

2007

Hydrogen Storage

Summary of Annual Merit Review Hydrogen Storage Subprogram

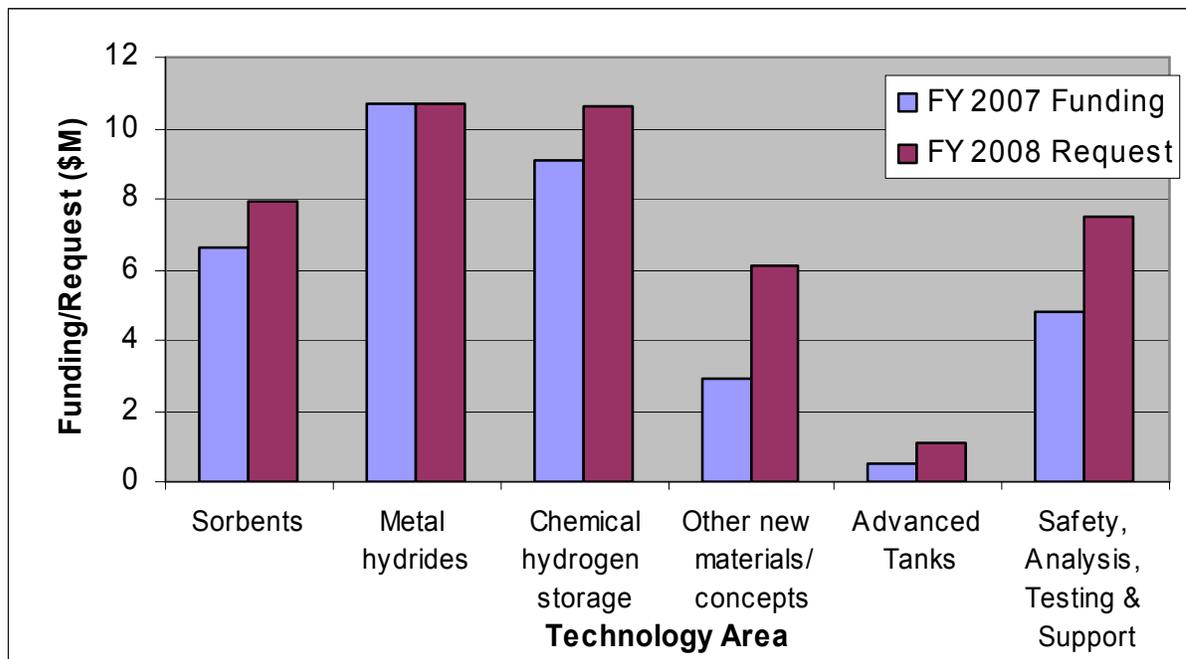
Summary of Reviewer Comments on Hydrogen Storage Subprogram:

Reviewers stated that the Hydrogen Storage subprogram was well focused with a robust R&D portfolio, clear ties to technical targets and well managed at all levels, both strategically and at the project level. Reviewer comments indicated that management of such a large and comprehensive effort with more than 80 projects requires coordination and sufficient program management resources. It was also noted that the Storage subprogram coordinates extensively with international activities as well as with the FreedomCAR and Fuel Partnership Technical Team and DOE's Office of Science. Reviewers stated that "the Center of Excellence approach on each main topic is an excellent and efficient way to pool resources for the R&D and provide clear focus to the participants." Of particular interest was the new Engineering Center of Excellence (CoE), which will help address systems issues often neglected by the other centers, and provide insight on the overall efficiency, cost, thermal management strategies, and the impact on system design and hydrogen delivery infrastructure.

Reviewer recommendations to the program included maintaining the processes to add new center and independent projects to ensure flexibility and agility. For the CoEs, it is important to continue to ensure transparency on the methods of operation and management (e.g. structure, decision process, communication flow & synergy among the sub-program areas, IP management). It is critical that the CoEs have mechanisms to share experiences and lessons learned particularly on cross-cutting issues. Engineering issues and tank system design could be further emphasized and the researchers should be encouraged to address them earlier on in the program. DOE was encouraged to continue reminding researchers that they must address system targets and not focus only on gravimetric capacities of materials. For example, the program should start emphasizing safety and toxicity issues for the benefit of all researchers as well as the role of such issues in the down-selection process. More emphasis was recommended on infrastructure issues and how various storage alternatives affect the well-to-wheels energy efficiency. Reviewers also recommended that the program start a review of the portfolio and assess the progress to date. Finally the CoEs should be encouraged to collaborate with each other as well as with independent projects and groups outside the DOE portfolio as appropriate.

Hydrogen Storage Funding by Technology:

The funding portfolio for hydrogen storage addresses primarily long-term materials R&D to meet 2010 and eventually 2015 targets for on-board applications. The requested EERE FY2008 funding profile, which includes the CoEs and independent projects, continues to address the National Academies' and FreedomCAR and Fuel Partnership's recommendations. Plans for FY 2008 (subject to congressional appropriations) include initiating a new Center of Excellence on applied engineering R&D to address system issues, as recommended by reviewers. The storage subprogram also plans to continue its annual solicitation to allow flexibility in eliciting new concepts and approaches that may not be in the current portfolio. A key milestone for FY2008 will be to down-select chemical hydrogen storage materials and accompanying regeneration processes. The chart below illustrates the funding in FY2007 for each major activity along with planned funding in FY2008 based on the Program's budget request.



Majority of Reviewer Comments and Recommendations:

Chemical Hydrogen Storage: Reviewers credited the Chemical Hydrogen Storage CoE with having a good understanding of the key barriers, and a well-formulated, well-focused approach to address critical issues. They stated that the CoE has applied a good mixture of experimental and computational tools and has good collaboration among partners. The CoE has made significant progress in understanding the hydrogen release mechanism in the ammonia borane (AB) system and in increasing both the kinetics and the amount of hydrogen released. However, continued effort is required to further optimize chemical additives and catalysts to increase the storage capacity as well as the kinetics for the 2nd equivalent of hydrogen. Guided by computational analysis, the CoE has developed a potentially energy efficient AB regeneration process. The CoE was also encouraged to continue the search for non-precious metal catalysts, to continue exploring and identifying new promising materials (including non-boron materials), and to maintain their focus on relevant material properties. The CoE was commended for actively applying self-regulating down-selection processes to reject unpromising materials and was encouraged to continue this practice including the narrowing down of regeneration pathways. There are some engineering efforts providing useful guidance for material development. Reviewers also encouraged wider application of up-front system and rough engineering analyses to help identify show stoppers at an early stage and guide material development to address critical issues. The reviewers commended the comprehensive assessment and analysis that was done to identify and rank promising sodium borohydride (SBH) regeneration approaches prior to experimental work. Work related to hydrolysis of SBH for on-board vehicular hydrogen storage will be reviewed in FY07 for a go/no-go decision. With regard to the organic liquid carrier work, it was recommended that systems analysis results be considered while continuing to improve overall capacity, efficiency and kinetics.

Sorbent-based Materials: It was generally recognized that the major accomplishment was the independent verification of metal organic framework (MOF) materials achieving >7 wt.% storage at 77K (MOFs developed by O. Yaghi). The reviewers recommended that DOE fully assess the implications of a cryogenic storage system to evaluate the potential of this class of materials. The other major promising approach is spillover materials, particular R. Yang's work. These materials have shown 1 to 3.5 wt%

material-based hydrogen storage capacity at room temperature and offer a promising avenue away from cryogenic methods. The reviewers recommended that this area of research be expanded to improve the understanding of underlying mechanisms and to improve material synthesis and testing reproducibility. Finally, the majority reemphasized the need to stress materials that lead to near room temperature storage of hydrogen at nominal pressure. Volumetric capacity, hydrogen uptake/discharge kinetics, and durability continue to be hurdles as well. The reviewers recommended that the portfolio be periodically reviewed to ensure that the projects emphasize these issues.

Advanced Metal Hydrides: In general the reviewers found that the Metal Hydride CoE was well-coordinated and organized with good collaborations between center partners. The fact that the center has “organically” down-selected materials which were not found to be promising for reversibility and/or meeting the DOE targets was considered a strength; however it was also felt that a clearer definition of criteria for continuing or discontinuing research on specific materials is needed. Two areas where the reviewers were especially encouraged by the past year’s accomplishments include the use of aerogel scaffolds with destabilized hydrides for lowering desorption temperatures and improving kinetics, and the use of organic adducts to aid in the regeneration of AlH_3 from Al. The reviewers were highly complimentary of the effort to determine the effects of gas impurities on long-term cycling of metal hydride materials and their degradation mechanisms. For the amide/imide materials the reviewers strongly suggested the need for quantification of ammonia release in the desorbed hydrogen. While theoretical modeling calculations were considered highly important and valuable, the reviewers suggested stronger collaborations with more center partners in all four of the key materials research areas and more effort in considering the reaction pathways versus predicted lowest energy end products. Since reaction kinetics is believed to be the major barrier to reversibility for a number of materials investigated, the reviewers recommend greater emphasis on catalyst research. Reviewers were encouraged by cross-center collaboration where expertise developed in one center can benefit the others, such as catalysis and alane regeneration. The majority of reviewers suggested further collaboration, especially with industry.

Tanks: Tank projects were not reviewed in FY2007 due to the reduced effort on tanks. Reviewer comments on the validation of the cryo-compressed hydrogen storage tank project (Lawrence Livermore National Laboratory) are presented in the Technology Validation subprogram of this report.

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

Note on Storage Report Structure:

Chemical Hydrogen Storage

ST-24 to 30 and STP-8 to 15 are partners of the Chemical Hydrogen CoE.
ST-23 is an independent project.

Sorbent-based Materials

ST-1 to 8 and STP-1 to 7 are partners of the Hydrogen Sorption CoE.
ST-9 is an independent project

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Advanced Metal Hydrides

ST-14 to 21 and STP-24 to 31 are partners of the Metal Hydride CoE.

Other New Materials and Concepts

ST-10

Testing, Safety and Analysis

ST-22, ST-31 to 33, STP-36

Cross-Cutting

STP-17

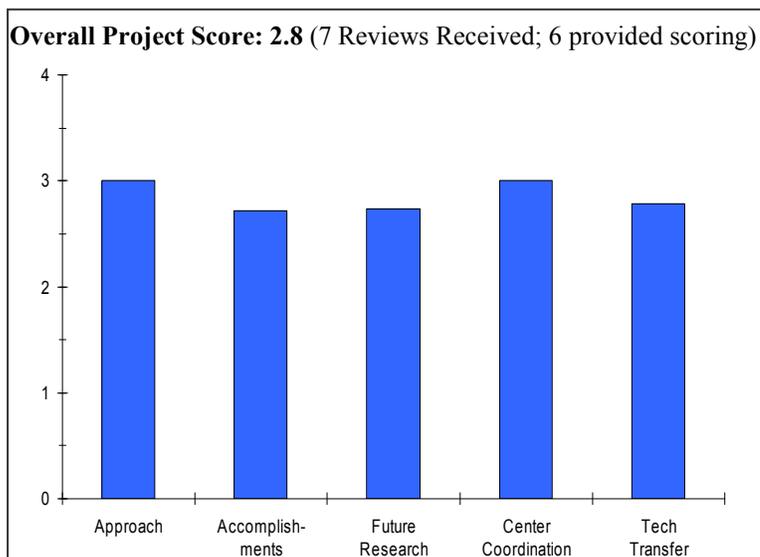
Project # ST-01: DOE Hydrogen Sorption Center of Excellence Overview

Mike Heben, Director (presenting); Lin Simpson, Co-Director; National Renewable Energy Laboratory (NREL)

[NOTE: This review 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 D. NREL's technical contribution to the center is evaluated in ST-02.]

Brief Summary of Project

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

**Question 1: Approach to performing the R&D**

This project earned a score of **3.0** in this criterion.

- This CoE has expanded its focus beyond carbon and is actively investigating a set of diverse physisorption materials. These new material classes that are being pursued present promising routes to improved storage properties. There should be more focus on identifying strategies/material classes having higher volumetric uptake (a major barrier typically associated with open, high surface area materials). The go/no-go decision-making process should be more fluid and integrated as a standard part of the program so as to effectively filter out the non-progressive work.
- Sound approach to address technical barriers, moving from theoretical modeling to material synthesis and development.
- Pooling of expertise, facilities; fostering of collaboration and complementary activities. Effective down selection and decision points have been set in the interest of the work. A good mix of technologies and technical capabilities. The CoE has shown the flexibility to change and adjust as new information is obtained.
- Diversified approach with integration where beneficial is a good approach at the high level. Diversification to more low temperature work and addition of other atoms than carbon as substrate is good. Still probably an excess of work on nanotubes and fibers. While go/no-go was mentioned, it does not seem to be an organic part of the program to the extent it is in the entire DOE program or other CoEs – this needs to be in the plan and seen as a good thing, this latter part is not clearly true in this CoE. Clusters are a nice way to organize the work and get more done. Theory guide is appropriate.
- Optimized binding energy and theory-guided research can effectively address most of the technical barriers. The “clusters” research approach is good in general. Too many activities within clusters and only some of them may lead to progress. Need [to] down select certain clusters and redirect the available resources to the most promising materials. Need more balanced and well planned activities among the five “disciplines” to best utilize the available resources.

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- Good scope expansion to chemisorption and "enhanced physisorption" on various adsorbents beyond carbons to increase probability of successful development of a system storing hydrogen above cryogenic temperatures.
- Excellent – the PI delivered an excellent talk as usual describing the direction and breadth of work covered.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **2.7** in this criterion.

- A significant increase in experimental output was shown which has enabled many more materials to be characterized and tested. Although many of the non-crystalline multi-dimensional materials are often more challenging to characterize, additional focus in this area is encouraged to conclusively determine the identity and understand the mechanism (a key to optimization) for each compound. Theorists should also more closely coordinate with experimentalists to ensure there are rational synthetic routes to prepare promising candidates.
- Good progress and a step forward as demonstrated by the promising data presented on enhanced uptake for specific surface area and by the validation of the spillover concept for developing C-based bridges to increase storage capacity. Materials discovery efforts intensified and led to the identification of a number of promising systems. The complementarities of theory and experiments have widely benefited the program.
- The spillover/bridging work has progressed significantly. The metal-C60's synthesis has progressed albeit the results at this point are a little short. The theoretical/modeling work is moving forward with coming up with new alternatives.
- Excellent synthesis and improving calculation work. Spillover has been confirmed only at much reduced level and remains a big question. Later poster showed confirmation. Synthesis of the fullerenes is excellent chemistry but of unclear value from an application view. Calculations of spillover are very interesting and help support that work more than the experimental work of late. The zeolite template work (outside the center) is very interesting, but needs confirmation. No real progress in the center in terms of capacity since last year on MOFs or spillover, almost the same slides actually. Still cling to the 12 hydrogens in Sc compounds even though results pretty clearly show that mostly cross linking occurs, not hydrogen binding. I believe progress has been better than what was shown in this talk.
- Progress has been made in certain areas. Improved fundamental understanding. All the accomplished materials/systems are still far away from DOE 2010 targets.
- Why is there so much focus on 77K storage? Is it practical? In general, progress of the CoE is good comparing to where it was 2 years ago (issues of reproducing capacity measurements on SWNT). Interesting leads have been demonstrated (e.g., storage by spillover that can be applied to various receptors). Good involvement of theoretical group from Rice. Still, need to speed-up no-go decisions (e.g. on [transition metal] TM-C60 systems).

Question 3: Proposed future research approach and relevance

This project was rated **2.7** in this criterion.

- Good to see expansion of MOF work through addition of new project. It is acknowledged that this CoE faces higher risk, more challenging synthetic routes. However, as much as possible, efforts should be devoted to candidates where there is a rational preparation route in place. Should perform variable temperature uptake for most promising materials to understand capacity-temperature tradeoffs.
- The proposed work is appropriate and it is the next logical step building on current experiences.
- Not clear if more work/resources will be devoted to spillover/bridge systems. Need to use the synthesis and test results to calibrate the modeling/theory (not clear the reverse feedback exists and if so, please give an example).
- Detailed plan. Most topics are appropriate and required.
- Future work plans are indeed built on the past progress. Hybrid material approach should be further explored to cover non-carbon based sorbent. Down select criteria were not well defined. Need to define what the unproductive directions are. Adding precious metal onto carbon is not a good way to overcome the cost barrier. Need to address the cost issue in the future research direction.
- Good proposal for the future involving non-carbon systems as well. Suggest more focus on developing materials capable of storing hydrogen at ambient temperature. Perhaps, conducting a theoretical screening of

potentially new MOF structures with enhanced heat of adsorption (>18 kJ/mol) that would work at ambient temperature.

- Key issues for this center include:
 - Volumetric efficiency – Not enough was highlighted this year (slightly better than last year) every presentation in this center needs to provide brief summary of how their material could reach decent volumetric densities – at least to surpass 350 bar technology).
 - Increasing storage temperature from 77K to room temperature – The center needs to understand that this is a priority and determine a way to report work at conditions of 298K and 350 bar (range more suitable for OEMs).
 - Explaining spillover effect and mechanisms – Many mechanisms were presented that adequately explain the phenomena or provide hypothesis- these hypotheses need to be validated analytically.
 - Explaining deviations from “Chahine rule” – Is it that nitrogen doesn't see all the sites or is there a double layer effect somewhere? This needs to be clarified.
 - Gravimetric storage capacity – Still unacceptably poor at room temperature.
 - Agreement of modeling to synthesis work – Models are providing molecules that are unrealistic to produce or become unstable after a few cycles – the experimentalists need to push back on modelers to provide simpler compounds that have a chance to be made cheaply.

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

This project was rated **3.0** in this criterion.

- All materials synthesis groups/efforts should have access to all measurement/characterization techniques. From the organizational charts, it is implied that only some synthesis groups are actively collaborating with groups possessing specific characterization techniques.
- The project has obviously benefited from pooling of resources. Progress appears to be followed up and controlled for effectiveness. Strong teaming, interaction and joint decision-making is mentioned in the presentation. Nevertheless, clarifications/more transparency may still be needed on how the CoE truly operates, how flexible it is and how its members are involved in the working clusters/groups/disciplines and in the crucial decision process and finally in the execution of these decisions. What is the internal/external information flow mechanism used and which are the terms of reference for the scientific/management board running the CoE (meetings, communication channels, level of participation of partners in the decision making mechanism, etc.)?
- Good communication, coordination and collaboration in general. The University of Michigan seems a bit of a lone program that others chase after to get data, as opposed to an open and willing collaborator.
- Demonstrated some collaboration. Need more collaboration between different clusters. Need to validate the measurement consistency between different groups.
- Good collaboration.

Question 5: Collaborations/Technology Transfer Outside the CoE

This project was rated **2.8** in this criterion.

- External collaborations with other CoEs and institutions appear to be well-developed.
- It is very encouraging to see the first signs of cross-fertilization of results and collaboration within the CoE itself but also across the CoEs.
- Seem to have good connections outside the CoE. Like all CoEs, could do better at communicating with other CoEs to learn both science and management strengths and needs there.
- Need more interactions with research groups outside CoE. Some of the foam materials developed with the center should [be] sent to the Metal Hydride CoE for them to incorporate with their materials.
- Perhaps, opportunity could be to enhance collaboration on MOFs with Yaghi's group [UCLA] as well.

Strengths and weaknesses

Strengths

- Strong, diverse, and competent team taking on high-risk and challenging materials synthesis.
- Partners' areas of expertise very complementary to one another.

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- Center's flexibility and willingness to take on new materials synthesis directions.
- Pooling of expertise and capitalizing on lengthy experiences in diverse fields.
- Good mix of theory/modeling and experimental work.
- Good pipelines of theoretically developed alternatives.
- The center management has shown flexibility and ability to change and adjust.
- Good team, good synthesis skills, Rice adds some good theory.
- Focused on fundamental understanding and bottom-up design.
- Area of adsorbents (enhanced physisorption and weak chemisorption) can potentially result in a winning storage material with enhanced storage energy efficiency (e.g., versus metal hydrides).

Weaknesses

- Experimental realization of targeted materials limited by their complex nature and non-intuitive syntheses.
- Go/no-go decisions seem to be externally applied and not part of the internal CoE process. Regular go/no-go decisions are important for ensuring that projects are progressing.
- The challenge of managing such a broad R&D portfolio involving so many and diverse research groups.
- Need to develop benchmarks for C60s and their derivatives.
- Feedback to the modelers to adjust after receiving actual data.
- Still too committed to original themes. Complex calculations continue to be done in absence of interactions with other fullerenes.
- Validation of some critical experimental results that might set future directions.
- There is no clear plan on how to move some of the promising work forward.
- There is no plan on how and when to make go/no-go decisions.
- Significant focus on storage materials at cryogenic temperatures.

Specific recommendations and additions or deletions to the CoE scope

- Future work could strive for a better balance between modeling and synthesis/testing.
- Operability/workable conditions need to be always kept in mind – adsorption must be addressed to occur close to ambient conditions rather than cryogenic temperatures (77K).
- Volumetric capacity is a critical issue and needs to be appropriately addressed.
- Enhance the interaction with related projects and international partners (outside the CoE).
- Agreement should be reached on reporting of adsorption data (e.g. total/excess/absolute uptake).
- More emphasis on validation testing.
- The most recent results from spillover/bridged materials warrant further resources to be devoted to this approach. NREL could provide much help to work on ways to improve the kinetics of the room temperature (RT) sorption.
- It is very important that the theory team, that have been doing the decorated C60, back up and learn from previous predictions vs. reality. Take, for example, the prediction that many TM atoms can be placed on C60, reality allows only one, they need to figure out why and adjust methods. Likewise they continue to do the calculation for a lone C60, but as was predicted by reviewers, the C60s crosslink through the metal atoms. The theory team needs to start making the calculation to see not only if the metal is stable on the C60, but also if there is cross-linking and can hydrogen still attach, otherwise the calculations are of much less value.
- Reorganize some of the research activities and focus the available resources to the most promising materials.
- Analyze data from all the "clusters of accomplishments" on the same basis, that is put all capacity plots in the form of isobars (e.g., at 100 bar), and see which materials are more selective towards storage at ambient temperature. This may help in selecting most practical materials that may not show all benefits at 77K.
- The center has adequate level of internal milestones and go/no-go decisions - however it seems only by force that they are implemented. The biggest disappointment of this center is that they are slowly moving back towards carbon nanotube and fullerene compounds. These compounds are expensive to make and their methods seem to employ complicated methods to functionalize these compounds. How could this ever be cost effective and scalable? Progress on MOFs and novel concepts were nonexistent this year. This center perhaps more than any other center has more opportunities for novel technologies that they are not fully looking into. They really need to take a deeper dive into the capabilities of organometallic chemistry and look to other industries for inspiration such as the medical and semiconductor industries.

Project # ST-02: NREL Research as part of Hydrogen Sorption CoE

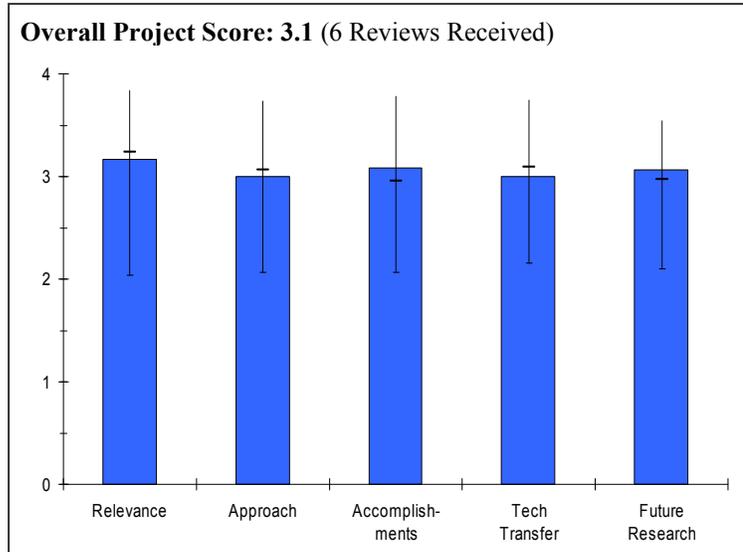
Anne Dillon, presenting; J. Blackburn, C. Curtis, M. Davis, C. Engrakul, M. Heben, K. Jones, Y. Kim, K. O'Neill, P. Parilla, L. Simpson, E. Whitney, S. Zhang, Y. Zhao, NREL

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

Brief Summary of Project

NREL is performing R&D and coordinating the Hydrogen Sorption Center of Excellence (HSCoE) to develop the applied science base and technology advances required to meet DOE's on-vehicle hydrogen storage targets. In FY 2007, NREL's research efforts have been refocused to:

- Using theory as a guide, actively pursue the synthesis of new promising compounds for reversible hydrogen storage with desired binding energies.
- Determine structures of new compounds and correlate the structure with adsorption mechanisms, desired binding energies and capacities (volumetric and gravimetric).
- Employ theory to explain and confirm observed experimental results as well as to establish optimized structures that have rational synthesis routes.
- Expand hydrogen capacity measurement capabilities for rapid screening to improve round robin process / sample exchange with partners.
- Continue theoretical efforts to predict / design new sorption materials consisting of light elements but not restricted to a carbon base.

**Question 1: Relevance to overall DOE objectives**

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

- Carbon-based adsorbents represent a viable option toward reaching the DOE objectives and thus, this research is aligned appropriately. The experimental targets (based on theory) for this project, however, are challenging and ambitious ones. Due to the complexity of these compounds, a great deal of time/effort will likely be devoted to trying to isolate, purify, and scale-up these materials.
- With ideal packing, the volumetric density of the majority of these candidate materials (for example, organometallic fullerenes) will not be close to achieving the 2015 volumetric target. This should be a primary focus for future materials selection.
- The sorption research is a critical approach to developing storage materials.
- The technical effort was redirected after the single-walled nanotubes (SWNT) go/no-go decision. New research directions generally support the DOE goals, but all approaches are high risk.
- The project directly addresses the DOE storage objectives. The presentation did not address directly how storage system targets will be met. It did not address either how Barriers A, C, E would be or have been addressed.
- Relevant to a greater extent now that they see their calling as physical adsorption rather than nanotube - fullerene adsorption.

