this area of research.
- Too much time was spent trying to create the DFT-predicted metal decorated materials in the laboratory.
- Presenters seem to be new to the field and are lacking in understanding of this field's history.
- Poorly thought out synthesis for Ti-polymer materials. Lack of awareness of current developments and perceived wisdom in the area means the group has spent time investigating systems either of low relevance to the DOE objectives (e.g., Mg nanoblades) or of theoretically predicted materials that are technically very challenging to make (Ti-polymer).

Specific recommendations and additions or deletions to the work scope

- Recommend no further work be done on DFT-predicted metal-decorated materials.
- The scope of project should be reworked for more innovation and connection to DOE goals.
- It is essential that this group build up collaborations with other key members of the CoE. This will help the group develop a more strategic focus. It is recommended that the Mg/MgH_2 nanoblade work be discontinued. The work on calcium borohydride is encouraged to continue. The group may wish to consider ways to produce nanostructured complex hydride systems.

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