Question 2: Approach to performing the research and development

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

- In principle, the approach is good, using theory to help guide the identification of experimental candidates. However, for many of these targeted compounds, it is still not entirely clear that there are rational synthetic pathways to their preparation. It is good that there is a heightened focus on experimentation that is helping to drive this project's potential success. In terms of theory, full evaluation of the stability of current and future structures should be routinely performed.
- A good mix of theory, synthesis, testing. Also showed flexibility to change and re-adjust approach.
- Multiple theoretical approaches for enhanced hydrogen adsorption are being pursued. There is a robust link between theory and simulation and materials synthesis and testing. This interaction allows timely evaluation of new concepts and predictions. Strong chemical synthesis capability is enabling the development of new carbon-based materials with potentially higher surface area and binding energy. The emphasis on OM-fullerene compounds (reactivity and sorption enhanced by metal on the fullerene) and B-doped SWNTs with higher binding energy for hydrogen—good extension and re-direction of work from 2006. Excellent characterization and analysis tools and capabilities support the synthesis effort.
- Clear focus of the research. Although the interesting results are mainly theoretical, the researchers are striving to the experimental realization of the compounds. Issues and problems were addressed frankly. Project plans retroaction between theory/experiment. The technical targets A, C and E were not addressed in the presentation.
- Theory guide is a good idea but it needs to be noted that the theory was isolated clusters, and others have correctly suggested 'chains' would occur several years ago. The theory does not seem reliable enough to really be a guide - They need to go back and figure out why the metal was predicted to put many atoms on a buckyball and only one goes on, and change the approach to get the right answer. Also need to calculate in an environment where balls can cross link. Movement toward non-carbon systems is wise.

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

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

- While an increased focus on synthesis has clearly been demonstrated, unfortunately not too much progress toward making the specific candidate materials has been shown, although the experimentalists are not faulted for this as the synthesis targets are extremely challenging. In general, there should be more focus on identifying experimental candidates for which there are known synthetic pathways.
- Good progress on synthesis albeit the actual results came short. Good continued work on the theory to guide future work.
- No significant progress.
- Impressive progress on OM-fullerene synthesis (NREL has successfully addressed a very difficult synthetic chemistry challenge). New results on Fe-containing fullerene are intriguing. However, there are serious concerns: binding energy is still too low; reactions involving multiple hydrogen adsorption/desorption cycles may likely be influenced strongly by contaminant poisoning and by fullerene-fullerene interactions and metal agglomeration. Also, it is surprising that the binding energy with hydrogen seems to be similar for different metal species. Enhanced hydrogen adsorption in B-containing SWNTs certainly is an encouraging result. It will be important to understand how hydrogen uptake scales with B concentration. Does simulation/modeling allow an estimate of maximum uptake that might be expected from B-doped materials (including the new metalloboranes)? New theory work on endohedral metallofullerenes suggests higher binding energies and enhanced uptake seems promising. Temperature dependence of sorption properties needs to be quantified.
- Excellent theoretical results - more experiments needed! Enhanced binding observed in metal doped materials. Experiments tend to lower expectations from theory. It is not clear how barriers C and E can be addressed within this project.
- Excellent synthesis work. The compounds are coming out fast - though the storage is low the temperatures are interestingly high. Li system did not clearly have much capacity at present but again a nice synthesis achievement from a science perspective. B work is a good idea though no progress yet in capacity; still this is a good thing to pursue some more to see what possibilities it has. At 1000K the metalloboranes do not sinter the metal, but will multiple fullerenes agglomerate at realistic operating temperatures? Rapid screening equipment is a nice technological accomplishment. Consider also that they have over 2 million dollars to achieve this; otherwise they would get a higher score.

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

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

- NREL is clearly supporting the sorption CoE greatly in providing measurements/consultation to various institutes. The personnel behind this project are an ideal combination of experimentalists and theorists leading to productive internal collaborations. Additional communication with the Rice group is encouraged regarding the C60 linking work as to avoid potential overlap.
- Theory is important to guide the experiment. But the opposite must happen too. In some cases the theoretical predictions look very hypothetical. A closer collaboration between theoreticians and experimentalists should take place.
- Good collaboration with other experimentalists and theorists both within the HSCoE and with the external technical community. This is definitely an activity that can benefit from collaborations across the entire HSCoE.
- Cross-collaboration looks excellent although it did not come through clearly (i.e. role of various partners) from the presentation. Very nice theory/synthesis/sorption property measurement integration.
- Well connected and using connections effectively.

Question 5: Approach to and relevance of proposed future research

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

- Proposed future research directed at investigation of simpler systems and chemical transformations is important toward experimental realization of intended more complex structures. However, hopefully these studies will not lead to an in-depth basic science research project which will detract from hydrogen storage materials research.
- Increased focus on conclusive structural determination is recommended.
- Development of rapid throughput of hydrogen storage capacity measurements is valuable for efficient materials testing and supports the sorption CoE partners.
- What is the approach for room temperature sorption? Cr-C60s? What are the benchmarks for C60s or metal-C60s? What results warrant more resources or vice-versa?
- 1 & 4 look very promising 2 & 3 not; but they needed for the final decision of the existence of these systems.
- Future work is a good extension of the efforts initiated in 2005/2006. Addition of new reactor(s) that enable higher B concentrations will be useful. Recommend additional modeling work that provides projections of hydrogen sorption properties at higher temperatures; and simulates how interactions among metal-containing carbon frameworks during hydrogen cycling will influence sorption behavior.
- Clear research objectives. Go/no-go decision on SWNT. The project's objectives have been refocused.
- Plans seem OK but I wonder if there really is a plan to get out of the C60 work if they can not see a route over 1%.

Strengths and weaknesses**Strengths**

- Implementation of both theory and experiment is an ideal approach toward hitting a "homerun". Expertise in these areas is clearly evident in this project, and there now seems to be a good balance in research effort allocated toward both.
- Strong theoretical basis.
- Also combined with a lot of synthesis work.
- Very strong theory/modeling and synthetic chemistry effort. The NREL team is attacking difficult technical problems in an innovative way.
- Excellent work being done to experimentally test predictions derived from theoretical work.
- Excellent synthesis work shows the team's ability to seek new materials for sorption storage.
- The team is strongly motivated to validate theory experimentally.
- Team clearly exhibits its capacity to refocus and push promising alternatives.
- Exciting theoretical results.
- Outstanding work overall.

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- Right energy range, good synthesis abilities. May generate higher temperature cryosorbents with the higher energy materials if the specific surface area (SSA) can be increased to where it "should" be.

Weaknesses

- A clear path to experimental realization of the theory-driven structures is not apparent.
- There needs to be more focus on strategies which enable these materials to reach the 2015 volumetric target.
- Not clear the pathway for RT sorption.
- C60-M-[C?]5H5 LDA theoretical calculation is not the state of the art, and due to symmetry not appropriate.
- The existence of metallaborane nanostructures is not proven yet. At some point the theoretical design must be also be guided by experimentalists.
- All approaches being pursued here are very high risk and involve fairly exotic materials and processes. This is not necessarily a weakness *per se*, but it is important that the ideas aren't "oversold" — i.e., a careful assessment of the large gap that currently exists between the proposed and demonstrated materials properties and the DOE goals must be made (i.e., what are the big roadblocks in getting from "here" to "there"? Is an incremental progress path acceptable or is there a discontinuity that requires an entirely different research approach?) The NREL effort would be enhanced greatly if this analysis and possible proposed mitigation strategies were made available to the community.
- Experiments still lag theory although noticeable efforts have been made.
- Cost issues not addressed.
- Still seem to be looking for a way to make SWNTs be the answer with no real success or justification. This probably holds the program back.
- Theory is holding the program back by predicting unrealistic things AND failing to go back and change the approach. The buckyballs MUST be calculated with the option to cross link. The theory needs to go back and figure out why they predict lots of metal atoms and reality allows only one.

Specific recommendations and additions or deletions to the work scope

- Clear decision-making points for continuing/discontinuing work on decorated C60 should be set. At what point is it time to move on?
- Need to develop benchmarks for various alternatives specifically the x-C60 and in general any molecules under consideration.
- Perform C60-M-C60 calculation in the LDA level and C₅H₅-M-C₅H₅ in MP2 and compare the results. Only in this way they can have size and method accuracy.
- Recommend de-emphasizing work involving highly reactive "bare" metal atoms on a C-framework structure. Although these structures may have encouraging performance from a theoretical standpoint, it is not likely that they will remain intact in their original reactive condition after multiple cycle processing.
- Less nanotube work; more non carbon work, more low temperature work.

Project # ST-03: Hydrogen Storage by Spillover*Ralph Yang; University of Michigan*

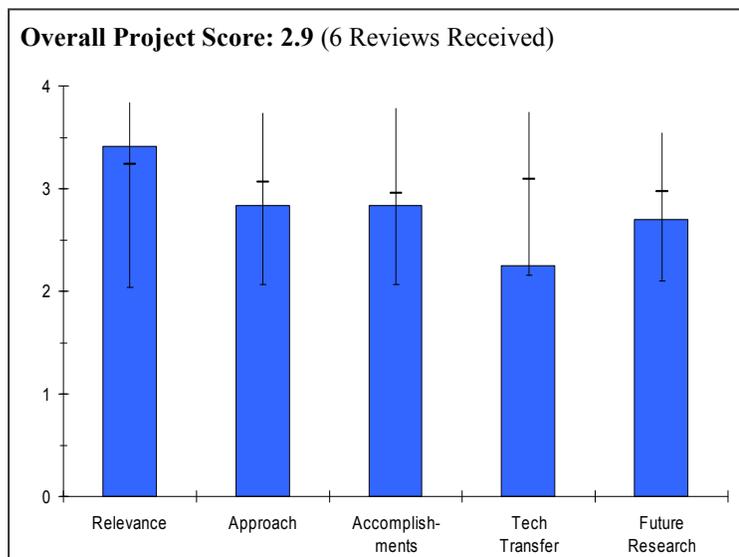
[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The overall objective of this project is to develop carbon-based hydrogen storage materials with capacities in excess of 6wt.% and 45 g/L at room temperature. This will be done by developing and optimizing new bridge-building techniques for spillover to enhance hydrogen storage. This will result in a mechanistic understanding for hydrogen spillover in nanostructured carbon-based materials for the purpose of hydrogen storage.

Question 1: Relevance to overall DOE objectives

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



- Concept of spillover could potentially be important towards taking sorbents from 77K to room temperature operation.
- Seems to be making negative progress (last year's results are "not reproducible", lower weight percents reported this year, no volumetric densities reported?)
- Don't know what this means that "desorption is enough to power a vehicle at 60 mph". DOE has set targets for hydrogen desorption rates – why hasn't the PI simply compared with these kinetic targets?
- Very promising mechanism.
- Room temperature hydrogen storage in a sorbent material is very relevant.
- The PI uses a novel bridge-building technique where catalyst supported on a receptor surface dissociates the hydrogen molecule and enhances sorption through increased diffusion. Understanding of the cluster / particle — support interaction is critical.
- This project has high potential to meet gravimetric and volumetric targets and possibly charge and discharge rates as well.
- If this can be shown to be real in the case of MOFs, then this is well aligned and important. If only the 1.2% on AX21 is real, then this work is not in line. As last year, external confirmation of high storage amounts is key.

Question 2: Approach to performing the research and development

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

- Like almost all the work in the sorbent area, this work needs to strongly focus on: 1) increasing binding energy to enable room temperature storage, 2) increasing gravimetric capacity, and 3) increasing volumetric capacity. All three must be achieved simultaneously.
- No sufficient theoretical explanation of the spillover phenomenon.
- Kinetic issues are being addressed.
- The PI is developing and optimizing the bridge-building technique by directing doping of the receptor.
- It is not clear what the approach will be to increase the hydrogen adsorption rate. Since this is a very promising approach, perhaps the HSCoE could be used to provide input for a broader perspective on future direction.
- Spillover is valid and real mechanism in chemical processing. Verification that this is really happening by some mechanism - say verifying H atoms on the surface, is still a very important task to prove that they are spilling

onto the substrate. Addition of the parallel calculations work is a big plus for this program. Needs to use a MOF that won't degrade; this is pretty clear, MOF-177 is not a good choice. Not apparently thinking about lowering Pt loading (way too expensive), need a better plan.

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

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

- Seems to be making negative progress (last year's results are "not reproducible", lower weight percents reported this year, no volumetric densities reported?)
- In general, the mechanism that is used to describe spillover seems to be a "kinetic" argument; however, the PI states that the effect is actually thermodynamic. Is there a contradiction here?
- Modeling results do not seem to agree with 20-25 kJ binding reported experimentally; however, PI claims that the results agree? Taking an average of the theoretical results for binding energies is simply not appropriate: a system with half of the sites with ~0 binding and half with ~40 kJ binding will behave completely differently from a system where all of the sites have ~20 kJ binding.
- At last year's meeting, there was a significant issue raised concerning the incompatibility between the proposed explanation of spillover and the proposed thermodynamics of spillover. The PI did not address this very serious concern in his presentation.
- Explanation for the lack of reproducibility of the MOF results was not convincing. It is likely that the method used to process the MOFs in this group (which is different from what other groups are doing) could be the source of the variability in the results.
- Not much progress from last year.
- How likely is it that the 2007 target of 4.5 wt.% will be met at room temperature with AX-21? Have all avenues for addressing the issues of MOF instability and reproducibility been pursued? Are MOFs being deemphasized prematurely?
- A number of receptors such as IRMOF-8, and activated carbon have been tried with significant improvement in hydrogen storage capacity. The experiments are well-coordinated with theory.
- These materials show great promise for meeting the DOE targets. It is clear the principal investigator is conducting his research with the DOE targets in mind.
- Technically this moved backward. However that dose of reality was needed in this project. The PI needs to be more open and share this program. There is rising doubt as to the reality of the 4% result. The binding energy was a very good thing to accomplish. Many of the slides are direct holdovers from last year.
- The calculation of hydrogen potential based on adsorption on all atoms was very speculative.

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

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

- PI could really benefit from close coordination with groups with more substantial expertise in MOF synthesis.
- Seems like this project is a little short on technology transfer and collaboration. Perhaps collaboration could help with the issues associated with IRMOF-8. Collaboration with spillover modeling being done at Air Products would be desirable.
- The project is well-coordinated with other groups/institutions/laboratories working on the project.
- Since this is such a promising approach, it would be good to see more interaction and parallel or complementary work at other institutions.
- This program has been secretive up until this year. Addition of parallel Rice work is very good, but the two programs seem virtually unconnected other than by Rice attempting to justify the published data. This still appears that it is not a collaborative or open program. It would be much more effective in moving forward if it incorporated other people and teams.

Question 5: Approach to and relevance of proposed future research

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

- It is not clear how the PI will get beyond the ~1 wt.% he reported this year at room temperature. What is the strategy to improve the storage capacity?
- PI wants to achieve 4.5 wt.% “system” level target in FY2007. This would require a nearly one order-of-magnitude improvement over the 1 wt.% results presented here. What is the strategy to achieve this (within the next few months)?
- Very good idea of performing spillover in MOFs and MILs and COFs.
- It is very important to obtain basic understanding of the spillover process including equilibrium and kinetics, using deuterium isotope.
- If AX-21 and other high surface area carbons do not have sufficient hydrogen capacity, is there a "Plan B"?
- The PI plans to study different receptors (MOFs, COF-1) and catalysts as well as direct doping techniques to achieve DOE targets. Also the future plan is a basic understanding of the spillover process.
- I would like to see a tabular description of what the future plans are for new MOFs, doping, and receptors.
- The proposed work is not inappropriate, but largely ignores the real questions of why no one can reproduce the 4% result, seemingly not even them, and why no one has shown conclusive evidence that H atoms are on the surface. Ignoring these critical questions is not appropriate for a managed program. Of the planned work the deuterium scrambling experiment may be the best. There is little detail to the plans and the program seems to move by response to observations not by intention or plan.

Strengths and weaknesses

Strengths

- Hydrogen storage at room temperature.
- New spillover mechanism for hydrogen storage.
- The spillover mechanism is a novel approach, and optimization of both catalysts and receptors may yield the derived storage material.
- Good science.
- Excellent focus on DOE targets.
- Promising results.
- Concept has great promise if it is really working and it is based on a known technology. The energy appears to be in the right range and the system works at room temperature.

Weaknesses

- The spillover mechanism is not understood yet.
- It would be nice to have more insight into why the spillover mechanism provides for room temperature hydrogen storage, whereas other sorbents only show significant hydrogen storage at 77K.
- The PI's reluctance to talk about the doping technique or dopants makes it difficult to assess its effectiveness. No discussion was provided on the line of thinking that makes one select the dopants, catalysts, or receptors. Poor understanding of why certain results are irreproducible. The basic understanding was poor.
- Since this work is so promising, I would like to see parallel and/or complementary work conducted at other sites.
- Program has done little to prove it is accomplishing what it claims (making atomic hydrogen on surfaces), and progress has been slow or backward since the initial claims. Not very forthcoming with those hoping to verify results or help them with their work, as best as we can see.
- This is one that has high potential and low performance for a year or more, the center or the DOE needs to step in and tune up the plans and improve the output of results.

Specific recommendations and additions or deletions to the work scope

- None.
- Emphasis should be placed on fundamental understanding of the spillover mechanism.
- This program desperately needs to reproduce the MOF result on an air stable, ultra high surface area substrate. I would avoid unstable MOFs no matter how high the surface area. There are air and water stable MOFs available and refusal to try stable substrates is tantamount to admitting the 4% result is erroneous.

HYDROGEN STORAGE

- The program needs to verify spillover is occurring by direct measurement. If need be by forming the hydrogen layer in a chamber attached to UHV tools by a gate valve, then quenching to low temperature to maintain the hydrogen layer and moving into a vacuum chamber to observe the state of hydrogen in EELS or other tools sensitive to atomic hydrogen bound to surfaces.
- To be clear, this area of work must be continued because it has much promise; but there is a need to direct it in a much better way. To prove H atoms are made, verify that the theory is correct by testing it in a system the theory was not fit to, and verify that the failure to reproduce is due to the MOF stability, not poor measurement.

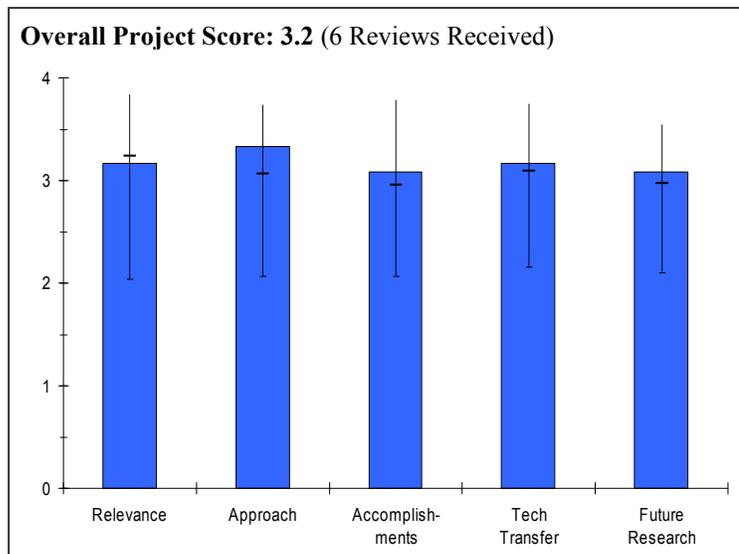
Project # ST-04: Theoretical Models of H₂-SWNT Systems for Hydrogen Storage and Optimization of SWNT Production

Boris Yakobson, presenting; Robert Hauge, co-PI, Rice University

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

Rice University is developing predictive models of material's interaction with hydrogen, in order to optimize their makeup for storage and assess the gravimetric and volumetric capacity. Rice will provide recommendations for the synthetic goals (e.g. diameter, type and organization of nanostructured materials). In 2007, Rice is preparing synthesis of metal- and electronegative group (F, BF₃) enhanced VANTA (vertically aligned nanotube arrays, contrast to fibers) for H₂ adsorption. They are also working on the theory of hydrogen spillover, its thermodynamics and kinetics: energy states, cooperative effects, and mobility.



Question 1: Relevance to overall DOE objectives

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

- Cryogenic sorbent materials are not likely to achieve the overall DOE objectives. Spillover or metal-doping to increase binding energies are two possible candidates for moving these sorbent materials to room-temperature storage. However, neither has really been reproducibly demonstrated to any significant capacity. Thus, it is not clear that the focus of this project is really in support of the overall objectives of the HFI.
- The methodology is interesting but the materials are not very promising for hydrogen storage.
- The objectives of this project support the DOE Hydrogen Fuel Initiative and R&D objectives in general. Connection to Yang's work at UM is valuable and has potential to yield suggestions for optimized systems.
- The PI is carrying out state-of-the-art calculations to understand the spillover mechanisms on a variety of systems. This understanding is essential for optimizing the catalysts and the support.
- This project would be more critical to the Hydrogen Initiative if carbon based materials, in general, had a reasonable chance of meeting even the 2010 storage "system" goals which will very likely require a materials storage capacity of at least 10 wt.% H to compensate for the balance of system components. The project generally supports the DOE RD&D vision for hydrogen utilization in vehicles by providing important insights into performance controlling issues for hydrogen storage materials, like binding energy parameters, additive aggregation, and spillover.

Question 2: Approach to performing the research and development

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

- The approach is interesting. Nevertheless studying spillover on surfaces is not a good approach.
- Approach sounds good in concept and is focused on technical barriers. The approach on spillover [effect] can be improved to predict the optimum receptor properties. Suggest to further explore accuracy of quantum chemical (and density functional theory [DFT]) predictions by validating with experiment.
- The PI is well aware of the limitations of the DFT and is using appropriate techniques to deal with dispersive forces. The barriers for diffusion are being calculated correctly.

HYDROGEN STORAGE

- The engineered 3-D foams, vertically aligned nanotube arrays, and cross-welding studies are fully consistent with the direction that research on carbon-based storage materials needs to take. The theoretical studies of the adsorption energy landscape constitute an inspirational piece of work that should widely benefit those working in the Hydrogen, Fuel Cell and Infrastructure Technologies (HFCIT) storage program.

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

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

- "Welding" of tubes and theoretically-predicted "foams" is an interesting idea, but wasn't this already presented at the last meeting [FY2006 APR]? Very interesting idea/mechanism proposed to explain the "thermodynamic problem" raised at last year's meeting. However, it does raise the question of how do these regions of high-level loading nucleate in the first place? What is the nucleation barrier, and is it plausible that one could overcome it with temperature? Could it be a heterogeneous nucleation mechanism (i.e., on defects in the structure)?
- No significant progress from last year!
- Demonstrated a best foam structure for better hydrogen storage. The recommendations from modeling should cover several scenarios rather than only the best case scenario.
- Effectiveness of computational calculation for [carbon nanotube] CNT-H₂ systems is shown well. Interaction between CNT and H₂ has been clarified with their technique. However, a solution to avoid aggregation of metal atoms is not proposed.
- The PI has demonstrated that metal atoms on carbon support aggregate, adversely affecting hydrogen storage. This effect has already been demonstrated by others, but the PI does not seem to be aware of it. An understanding of spillover kinetics is provided.
- The computational aspects of this program define pathways to improved performance and to overcoming technical barriers to meeting program targets. The carbon materials synthesis work focuses on aspects of carbon nanostructure development that seem appropriate if carbon in some form has any chance of meeting H-storage system targets, i.e., increasing dimensionality, reducing "dead" space, and optimizing spillover.

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

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

- Need to collaborate more with experimental group so that the results from this project can be used by others. Most of the time, theory-predicted optimized condition can not be achieved experimentally. The modeler needs to consider the feedback from experimental group and put them into the modeling assumption.
- The PI works effectively with experimentalists and the work is well coordinated with other members of the group.
- It seems that workers in the HFCIT H-storage program are picking up on the implications and general usefulness of the results in FY 2007. Those that haven't soon will to be sure. Collaborations with NREL, Air Products and NIST are ongoing. Others with the University of Michigan and the University of Nevada Las Vegas are emerging with good reason. One should expect even more to follow.

Question 5: Approach to and relevance of proposed future research

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

- Like many of the results in this field (of sorbent materials), theoretical predictions far exceed what has been currently synthesized. For the 3D-foam results, the likelihood of synthesis should be critically assessed before investing a lot of time and effort in doing more detailed MC simulations. The work on spillover has proved fruitful, and should help provide a mechanistic understanding which can be either proved or disproved experimentally. Not clear how the metal-doping work will significantly add over the analogous work that is currently going on at NREL.
- The spillover model is not correctly formed. Spillover cannot be studied in a single layer graphitic surface.

- Plans are built on past progress. Need fundamental understanding and experimental validation of the spillover dynamic effect. Suggest omitting the pure carbon VANTA/foam MC simulations as binding appears to be too weak unless metal hetero-atoms are incorporated.
- The proposed future work for the most part represents a logical and appropriate extension of what was reported at this Peer Review. The entire hydrogen storage program would benefit from an expansion of the adsorption landscape energetics computations to include other types of storage media where spillover could come into play. If the optimum spillover architecture is now known, it is then necessary to prove that it can be constructed and maintained (e.g., against agglomeration). Systems with $H/C > 1.0$ need to be emphasized.

Strengths and weaknesses

Strengths

- Theory prediction can effectively direct the experimental design to achieve the optimized material properties.
- Their extensive experience in computational technique.
- Interaction with people on experimental side through the CoE activity.
- Good understanding of experimental needs and sound theoretical approach.
- The presenter is very knowledgeable and perceptive about how to attack the issues without doing lots of meaningless physicochemical measurements.
- The project integrates considerations of both thermodynamics and kinetics. That's important because both are in play in the hydrogen storage "game".

Weaknesses

- C_nH_n is a hydrocarbon model and not a model for H @ C material.
- Lack of communication with experimental group to address the technical feasibility.
- The PI should do a better job in handling van der Waal's interaction and be more critical of commercial packages.
- At the present level of funding, progress may not be as rapid as it deserves to be in the coming years.
- Otherwise, there are no obvious weaknesses.

Specific recommendations and additions or deletions to the work scope

- Suggest adding some study on the effect of different nano pores and channel orientation rather than 1-D structure.
- The entire H-storage program would benefit from an expansion of the adsorption landscape energetics computations to include other types of storage media where spillover could come into play.
- If the optimum spillover architecture is now known, it is then necessary to prove that it can be constructed and maintained (e.g., against agglomeration).
- Systems with $H/C > 1.0$ need to be emphasized.

Project # ST-05: Cloning Single Wall Carbon Nanotubes for Hydrogen Storage

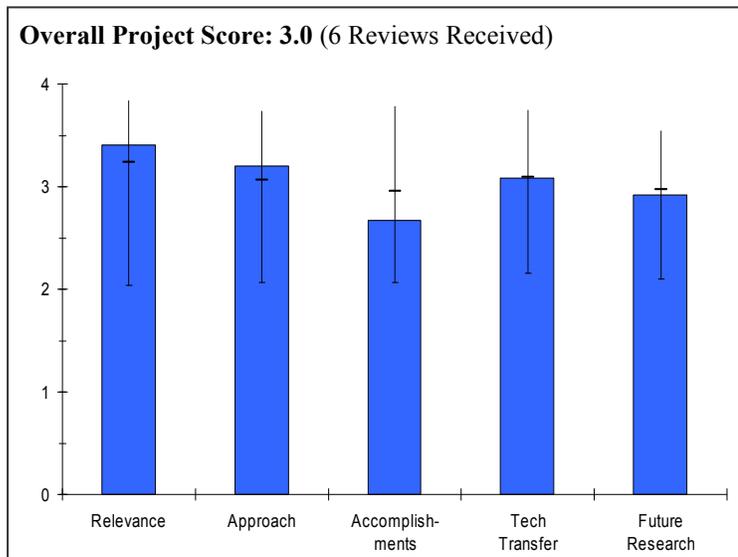
Jim Tour, presenting; Carter Kittrell, Co-PI; Rice University

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The overall objective of this project is to develop nanostructures and nano-engineering processes that enable synthesis of hydrogen storage materials that can be used to meet the 2010 DOE gravimetric (6 wt.%) and volumetric (45 g/L) system goals, with excellent uniaxial thermal transport properties. This will be accomplished by developing processing techniques to produce specific types of nanomaterial structures with increased available surface area. In 2007, the objectives of this project are:

- Investigate the 2-times steeper slope for “Chahine rule” for H₂ uptake and the concept of high temperature condensate. Determine uptake properties of the precision sp² pore.
- Develop alternative spinning methods and solvent extraction methods to increase available pore volume.
- Develop non-acidic lithium/ammonia based fiber expansion and cross-linking methods to circumvent oleum acid extraction problems and generalize the nanoengineered sp² pore methodology.
- Begin development of lithium intercalation of rigid nanotube scaffold for Kubas-type binding of H₂ at ambient temperatures.



Question 1: Relevance to overall DOE objectives

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

- This project represents one of the more promising experimental work/approaches toward achieving the DOE objectives for this class of carbon-based physisorptive materials. The design strategy (of linking SWNT [single walled carbon nanotubes] into a 2- or 3-D scaffold) and ability to modify these structures (through linker functionality/geometry or dopant additions) distinguish this project and reveal a new avenue toward potentially achieving the goals of the DOE RD&D plan using SWNT as structural building blocks. It does, however, seem as though this project is still in more of a research stage.
- Nanoengineering seems to be the only solution to hydrogen storage problem. Cloning nanotubes (NT) is a very interesting idea. Cloned NTs decorated with metals look [like] promising materials for hydrogen storage [because of] pi-systems, large surface areas and metal binding sites.
- The project scope supports DOE H₂ initiative and overall R&D objectives. The rigid scaffold developed from cross-linking methodology may generate some promising results and lead to a new direction.
- Cost targets seem to be difficult to achieve using SWNT.
- This project is well aligned with the "hydrogen vision" for carbon based materials. It's focused on the intelligent design and synthesis of carbon-based structures containing many of the characteristics that are generally regarded as being beneficial for hydrogen storage by a sorption-type material, namely, a compact, three dimensionally interconnected, high effective surface area, small pore size architecture with under coordinated metal atom inclusions or a similar hydrogen attractor.

Question 2: Approach to performing the research and development

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

- Designing chemically 'cross-linked' SWNT is novel approach toward creating multi-dimensional materials having uniform pores whose size, shape, and chemical composition can be modified through linker geometry/length, chemical functionality of pores, and/or addition of dopants. Such control over the size/chemical make-up of the pore structure is important for property optimization. More clarification on the characterization is advised. For example, how uniform/predictable is the degree and location of cross-linking? Has the pore size distribution been performed to ensure that uniform pores have been created? What characterization methods are being used to determine the structure type (i.e. distinguish different potential 2- and 3-D rod-packed structures)?
- Cloning nanotubes is a very interesting idea. Cloned NTs decorated with metals look promising materials for hydrogen storage since pi-systems, large surface areas and metal binding sites.
- General approach is novel. Using model system to study the pore size effect is a good strategy. The cost barrier was not addressed in the approach.
- Approach for solvent removal is a critical item and the activation procedure and absence of residual solvents need to be illustrated prior to hydrogen uptake measurement. Cost targets could be hard to reach.
- The approach embraces just about all the accepted notions regarding what has to be done to achieve DOE RD&D storage targets with a carbon-based material. The research seems to be well thought out and skillfully performed.

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

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

- While the approach seems solid, the current progress and results for the synthesized materials are unclear. For example, only slide 9 pertains to hydrogen capacity, and it is not clear which specific samples those graph points correspond to. Need clarification on which samples have been synthesized, which have been tested, and how they perform. Additionally, other examined properties, in particular, the volumetric capacity and kinetics should also be included. In general, more emphasis should be placed on property evaluation for the synthesized materials and an understanding of why certain materials performed better/worse than others (develop structure-property relationships).
- No significant progress from last year. Li does not perform Kubas binding.
- Demonstrated some progress and achieved some promising results. Need fundamental understanding of the material behavior.
- They have not achieved the 2010 target based on their approach. However, it is important for development of materials for hydrogen adsorption that they prove enhancement of heat of carbon material-hydrogen interaction.
- Since the initial results show 2-times slope vs. "Chahine rule," focus is recommended on increasing the surface area which would be by opening the tubes and optimization of the cross linker for porosity control. Hydrogen uptake results need to be shown at room temperature.
- Results were presented that exceed the "Chahine" predicted surface area rule—a step in the right direction. They tested and/or developed some new synthesis methods for cross-linking and lithium addition. They created a new 3-D nanoengineered carbon scaffold. They may be leaning a bit too hard on their extrapolations. Better to get results that leave no doubt about their ability to achieve 6.5 wt.% H and 55 g/L.

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

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

- Work within Rice seems to be diverse and strong. Collaboration with NREL also appears to be a valuable component of their research in terms of testing, and hopefully this relationship will produce even more property data. Additional communication with NREL is important in regards to the C60 linking work, as to avoid duplication of research.
- Certain coordination within the center exists. Need communication with other CoEs to see whether this foam structure can be used by other centers, such as the metal hydride CoE.
- Suggest more collaboration with theoreticians within the center to better select appropriate cross linkers to control the porosity.
- Other than their colleagues at Rice University (Yakobson et al.), it isn't clear how much meaningful interaction they have with their other stated collaborators in the Sorption CoE. Perhaps they should spell this out more clearly in future years.

Question 5: Approach to and relevance of proposed future research

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

- As indicated in their future plans, more testing of properties (H_2 uptake, binding energy, kinetics, cycling, etc.) on the various synthesized samples, structure-property relationship determination, and continued work on scale-up would be highly valuable.
- The nanotube scaffold idea looks promising, for the rest I vote 'no-go.'
- Plans are built on past progress and may lead to some improvement. Need to focus on more promising materials/systems rather than only SWNT. Need to explore the possibility of applying this concept to other types of materials.
- Their proposed future research is considered to be the best one at present stage.
- For the most part, the FY 2008 plans are a logical extension of their work to date. Next year they should give more detail on the nature of their collaborations within and outside the Sorption CoE. A major point of emphasis should be to get some kind of reasonable hydrogen sorption result near ambient temperature.

Strengths and weaknesses

Strengths

- Strong approach and creative design strategies are in place and are providing a fruitful composition space for synthesis.
- Nice to see work devoted to scale-up and improvement in the production process of these materials.
- The general approach is novel and is focused on overcoming most of the technical barriers.
- Interaction with people on the computational side and the measurement side through the CoE activity.
- Their technology for synthesis of nano-structured materials.
- Cross linking possibility could be applied to other carbon based materials.
- This group is a world leader in the synthesis of nanoscale carbon structures.
- Their close proximity to the Yakobson group serves them well.

Weaknesses

- More emphasis should be placed on hydrogen storage property evaluation and the deduction of structure-property relationships toward materials optimization. It is additionally important to evaluate and include the properties of materials which have been synthesized in terms of volumetric capacity, response to cycling, kinetics, and binding energy (i.e. the DOE targeted criterion).
- Li does not perform Kubas binding. It enhances the H_2 binding by charge induced dipoles. A better understanding of the phenomenon is needed.
- The cost barrier was not addressed in this project.
- There are no obvious weaknesses in this project. The overall approaches and capabilities are among the best one will find in any of the hydrogen storage CoEs.

Specific recommendations and additions or deletions to the work scope

- Overall scope of project is aligned. Shift toward property evaluation recommended. Additionally, continued communication between Rice and NREL is recommended in regards to the work on C60 to avoid duplication of research.
- Suggest adding the scale-up issue to project scope.
- Suggest sending some foam materials to MH center to incorporate their result.
- Kubas-type binding proof of concept illustration is recommended for the 2007 work to support a "go" decision
- It's not too early to start thinking about what can be done to get upwards of 10 wt.% H and 100 g/L for carbon-based materials because it will probably take these kinds of material storage levels to meet the 2010 system targets once the balance of system is taken into account. A compensation factor near 2.0 is emanating from systems studies reported in other presentations at this year's Peer Review. If that is out of the question for carbon-based materials, someone should be prepared to "step up and say so".

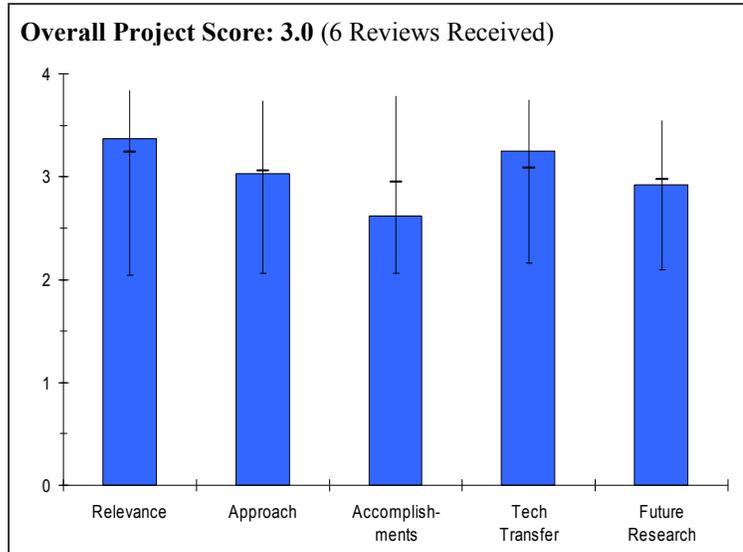
Project # ST-06: Metal-doped Carbon Aerogels for Hydrogen Storage

Ted Baumann PI, presenting; Joe Satcher, Co-PI, M. Worsley, J. Herberg, Lawrence Livermore National Laboratory (LLNL)

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

Designing new nanostructured carbon-based materials that meet the DOE 2010 system targets for on-board vehicle hydrogen storage of 6 wt.% H₂ is the objective of this LLNL project. Metal-doped carbon aerogels (CAs) will be prepared, characterized and evaluated for their hydrogen storage properties. Mechanisms associated with hydrogen adsorption in these materials will be investigated using advanced nuclear magnetic resonance (NMR) techniques. In 2007, LLNL incorporated dopants, such as boron or metal nanoparticles, into CAs to increase H₂ binding energy (> 10 kJ/mol).

Question 1: Relevance to overall DOE objectives

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

- Project focus is on low cost, high efficiency storage materials. However, it is unclear why carbon aerogels would provide any performance benefits as compared with other adsorbents.
- Fits well into DOE objectives and President's HFI. Focuses directly on targets and goals of HFCIT multi-year RD&D program plan (MYPP), especially the most important gravimetric and volumetric H-densities. A few comments on cost would have been useful; presumably aerogels can be manufactured at lower cost than some other forms of carbon.
- Carbon aerogels will only have significant hydrogen storage capacity at 77K, and not room temperature. Carbon aerogels will likely not meet the 2010 volumetric storage targets.
- The project is closely related to the DOE Hydrogen Initiative and overall objectives. The design of new CA materials with the flexibility of incorporating dopant is critical to overcome the technical barriers.
- Project is highly relevant to storage targets. Barriers A, C, P addressed.

Question 2: Approach to performing the research and development

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

- One of the advantages was stated to be incorporation of dopants into sol-gel precursors in the stage of synthesis of aerogels, then it was stated that this method would not work because of activation process. If that is the case, there seems to be no advantage versus other carbon materials.
- Controlled aerogels complements other carbon projects. Good porosity control of C-nanostructures. Metal doping seems to be a highly worked area; this work can perhaps complement other DOE carbon project efforts, but project should take care to avoid duplication. Use of controlled C-aerogels as scaffolding for hydrides is an excellent idea, perhaps more valuable than use as an H medium *per se*.
- Trying to further manipulate the porosity morphology in carbon aerogels may have reached the point of diminishing returns.
- The approach is focused on technical barriers and enables surface modification of carbon.
- Pore size distribution can be easily controlled to a certain range with this approach.

HYDROGEN STORAGE

- The approach is scalable.
- The cost issue was not addressed in the approach.
- The approach is sound and interesting, definitively worth investigating. Offers an interesting alternative to activated carbons and other nanocarbon materials. Excellent team.
- The barriers identified in 2006 are tackled which led to improved wt.% hydrogen uptake-very good progress!

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

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

- Advantages over other carbon systems have not been demonstrated. In fact storage characteristics were inferior to other known "physical" adsorbents.
- Have demonstrated excellent ability to control aerogel microstructures, pore size, surface area, etc. Room temperature data not yet obtained, but one can probably predict aerogel carbons will not have very useful capacities at ambient temperature. M-doping seems to have only marginal benefit, at least so far at low temperature. Good progress in technical understanding. Progress in H-storage capacities suggest DOE targets will not easily be met with the M-doped, but the idea to use C-aerogel as MH scaffolding may be a much better approach.
- Very good progress on pushing the carbon aerogel hydrogen storage capacities at 77K. Relatively little progress in using metal additives to the aerogel to increase storage capacity.
- Demonstrated good improvement in hydrogen storage, compared to standard carbon aerogel materials.
- The best material achieved is not as good as activated carbon in terms of desired pore size distribution.
- Some improvement of binding energy, still below stated objective. Good storage densities for cryosorption, however the results are similar to activated carbons (minor effect of doping so far).
- Porosity control methodology needs to be focused on more. Hydrogen uptake of 5.3 wt.% due to activation is a good improvement from last year's results.

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

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

- Useful collaborations, at least on paper. Source of collaborative data not always clear in presentation. No NS [neutron scattering?] or NMR results shown. Collaboration with HRL (aerogel scaffolds) is a great plus. Is this effort a direct component of the HSCoE?
- Project is seeking out other possible uses for aerogels, such as scaffolding for higher capacity hydrogen storage materials.
- Good collaboration with other groups.
- Need to explore the possibility of using the materials developed in this project for other applications.
- Clear collaborative framework. Good collaboration with others within the DOE program (i.e. HRL).

Question 5: Approach to and relevance of proposed future research

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

- "Scaffolding" metal hydrides in the framework would not significantly improve basic characteristics of metal hydrides (except kinetics, perhaps). (Refer to earlier work by NREL on SWNTs loaded with hydrides).
- Future work is built on past results and is logical to complete the fundamental understandings of C-aerogels. Further doped- C work may not be very productive toward breaking the technical barriers.
- Expansion of original effort to MH scaffolds seems the most value for a breakthrough (HRL connection).
- Good, but there doesn't seem to be very many avenues identified for improving the storage behavior of the metal additive doped carbon aerogels.
- The plans are built on past progress.
- The PI needs to layout a strategic and realistic approach in choosing the dopants.
- The PI needs to consider how to improve the thermal conductivity of the material.

- Boron work could be interesting. Difficult to see yet how substantial improvements over activated carbons could be achieved. The team is proposing an interesting refocus: scaffolding strategy interesting.
- Path to tune the porosity is not clear and might not be simple; this could be a show stopper for utilization of aerogels as hydrogen storage materials.

Strengths and weaknesses

Strengths

- Use of relatively low-cost materials.
- Is doing work on C-aerogels, a complement to similar work elsewhere on other types of C?
- Offers a potentially low-cost alternative to other carbons, such as nanotubes.
- Offers an important extension to using the aerogels as scaffolds for MH, not as H-storage media themselves.
- Excellent expertise on the aerogels and their synthesis.
- Carbon aerogels can be made with high surface area.
- Carbon aerogels are potentially relatively inexpensive materials.
- The approach is simple and scalable.
- May offer a practical pathway to doping carbon structures (compared to activated carbons).
- Improvement of activation procedure and consequently improved wt.% hydrogen uptake.
- Collaboration with others within the DOE program.

Weaknesses

- Essentially all capacity measurements were done at 77K that may not demonstrate any potential leads towards more practical applications at ambient temperature.
- Like all C adsorbent work, this does not seem like a likely route to reaching DOE 2010 gravimetric and volumetric storage targets.
- At best, undoped or metal-doped aerogel storage will probably require cryogenic containers.
- Carbon aerogels are likely to have relatively low volumetric hydrogen storage capacities.
- Incorporation of effective metal dopants into the aerogels to increase storage capacity appears to be very problematic, and may not be feasible.
- The theoretical limit of this kind of material in terms of hydrogen storage capacity, how it compare to activated carbon and MOFs was not addressed.
- Difficult to imagine how the pure materials will be able to achieve the DOE targets.
- Need to clarify path suggested to enhance and control porosity of the aerogels.

Specific recommendations and additions or deletions to the work scope

- Consider evaluating the spillover effect and capacities at ambient temperature and move on to a go/no-go decision.
- There should be a go/no-go decision point during the next year concerning the viability of using C-aerogels (undoped or doped) as H-storage media.
- Further increase project scope and direction in the direction of using C-aerogels as MH scaffolds.
- None.
- Very interesting and recommend to continue funding.
- Need to clarify path suggested to enhance and control porosity of the aerogels.

Project # ST-07: Enabling Discovery of Materials with a Higher Heat of H₂ Adsorption

Alan Cooper, presenting; H. Cheng, M. Foo, J. Zielinski, C. Coe, G. Pez, Air Products & Chemicals, Inc.

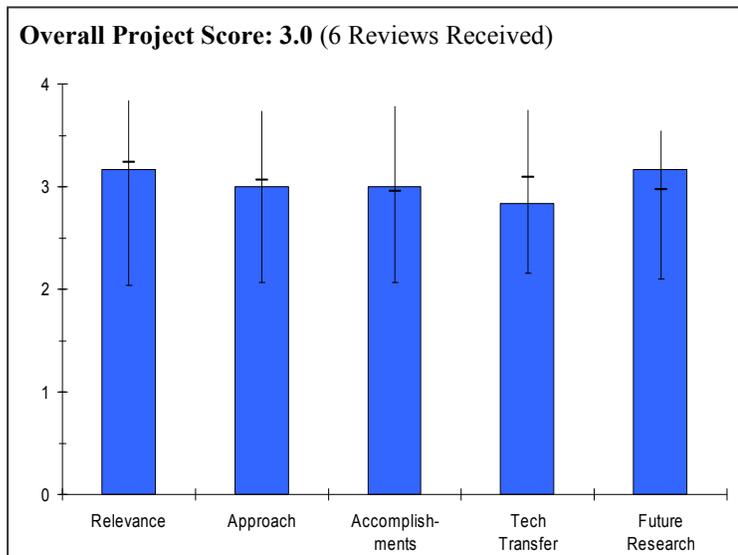
[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The objectives of this project are to:

- Develop enabling technologies for H₂ storage materials development;
 - o Accurate, predictive computational methodologies for new materials discovery and mechanistic understanding,
 - o Characterization tools for accurate H₂ storage measurements,
- Develop and test of new materials with high H₂ storage density and appropriate enthalpy of hydrogen adsorption.

The overall goal of this project is reversible adsorption of hydrogen at near-ambient temperatures at densities that will enable meeting the 2010 DOE system-level targets for hydrogen storage.



Question 1: Relevance to overall DOE objectives

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

- Aligned and relevant to the DOE objectives. Even though not critical, still instrumental for the success of the Sorption CoE projects. Provides data and guidance on the limitations and performance improvement possibilities of carbon based materials.
- Project fits within President's Hydrogen Fuel Initiative. Project generally directed toward HFCIT MYPP, mainly gravimetric H-density. Other target parameters (e.g. volumetric H-density) not discussed much.
- The project involves a combined theoretical and experimental study where theory predicts promising materials and experiment develops and tests these new materials.
- The work is too preliminary to assess relevance with respect to the DOE goals for storage.
- High degree of relevance to guide the development of new materials that could meet the storage targets and to the understanding of physical processes needed.
- Understanding the hydrogen spillover mechanism could lead to the discovery of improved hydrogen storage materials. This is a key mechanism to understand for almost all adsorbent based materials.

Question 2: Approach to performing the research and development

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

- Well-thought approach. It involves predictive computational modeling for screening materials with respect to their hydrogen storage capacity and adsorption energy prior to synthesizing and testing them. Valuable contribution to the improvement of accuracy of adsorption measurements - this is of particular importance to the microporous materials.
- Part of project's approach is to support various HSCoE efforts with theoretical (computational) aspects of H-spillover. That is valuable to help decide if spillover has any hope of overcoming weight-volume barriers. PI notes the advantage of close connections between calculation activities and experimental. Project activities are rather diverse and scattered, but should contribute in a useful manner to the H-program. Project's emphasis on identifying new and different materials is very important.

- The theoretical methods and software used are standard and the energetics are computed efficiently. However, the results are not well integrated with experiments and other research.
- Several different systems have been considered, either experimentally or theoretically, but it is not clear what the overall program direction is.
- Very interesting results obtained using ab-initio approach. Some validation is shown, however should be complemented by experimental work by partner organization.
- Using appropriate modeling tools to understand the binding energy discrepancies in the various stages of the spillover mechanism - an adequate explanation must be provided in order to give credence to this mechanism. Modeling will need to be followed up with real analytical tools to observe and validate the hypothesis put forth.

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

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

- Sound progress and satisfactory degree of achievement with respect to objectives and original planning. Identification of promising storage materials that could demonstrate practical hydrogen adsorption enthalpies at high hydrogen loadings and could be synthesized in the lab. First insights into the hydrogen spillover mechanism.
- A good and more complete story on the mechanism of hydrogen spillover has been accomplished. It seems, at least relative to carbon and Li-intercalated C, that the calculational results are rather negative relative to meeting MYPP RD&D targets. For example, it appears that it will promote strong C-H bonds that may require excessive temperatures to break. It is not clear what the PI recommends for the future of other DOE projects involving spillover. Is there hope of reaching DOE targets at room temperature? The prediction of a new material (N-F-graphite) gives great hope of overcoming the weight barriers. This is a valuable result that should be experimentally confirmed ASAP. It is hard to judge this project against its own schedule and milestones, which were not given in the presentation.
- Theory has identified possible synthetic routes to produce porous nitrogen-based graphite intercalation complexes. There is no clear demonstration that the theoretical prediction has resulted in the discovery of new materials.
- The technical progress was not clearly summarized in the presentation. Only a few systems were examined using modeling tools but there was not much to report on new material development and testing.
- Shows possible pathways to achieve the DOE storage targets. Good contribution to understanding the mechanisms of spillover and related phenomena. Proposes new promising materials for sorption based storage that could meet the DOE targets. Proposes bridging/storing class of materials to improve spillover mechanism.
- Good explanations of Pt clusters provided and how large clusters must be in order to propagate the spillover mechanism. PI should offer some insight as to how the spillover mechanism is initiated (not just propagated). Can surface defects provide the initiation sites?

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

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

- Already well connected to a number of CoE members involved in the same research field and in anticipation of enhancing these collaborations and establishing interactions with others.
- PI lists NREL, ORNL and Penn State as collaborators, but does not really define their roles. PI lists possible future collaborations, but does not really define their roles. Collaborations seem to be mostly within the HSCoE.
- The project is not well coordinated with similar work being carried out at other institutions modeling spillover mechanism.
- It is not clear what the next step will be in the program if the nitrogen-doped carbon materials are not effective. It is not clear how this work has enabled others in the CoE.
- Degree of input of other partners seems low or has not been clearly expressed in the presentation. The project would benefit from collaborations with other program funded projects.
- Air Products is always limited in their collaboration. However, they have the appropriate level of in-house expertise to conduct such work.

Question 5: Approach to and relevance of proposed future research

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

- Sound & targeted future planning building on recent progress and moving a step forward.
- Future work is based on past results and aimed toward technical barriers. Work on N-F-graphite and computational identification of new materials is good. Spillover work seems about finished. It would have been useful to clearly state the PI's conclusion from the calculations – does spillover offer much hope for developing a C-based material that can meet DOE targets for 2010 or beyond?
- Complete synthesis of graphitic carbon materials with nitrogen doping and using these materials to generate fluoride intercalation will be very worthwhile project.
- The future work has limited scope and there is not clear pathway forward if the next system, the nitrogen-doped graphite, does not have success.
- Excellent progress, logical next steps.
- They need to clarify if they will pursue some of these fluorinated compounds and to what extent.

Strengths and weaknesses

Strengths

- Lengthy experience and competence in the field.
- Strong collaborations pulling expertise and forces within the CoE, particularly in the field of synthesis.
- Project has good people with good new ideas and excellent technical and industrial experience.
- Project aims at identifying new and very different materials through calculational modeling. Yes, other projects are also doing that; but this project's methods seem somewhat different.
- Experiment is aiming at synthesizing theoretically predicted materials.
- Difficult modeling work was completed.
- Interesting quantum chemistry study of the spillover mechanism.
- Proposes strategies to enhance the effect.
- Exciting results for carbon-nitrogen-fluorine structure (strong binding physisorption).
- Air Products is an industrial company that is motivated to produce hydrogen storage materials for their own gain. They have a good understanding of automotive and industrial requirements and choose their research directions wisely based on real-world economics and knowledge.

Weaknesses

- Validity and reliability of the ab-initio molecular dynamics simulations presented.
- Identification of limitations/downsides of proposed methodologies – for instance difficulty in removing the THF solvent in the process proposed for the Li-building carbon materials.
- Volumetric and other DOE targets hardly mentioned. In addition to calculating gravimetric H-densities, we should see some simple calculations on volumetric densities. Can this general volume barrier problem be overcome with sorption materials based on carbon?
- This reviewer would like to see hydrogen expressed in wt.% rather than cc/g (Li-doped SWNT slide).
- Collaborations are not clearly defined.
- Some of the work is not very relevant to the program goal. For example, studies of hydrogen interaction with free Pt clusters does not elucidate spillover mechanism as it is the supported metal cluster that is important.
- The project would benefit from a clearer program plan, both with respect to material development and for enabling interactions with other CoE participants.
- Lack of experimental work.
- Limited validation.
- Clearly needs experimental feedback.

Specific recommendations and additions or deletions to the work scope

- Benchmark computational modeling data with experimental data; check their validity.
- Consider accelerating the material synthesis and testing program.

- A general comment – there is a strong need to reach an agreement on how storage capacity data are presented – excess, total or absolute hydrogen uptake?
- Phase out spillover work and increase efforts on experimental confirmation of identified new materials.
- Focus on new N-F-graphite. It seems to offer greater hope for a "breakthrough", as suggested by the preliminary calculations of $\Delta H = -20.2$ kJ/mol and wt.% = 7.4. Look for new and different materials.
- Efforts should be more coordinated between theory and experiment relevant to the program goals and between various groups working on similar problems.
- Collaboration with Yakobson and Hauge from Rice strongly suggested in order to coordinate theoretical activities on spillover.

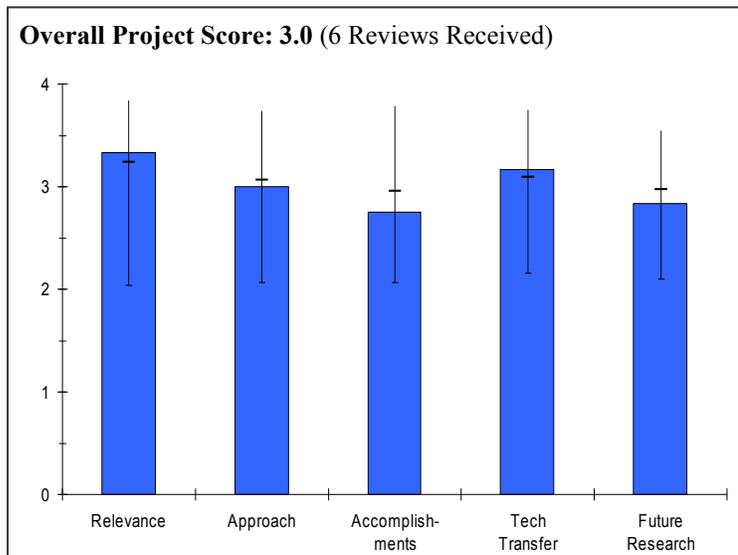
Project # ST-08: Advanced Boron and Metal Loaded High Porosity Carbons

Mike Chung, Presenting; Peter Eklund, Hank Foley, Vincent Crespi, Co-PIs, Pennsylvania State University

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The overall objective of this project is to develop advanced hydrogen physi/chemisorption materials that are reversible, have high gravimetric and volumetric capacity and favorable thermodynamics. The goal is to achieve reversible storage of ~6 wt.% at 200K, 100 atm by 2008. High specific surface area (SSA) carbons are the focus of this work. The carbon framework will be chemically modified for enhanced H₂ binding energy. Boron will be substituted to enhance the binding energy of hydrogen. Boron is a light element and the only one known to substitute in the sp² framework without serious structural distortions.



Question 1: Relevance to overall DOE objectives

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

- The effort of chemical modification of carbon to adjust H₂ binding energy is good and relevant for efficient storage. Too much focus on achieving good capacity numbers at cryogenic temperature which has little relevance to potential commercial applications for on-board storage.
- There is some doubt that this approach can meet the 2010 targets, even at 77K.
- The project is closely related to DOE HFI and overall objectives. Synthesizing the B/C materials with desired B content and SSA is critical in overcoming the barriers.
- The project is highly relevant to the DOE RD&D objectives. Barriers A and P have been addressed in the presentation.

Question 2: Approach to performing the research and development

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

- Increasing boron content and enhancing SSA is the right approach for doped carbons. However, more studies should be done at temperatures other than cryogenic.
- There needs to be more emphasis on ways to incorporate higher binding energy species into the B-C structures. What is the strategy for incorporation of these species?
- Theory guided experimental design is a good approach. The experimental approach is scalable. The PI needs to address how to control the structure and content of the final product in the approach.
- The approach to meet the project objectives is sound.
- Molecular reaction and electric arc appear to be brute force approaches to synthesis and do not show any path forward to controlling the boron concentration on an atomic scale. Polymeric precursor route to boron modified carbon appears to be only path to control boron concentration. There are no systematic experiments planned or discussed with respect to the polymeric precursor route. There needs to be a controlled set of experiments to evaluate boron concentration effects as well as surface area. There needs to be some determination of the theoretical limits of boron exchange in the graphene layers.

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

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

- Still, best boron-doped carbon demonstrates significant disadvantages in capacity versus other materials such as MOF's and high SSA carbons. There is a good correlation of boron content and "specific" capacity - 5.7% boron gives ~ 330 m² per wt.% capacity, and 8% boron gives ~ 244 m² per wt.% capacity (compare MOF ~ 840 m²/g and commercial carbon ~500 m² per wt.% capacity). Assuming trend continues with the increase of boron, a weight capacity of 10% could be feasible if SSA increased up to 1700 m²/g. It is challenging but not unrealistic, however, this would be at cryogenic temperature. Progress isn't enough to anticipate meeting the targets for storing hydrogen at ambient temperature.
- Boron additions do show some level of improved hydrogen adsorption, but not enough to get "excited" about. Multiple synthesis techniques for incorporating boron into the carbon structures have been developed. The high temperature synthesis of boron-carbon nanoparticles is interesting.
- Demonstrated certain progress towards the target. Room temperature hydrogen uptake at less than 1 wt.% should not be used as a measure for accomplishment. The PI needs to specify the size of error bar for 0.5 wt.% hydrogen uptake.
- Substitution of carbon material with B, C, Al etc., considered to be one of effective techniques. However their strategy and result do not suggest certain achievement of hydrogen capacity over 6 or 9 wt.% .
- Promising storage densities have been achieved experimentally (taking into account the specific surface). Lower end of H₂ binding energy of project objective has been achieved. Interesting theoretical work.
- The technical accomplishments are minimal. Only the chemical synthesis method has generated any material with substantial boron levels. The hydrogen storage is not better than that of any other carbon material. The boron additions increased the binding energy and to some degree the hydrogen storage capacity. At what point is the binding energy too high for this to be a useful material?

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

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

- List of partners is very limited, however, membership in the CoE should help enhance collaborations.
- There is good collaboration to characterize the materials being produced.
- Certain coordination within the CoE exists. Need more collaboration with other groups.
- Good Penn State team integration, not as clear from the presentation what the contribution of the other partners were.
- Collaborators were listed but there was no mention of how the team interacts with the CoE or the collaborators. Detail is lacking.

Question 5: Approach to and relevance of proposed future research

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

- Proposed future research is good, but there appear to be no radically new approaches proposed to increase the hydrogen storage levels from where they are now, except to pursue the addition of selected metal atoms to the boron-carbon structures.
- Plans are built on the past progress and sound good. Need to layout a specific pathway to execute the plans.
- It is expected that they find a pathway to improvement of hydrogen capacity over 6 or 9 wt.% in system by increase of heat of adsorption.
- Logical next steps are considered.
- The future work lacked a detailed explanation of how they are to achieve their results. The future work was to achieve a certain boron level by a certain date or a certain storage capacity by a certain date. The details of how they plan to get to these levels or if these levels are possible were lacking.

Strengths and weaknesses

Strengths

- Good lead in terms of increasing "specific" capacity (SSA per wt.% storage).
- Very good scientific approach to explore boron additions to carbon to improve hydrogen storage.
- Multiple synthesis avenues are being pursued.
- Hydrogen storage reversibility should be good for these types of materials.
- Theory guided experimental design is very effective.
- The approach is scalable.
- Assuming that the specific surface can be scaled up to 2800 m²/g then a storage density of about 11% could be achieved for cryosorption (may meet the 2010 DOE storage density system target).
- Net increase of H binding energy.
- Polymer precursor route to boron modification of the graphene sheets is interesting.

Weaknesses

- Low probability of success if storage at ambient temperature is considered instead of cryogenic.
- It is not clear that the boron addition approach will be sufficient to achieve 2010 storage targets.
- Lack of specific technically feasible pathway to execute the plans.
- Room temperature adsorption remains low (cryosorption needed).
- The materials produced need to be more fully characterized to determine where the boron resides and how it impacts the crystal structure. Boron NMR would be the first step as would TEM.
- Systematic studies of boron concentration effects need to be implemented to determine if there is a critical boron concentration.
- Material produced to date is of low surface area. Surface area increased by CO₂ activation. PI needs to understand that boron additions make the carbon structure more stable to activation and more difficult to increase the surface area. This looks like a "dead-end" approach.

Specific recommendations and additions or deletions to the work scope

- Include other elements as dopants in the search. Boron will most likely to help achieve targets at 77K but not at 25°C.
- The study of non-stoichiometric carbon-rich B₄C might prove interesting.
- Determine what is the desired structure (pore size, BET, etc.) and feasible B/C ratio. Determine whether there is a structure change compared to pure carbon materials.
- Eliminate electric arc and molecular reaction synthesis routes as they do not appear to demonstrate to control boron concentration.
- Some in depth characterization of the structure with boron is needed.
- There are no systematic experiments planned or discussed with respect to the polymeric precursor route. There needs to be a controlled set of experiments to evaluate boron concentration effects as well as surface area.
- The materials produced need to be more fully characterized to determine where the boron resides and how it impacts the crystal structure. Boron NMR would be the first step as would TEM.
- Systematic studies of boron concentration effects need to be implemented to determine if there is a critical boron concentration.

Project # ST-09: Carbide-Derived Carbons with Tunable Porosity Optimized for Hydrogen Storage

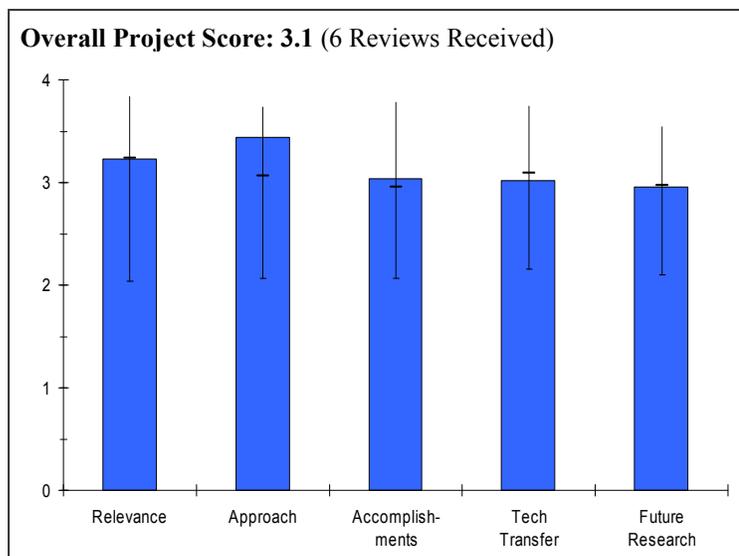
Jack Fischer, presenting, University of Pennsylvania; Yury Gogotsi, Co-PI, Drexel University; Taner Yildirim, Co-PI, NIST

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

Brief Summary of Project

The objectives of this project are to:

- Develop and demonstrate efficient, durable and reversible hydrogen storage in carbide-derived carbons (CDC) with tunable nanoporosity (2004-2005).
- Determine the optimum pore size for hydrogen storage using experiment and theory (2005-2006).
- Identify post-processing strategies and catalytic additives which maximize the performance of CDC-based hydrogen storage materials, using experiment and theory (2006-2007).
- Finalize the design of a CDC-based H₂ storage material that meets 2010 DOE performance targets and commercialize it (2007-2008).

**Question 1: Relevance to overall DOE objectives**

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

- Project focus seems generally aligned with DOE objectives.
- The project aims to develop durable, efficient, and reversible hydrogen storage using carbide-derived carbon with tunable porosity.
- Clear relevance. Barriers A, F, Q addressed in the presentation.
- Directly addresses one approach to materials-based hydrogen storage.
- The stated objective is to develop a system that will satisfy 2010 goals and commercialize it (by 2008). It is not at all clear how the PI will do this (either achieving the 2010 goals, nor commercialization). The specifically tailored pore-sizes could be useful for a variety of purposes; however, it is not clear that changing the pore size will get this idea to room temperature storage (much less a 6 wt.% system at room temperature).
- Project generally supports DOE goals. However, the pathway to achieving the gravimetric and volumetric goals at non-cryogenic temperatures is unclear.
- There may be inherent limitations in capacity and binding energy that could limit reaching goals.

Question 2: Approach to performing the research and development

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

- A variety of purification/activation and chemical modification studies have been performed and shown to be effective for tuning the pore size distribution and surface areas of these materials. Fundamental understanding of the structure and hydrogen binding would help to guide and understand research. Additionally it is important to determine the theoretical upper limits for gravimetric/volumetric capacity for these materials?
- This is a unique and interesting approach for fabricating nanostructures with controlled pore size. The ability to tailor the pore size is a promising way to synthesize and test sorption materials with controllable sorption properties. It is highly questionable as to whether these materials will be effective adsorption media at non-cryogenic temperatures. The strong synthesis and characterization effort is enabling rapid progress toward

establishing the efficacy of this approach for enhanced hydrogen sorption. There is good support from theory to describe how changes in structural properties affect sorption behavior. This will continue to be important for understanding and optimizing sorption enhancement by doping and chemical modification.

- Approach involves creation of pore structures, optimization of the size and shape of the pore, and developing techniques for purification and doping.
- Approach ("designer pore structure") is sound and interesting. Nanodiamond studies were an excellent idea to qualify surface modification strategies.
- Unique approach in tailoring pore size distribution to enhance hydrogen uptake by starting with carbide as a precursor. Emphasis on post-processing strategies to enhance hydrogen capacity has yielded improvements in hydrogen capacity. Should increase efforts toward increasing the hydrogen binding energy. Use of macroscopic configurations (e.g., rolling peels, pellets) excellent approach to enhancing volume density.

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

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

- Post-treatment purification of samples using NH_3 or H_2 gas was used for removal of Cl-based byproducts. While necessary, the purity of the effluent H_2 gas needs to be examined. That is, what is the remaining amount of trapped Cl_2 gas (" <1 wt.%" needs to be quantified further)? Does annealing under NH_3 result in trapped/bound/adsorbed NH_3 which would be released? It is good that strategies for improving volumetric capacity are being considered and evaluated. A great deal of progress on gravimetric capacity since 2006 has been demonstrated. Cycling/reversibility studies for these materials are necessary to demonstrate that the chemical (dopants/surface treatments) and structural (pore size/surface area) integrity (and thus properties) are maintained over multiple cycles.
- The accomplishments look scientifically promising, but don't show a real pathway towards improving the technology, or progressing towards DOE targets. Surface chemical modification (to increase binding) results look like a promising avenue to pursue. Li doping studies do not look like a promising approach. Not clear how modeling studies have really significantly taught anything new beyond what was already known from NREL studies.
- Excellent progress on synthesis of a wide range of CDCs with different pore characteristics. Impressive results on enhanced adsorption at 77K. Chemical modification of pore surfaces and synthesis of doped material are promising approaches to achieving improved sorption performance. Control of reaction with Li to achieve high coverage without agglomeration is likely to be problematic. Are theory/modeling predictions available that show which pore size and pore size distribution would be optimum? If so, the project should rapidly focus on those conditions for testing/validation.
- Purification by removing elements that block access to the pores. Chemical modification of the interior pore surface to increase binding. Doping with metal atoms to increase Kubas binding.
- Optimization of pore size distribution and specific surface. Li-doped disappointing at moderate pressures (Li clustering reducing accessible pore volume?) Challenges well identified. Ti dispersion in pores not achieved. Enhancement of the volumetric capacity through compression has been achieved.
- Important results achieved on volume density by compressing powders. Good progress on tuning porosity and cleaning materials, but most of this work was from last year? Major result this year was using ammonia in post process purification treatment. Still limited on volume and weight capacities. Needs further work and accomplishments towards enhancing hydrogen binding energies in these materials to raise the operating temperature. No measurements shown above 77K.
- Although good progress has been made to date, significant improvements in storage densities and binding energies will be needed to meet DOE targets.

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

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

- Good collaboration between experimentalists and theorists within the independent project. Recommend initiating interactions with investigators in the HSCoE (there's common ground between this project and the HSCoE activities; both groups could benefit from these interactions). There may also be some good

opportunities for collaborations with MHCoe researchers on the use of these materials as support structures for enhancing the metal hydride reaction kinetics.

- The PI is interacting with theorists to achieve a fundamental understanding of the hydrogen binding to metal doped pores.
- Collaborations and role clearly discussed.
- Some collaborators in specific technical areas. Some leveraging with BES funded activities.

Question 5: Approach to and relevance of proposed future research

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

- Future goals such as increasing the heat of adsorption (toward more ambient temperature storage) are valuable; however, it was not clear what the approaches are. As mentioned above, cycling and hydrogen purity studies are important as well as a continued focus on increasing volumetric densities.
- The proposed future research is focused in the right direction (increasing binding, moving towards room temperature adsorption, etc.), but seems a bit unimaginative. It is not clear that the proposed theoretical work will really help move the project forward (particularly in the last year of the project).
- Good science-based approach to optimizing sorption properties is planned. It is important to consider methods for preparing more reactive sites for metal incorporation; however, no specific plans were outlined. Recommend quantification of hydrogen confinement capacity as a function of temperature (e.g. 77K to ~50 deg C)
- Exploit metal-hydrogen reaction to increase hydrogen binding.
- Clear strategy to move forward. Looking forward to the results on the pore structure (proposed neutron scattering experiments and use of reverse MC simulations)
- FY 08 plans very ambitious. Not clear if all could be accomplished. Right direction for some of the FY 08 activities - increasing binding energy and continuing with improving volumetric density.

Strengths and weaknesses

Strengths

- Vast experimental space to investigate and tune materials properties (i.e. numerous activation, purification, doping, and surface modifications being explored).
- Demonstrated control over pore size and surface area properties using above methods.
- Novel approach for preparing unique sorption materials with controllable pore characteristics.
- Strong R&D team comprising both theorists and experimentalists.
- Good possibilities for expanding effort by collaboration with CoEs and other independent projects.
- Knowledge guided approach for optimizing pore size and metal doping.
- Ability to optimize the pore size distribution is demonstrated.
- Substantial enhancement of the isosteric heat of adsorption with respect to conventional carbon structures.
- Designer pore size distribution is an appealing strategy.
- Good approach of forming compressed structures to increase volume densities of these relatively low density materials that might be applicable to other types of adsorption materials.

Weaknesses

- It is not clear that a rational materials design approach has been developed. That is, the effects of the reactants (metal identity) and sample treatments (activation, purification, and surface modifications) on the resulting product structure need to be understood. This would clarify the path forward toward improved properties.
- Operation at non-cryogenic temperatures is a critical issue and potential showstopper for this approach. This should receive greater emphasis.
- The theoretical work is not relevant to project goals. Using $C_2HA(Ti)_2$ to understand what happens in Ti doped pores is inappropriate.
- Doping these structures appears problematic.
- Needs higher temperature capacity measurements on doped samples.
- Not clear how modeling works into experimental work.

Specific recommendations and additions or deletions to the work scope

- The challenge of modeling these amorphous, non-periodic systems was acknowledged and potential options introduced. It would be beneficial to try to incorporate some theoretical aspects (identification of best dopant or surface functionalities) to better guide their research.
- Experiments which investigate hydrogen gas purity and reversibility should be incorporated.
- None.
- The PI should be more critical of theoretical models and encourage calculations that are appropriate for the experimental morphology. Efforts should be made to determine if metal atoms inside pores cluster or remain isolated.

Project # ST-10: Hydrogen Storage in Metal-Organic Frameworks

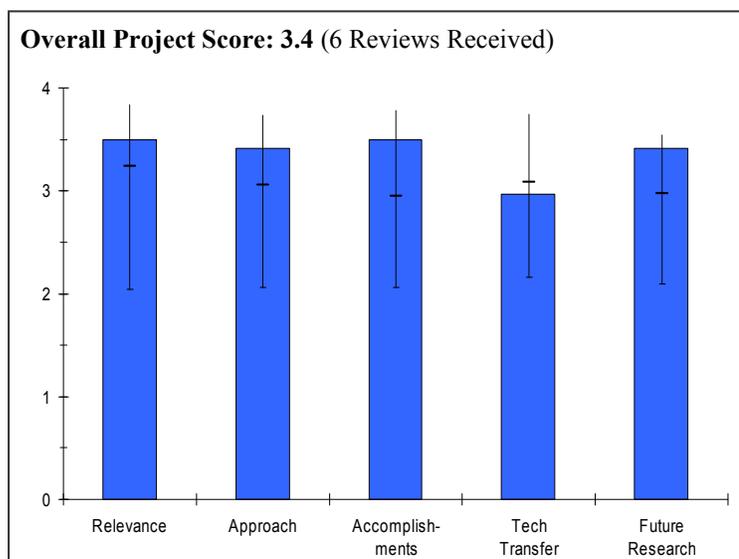
Omar Yaghi; University of California, Los Angeles (UCLA)

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

Brief Summary of Project

The overall objective of this project is to develop strategies for achieving metal-organic frameworks (MOFs) that have increased uptake at higher temperature. This is being done by utilizing new concepts for increased surface area, implementing strategies for higher adsorption energy, and developing strategies for increased hydrogen density. Progress in 2007 included:

1. Tuning porosity led to tripling of hydrogen uptake in MOFs (excess 7.5% wt., absolute 12% wt.);
2. The 35 grams H₂/L achieved in MOF-177, indicates that dead volume is not a major issue for MOFs;
3. MOFs exhibit fast kinetics (1-3 minutes for charging and discharging);
4. MOF material porosity and uptake are stable to charge/discharge cycling;
5. Cubic meter scale of useful MOFs is now being developed by BASF.

**Question 1: Relevance to overall DOE objectives**

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

- Research directions followed are generally aligned to program's objectives and support the Hydrogen vision.
- High surface area materials are an important part of the DOE storage objectives and this program is addressing this issue.
- Project is well-directed toward objectives of President's Hydrogen Fuel Initiative. Project focused on DOE objectives and HFCIT RD&D Plan (i.e. MYPP). Project looks closely at both gravimetric and volumetric targets, as well as kinetics.
- The project involves designing the porosity of metal organic frameworks and doping with metal atoms as well as impregnating with polymers to increase the binding energy of hydrogen. Theoretical calculations provide input regarding the metal atoms to be doped.
- Work is directly related to the development of adsorbent materials for hydrogen storage.
- This project brings the concept of reticular coordination chemistry into the DOE Hydrogen Initiative. While it is not likely that metal-organic frameworks (MOFs) in their present state of discovery will meet hydrogen storage targets, the extended study of the first generation of MOFs has stimulated much research into reticular chemistry. The possibility that a reticular structure could meet the storage requirements deserves exploration.

Question 2: Approach to performing the research and development

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

- Well-thought, reasonable, systematic approach profiting from the PI's lengthy experience in the field.
- The approach has been focused primarily on 77K sorption condition despite emphasis by reviewers last year to work on room temperature [RT] materials. Some of the proposed approaches towards RT sorption such as Li-

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insertion (as shown in the sorption CoE) have been tested with limited success. Need to look at the bridging/spillover phenomenon as developed by R. Yang.

- This effort is well-focused on a large and versatile family of high-surface sorption materials, MOFs and related structures. It is systematically looking at a large variety of MOFs relative to technical barriers. Project aimed at understanding and modifying structures for maximum hydrogen storage capacities with minimum dead volume. This is an important and needed feasibility test for MOFs. Good systematic thinking.
- The PI uses novel chemistry to design materials with different pore sizes and modifying the chemistry of the pores through doping. Fundamental understanding of the science is sought from theoretical collaboration.
- These structures have demonstrated the highest hydrogen capacity of adsorption materials. Has a plan for improving volume and weight densities, as well as increasing hydrogen binding energy - interpenetrating structures, maximizing surface area while reducing large volume, impregnation, etc. New collaboration established with Goddard for theoretical modeling.
- The approach involves the synthesis/construction of strongly bonded, stable, molecular frameworks with controlled pore architectures, dimensionalities, and hydrogen sorption properties. Measurements of the hydrogen uptake and release properties of said molecular frameworks are made routinely. Studies of open metal incorporation, interpenetration effects, combination of MOFs with other framework-like media, and metal atom impregnation are underway. Stability studies are also done as appropriate.

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

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

- A very significant step forward. Demonstrated reproducibility of hydrogen adsorption experiments and independent verification of the saturation hydrogen uptake in MOF-177. Proposed a benchmark adsorber: MOF-177 in view of its well-known structure and hydrogen uptake performance. Equally exciting are the possibilities opened by the large free volume in interpenetrating networks – could these hold the secret to a storage solution?
- No significant progress has been made on room temperature sorption materials. The results are not significantly different from what was presented in 2006.
- PI and many coworkers have looked at a large number of materials via theory and experiment. Group has shown up to 7.5 wt.% and 30+ g/L capacity at 77K, i.e., a fair fraction of the DOE system targets. Of course, systems must accommodate reductions from the materials' properties. Group appears to have got a good start on cataloging MOF possibilities in a relatively short time and reasonable cost. Good reversible absorption/desorption kinetics demonstrated. In summary, good progress has been made against the technical barriers.
- 7.5 wt.% reversible hydrogen storage is achieved at 77K. The synthesized materials exhibit fast kinetics and stability. Efforts are made to scale up production.
- Major effort this year towards interpenetrating structures (IRMOF-62 ~7 wt.%). Increased capacity by opening up metal sites. Still relatively low volume density of these materials relative to e.g., hydrides. Still relatively low hydrogen binding energies with poor room temperature uptake. Soft chemisorption covalent framework studied but only preliminary results. No evidence of high capacity with increased binding energy. Binding energies still remain low in the materials to date.
- The PI has a large group and is broadly funded by several agencies. In future presentations, a slide showing exactly what was done for the project under review would help the reviewer to properly evaluate this metric. Assuming the information on Slide 67 is in fact what was done specifically on the project under review, the progress has been very good. Absolute hydrogen uptake levels at 77 K are now in the range needed to meet system targets for hydrogen storage. The kinetics at 77 K are very good. However, getting reticular frameworks to function effectively and meet targets at ambient temperature is still not achieved.
- The stability results, particularly in aggressive media for some selected structures are impressive.

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

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

- Strong interaction and significant technology transfer appears to take place with BASF. However the degree of collaboration with other carbon researchers and institutes is not clear; neither is the link with the Sorption CoE (still important even though the project is outside the CoE).
- Work on MOFs fits well in the R&D roadmap. There are no fixed partners and very limited information on future partners and their roles in the effort.
- The PI collaborates effectively with theorists and is willing to lend expertise and advice to others working on MOFs and COFs.
- Limited collaborations. New collaboration for theoretical modeling. Has collaborated with SwRI on MOF-177 validation and additional testing.
- This project is not part of the Hydrogen Sorption CoE and it is not clear why that is. Other than the Goddard collaboration and the outside testing of a few MOFs, the effort of this project seems to be a “closed shop” operation.

Question 5: Approach to and relevance of proposed future research

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

- Future research plan builds on current experience and it is appropriately drawn for further progressing towards reaching the objectives.
- The pathway to room temperature sorption materials is not clear.
- PI shows an ambitious and well-considered list of future materials and ideas. Future work built on past results and aimed and weight and target volumes.
- Future work is aimed at increased binding energy for room temperature applications by metal doping, and impregnating with polymers. Testing of new materials (ZIFs and COFs) is likely to enhance the chances of finding suitable materials.
- One senses that the PI has a firm plan for the future that won't be “budded” by recommendations from a reviewer. Nonetheless, getting the reticular structures and/or hybrid structures to meet hydrogen storage target levels at ambient temperature must be the primary future direction for this particular project within the larger Yaghi program. Working on frameworks that might have higher hydrogen absorption energies seems to be essential for this project. The lithium addition and polymer impregnation studies look like good avenues to pursue as well.

Strengths and weaknesses

Strengths

- The PI's and his co-workers' high caliber expertise in the field.
- Strong background in developing novel materials with very high SSA.
- There is a large and fascinating spectrum of MOFs (and related materials) to look at.
- PI, support and students have very high expertise and potential to fully explore these potentially important materials.
- The project is innovative and the PI is always searching for materials with better performance.
- Very innovative work with large group having good success in synthesizing novel structures.
- Hydrogen program likely benefits from leveraging of resources that the group obtains from other sources.
- A highly leveraged project spearheaded by a determined PI.
- An approach that offers many interesting possibilities for future developments in nanoporous material development.

Weaknesses

- Reproducing this high performance under workable conditions, suitable for transport applications.
- Interaction with carbon research community.
- Scalability?
- Lack of progress in room temperature sorption materials.

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- It is uncomfortably apparent that this family of materials may never be practical at room temperature. That is they seem to offer no obvious advantages over other high-surface-area media, except perhaps volume. To be fair, PI expressed some hope for 4-5 wt.% H for Li- or Ti-doped MOFs.
- Focus should be given to keeping the open metal sites from reacting with anything but hydrogen.
- The project might benefit from more interaction and collaboration (where appropriate) with other PIs (e.g., other modelers/theorists, HSCoE PIs).
- The absence of a meaningful interaction with the Hydrogen Sorption CoE seems to be a drawback. Better coordination might help to focus the project on the specific needs of the larger HFCIT program.
- Presentation set of slides are too long and don't follow guidelines.

Specific recommendations and additions or deletions to the work scope

- Enhance interaction and collaboration with the carbon research community and liaise with Sorption CoE.
- Examine the effect of hydrogen impurities on the reversibility, kinetics, durability.
- Investigate MOFs that could have open metal sites and are at the same time interpenetrable.
- This project has delivered excellent results with developing very high SSA materials. However, it has failed to translate this property into useful hydrogen storage materials.
- It is recommended to focus the remaining time and resources to address the room temperature sorption.
- Consider adding collaborative partners.
- Are there possibilities of interest from industry?
- Doping with transition metal atoms should be aggressively explored.
- The work on this particular project should be more narrowly focused to strictly meet the needs of the Hydrogen Initiative.

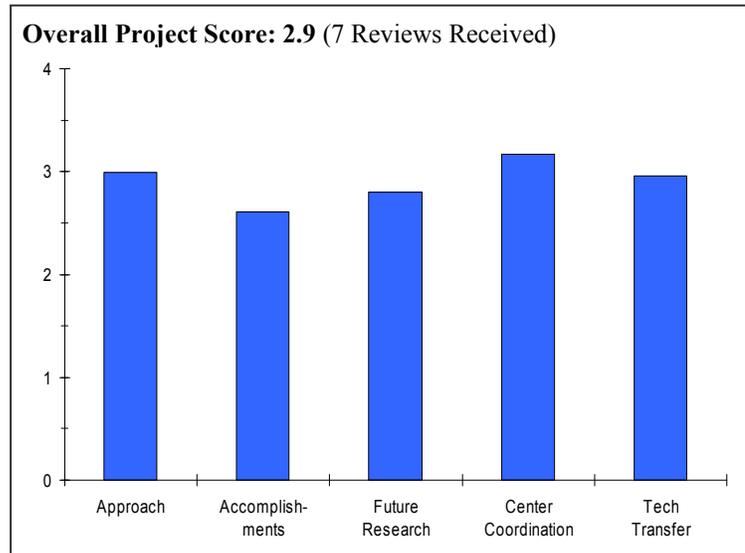
Project # ST-14: DOE Metal Hydride CoE Overview

Lennie Klebanoff, Director; Jay Keller, Co-Director, Sandia National Laboratory (SNL)-Livermore CA

[NOTE: This presentation was to evaluate the entire Metal Hydride Center of Excellence as a whole. A separate review form was used and can be found in Appendix D. Sandia's technical contribution to the center is evaluated in ST-15.]

Brief Summary of Project

Sandia National Laboratories is the lead partner in the DOE Metal Hydride Center of Excellence, which is composed of 8 universities, 3 industrial partners and 5 other national/federal laboratories. The center is focused on developing new reversible metal hydride materials capable of achieving at least 6 wt.% system hydrogen capacity, improving kinetics of absorption and desorption and thermodynamic plateau pressures, and improving processing and doping techniques that will lower cost. Current materials under study include destabilized binary hydrides, complex anionic materials, amides/imides, and alane (AlH₃). In addition to new materials discovery, Sandia will work with all center partners in fundamental modeling, materials synthesis and modification, testing of hydrogen storage and delivery characteristics, and engineering science and process development to support and guide the materials discovery efforts.

**Question 1: Approach to performing the R&D**

This project earned a score of **3.0** for this criterion.

- The center activities and project scopes are sharply focused on the DOE objectives, making it a key contributor to the overall Hydrogen Initiative. The center's approach combines synthesis/experiment, theory, and systems analysis, all vital components of a high-impact collaborative hydrogen storage research effort.
- The CoE and the work plan are well-structured with an effective increased contribution of system-related analysis (Project E).
- The program management and the overall revision process are adequately presented with effective selection of promising materials.
- The milestone management style is well aligned with DOE milestones.
- I like the management structure and approach.
- The general approaches are focused on overcoming the technical barriers.
- A lot of activities are directed to address the regeneration/reversibility issue of the materials.
- The center is well organized and is willing to self down select without pressure from DOE or the tech team. The project and program work is well divided in terms of partner capabilities. The work is directed at appropriate questions, such as higher capacity and lower enthalpy of release, though a clearer plan for fast progress on enthalpy and kinetics might improve the center slightly. Theory is well used to help guide experiment; the feed back to theory is present but might be improved a little.
- Organic down select is organic, so far no need to force a down select but council will step in if needed.
- Technical feasibility of metal hydrides is very limited for on-board storage primarily due to low storage energy efficiency, and therefore, low potential of most of metal hydrides studied by the center to meet the program objectives. Only [just] a few leads may be considered as potentially feasible, such as alane that still requires off-board regeneration.

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- The strategic focus of the CoE is not critically described by the Coordinator in relation to the DOE technical barriers.
- The down-selection approach needs more specifications and clarity: no criteria have been presented, even during the discussion.
- There are not clearly justified duplication/overlapping in the theoretical material selection approach: various methods are applied in different CoE projects with no clear comparison and integration among them (Monte Carlo, Combinatorial, First Principles). The Theory Group must better describe the way the methods and the efforts are effectively combined.
- The Management cost share (13%) is not adequately justified by the actions described.
- The overall R&D approach must be more tuned with the application-oriented approach of the DOE Hydrogen Storage Subprogram, instead of the used research-oriented approach.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **2.6** on this criterion.

- The progress has been well summarized, showing relevant results in term of scientific (62 publications) and IP (10 patents) production.
- The center has shown certain progress in overcoming barriers.
- Some promising results have been demonstrated.
- Significant progress has been made, but using a fairly large budget 8.2M\$. Multi-hotplate device is about “ready to roll,” but after a rather long generation cycle. $\text{Ca}(\text{BH}_4)_2$ work is quite an interesting result, though a lower desorption temperature is required. Getting Mg in aerogel is a nice accomplishment; LiBH_4 in aerogel did help kinetics. Alane work is appropriate though not much progress this last year. Tank work analysis is appropriate and may be helpful in future when proven out. Theory work is good, but needs to incorporate multi-step nature of reactions - not average over all steps - as its output.
- It is clear, since the presenter mentioned it several times, that they are focused on the DOE goals and aware of the gaps.
- There has been good progress and research devoted to alane regeneration with several different avenues being concurrently explored. Additionally, the modeling portion (particularly that regarding mixed borohydrides) of this center seems to have really aided in providing promising 'leads' to the experimental projects. It is however, important for the theorists to evaluate the stability and step-by-step decomposition energetics of all compositions (rather than just the reactants to products average). Independent and/or internal cross-validation of experimental measurements between partners is also encouraged.
- No/little progress has been demonstrated in the area of complex metal hydrides, amides/imides and destabilized hydrides. These materials may be considered for a quick no-go decision due to low potential for increasing useable storage capacity.
- The progress has been only partially analyzed with respect to DOE objectives and barriers.
- The presentation gives more emphasis to the progress of materials selection and less to the effective possibility to overcome DOE Program barriers.
- All the accomplished materials are still far away from DOE 2010 targets.
- Lack of a well defined pathway to achieve DOE targets.
- There should be more accomplishment with the \$8 million spending.

Question 3: Proposed future research approach and relevance

This project was rated **2.8** for this criterion.

- Future plans are appropriate but a deliberate focus on kinetics, enthalpy, and release temperature might yield a better plan. As mentioned above feedback to theory should be planned to a greater extent.
- The timing for the materials down-selection process is reasonable for the DOE target dates.
- I was pleased to learn the CoE structure is flexible and can be reorganized, as appropriate, based on promising new materials.
- A detailed description of future work was not clearly communicated in the presentation. Continued work on higher-valent borohydrides (and mixtures containing them) is promising. Alane regeneration method work

should also continue to be explored in more detail. More importantly, kinetics seems to be a (the) major barrier in the center and should emphasize or devote resources to this problem. Should clarify more how internal go/no-go decisions are made.

- The future plans are not clearly presented.
- The revision and contingency plans to dynamically modify the CoE activities are not adequately planned.
- Time planning showed in slide 24 seems too slow to well address results and efforts toward the final 2010 target.
- It is suggested to concentrate on materials potentially meeting more DOE technical objectives, extending the analysis also to cost aspects.
- The continuous update of material focus may require plans to involve other participants and/or projects in the CoE R&D effort, but it does not seem to be considered.
- The work plans are built on past progress.
- The down selection criteria were not well defined.

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

This project was rated **3.2** for this criterion.

- Communication between center projects is well coordinated and organized. Examples of cross-project interactions were presented to exemplify this established dialogue. Materials systems appear to be rapidly screened and efficient go/no-go decisions made to focus effort on the most promising materials systems.
- Good collaboration and alignment with partners and DOE milestones.
- The coordination and collaboration is well structured.
- Demonstrated good coordination within CoE.
- The composition of the Coordination groups and projects show well organized exchange of information and expertise, well supported by the Coordinator communication plans.
- Based on the information provided, coordination and collaboration appears to be very good.
- It is not clear how intellectual property (IP) aspects have been regulated to improve faster and more effective collaborations.
- Generally well coordinated internally and externally. Would prefer to see a bit more integration of fast throughput into the overall work of the group. Other subcontracts, say LLNL, or HRL, or the theorists seem to help out team members or share their thrusts and expertise regularly. Integration of combinatorial and theory work would seem appropriate to do. SRNL and Intematix in particular seem rather “close to the vest” on science (not engineering, SRNL is open there).
- The Theory Group may reduce apparent efforts [and] duplication by comparing and optimizing the use of theoretical methods for material selection applied in the different projects.
- Need more collaboration between modeler and experimentalist. Certain experimental restrictions and feedback need to be filtered through the modeling work.
- Collaborations between the project and researchers are not visible for their presentation even it is emphasized in this presentation.
- More close discussion of approach and target discussion is necessary.

Question 5: Collaborations/Technology Transfer Outside the CoE

This project was rated **3.0** for this criterion.

- The Coordination with the other CoEs is conveniently increasing.
- External communication seems good. Greater leverage by use of outside partners might be a way to improve slightly.
- Certain collaboration with other CoE exists.
- Discussion meetings between the MHCoE and other CoEs seemed to be scheduled for 07.
- The coordination and collaborations with external organizations (even international) is not yet planned as a CoE need, but it is left to the various projects and participating organizations (as in the case of UH through IEA).
- Need more coordination with other groups.
- It was not clear from the presentation if any technology transfer occurs outside the CoE.

Strengths and weaknesses

Strengths

- The CoE is well structured with an excellent integration of expertise and competence to be conveniently integrated on specific topics.
- The coverage of the key most promising materials is guaranteed by the level of competence of the participating organizations.
- The scientific approach is excellent.
- The contribution of the engineering analysis and design adds value and gives substantial tools for material selection towards DOE 2010 objectives.
- Strategy of material research toward the system target.
- The flexible overall structure and the milestone management style enable effective research.
- Good communication and collaboration within the center.
- Team, organization, theory guidance.
- Good approach to project management.
- The CoE is flexible to change as the down-select procedure narrows the group of potential materials.
- Strong group of expert partners with diverse capabilities. Projects are organized, well managed, and have an accurate perspective on the key development areas. Close coordination between theory and experiment has been useful in characterizing existing and guiding new materials research.

Weaknesses

- Unfortunately, project scope is limited by materials (metal hydrides) that have very little potential for large scale commercial on-board applications with the exception of just a few options.
- The CoE does not seem to be well organized, according to the hard-to-follow presentation.
- Lack of clear decision processes and criteria for material selection.
- Risk of overlapping/duplication of theoretical analysis for material investigation, with no clear directions from the Theory Group.
- Lack of a clear and well defined pathway to achieve DOE 2010 targets.
- Down-selection criteria were not well defined.
- Tough problem to solve. Internal communication could improve, for example SRNL science seems almost independent.
- Clear future directions are not completely apparent, however the partners are highly innovative and therefore research is expected to be fairly well-guided. Some additional cross-validation of measurements should be initiated, especially between SNL and the other partners.

Specific recommendations and additions or deletions to the work scope

- Have they considered adding a group to look at binary or ternary systems discussed in other presentations?
- Facilitating go/no-go decisions regarding complex metal hydrides, amides/imides and destabilized hydrides. Perhaps, more effort can be shifted towards AlH_3 (including synthesis, modification and regeneration) and engineering as well as more exploratory work for lead generation.
- Only projects D (AlH_3) and E (Engineering) seem to have enough potential to continue.
- The system-related approach (Project E) must be extended and used as a selection criterion of the investigated materials in any CoE Project.
- The focus on very promising materials requires the definition of clearer plans for material selection or cancellations, in agreement with DOE targets and barriers.
- The various materials with promising performance must have a critical review analysis with relation to the complete set of DOE objectives and technical barriers (not only hydrogen density) to accelerate selection and screening.
- The high theoretical capacity must be better utilized by giving a substantial role to the Theory Group.
- External collaborations in the key research areas of the advanced hydrides investigated must become a central activity of the CoE and not a casual opportunity of single participant contacts.
- Need to leverage the expertise from Sorption Center to develop more innovative ideas.

- A more structured exchange of information and contacts with external potential contributors should be part of the scope of the CoE work to better assist internal R&D.
- The theory predictions need to break down by each step rather than averaging all the steps.
- Incorporate routine theoretical examination of stability and reaction pathway energetics for all compositions to provide experimentalists with best possible material candidates.
- Specific program to refine theory with combinatorial program to test predictions of delta H and decomposition temperature and reversibility.
- Include kinetics component to work portfolio.
- Need to focus on kinetics improvement.
- In the future this talk needs to be more on the management of the center and less on the technology which your PIs will talk to later in depth. Technical accomplishments should be more how the progress relates to goals.

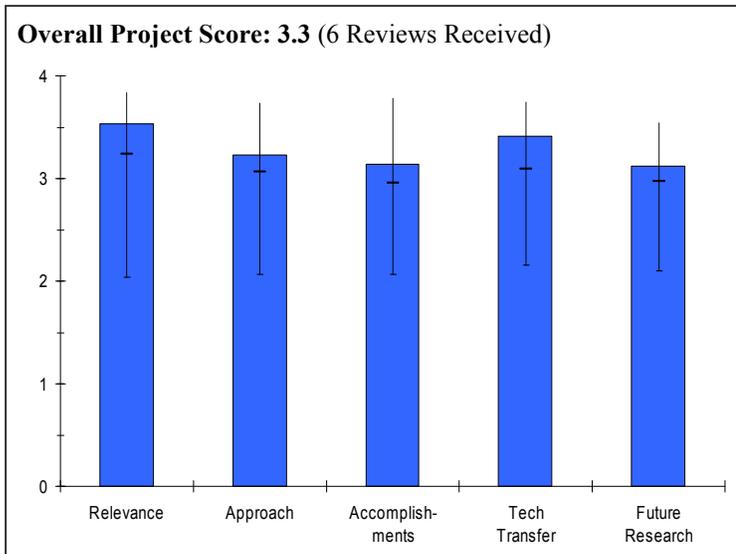
Project # ST-15: Sandia Research as part of the Metal Hydride CoE

Ewa Ronnebro, Eric Majzoub and Tony McDaniel, presenting; Lennie Klebanoff, Mark Allendorf, Jay Keller, Sandia National Laboratory (SNL)-Livermore CA

[NOTE: This review is for Sandia’s technical contribution to the MHCoe.]

Brief Summary of Project

Metal hydride research at Sandia National Laboratories continues to develop new high-capacity hydride materials capable of achieving at least 6 wt.% hydrogen for vehicular applications (system basis). Sandia employs a parallel approach through work in each of the following areas: (1) Investigate new complex hydrides and other reversible hydride-based materials to achieve higher capacities; (2) Develop new synthesis and doping processes to improve both absorption/desorption kinetics and ultimate capacity; (3) Experimentally characterize the materials’ properties; (4) Determine hydriding mechanisms through experimental analysis and modeling; and (5) Determine important engineering materials properties to ensure that complex hydrides are on track for eventual commercialization.



Question 1: Relevance to overall DOE objectives

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

- As a member of the MHCoe this project is focused directly on the DOE storage material performance targets.
- This project is apparently playing a key role in MHCoe activities.
- The project is well committed to reach DOE objectives by concentrating on best materials adapted to targets and discovery of new ones.
- The new hydrides can be faster and better screened with the newly developed equipment: this may reduce selection time.
- Identifying new and promising reversible metal hydrides is very relevant to meeting the 2010 targets.
- Materials being studied appear to have potential to meet DOE objectives.
- Relevant work because these are high capacity materials. However the energy required is very high and must be attacked aggressively.
- Project is relevant to DOE objectives.

Question 2: Approach to performing the research and development

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

- The approach is well-balanced between theory and experiment.
- The present emphasis on Ca-B-H system at 700 bar after no-go on Na-B-H system demonstrates flexibility and adaptability in the approach.
- The approach is adequate and some suggestions can be referred to the possibility to better focus, immediately after the synthesis and optimization of new materials, to operating conditions (temperature for example) closer to the DOE targets.
- The Monte Carlo method should be compared with the other theoretical methods applied in other projects of the CoE.

- New materials and catalysts are needed and they seek them. This is good. Theory guided experiment is also a good approach to use. Not looking for a CaLiB system is a good example.
- All the "low hanging fruit" aspects of the metal hydride systems have been explored, so the project is seeking to widen the search through a combinatorial approach guided by theory.
- I like the combinatorial approach but would like to have seen more substantial progress on new materials compared to last year.
- Micro-reactor approach has advantages and disadvantages; possible limitations of the approach have not been discussed in detail.
- Stability assessments provide valuable basic information; this work should be continued.
- It is not clear whether the solid-state approach can be scaled up.

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

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

- Good progress to date in both theoretical and experimental efforts.
- New high throughput/combinatorial methodology is a strong addition to the experimental effort.
- The progress is well described with a clear vision of the potentialities (closing activities on Na-Si-H is an example of the vision).
- The identification of the reversible calcium borohydride material is interesting, and potentially important if temperatures and regeneration pressures can be reduced.
- Good progress has been made on the combinatorial synthesis system.
- Ca(BH₄)₂ system is a good result but needs to be modified to lower temperature and pressure obviously. The Monte Carlo theory work has come along nicely and is contributing in a meaningful way – probably the best result of the period. It is good that the hot plate system is working but it has taken rather a long time to get going. Ge hydride may have a future – it is odd that the TGA is known but the capacity is not.
- \$1.8M budget, so should get a fair amount done, score would be higher if this was done on a more modest budget with fewer people.
- Technical accomplishments are at a very high level. However, there are gaps in the understanding of chemical processes taking place during the operation.
- Theoretical assessments require additional experimental support.
- High-throughput screening requires additional validation.

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

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

- In association with the Metal Hydride Center, the project has many important collaborations in place.
- Significant collaborations both within and without the CoE.
- A patent application has been filed.
- The focus is mostly on research activities with adequate collaboration described with research organizations.
- There is no clear description of possible industry involvement, due to the early stage of development and IPR concern.
- Highly connected with team members of the center, but also with outside groups. Could improve by using those connections more frequently and directly to get results.
- Collaboration with academic institutions is very good. However, there is plenty of room for the collaboration with industry.
- Technology transfer is good within SNL but it was not clear from this presentation if any technology transfer is occurring outside SNL.

Question 5: Approach to and relevance of proposed future research

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

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- Future plans thoroughly developed and appropriate.
- The future plans are clear and well organized.
- There are a few doubts about the way some technical limitations of present materials will be solved or addressed (as, for example, in the case of amides).
- If the December 2007 decision is a no-go on the complex hydrides currently under study, then the project is essentially back in search mode for complex hydride materials that have a possibility of meeting the 2010 targets.
- Will there be enough information known about significantly reducing the temperature and pressure of the calcium borohydride by the materials down-select date?
- The combinatorial system for elevated temperature synthesis uses a silicon container. Are reactions with silicon a limiting factor for exploring some systems?
- The ability to drop unfruitful research is laudable and shows planning and the ability to follow them. Theory guide to research is a good move. Plans are clear and appropriate with the exception of what I think is insufficient emphasis on catalysts.
- Future work is formulated in very general terms. It is not quite clear which materials are going to be studied in detail.
- Nano-engineering: no explanation is provided; it is not quite clear how the group is going to design novel nano-materials.

Strengths and weaknesses

Strengths

- Strong team with demonstrated expertise in their respective areas of responsibility.
- The project is well organized and directed with a well-justified approach and with high level of competence and skills.
- The resources are adequate with a very good complementarity.
- Well planned and coordinated project.
- Materials that have little chance of working are quickly discontinued.
- Combinatorial synthesis technique should lead to rapid screening of potential candidates.
- Calcium borohydride is a promising material if rehydriding step can occur at less severe pressures.
- Theory is making good progress and they are developing new materials. They have repeatedly shown they can cut off lines of work that are complete or unproductive. High capacity of targets is suitable. Use of theory to scan formulations and enhance "hit rate" is very good, keep the computer busy!
- Team communicating and functioning better than last year, they are back on track and that is good to see.
- Collaboration with research organizations is quite impressive.
- Theory-experiment relationship.
- High-throughput screening approach may become extremely useful.

Weaknesses

- Does theory lead or follow the experimental work? To date it appears the focus has been to use experimental data to validate the theoretical model-hopefully in the future the theory work will be used to guide and direct the experimental effort.
- Project seems to be a little short on creative ideas.
- Energy and temperature "sum it up". Delta H "kills" systems at release temperatures above 100°C because all the energy must come from stored hydrogen as the team is well aware. They need to find lower enthalpy and temperature materials to succeed. Combinatorial system was rather slow in coming on line.
- Marginal collaboration with industry.
- Understanding of chemistry involved in the operation of B-based materials has room for improvement.

Specific recommendations and additions or deletions to the work scope

- I presume that work involving calcium borohydride rehydriding has occurred with high purity hydrogen. They could consider looking at less pure hydrogen systems to see if there are inhibitors or synergies in the rehydriding step.

- The preparation of $\text{Ca}(\text{BH}_4)_2$ in the solution should be explored in more detail.
- Since diborane is usually accompanying transformations of borohydrides, its formation during the operation of potential candidates should be evaluated in very early stages of the research.
- Need to approach catalysis more formally. So far the so-called mixed or destabilized hydrides have not lived up to their thermodynamic possibilities in part because the kinetics behave as if the energy barrier is unaltered, and this is not so unlikely as the thermodynamic advantage comes on the products end of the reaction – transition states may be only weakly influenced by the modifications. Use hot plate to look at catalysts rapidly.
- None.

Project # ST-16: Lightweight Intermetallics for Hydrogen Storage

J. C. Zhao; General Electric

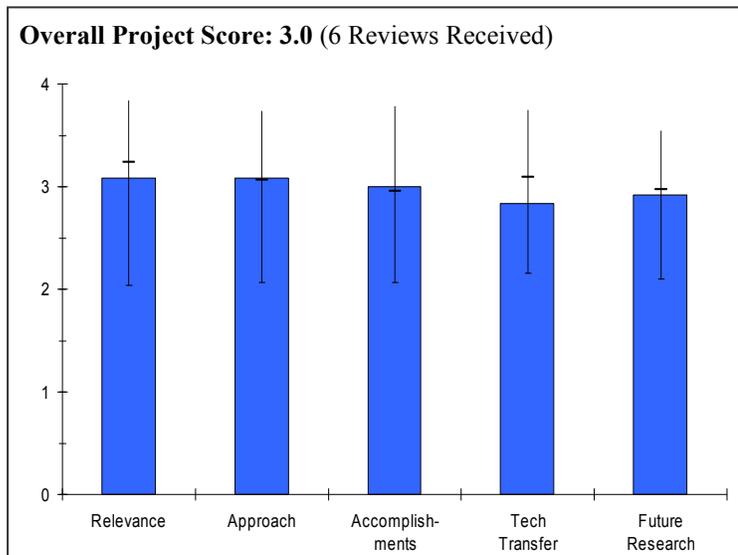
[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The objective of this project is to discover and develop a high capacity (> 6 wt.%) lightweight hydride capable of meeting or exceeding the 2010 DOE/FreedomCAR targets. Specific objectives for fiscal year 2007 include performing combinatorial and computational screening of catalysts, dopants and complexes for $Mg(BH_4)_2$, and exploring ways to make the materials reversible.

Question 1: Relevance to overall DOE objectives

This project earned a score of **3.1** for its relevance to DOE objectives.



- This project clearly conforms to the President's Hydrogen Fuel Initiative and DOE's Multi-Year RD&D plan by seeking a new and cheap high-capacity storage material with low-temperature H₂ recovery and critical reversibility.
- High wt.% push stated, but little said on volumetric and other properties.
- Work is relevant to DOE goals for gravimetric and desorption goals but it is not clear what has been accomplished for volumetric and refueling goal.
- I assume that cycle life would be affected by by-products, but it was not clear from the presentation if this is being considered.
- High capacity materials that are not made from expensive precursors are good. Need to seek lower delta H while also seeking reversibility - not an easy task.
- Project is relevant to DOE objectives.

Question 2: Approach to performing the research and development

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

- The project has progressed to the point of down-selecting to three materials that can meet weight targets: $Mg(BH_4)_2(NH_3)_2$, $Mg(BH_4)(AlH_4)$ and $Mg(BH_4)_2$. These are basically different from materials in most other DOE programs.
- This is an acceptable high-risk approach. All of these materials have significant problems to overcome, not the least of which is reversibility. Project is focused, for sure.
- High-throughput screening is useful.
- Efforts spent on catalyzing $Mg(BH_4)_2$ are not clear. Thermodynamics limitations of the borohydride stability have to be addressed first.
- Reasons for using borohydride based catalyst, synthesis routes for $Ti(BH_4)_3$ and its stability are a concern!
- Theory base is not made clear. Seems more or less like mixing the usual suspects - not all bad, but not highly enlightened either. High throughput work is a good way to improve progress.
- Too strong emphasis on a Mg-B-H system.
- New ideas are highly desirable.

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

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

- Significant progress has been made in understanding the three down-selected materials relative to the technical barriers.
- Catalysis has shown some beneficial effect, but $\Delta T = -50^\circ\text{C}$ seems disappointing.
- Most RGA outgassing results show traces of boranes and $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$ shows significant NH_3 (and related NH_2). Does this mean that supplementary H_2 purification will be required at an increase of system weight?
- Finding new materials through the high-throughput method is very smart.
- Energy to generate hydrogen seems too high, need to find either a low temperature or low energy material.
- It would be good to see more work on the reformation reactions.
- I would like to see catalysis work to smooth out the $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ desorption curve.
- The catalysts did not lower the desorption temperature very much for $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, so more work here would be useful.
- Assumptions of compound formation need to be differentiated from confirmed formation of compounds or structures, i.e. $\text{Mg}(\text{BH}_4)\text{AlH}_4$ type of compound is just an assumption and this need to be more clear in the presentation.
- Catalyst studies purposed for both $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$ and $\text{Mg}(\text{BH}_4)_2$ when the main problem is of a thermodynamic nature, the reason is not clear.
- Getting some reversal in the system is good and the materials being tried are not unreasonable. Appropriate to look for catalysts, no huge change in hydrogenation but a needed search. Structure determination seems to be more of basic science interest, not of much practical interest. Still need to find a reversible system – did improve some in this regard.
- NH_3 and AlH_4 incorporation was worth a try. Did improve the release temperature this way.
- An excellent work on the preparation and characterization of $\text{Mg}(\text{BH}_4)_2$.
- High-throughput screening is not discussed in sufficient detail.
- Scalability of $\text{Mg}(\text{BH}_4)_2$ synthesis has not been discussed. Is the synthesis scalable?
- $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ is not sufficiently characterized.

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

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

- Good collaborations shown nicely in slide 2 and the various results slides.
- Useful position, at least on paper, in the MHCoe.
- Given the fact BNL (Brookhaven NL) is listed as the source of data on several results slides, why is it not listed as a formal collaborator in slide 2?
- Since this project is in an early phase, technology transfer to other groups is likely not appropriate at this time.
- Collaboration with other members synthesizing borohydrides, amides and alanates systems is not so visible.
- Seems well connected but a more "cards close to the vest" program than most in the center, possibly because of corporate IP concerns. Could be improved, but not likely to occur.
- Collaboration with other research institutions is at much higher level than that with materials manufacturing industry.

Question 5: Approach to and relevance of proposed future research

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

- In spite of high risk, no changes suggested in work plan for future.
- Plans clearly based on past results and are sharply focused on technical barriers.
- Reviewer appreciates the built-in go/no-go decision points. It would be even better if they could be made more quantitative.
- Guidance of future materials research is not clear

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- It would be useful to see goals and plans for reformation work since it was stated that no catalyst has been found to enable the $\text{Mg}(\text{BH}_4)_2$ reaction and $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$ is only partially reversible.
- Fairly suitable as far as it was detailed, but not fully clear exactly what will be done from the plan listed. Should try to decrease delta H.
- Future work is formulated in very general terms.
- It is not quite clear why work on Mg-B-H system should continue. Experimental results presented suggest the opposite.
- New ideas could significantly benefit this project.

Strengths and weaknesses

Strengths

- Looks at high-capacity borohydrides capable of meeting system weight targets.
- Good researchers and collaborations.
- Efficient combinatorial experimental approach.
- High throughput equipment seems to speed up the searching process but need idea.
- Good program for looking at desorption.
- Good system to focus on based on capacity.
- Collaboration.
- Very solid experimental work.

Weaknesses

- The borohydrides are a difficult and high-risk approach, with many problems to be solved, including high desorption temperatures, poor reversibilities and impurities in the H_2 released.
- This reviewer would have liked to see more information on volumetric H-densities.
- Need more work on material reformation.
- Addressing the real problems related to the materials researched.
- May never get full value due to isolation they seem to need for internal reasons. Energy requirements are a big problem in these systems and catalysts are sorely needed.
- Focus on only one group of materials.
- Since diborane is usually accompanying transformations of borohydrides, possibility/extent of its formation during the operation of potential candidates should be evaluated in very early stages of the research.
- Marginal collaboration with materials manufacturing industry.

Specific recommendations and additions or deletions to the work scope

- Why not consider partially substituted $\text{Mg}(\text{BH}_4)_2$ rather than catalyzed $\text{Mg}(\text{BH}_4)_2$?
- With significant ammonia formation, why continue with $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$?
- Recommend to confirm formation of $\text{Mg}(\text{BH}_4)(\text{AlH}_4)$ prior to any catalyzed trials.
- Recommend to collaborate more with other members of the center.
- Focus more on catalysts and getting reversibility. Also need to focus on lower delta H. Theory guide may help here. Consider carefully what the criteria are for getting out of the Mg-B area. Leave off some of the interesting but un-used testing such as structural determinations.
- go/no-go decision about $\text{Mg}(\text{BH}_4)_2$ should be met as soon as possible; preferably by July-August 2007.
- No change.

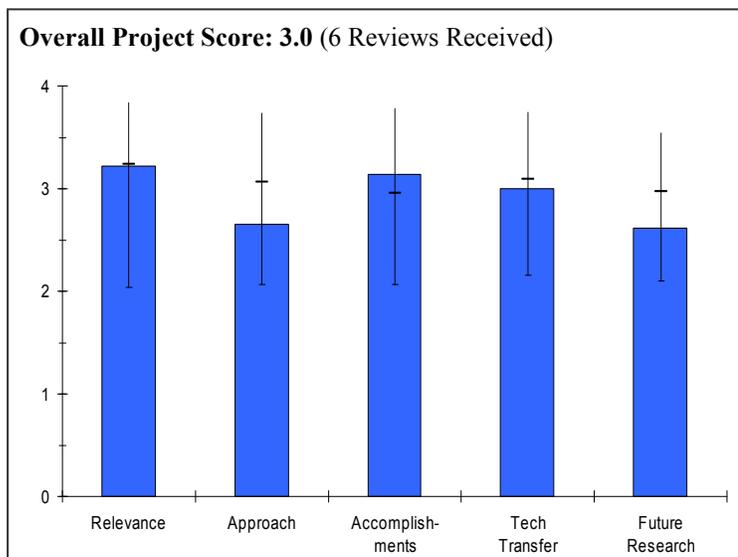
Project # ST-17: First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems*Karl Johnson; Univ. of Pittsburgh, David Sholl, Co-PI, Carnegie Mellon University*

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The objectives of this project are to 1) compute thermodynamics of metal hydride systems, 2) compute interfacial properties of hydrides, and 3) address fundamental processes in hydrogenation. Specific objectives for fiscal year 06/07 include:

- Identify promising complex hydride materials through computational screening of the heat of reaction ΔH ;
- Develop an automated approach for identifying all possible compounds from a given set of reactants and products;
- Screen doped hydrides for phase stability;
- Initiate calculations for ΔH of substituted (doped) complex hydrides, including $Mg(BH_4)_2$ and $Ca(BH_4)_2$;
- Compute surface reactions as relating to poisoning and initial kinetics of hydrogenation/dehydrogenation;
- Contribute to the development of CALPHAD databases for metal hydrides.

**Question 1: Relevance to overall DOE objectives**

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

- In the metal hydride field, one thing that is needed is high capacity reactions with suitable thermodynamics for efficient thermal management considerations. This work is directed at this goal.
- The project involves computational studies of metal hydride system thermodynamics, interfacial properties that relate to adsorption/desorption of hydrogen, and energetics of hydrogenation. This type of information has great value in the context of what the CoE for Metal Hydrides is trying to accomplish.
- The project provides valuable screening capability that can sort through large numbers of chemical phases in search of the most promising candidates for hydrogen storage.
- A variety of issues related to hydrogen storage that require information on molecular energetics are under study.

Question 2: Approach to performing the research and development

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

- Predictive modeling approach is a promising, cost-effective way to accelerate discovery of novel storage reactions.
- Modeling needs to address not only candidate hydride materials, but a systematic predictive method for identifying the lowest-energy thermodynamic pathways. This latter approach is missing in the current project, and has led the PIs to predict spurious reactions.
- It is not clear on what basis the selection criteria were chosen. Based on previous DOE presentations, it is recommended to narrow down the selection to 0-100C equilibrium temperature and 15-30 kJ/mol H_2 enthalpy.
- >160 solid materials, ~350 reactions ... This is not an efficient approach. On the other hand the theoretical methodology is the state of the art.
- State-of-the-art DFT packages are used to perform calculations of free energies and other thermodynamic quantities for a wide variety of chemical compounds and molecular architectures.

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- Wherever possible, the computational results should be compared with existing experimental data. Agreement with experiment adds credibility to all aspects of the work.

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

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

- The prediction of novel high-capacity reactions is quite important and will help direct experimental efforts towards promising materials. However, the PIs appear to be using mainly chemical intuition to describe the lowest-energy decomposition pathways. This intuitive approach has led in several cases to predicted reactions as being "single step" reactions with suitable thermodynamics, when in fact they are thermodynamically "multi-step" reactions, each of which has unsuitable thermodynamics.
- A lot of work has been done. The database will be useful.
- Kinetics of multiphase reaction systems is expected to be controlled by solid-phase diffusion as well as surface reaction. They should consider easiness of solid-phase diffusion in the system studied.
- The poisoning studies of complex metal hydrides are very useful.
- Thermodynamic quantities are computed with reasonable accuracy.
- Several potentially interesting reactions have been identified.
- A broadly useful data base is evolving from this work.
- The interfacial energy calculations are particularly worthwhile for sorting out hydrogen uptake and release issues.
- It's no big surprise to find out that elements that "like" hydrogen also "like" oxygen.

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

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

- It was not clear who is the end-user of this work and how the data impacts their work.
- Can the PI provide specific examples on how this work helped the synthesis/experimentalists in the center?
- A stronger collaboration with experiment will help in strategy.
- Collaboration apparent with HRL, University of Utah, GE and SNL.
- There was some mention that experimentalists in the Metal Hydride CoE are following up on the findings from this project. That's what should be happening.
- The level of collaboration should be broader than is obvious from the presentation. For a project like this, i.e., one that provides both screening results and energy parameters, there should be cross-collaboration in virtually all task areas.

Question 5: Approach to and relevance of proposed future research

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

- Future work seems to be largely comprised of "concluding" or "completing" various tasks, rather than novel, creative approaches.
- The development of an automated approach will not solve the hydrogen storage problem!
- The database will be generally useful.
- They should include an activity to investigate the effect of solid-phase diffusion in their system.
- The proposed future work on Slide 21 is presented in a very general way. Try to be more specific in the future. What will be done? Why? Which other CoE projects will it contribute to?
- The doping studies and the interfacial studies should be emphasized.
- Any calculations you can do that relate to or give information about kinetics will have great value.

Strengths and weaknessesStrengths

- Computational capabilities.
- The PI is very knowledgeable.
- The publication record is impressive—particularly the Science article. That's a “kudo” for the CoE.
- Much is learned per-dollar of funding in projects like this one.

Weaknesses

- Methodology.
- Information exchange on reaction in solid phase between the theoretical side and the experimental side seems not to be so effective.
- There are no obvious weaknesses in this project, but a more explicit demonstration of the interplay with the rest of the CoE would raise the project's visibility level.

Specific recommendations and additions or deletions to the work scope

- A more strategic and efficient approach is needed.
- Support understanding and directing experimental results with aid of calculations is definitely recommended to continue.
- See the recommendations given in the comment boxes above.
- Modeling needs to address not only candidate hydride materials, but a systematic predictive method for identifying the lowest-energy thermodynamic pathways. This latter approach is missing in the current project, and has led the PIs to predict spurious reactions.
- Need to further validate the model with established samples within the above range. (0-100°C equilibrium temperature and 15-30 kJ/mol H₂ enthalpy).
- In next year's presentation, provide indications of how each computational task relates directly to ongoing experimental work within the CoE or is connected to an issue of importance to other CoE projects.

Project # ST-18: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

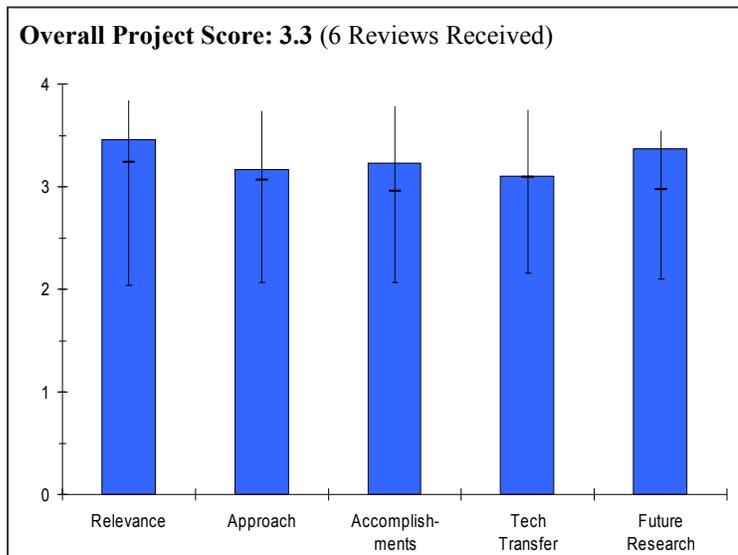
John Vajo, presenting; Ping Liu (PI); HRL Laboratories

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The overall objective of this project is to develop and demonstrate a safe and cost-effective light-metal hydride material system that meets or exceeds the DOE goals for reversible on-board hydrogen storage. Specific objectives for FY2006/2007 include:

- To identify and test new high capacity Li- and Mg-based destabilized hydrides;
 - o Screen candidate $\text{LiBH}_4 + \text{MgX}$ destabilized systems and evaluate energetics and kinetics,
 - o Down-select systems for additional work;
- To apply nano-engineering methods to address kinetics limitations;
 - o Determine hydrogen exchange rates in nanoscale MgH_2/Si ,
 - o Evaluate sorption kinetics and thermodynamics of LiBH_4 and Mg in carbon aerogel scaffolds,
 - o Assess capacity penalty for hydrides in scaffolds (can they be practical?).



Question 1: Relevance to overall DOE objectives

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

- The objectives are relevant to DOE's overall objectives in pursuing the Hydrogen Fuel Initiative.
- The project is well in line with DOE objectives.
- The conclusion of the project at 2010 makes slightly unclear possible references to 2015 targets (in extra slides).
- Project conforms very well to President's HFI and DOE Multi-Year RD&D plan.
- Project aims at meeting targets for weight, volume and H_2 delivery temperatures, as well as cost and safety.
- The $\text{LiBH}_4 - \text{MgH}_2$ system may have a possibility of meeting the 2010 targets.
- The project, aiming to develop a high-capacity storage material working at ambient temperature, fits well to the DOE objective.
- Highly relevant work, one of the key thrusts in the center now.

Question 2: Approach to performing the research and development

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

- The project is a difficult one. It may have high payoff.
- The PI needs to focus on 1) Mg-in eutectic 2) catalysts 3) effect of high pressure on aerogel.
- The approach is acceptable with clear steps to improve key performance and limitations.
- The emphasis on cost and safety is not yet considered.
- Effort is focused on two most important technical barriers associated with light metal hydrides - thermodynamics and kinetics.
- Thermodynamics controlled by "destabilization", the mixing of secondary reactants (e.g., MgH_2 to LiBH_4) to provide an exothermic contribution to the otherwise highly endothermic desorption.
- Kinetics controlled by nano-sized particles.

- Carbon scaffolds applied to maintain small particle sizes.
- Very good combination of approaches to attack barriers.
- Scaffold approach is a good one to attempt to maximize the kinetics of the $\text{LiBH}_4\text{-MgH}_2$ system.
- Approach based on their own concept of 'destabilization' is successful for exploring reactions with small reaction enthalpy.
- Poor kinetics is the most serious problem. Nano-engineering that they started is expected to provide some knowledge about the effect of particle size and diffusion distances.
- Solid approach, might benefit from greater guidance from the theory team in the center. For some reason the thermodynamics used are not working as expected and perhaps a different level of theory [guide] would help.
- Scaffold use is another center showpiece that came from this group.
- Willing to make or accept a no-go on their own work.
- Some indication that there is a thermodynamic improvement too, likely due to chemical interaction.

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

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

- This project is an excellent example of following the work plan, objectively reporting both negative and positive results, and eliminating R&D directions that are clearly not promising.
- Since it is a difficult project, a lot of work is needed to show progress. Using nanophase brings up the issue of safety, which was not addressed.
- The results and the progress are interesting.
- The operating conditions (e.g., 300°C) are not compatible with the DOE targets.
- Project has accomplished much of what was planned, with both positive and negative results.
- $\text{LiBH}_4 + \text{MgX}$ combinations, so far, not very useful for destabilization.
- No-go decision made on $\text{MgH}_2 + \text{Si}$ system. Attempts to utilize several approaches failed to achieve reversibility.
- Preliminary results to test C-aerogels as scaffolds are very promising relative to decreasing desorption temperatures and increasing kinetics (better thermodynamics?). Cyclic capacity loss still a problem, as well as carbon scaffold penalties.
- No new destabilized LiBH_4 systems have been identified, other than the MgH_2 destabilization.
- Looks like it is difficult to get Mg into the carbon aerogel, but multiple approaches are being pursued to address this.
- Possible evidence for aerogel scaffold effects on the thermodynamics of LiBH_4 .
- The result of exploring new combination for 'destabilized' reaction is rather poor.
- The trial using carbon aerogel as scaffold shows good indications for desorption pressure and kinetics.
- Scaffold work to reduce [attach] temperature of dehydrogenation is very good. Pore size work is likely giving clues as to the optimal function of the aerogel, for this application and perhaps generally. Getting Mg in carbon aerogel is a difficult thing to do and they appear to have done it, results will be interesting.
- Also did work on MgSi and 2 other systems that did not produce a winning compound but were reasonable systems to try based on theory.

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

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

- The coordination and roles of participating organizations is very good and adequate to the needs.
- Good collaborations within MHCoe and outside.
- Very good collaboration with regard to carbon aerogels.
- Collaboration with the groups synthesizing scaffolds works well.
- Well connected internally and externally.
- Positive results with LLNL aerogels cited, but LLNL is not listed as a formal collaborator in Slide 2.
- PI needs better collaboration with partners.

Question 5: Approach to and relevance of proposed future research

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

- Looks good.
- The future plans are well consistent with the current limitations.
- Plan builds nicely on past results and stays completely focused on technical barriers.
- PI's Program Direction matrix slide (16) is an excellent display of past, present and future.
- Future work with the carbon aerogels is well-structured.
- What is the "Plan B" if the carbon aerogel approach does not work out?
- Approach using scaffold materials should be more focused and done more systematically.
- How to explore the combination of materials for 'destabilization' is not necessarily clear.
- More attention to DOE targets is required.
- Appropriate. Working on thermo, kinetics and capacity.

Strengths and weaknesses

Strengths

- The project has good potential.
- Clear vision of the current material limitations with reasonable research plans.
- Destabilization and the concurrent use of nanoporous scaffolds represent an important approach to attack the thermodynamic and kinetic barriers. In spite of inherent metallurgical problems (see below), the project must be completed as planned.
- Project participants are very competent and unusually skillful at designing and executing a multifaceted R&D approach.
- The $\text{LiBH}_4\text{-MgH}_2$ system has the potential to meet the 2010 targets, if the kinetics can be significantly improved.
- The PI has started to prove their original idea of 'destabilization'.
- Great ideas and strong team

Weaknesses

- The proposed research lines do not guarantee the reach of the targets.
- The only project weakness is nature itself. It will be very difficult to get good room-temperature reaction kinetics when the diffusion of metal species is involved. Nano can only go so far.
- There may be no other destabilizers for LiBH_4 other than MgH_2 .
- Approach for improving kinetics is limited.
- Needs a lot of work.

Specific recommendations and additions or deletions to the work scope

- Maybe testing more chemical systems in the scaffold would be good.
- Introduction of supporting cost and system analysis as a mandatory task of a member of the MHCoe.
- No changes recommended.
- None.
- Exploring of 'destabilized' reactions should be tailored to some new kinds of materials.
- Get the theory team at the center to try to refine the destabilization predictions so as to make it a more accurate guide.

Project # ST-20: Synthesis and Characterization of Alanes for Automotive Applications

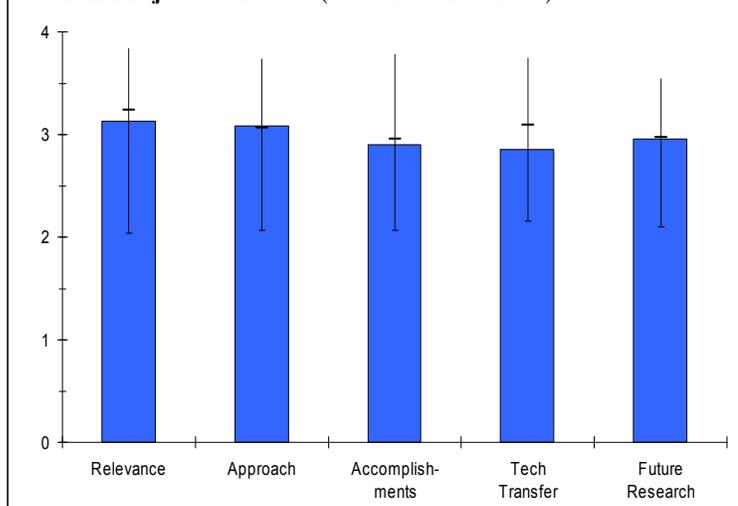
Jason Graetz (PI), presenting; Jim Wegrzyn (co-PI), J. Reilly, J. Johnson, W. Zhou, Brookhaven National Laboratory (BNL)

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The objective of this project is to understand the strengths/weaknesses of using aluminum hydride (AlH_3) as a storage medium by quantifying the reaction kinetics, thermodynamics, and energy requirements for regeneration. This will be done by synthesizing 3 polymorphs of AlH_3 (α , β and γ) with material capacities $\geq 8\%$ $\text{kg-H}_2/\text{kg}$ (grav.) and ≥ 0.10 $\text{kg-H}_2/\text{L}$ (vol.). AlH_3 polymorphs with suitable H_2 pressures at temperatures near the operating temperature of a proton exchange membrane (PEM) fuel cell ($\sim 85^\circ\text{C}$) will be identified and it will be determined if AlH_3 can be formed by direct high-pressure hydrogenation of Al powder at pressures < 103 bar. Specific objectives in fiscal year 2007 include:

1. Produce aluminum hydride with 9 wt. % H_2 and 0.13 $\text{kg H}_2/\text{L}$ (material capacity);
2. Develop practical and economical process for the regeneration of AlH_3 from the decomposed Al;
3. Assist in the design for an on-board fuel tank delivery system.

Overall Project Score: 3.0 (6 Reviews Received)**Question 1: Relevance to overall DOE objectives**

This project earned a score of **3.1** for its relevance to DOE objectives.

- High capacity and low enthalpy of dehydrogenation make alane a viable option to investigate for on board storage.
- The objectives are relevant to DOE's overall objectives in pursuing the Hydrogen Fuel Initiative.
- In line with RD&D program objectives and addresses a number of key barriers.
- Very relevant. Addresses one of the main barriers to commercialization of H_2 vehicles.
- The high capacity meets the DOE target. Studying possibility of using this material is relevant to the total program.
- Good program direction; well aligned to goals. A good material to study.

Question 2: Approach to performing the research and development

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

- Excellent idea of using organic adducts to lower the pressure for hydrogenating Al.
- Perhaps needs more systematic approach for developing most optimal organic adducts that would be easier to remove from AlH_3 without loss of hydrogen (modeling?).
- The project is well designed. AlH_3 has potential, but regeneration is a big problem.
- Addressing the problem via liquid organometallic is good.
- Reasonable and well-thought-out approach focused on regeneration and possible routes.
- Regeneration energy requirements established for the screening on possible pathways.

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- Addresses a key issue for alane system-regeneration.
- Have identified a regeneration approach that is promising.
- Focused approach-have eliminated work on LiCl splitting due to energy requirements that are too high.
- Characterization of the material is essential to know possibility of its use.
- Rehydrogenation is a real key issue and needs to be focused on.
- Seem to understand the key questions and are focused on improving those aspects (temperature and reversal in particular). Regeneration target energy is a bit higher than I would like to see. For example, it is higher than gas compression and slightly higher than liquefaction.

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

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

- Project seems to be on track, however at this early stage it is difficult to predict if most important targets could be met with the approach.
- Good.
- Good progress in understanding the regeneration process and properties of AlH_3 for H_2 storage.
- Significant accomplishment with the direct hydrogenation of activated Al powder with a ten-fold reduction in pressure and a yield of almost 100%.
- Have reduced hydrogenation pressure and temperature by using tetraethylenediamine complex (TEDA), but have not demonstrated decomposition of TEDA adduct to give back AlH_3 .
- Structural/thermodynamic studies provide needed information.
- Progress toward a useful reversible system is slow.
- Characterization has been almost accomplished except for detailed investigation how kinetics is controlled by the surface condition.
- The trial of regeneration in organic route has a lot of problems to be solved.
- Some progress on recycle, making $\text{AlH}_3 \cdot \text{TEDA}$. Did finish phase study. Progress might have been greater based on funding level.

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

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

- Strong collaborations within the Sorption CoE, the Chemical Hydride CoE but also at international level.
- Thanks to its networking this project profits from wide-range, top-class expertise and access to unique material characterization facilities.
- Collaborations evident in structural studies.
- Additional collaboration with theory group and chemical hydrogen storage center would be beneficial.
- International collaboration present.
- No results from collaborations with SRNL and UH on regeneration yet.
- PI needs more collaboration with partners.
- Collaboration works well on both characterization and exploring various way of regeneration.
- Good outside and inside connections, probably better outside actually.

Question 5: Approach to and relevance of proposed future research

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

- Looks good.
- The path forward is planned in a sensible manner based on findings to date and capitalizing on the expertise of collaborators.
- Clear milestones and go/no-go decision points have been set.
- Collaboration with Chemical Hydrogen storage center should be beneficial.
- Not sure what additional fundamental high-pressure studies are planned and what benefits they will provide – a better description of planned high pressure work would be helpful.

- Pursuit of alane adducts may be beneficial, but it will be difficult to find an adduct with the high hydrogen storage density needed. Must be careful in adduct choice so that elimination reactions upon adduct decomposition do not occur (would lead to impurities in H₂ and Al-products that would be more difficult to convert back to AlH₃, and would probably need off-board regeneration).
- Focusing on rehydrogenation is reasonable. Trying to find a complex containing AlH₃ is one approach.
- The proposed 'reversible metal-organic hydride' seems difficult to achieve the target of gravimetric capacity.
- Appropriate, though not clear that it comprises \$0.9 million in work.

Strengths and weaknesses

Strengths

- Seems to be most relevant approach within Metal Hydride CoE.
- PI has good group.
- Networking and pooling of expertise, technical resources, unique facilities and instrumentation.
- Have made some progress in regeneration, decreasing H₂ pressure needed to a relatively low 35 bar.
- Strong activity and experience for characterization of materials.
- Excellent material and talented team.

Weaknesses

- Lack of strategies for removing TEDA from the AlH₃ other than simple evacuation that would result in losing hydrogen. Perhaps needs some more effort towards understanding of the potential of chemical removal of TEDA.
- AlH₃ has been studied extensively with not much hope.
- Recycling - adapt synthesis route to reuse/reduce byproducts.
- Challenge of tuning the decomposition kinetics.
- It is open question if off-board regeneration of solid hydrides is realistic.
- Cost effectiveness.
- Regeneration is a challenging issue. Solid-gas reaction is most preferable, but energy consuming in pressurized gas.
- Equilibrium T-P curve shows P_{eq} is around 50 bar at 77K. This means AlH₃ system has a larger capacity than the best sorbent materials found so far when using at 77K.

Specific recommendations and additions or deletions to the work scope

- Perhaps need more focus on the use of alane in addition to regeneration/synthesis. Alane is thermodynamically metastable at 25°C below 7 kbar pressure, and may create substantial safety issues for users.
- Since AlH₃ is thermodynamically metastable system at ambient temperature, it would be worthwhile to check the potential for run-away pressure build-up at operating conditions.
- More modeling to define optimum alane-base adduct bond energy to drive hydrogenation but allow recovery of pure AlH₃ would be helpful.
- Feedback from the AlH₃ Theory Group is required - to calculate gas-phase complex stabilities to guide BNL regeneration efforts.
- Explore other activation processes (and use of catalysts) for the Al powder.
- Associated regeneration costs could also be addressed.
- Increase interactions with the chemical hydrogen storage center on regeneration issues and potential hybrid schemes.
- Increase interaction with the theory group.
- The low desorption rate at 80°C is another problem. Kinetics depends on the surface conditions. More detailed investigation of the surface effects on the kinetics is needed. It should be noted that the surface condition would depend on the hydrogenation (regeneration) process.
- A little more planning on what would be the theoretically optimal or better than current ligands would be a wise move, get help from center partners if need be. Still would like a higher efficiency target, in concert with DOE goals.

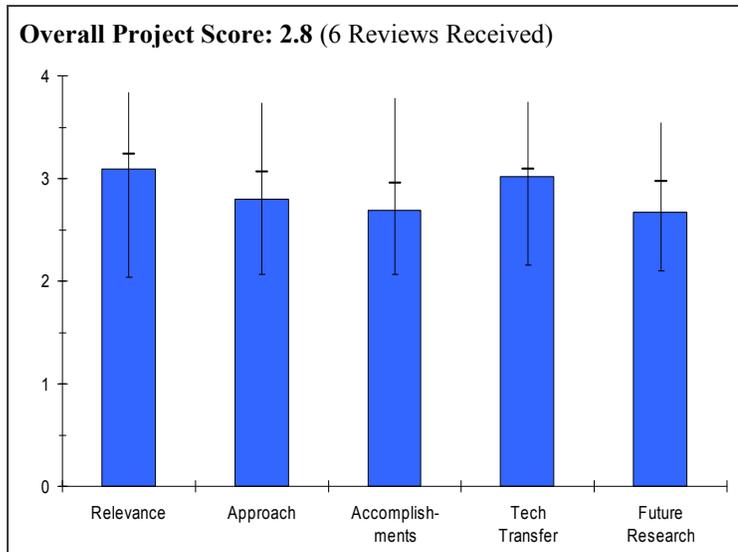
Project # ST-21: Chemical Vapor Synthesis of Nanocrystalline Binary and Complex Metal Hydrides for Hydrogen Storage – Understanding and Discovery of H₂ Storage Materials Involving Metal Amides

Zak Fang; University of Utah

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The objectives of this project are to discover new solid hydrides that meet reversibility and kinetics requirements, to develop a chemical vapor reaction process (CVS) for synthesis of nano-sized solid metal hydrides, and to demonstrate the effectiveness and unique properties of nano-sized solid hydride materials for hydrogen storage. Specific objectives for FY 06/07 include: 1) discover and study new materials based on lithium alanates destabilized by light metal amides, 2) synthesize new materials using high-energy high-pressure reactive milling process, and 3) synthesize nano precursor and hydride powders using Chemical Vapor Synthesis (CVS) process.



Question 1: Relevance to overall DOE objectives

This project earned a score of **3.1** for its relevance to DOE objectives.

- The basis of this project is relevant to the scope of the DOE objectives in that it involves both explorations of novel complex hydride combinations as well as new routes for generation of nanocrystalline materials.
- The objectives are relevant to DOE's overall objectives in pursuing the Hydrogen Fuel Initiative.
- Aimed at addressing a number of key objectives from the DOE plan.
- This work is directed at an important goal of reversible metal hydrides: discovery of novel combinations of hydride materials that will produce high-capacity reversible reactions with low enthalpies of decomposition.
- Project is consistent with President's HFI and DOE's Multi-Year RD&D plan.
- Focus on kinetics, H-content and synthesis is good.
- Could perhaps have additional focus on volumetric H-content and processing cost.

Question 2: Approach to performing the research and development

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

- While the approach to chemical vapor synthesis (CVS) is novel and has been experimentally proven, the approach toward selection of the two-component complex hydride systems is unclear. On what basis were these compositions chosen?
- Their approach toward characterization and property evaluation for storage compositions involves access to a variety of different (and valuable) techniques (through center collaborations). Nevertheless, given this access, it is not evident that all pieces of data are being interpreted properly or used collectively to clearly deduce reaction mechanisms.
- The project addressed technical barriers such as inadequate kinetic properties and lack of robust synthesis methods, but left out the contamination due to milling process. Previous year suggestion to move away from alanate / amide systems was good, and was not incorporated.

- The PIs appear to have had a few clever ideas of combining two existing ideas in the literature: decomposition of Li_3AlH_6 , and the combination of LiH with metal amide materials (LiNH_2 and $\text{Mg}(\text{NH}_2)_2$). The results look quite interesting, though it is not clear how the combination of these two materials will really give results significantly better than the materials separately.
- Very good to see experimental groups quickly synthesizing and testing predictions from the theoretical efforts of the center.
- Although not completely clear in Slide 2 (Barriers), work is properly aimed at important weight and desorption temperature problems with metal hydrides.
- Sensible, targeted approach for exploring the metal amides as hydrogen storage systems.
- The main direction of the project is looking at mixtures of alanates (particularly Li_3AlH_6) and amides (particularly LiNH_2 and $\text{Mg}[\text{NH}_2]_2$). It seems like the limited potential and NH_3 problems of these systems mitigate against full success in metering system targets.
- Work on new materials (e.g. LiMgN) is good, with hopefully lower NH_3 .
- The vapor phase synthesis work, particularly in support of the MHCoe seems useful.
- Barriers to utilization of amide systems are not well tackled. Analysis of gases evolved from destabilized/amide based systems should be incorporated in the initial testing steps.
- Purpose for utilization of known synthetic methodology which utilizes high energy high pressure synthesis need to be clarified more, i.e. plan to regenerate AlH_3 !

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

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

- In regards to the amide-alanate work, the progress and technical conclusions are lacking. It was not clear what new knowledge has been gained for the Li_3AlH_6 - LiNH_2 system as compared with FY06. Additionally, a variety of their accessible techniques (i.e. IR and PCT data) did not seem to be included, yet could aid in clearly determining the reaction mechanisms for these amide-alanate systems. There were also several inconsistencies between data and proposed mechanisms (e.g. plateau pressures and extracted ΔH 's inconsistent with proposed reactions and observed reaction species that were not in mechanisms).
- It was good to see consideration of durability for the materials as exemplified by cycling study.
- The CVS synthesis project seems to greatly support the efforts of the entire center through preparation of precursors. It would be helpful to know the scale and purity of this method.
- The negative accomplishments mentioned, such as limited reversibility of lithium alanate and problems using amide alone are well documented. Using combination of alanate & amide will create problem of NH_3 and should be addressed.
- Significant progress has been accomplished in line with the project objectives.
- Demonstrated potential & possibilities opened by new material systems with reversible storage capacity.
- Experimental verification of the reaction of alanate destabilization with amides and of the reversibility of the process.
- Successful nano-sized metal powder precursor synthesis via the CVS technique.
- The Li_3AlH_6 + amide reactions are interesting, in that the PIs have demonstrated reversibility in Li_3AlH_6 , whereas no other groups have been able to demonstrate this. However, these combined reactions are likely to produce a combination of the drawbacks of the two separate reactions: One reaction with an enthalpy that is likely too low (Li_3AlH_6) and another that is likely too high (LiH + amide).
- PI has presented a lot of interesting mechanistic results, but it seems that the results have not moved the hydride world much closer to surmounting the barriers and meeting DOE RD&D targets.
- The alanate-amide results show improvements, but the present thermodynamic and capacity properties seem little better than "many-year-old" doped nano-Mg (e.g., see Slide 19).
- At the 2006 Peer Review, there were worries about ubiquitous NH_3 emissions from amide systems. While PI has demonstrated NH_3 is apparently low enough to minimize cyclic capacity loss, this reviewer is disappointed that the absolute levels of NH_3 in the exit H_2 has not been yet quantified vis-à-vis PEM fuel cell tolerances.
- The efforts to synthesize nano-powders for the MHCoe are useful.
- Preliminary reversibility illustration of Li_3AlH_6 is a good result.

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

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

- Very strong coordination between this program and the remaining center activities. In particular, collaborations appeared to be developed for characterization experiments. Additionally, this program's CVS project supports center through supply of nano-powders.
- Substantial networking and collaborations with a good blend of expertise.
- Good to see this group quickly testing theoretical predictions, which can then either be pursued or discarded.
- This group's collaborations within the MHCoe seem outstanding.
- Recommend strong collaboration with SNL. They have extensive experience with amide systems. Poor collaboration with partners.

Question 5: Approach to and relevance of proposed future research

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

- Future work scope should include reproducibility studies (especially in regards to reversible capacity) and purity determination and as stated, determination of the thermodynamic and kinetic properties for each reaction and reaction step. For the first reaction ($\text{Li}_3\text{AlH}_6\text{-LiNH}_2$), it is unclear why these experiments remain outstanding as it was 'future work' from FY06-07. Would encourage more collaboration with theoretical projects in center to help characterize current research as well as guide future work.
- Good to see intended continuation of support in regards to CVS synthesis of nano-powders.
- Materials selection is focused to alanate and amides. This question has been raised before and should be addressed. CVS synthesis of Li/Mg powders should be given more emphasis.
- The future plans are appropriate and justified by the experimental results produced so far.
- Not clear that the PIs have really good, novel creative ideas to build upon their previous results. They seem to be promising that they will continue working in the same area, but don't provide any details of how they will improve upon these reactions.
- This reviewer doubts that N-containing hydrides can be made to achieve DOE targets, but agrees with PI that it may be useful to continue keeping some amide work within the overall DOE program.
- The quantification of NH_3 should be given the high priority.
- The group's movement toward non-N systems may be wise.
- Work on CVS and high-pressure ball milling with help the MHCoe and should be continued.
- Reversible systems are important but energy efficiency is a key to on-board storage, focus should be perhaps redirected to other potentially less stable combinations.
- Recommend to clarify the purpose and show how rather known HEHP milling would help the synthetic efforts.

Strengths and weaknesses

Strengths

- The compositions and synthetic methods under investigation are relevant and promising. Additionally, the diverse set of characterization and property evaluation techniques that are in place are very valuable toward (further) clarifying the mechanisms and properties of storage materials.
- The PI is well-placed for the proposed work.
- Still exploring opportunities within the amides family.
- Good, solid collaboration record.
- The project serves as a useful contribution to the MHCoe.
- Overall good technical approach utilizing several characterization techniques.

Weaknesses

- The pace and degree to which the details (mechanism and properties) of each composition are being clarified is somewhat slow.

- The multitude of experimental techniques should be used collectively to confidently determine the reaction mechanisms. First-principles calculations should also be used to characterize existing and direct future research efforts.
- The PI does not like to change the emphasis related to materials.
- Release of ammonia is detrimental to the PEM fuel cells; it constitutes a significant drawback for amide-based systems and their use as hydrogen storage media.
- Work with amides has turned out to be problematical from a H₂ purity point of view, vis-à-vis PEMFC tolerance.
- Focus on higher stability systems/combinations is not considered.
- Concerns of ammonia formation and its measurement as a 1st step should be of higher priority.

Specific recommendations and additions or deletions to the work scope

- Quantify the ammonia concentrations involved and evaluate viability of material for storage applications - is it worth pursuing it as practical on-board hydrogen storage solution?
- There should be a go/no-go decision point for amide-containing systems during the next year, based on the upcoming NH₃ measurements. The level of NH₃ measured should be less than say 10 times what a PEMFC can tolerate. For example, if the PEMFC people require <1 ppm, then PI must demonstrate <10 ppm or ultimately abandon his systems.
- Alternatively, the project could accept the inevitability of unacceptable NH₃ levels and add a purification component.
- Recommend to shift focus to potentially less stable combinations.
- Confirm/measure ammonia formation as soon as possible.

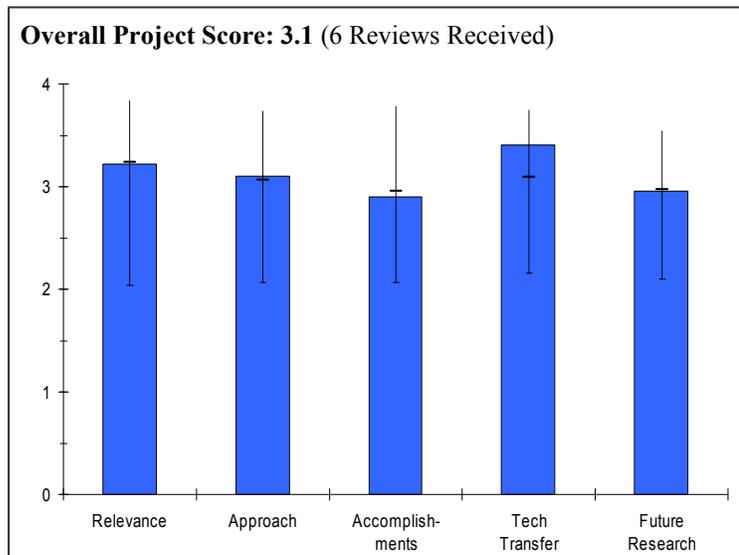
Project # ST-22: Fundamental Safety Testing and Analysis of Hydrogen Storage Materials and Systems
Don Anton; Savannah River National Laboratory (SRNL)

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

Brief Summary of Project

The objective of this project is to fundamentally understand the safety issues regarding solid state hydrogen storage systems through:

- Development of standard testing techniques to quantitatively evaluate both materials and systems
- Determining the fundamental thermodynamics and chemical kinetics of environmental reactivity of hydrides.
- Development of amelioration methods and systems to mitigate the risks of using these systems to acceptable levels.



Question 1: Relevance to overall DOE objectives

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

- This is a very important aspect of the program that has not been addressed.
- The outcome of the work should be used as a guideline for go/no-go decision on materials selection for all centers.
- Extremely important to pursue in parallel with development of new materials.
- Safe handling of hydrogen carriers/fuels is a major issue for the introduction of hydrogen-powered vehicles to the public. Therefore, projects that address this issue at any point during the supply chain will be an important determiner of which carrier should be used.
- Important point made by one member of audience: that on-board vehicle storage should also be included for greater fit with DOE objectives as at the moment the project appears more directed towards the mass transport of the carrier.
- Relevant to all metal hydride storage projects and other materials projects as well.
- Provides a safety program that will allow safety screening of materials, including novel/previously unknown materials.
- Quantifies or at least semi-quantifies safety.
- This project is critical for ensuring that systems can be developed for safely utilizing new hydrogen storage materials that meet DOE targets.
- Assessing the potential risks of solid-state hydrides and mitigating technologies/techniques is imperative.
- This work is premature given the intent of the project.
- Developing standards and codes when suitable materials have not yet been identified provides the danger of precluding materials that are otherwise interesting.
- There are no solid-state materials (other than the well characterized AB₂ and AB₅) that are suitable for automotive use. This kind of testing is overkill at this point.
- At this point a simple material MSDS and good engineering intuition will suffice for this stage of development.

Question 2: Approach to performing the research and development

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

- The current approach is good but needs to be expanded.
- Need to consider partially depleted materials.
- Need to address carcinogenic, mutagenic, respiratory, and in general toxicity of all potential storage materials.
- Good international partners and cooperation of tasks appropriate.
- Improvements could be made in process to ensure developments in H₂ storage materials are identified. Concerned that relying on attending conferences, H₂ storage committees, etc. is ad hoc, and would prefer to see more structured approach. However, understand this could be difficult.
- Maybe use checklist/database of materials that can be updated regularly. This could be an initial assessment of all the compounds currently under development with their evaluation status (whether the compound could meet the targets for commercial viability), i.e., under investigation, possibly viable compound, etc., with comments as to position in this project's analysis, i.e., if used in this project, why, and if not, why not analyzed?
- Generally believe they have identified most of the technical barriers although some more work could be done to understand the test standards for onboard storage and investigate mitigation requirements for this standard.
- Confused as to the pathway of the project. It may be helpful to provide/develop process showing potential outcomes.
- The project uses identification/mitigation methodology, which is very appropriate for safety studies (a "practice what you preach" approach).
- The actual series of testing methodologies include many proven processes.
- I especially like the methodology of mitigation testing and interaction with standards organizations.
- The technical approach is good and will systematically address key properties of the materials studied.
- The mechanism for ensuring that new materials emerging from other storage projects (and that are becoming prime candidates to meet DOE targets) are identified and provided to this project is less clear and will need some attention and support from DOE through the life of this project.
- They are not conducting tests that are performance related to automotive systems. A simple pyrophoricity test by dropping material in an air environment does not accurately describe how the material will react when packed into a tank in the case of a rupture.
- Additionally, containment methods today (pressure vessels) likely do not represent what will be used in the future, until we have identified suitable systems, I fear that most of this testing will become redundant or obsolete!
- They really need to collaborate with appropriate automotive safety groups, such as NHTSA, FMVSS and SAE to develop appropriate and useful test plans and procedures.

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

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

- Project relatively new so results limited.
- Have some quantitative data.
- Apparently have acquired equipment.
- Difficult to fully score here as only 10% complete after 2+ yrs although the project manager appears to have a reasonable understanding of the tasks and responsibilities – would expect greater % completion not sure if there were issues here that affected completion.
- Starting to get some good results – although it appears to be starting slowly (looking at the funding levels, it appears that this may be the reason).
- This is an ongoing process which should prove invaluable to materials testing and safety within the program.
- Showing some interesting thermodynamic pathway data. This will likely prove valuable.
- Good progress in the early project stages at the level of funding provided to date.
- Program has just started; but I don't see what novel work they will present.

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

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

HYDROGEN STORAGE

- Via DOE program managers, this project should be able to interact with other centers and independent projects to acquire safety and toxicity information.
- Fine team of international partners.
- Tied-in with IPHE.
- ICHS paper good.
- More could be done in terms of communication between partners to ensure that overlaps in undertaken research are reduced and so that each group could learn more from the other areas.
- Expect communication to improve and believe the idea given by the presenter for webshare would be a very good idea. Not sure of how regularly meetings are held but maybe also regular presentations via video conference or internet of each group's status and achievements could also prove useful within the group.
- Addition of regulatory body representation may provide useful advice on how the results of this project could be directed to a standard document – may also assist in providing structural focus to the research and mitigation strategy.
- Excellent international collaboration process – will greatly aid transfer of technical and safety data on an international basis.
- They need to ensure that lessons learned and safe practices methodologies are shared between participants.
- Very strong team of partners that also includes lead lab for the MHCoE.
- Participation of Sandia will help with identification and access to new materials being developed and as needed for testing but mechanism for such will need some attention.
- They have teamed with Dr. Fitchner of FZK in Germany, who has completed similar work in the past with guidance from OEMs.
- They really need to team further with OEMs when/if OEMs decide this work is ready to be conducted.
- They need to collaborate with appropriate automotive safety groups such as NHTSA, FMVSS and SAE to develop appropriate and useful test plans and procedures.

Question 5: Approach to and relevance of proposed future research

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

- Need to develop test matrix.
- Try to get fundamental relationships between quality of storage material and energy release.
- A matrix of the recommended test techniques for each of the storage materials relative to mass transport or on-board storage maybe a useful outcome for future. This may not be complete, but it may be a useful tool in identifying any gaps, etc.
- They are fairly early on in the process and still building.
- The path forward looks reasonable.
- I especially like the establishment of an internal website to share safety happenings/incidents, etc.
- This is a focused project with strong players and capturing the current knowledge base.
- Delay project until OEMs are ready and define what they need.
- Then team up with automotive safety related groups.

Strengths and weaknesses

Strengths

- Partners.
- Communication.
- Attempting fundamental understanding.
- Project is beneficial and required to assist in the safe market entry into hydrogen powered market.
- Strong international team.
- PI has much experience in this area.
- Well thought out approach/methodology.
- Dr. Max Fitchner.
- Technical expertise as represented by the PI and partners.

- Appreciation for need to develop sound and even novel technologies/techniques for risk mitigation associated with use of these materials.

Weaknesses

- Large scope.
- Probably underfunded.
- Ensure coordination among partners.
- Addition of industry and regulatory organization (codes & standards) advice may provide more breadth on risk mitigation perspective and industry introduction of standardized document.
- None that are obvious, other than things seem to be starting slowly – but looking at funding levels, this may be the reason.
- Path forward for interaction/collaboration with other storage projects less clear at this stage, but I am highly confident that this will be addressed by this team.

Specific recommendations and additions or deletions to the work scope

- This is a much-needed project that is long overdue to address the safety issues and metrics.
- It is recommended to increase the scope of this project to develop safety guidelines and targets used in down-selecting storage candidates.
- Currently this project appears underfunded. It is recommended to increase funding resources commensurate with scope expansion.
- Consider fire suppression techniques as part of task 3. Both lab, vehicle, and storage manufacturing scale.
- DOE should adequately fund.
- HSP should review safety plans for SRNL and UTRC and other U.S. collaborators – consider a site visit.
- Addition of industry and regulatory organization (codes and standards) advice may provide more breadth on risk mitigation perspective and industry introduction of standardized document.
- Review standards on onboard storage safety – on and off road vehicles.
- Matrix summary of status of each material and issues per material.
- Share learnings/best practices with the hydrogen community as a whole – via a website, maybe like h2incidents.org or similar.
- Per the discussion of Task 3 and the consequences of exposure-to-air and humidity for these materials, work on identifying and testing appropriate fire suppression agents for new materials should be considered.
- SwRI is serving as a testing laboratory for new materials coming from the Storage CoEs. Although their scope is different from this project, some interaction might be fruitful for both projects.

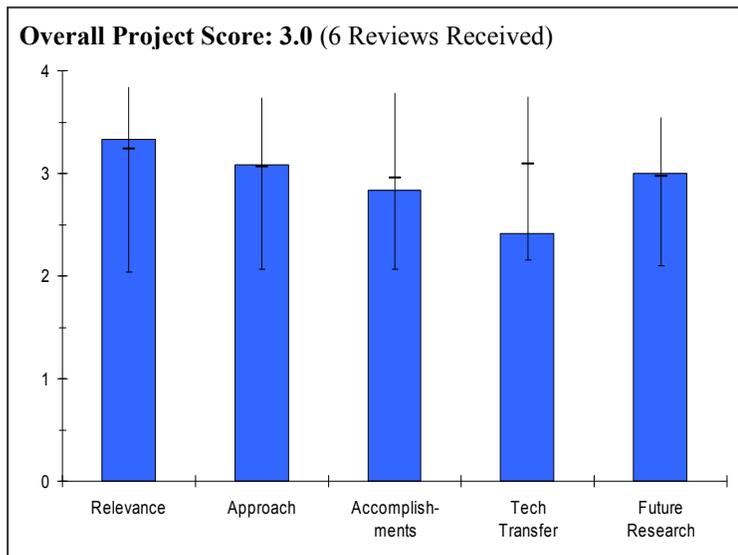
Project # ST-23: Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers
[Official project title: Design and Development of New Carbon-based Sorbent Systems for an Effective Containment of Hydrogen]

Alan Cooper; Air Products & Chemicals, Inc.

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

Brief Summary of Project

This project is dedicated to the development of reversible organic liquid-phase hydrogen carriers for the delivery and storage of hydrogen. These liquid-phase carriers can be used to transport hydrogen from production sources, using the existing liquid fuels infrastructure, to sites where they can release hydrogen by dehydrogenation for stationary power applications or be dispensed to H₂-powered vehicles. The overall objective is the development of liquid-phase hydrogen storage materials with capacities of >7 wt. % and >60 g H₂/L and associated dehydrogenation and hydrogenation catalysts, and scale-up of liquid carriers for use in systems engineering activities as part of an associated DOE production/delivery project.



Question 1: Relevance to overall DOE objectives

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

- This project attempts to develop a liquid hydrogen carrier that would have definite benefits for hydrogen on-board storage.
- Organic liquid carrier concept has real potential to become a viable hydrogen storage technology. The PIs are aware of the main challenges: lowering the temperature or heat input for desorption, improving catalyst effectiveness, and improving the capacity beyond the 7 wt.% "barrier". All of these will be non-trivial to overcome, but the PIs are working in the right directions.
- Having a (low-pressure) liquid fuel and liquid spent fuel is a significant advantage of this approach.
- Gravimetric performance is not close to the final target but this approach seems quite practical both for the on-board and off-board hydrogen delivery.
- Finding a high density liquid storage system with acceptable thermodynamics could significantly benefit the OEMs
- Finding a combined (exothermic/endothermic) system is an interesting approach to design systems with the appropriate systems
- The organic liquid hydrogen storage materials appear to have one of the best chances of leading to an H-storage system that meets DOE capacity targets.
- Air Products and Chemicals, Inc. (APCI) is making a concerted effort to identify and examine the most likely candidates.
- Lowering dehydrogenation temperature and carrier volatility are important longer range programmatic considerations.

Question 2: Approach to performing the research and development

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

- The approach seeks to develop novel, liquid-based hydrogen storage as a substitute for gaseous storage. The approach, while it must be considered high-risk, would have definite advantages particularly in terms of volumetric density of the storage system.
- Very effective use of combined experimental/computational approach. Should be used as an example for other projects, in this regard.
- APCI is also exploring a new auto-thermal on-board process.
- Autothermal process is an interesting idea that would help overcome the barrier associated with the high enthalpy materials. This idea should be pursued in the coming year, and next year it would be nice to see a bit more in terms of the overall energy efficiency of such an approach, and more specifics about the viability of such an approach.
- The approach considers using both on-board waste heat for dehydrogenation of the liquid carrier and an alternate autothermal configuration.
- New concept reflect to the biggest problem of chemical storage, how to get heat for dehydrogenation.
- The autothermal approach has the issues of reduced storage efficiency since some liquid carrier would be used for dehydrogenation heat and thus reduced volumetric and gravimetric densities. But may be required if there is not sufficient on-board waste heat from the fuel cell power system.
- While the combined exothermic/endothermic approach is commendable. I fear that the autothermal approach will bring us back to the point of on-board reforming systems. I highly doubt that they will be able to engineer a compact/efficient and cost effective system that meets our requirements.
- Storage and release of hydrogen in/from organic liquids with loosely bound hydrogen atoms is under study. The work involves identification of (1) organic liquids with suitable H uptake/release properties and (2) effective catalysts for the release process.
- APCI is investigating modified catalyst embodiments to improve dehydrogenation effectiveness.

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

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

- Good progress has been made in identifying and characterizing potential liquid carriers. Progress in the dehydrogenation of the various liquid carriers aided by catalytic additives was reported.
- A number of new liquid carriers are under study, including ones with >7 wt.% Hydrogen theoretical capacity.
- Several new concepts in the catalysis and thermal balance areas were reported on, but these are still works in progress.
- New concept of autothermal hydrogen release has been demonstrated that may help resolve the on-board storage efficiency issues, however, it moves the energy efficiency problem off-board (to the re-hydrogenation step) where additional "waste hydrogen" still needs to be put in the molecule that would be used on-board to compensate for the heat effect upon dehydrogenation. Another potential to reduce the efficiency problem would be to use other reducing agents (e.g., natural gas, etc).
- They have identified proven materials that work effectively in concert with each other to make the system work and provide the appropriate thermodynamic window.
- Better yet, the material combination is also taken into account for regeneration schemes.
- The only problem is that air is a required input.
- Given the funding level, the progress on this project has been modest in the past year. Earlier years seems to be filled with new results, new ideas, and new molecules.
- The presentation did not give a clear picture of the amount of real progress towards an operating system over the past year. A graphic showing how the program is moving towards its end-state goals on an annual basis might help clarify this.
- There is less than a year left for this project and over \$6M will have been spent. It doesn't seem that APCI will come very close to meeting the original expectations of the program. Will we have a liquid carrier that can meet at a minimum the "system" capacity targets for 2010?

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

This project was rated **2.4** for technology transfer and collaboration.

HYDROGEN STORAGE

- There appears to be little collaboration on this project, perhaps due to the proprietary nature of the work at Air Products. However some collaboration with ANL was mentioned and input was requested from the auto OEMs.
- Not clear that this project is significantly interacting with any other projects. It could be interesting to see a more substantial interaction with one of the automakers, for instance.
- Typical Air Products – not much collaboration. But then again, they really don't need it; they have excellent resources in-house for the job.
- There doesn't seem to be any meaningful collaboration outside APCI.
- It is not clear to this reviewer why this project is not more closely connected with, or even an actual part of, the Chemical Hydrogen CoE.

Question 5: Approach to and relevance of proposed future research

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

- Presentation ST-31 reported a compensation factor of about 1.6 for gravimetric material H-storage capacity for organic liquids compared to system gravimetric capacity. That means the 2010 goal can be achieved for a liquid with H-storage capacity around 10 wt.%. In light of this, it seems prudent for Air Products to focus their attention on compounds that have a chance to deliver at least 9 wt.% H. There seems to be little point to experimenting with compounds that can't at least in theory release 9 wt.% H.
- Highest priority emphasis should be on identifying liquid carriers that can meet H-storage targets.
- Considerations related to releasing all of the theoretically available hydrogen should follow the above.
- Issues related to release temperature, energy balance, and volatility should come after that.
- Catalyst research is also necessary to pursue for potential improvements of system weight and volume and kinetic characteristics.
- Autothermal dehydrogenation has a potential to resolve major energy efficiency issue on-board
- At the same time, search for new carrier(s) with lower dehydrogenation enthalpy is also necessary to improve overall efficiency
- Please find away to eliminate any outside inputs such as air or water; this complicates the reactor significantly in terms of after-treatment.
- The project was reported to be 75% complete at this point. Future plans for the remainder of the work seem to be reasonable, but a lot of work is needed to fully evaluate the full potential for liquid hydrogen carriers.
- Future work is focused on the most critical barriers; however, the plan to overcome these barriers is not clear. For instance, improved catalysts are certainly needed, but how do the PIs propose to find them?

Strengths and weaknesses

Strengths

- Use of hydrogen carriers for both on board and off-board applications.
- Improved safety as compressed hydrogen is not utilized.
- There is a potential to overcome on-board storage efficiency issues with the autothermal dehydrogenation approach.
- Novel ideas (unlike other projects in portfolio).
- Liquid fuel (could use conformable tanks).
- Great combined use of experiment/computation.
- This is a very innovative concept from a practical point of view.
- Novel.
- Functional.

Weaknesses

- Relatively small progress being made towards the discovery of new carriers with increased capacity and reduced enthalpy of dehydrogenation.
- System start-up and transient response may be serious issues to resolve on the system development stage.
- Capacities for these molecules (at least for low enthalpy) appear to be significantly limited by H:C ratio.
- Progress in this project was initially quite fast, but seems to have slowed recently.

- Material seems solid in the low room temperature
- Autothermal concept requires air!
- APCI seems to be working alone in this project. What has prevented the development of close ties with related projects in the Chemical Hydrogen CoE?

Specific recommendations and additions or deletions to the work scope

- None.
- A decision on whether or not to pursue the autothermal approach should be made as soon as possible in order to focus the remaining effort. Suggest that emphasis should be on selecting a specific liquid carrier and fully characterizing the dehydrogenation and regeneration of the selected carrier.
- The PIs should be encouraged to try and demonstrate this autothermal concept; it could potentially remove one of the significant barriers associated with this approach.
- See recommendations in the "comment" boxes above.

Project # ST-24: DOE Chemical Hydrogen CoE Overview

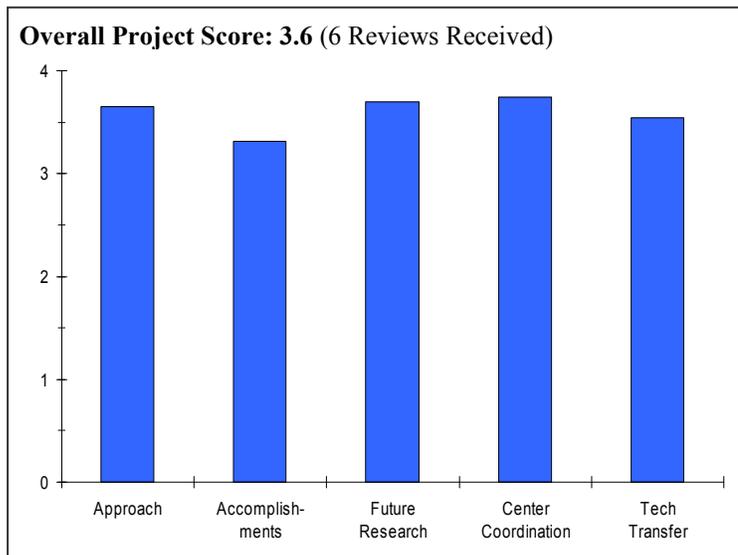
Bill Tumas; Los Alamos National Laboratory (LANL)

[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 D. LANL's technical contribution to the center is evaluated in ST-29.]

Brief Summary of Project

The Chemical Hydrogen Storage Center of Excellence (CHCoE) involves two national laboratories, seven universities, and four industrial companies. The objectives of the center are 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 to 2015 goals:

- Develop materials, catalysts and new concepts to control thermochemistry and reaction pathways;
- Assess concepts and systems using engineering analysis and studies;
- Select most promising chemical systems for engineering development.



Question 1: Approach to performing the R&D

This project earned a score of **3.7** for this criterion.

- Center very well organized and focused on challenges.
- Aimed squarely at the barriers and well designed for partner strengths. Clear go/no-go structure and internal goals. Fairly diverse set of approaches now.
- Strong management team.
- Important that the center is actively stopping work (down select process) on materials that don't show potential, so scarce resources is not wasted.
- Generally, I like the management structure and approach. Although reactor engineering is part of their future plans, I would appreciate seeing upfront calculations using a template material, rough engineering, and a cost study to see if there are any obvious show stoppers. This could also be used to help set qualitative practical targets for regeneration, storage, and hydrogen release.
- Pathway to promising advanced technologies as well as borohydride and ammonia borane is considered in this CoE.
- The scope of the center is largely limited to boron chemistry. Boron is light element, abundant enough in nature that demonstrates very rich chemistry. This opens the door to a variety of ways for storage and regeneration. At the same time little effort is devoted to exploratory advanced concepts other than boron.

Question 2: Technical accomplishments and progress toward DOE goals

This project was rated **3.3** for this criterion.

- Aminoborane work shows excellent progress to overcoming key challenges and targets.
- Establishment of regeneration process from spent fuel should be accelerated as well as system study for hydrogen generation to clarify requirement to material properties.

- Significant progress has been made toward goals, but there is still much to do. Spent fuel regeneration is moving along. Some systems have been taken to a point where they are sure there is no need to go further. MBN systems are a good addition. Adding combinatorial catalysis system is also a needed ability.
- If the data are available, I would like to see some overall yields for the forward and reverse reactions to assess the overall cycle efficiency.
- Still, a lot of technical barriers exist to be overcome that are associated with boron ranging from use and regeneration of NaBH₄ to kinetic issues of H₂ release from and regeneration of ammonia boranes. Perhaps, a go/no-go decision on NaBH₄ can be facilitated based on both on-board operability and off-board regeneration efficiency issues. (Note: DOE's go/no-go decision on NaBH₄ in FY07 will be facilitated based on both on-board operability and off-board regeneration efficiency).

Question 3: Proposed future research approach and relevance

This project was rated **3.7** for this criterion.

- Good focus on exploratory / innovative research to invent new materials and concepts.
- Down-selecting the best materials and continuing to pursue elements with high (2+) hydrogen release rates should maximize the results of this CoE.
- The timing for materials down-select process is reasonable for the DOE target dates.
- Seems like a suitable plan though the backup plans, as with all centers, seem scant.
- It isn't clear if focus should be on improving efficiency of regeneration schemes for AB until a go/no-go decision is made.

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

This project was rated **3.7** for this criterion.

- Excellent communication within the CoE is apparent.
- Based on the information provided, coordination and collaboration appears to be very good.
- The CoE considers correlation with other CoEs well.
- The CoE promotes "Engineering Assessment and Coordination Crosscuts Center Activities" for better cooperation between engineering and scientific research.
- Coordination and communication seems largely good. There are still some players (at the poster session) who seem adrift doing their small sub-segment and just counting on someone else to make whole system work without even really knowing what that entails; but generally communication is good.

Question 5: Collaborations/Technology Transfer Outside the CoE

This project was rated **3.5** for this criterion.

- As material selections from other CoEs converge, more communication between the CoEs will be crucial to ensure work is not being duplicated/repeated.
- The CoE have tried to expand the possibility of chemical hydride by means of collaboration with researchers in foreign countries through the IPHE framework etc.
- All centers could do this more, but there is communication, it could be significantly more frequent and addressed with greater intent to benefit the overall program. Metal Hydride CoE and Chemical Hydrogen Storage CoE are working together on alane now. Organic chemists are exchanging ideas across teams.
- Although not clear from the presentation, the Q&A uncovered interactions between this CoE and the CoE for metal hydrides.

Strengths and weaknesses

Strengths

- The network with foreign researchers through IPHE.
- Strong leadership is apparent in the progress being made at this center.

HYDROGEN STORAGE

- Strong management across the whole center.
- Right team for the area. Good management model.
- Good approach to center project management.
- Technical issues appear to be well understood.
- The CoE is flexible to change as the down-select procedure narrows the group of potential materials.
- Innovative ideas and healthy pipelines of new candidates.
- Excellent combination of theory, experimental, and system cost/analysis.

Weaknesses

- Still very dependent on BO to BH chemistry, and while a quite interesting approach to this is being worked out it is far from a sure thing, so further diversification would seem a good course.
- Probably would benefit from actual collaboration with Production/Delivery team because this system has the added need to return spent fuel to the maker.
- Would like to see more upfront cost analysis and to use this information to qualitatively set some of the technical targets.
- Although it does not really fit into this category, I felt that the presenter had too many slides and the presentation was rushed. I would suggest narrowing the range of topics covered and focus more on high level messages.

Specific recommendations and additions or deletions to the work scope

- Center members seem to have different visions of appropriate efficiency. This should be uniform.
- Materials that meet the requirements for on-board operations can be down-selected for dedicated regeneration studies, as opposed to addressing regenerability issues for majority of the materials under investigation.
- Good approach for analysis and selecting optimal regeneration process has been demonstrated by Rohm & Haas that could be applied towards material selection for storage as well.

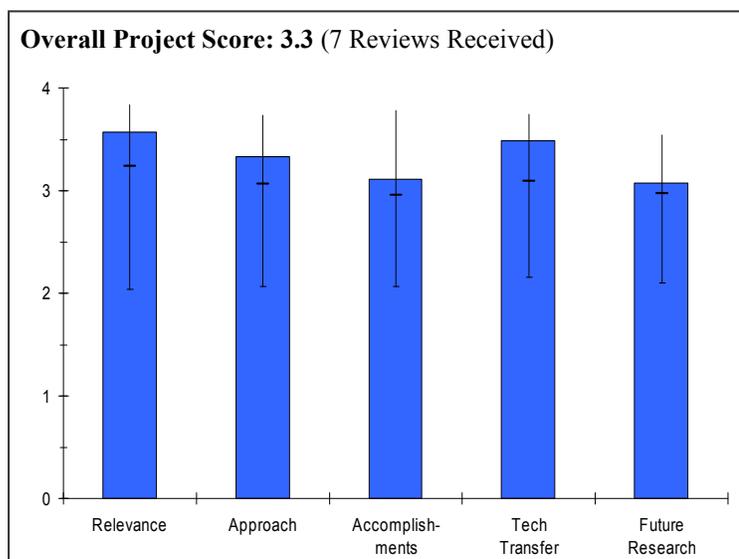
Project # ST-25: Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides*Suzanne Linehan; Rohm and Haas*

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The overall objective of this project is to define and evaluate novel chemistries and processes to produce chemical hydrogen storage materials that meet DOE 2010 targets, and that have the potential to meet 2015 targets.

- The primary focus is to identify energy efficient and cost-effective options for B-OH to B-H conversion.
- A secondary objective is to leverage Rohm and Haas' expertise and experience across the entire center, assessing engineering requirements, economics, and life cycle inventory of hydrogen storage materials other than borohydride.
- A third objective is to support DOE's Chemical H₂ Storage Systems Analysis Working Group.

**Question 1: Relevance to overall DOE objectives**

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

- Consistent with President's Hydrogen Fuel Initiative.
- The lessons learned in this program represent a valuable contribution to the DOE's Hydrogen Program.
- Important to the chemical hydride effort in DOE's Multi-Year Research Development & Demonstration plan by carefully examining the technical and economic aspects of NaBH₄ regeneration from spent borates (i.e., after the Millennium Cell on-board hydrolysis process).
- Presentation addressed broadly, but very well, the goals of the national initiative.
- This exhaustive (dragnet) approach to determining all possible NaBH₄ regeneration methods is absolutely necessary to put true closure on the question of the feasibility of economically viable NaBH₄ regeneration.
- A stipulated overall objective for this program is to examine chemistries that can meet the 2010 and possibly the 2015 H-storage system targets set by DOE. Rohm & Haas has done an admirable job of assessment, analysis, and experimentation on the NaBH₄ system as a hydrogen storage material. All indications at the present time are that it will barely meet the 2007 targets. In short the SBH system is at best a test case for the boron-based materials and for slurry type approaches.
- Necessary to do this sort of analysis to sort out the possible efficiencies for NaBH₄ regeneration.
- Probably the critical challenge for these systems is recycle energy and engineering the system.

Question 2: Approach to performing the research and development

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

- Good focus and start on quantifying the thermodynamics and cost of NaBH₄ regeneration from spent borates.
- Thermodynamic modeling followed by experimental confirmation is an excellent approach and greatly needed by DOE for the go/no-go decision on NaBH₄ hydrolysis.
- PI and collaborators have competence and skill in attacking this long-standing regeneration problem.
- Very professional presentation and analysis of the project.

HYDROGEN STORAGE

- Experimental and theoretical approach – very well described.
- Plan, etc., were very well presented. Efficiency analysis was similarly well documented.
- Paper study of approximate energy is appropriate. Metric for overall weighting is arguable (everyone has their own weighting) but useful.
- Excellent that as many different routes and chemistries were considered.
- Weighting system seems a bit arbitrary (as is inevitably always the case) however it seems reasonably well aligned with DOE's goals.
- Why an internal regenerating efficiency of 60%, FreedomCAR/DOE targets are higher.
- The work involves finding a cost-effective way to convert borates to boranes. The tasks cover literature searches, screening and evaluation, development of flow sheets and cost estimates, and laboratory demonstrations of key process steps.
- The approach taken in this program has been well thought-out from the beginning. The problem is that the H-storage "system" targets are set at a high level and very few H-storage material concepts have a chance of meeting them.

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

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

- R&H has done an excellent job of scoping and evaluating the regeneration options. The respective options have been examined in considerable detail, quantified, and ranked in a sensible way.
- Judging from this presentation and related NaBH₄ presentations and posters, it is clear that R&H is making an honest, forthright effort to put NaBH₄ technology in proper perspective.
- Excellent and exhaustive work conducted (literature study).
- All obvious regeneration processes have been studied in detail, at least on paper. Good presentation. Moving well toward the one intent of the project, namely to help DOE in making the go/no-go decision on NaBH₄ hydrolysis.
- Results are likely to be very useful for the go/no-go decision.
- Weighting factors of the various contributions seem to be somewhat "underweighted" on the environmental/CO₂ impact of the regeneration strategy. This leads to some skepticism of the final ranking of the regeneration processes.
- Group has determined that metalothermic reduction is the most promising regeneration route. This is consistent with Prof. Suda's conclusions of the last few years. Why was that Japanese work not cited? Does PI think Suda's projection of \$2/kg NaBH₄ is possible?
- Other possibilities quantified.
- Important cost projections not quite ready. These are needed soon and will be critical.
- Details were not really provided in the presentation except for the various projections and feasibility analyses.
- Clearly, the results are positive for the metal hydride and metal reduction routes to regeneration.
- Provided some lab evaluations such as the metal based regeneration of boron wastes. Generated information to set rankings and ranked the efforts. Paths elucidated and energy, complexity, etc. evaluated. Seems like perhaps more might have been accomplished on a largely paper study with this budget.
- Would like a little bit more validation by real world results or studies (perhaps also obtained from literature).
- The calculations done seem quite simple, and it's not clear why such a large amount of funding was necessary to produce these results.
- Does not appear as though they have delivered on the milestones promised in Q1 FY07 (still listed as "ongoing").

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

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

- Excellent.
- Excellent collaborations and tech transfers through the CHCoE.
- Excellent collaboration with CoE partners.

- Other services beyond NaBH₄ useful to the CHCoE.
- Interacting well as center partner.
- R&H has a set of collaborations within the CHCoE that support and augment their effort in meaningful ways.
- Perhaps their collaborations will lead them to a new or at least revised direction that has a better chance of meeting storage targets than NaBH₄.
- Why are there no collaborations with Suda/Japan?

Question 5: Approach to and relevance of proposed future research

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

- The cost estimates are really a critical contribution, and will be necessary for an informed go/no-go decision. Thus, this work should be completed ASAP.
- Very nicely consistent with past results and very well focused toward the NaBH₄ regeneration barrier.
- This reviewer (and presumably DOE) is anxious to get some cost estimates for regeneration.
- This is based on a series of excellent analyses.
- Appropriate.
- Please add some extra calculations as to what further inefficiencies occur with removal/pumping and shipping the fuels from the vehicle, to fueling/reprocessing plants.
- The R&H path in the future will depend on the outcome of work over the next few months. In the short term, they need to pour their efforts into putting their NaBH₄ technology in the best possible light. The outcome of the go/no-go decision process will determine how they proceed beyond September of 2007.
- In parallel with the NaBH₄ work, they should work with their CoE collaborators to define a follow-on path for their storage work if NaBH₄ is discontinued or modified in scope.
- Amino-boranes may be the way to go in the future. Systems with a ratio of H to other atoms equal to or greater than 2 seem to be the most promising.
- Not exactly clear what actual chemistries they will try to validate or why? Their results show that there is no route that is sufficiently energetically efficient to meet their own criteria, let alone the more stringent DOE Criteria.
- Not completely clear what will become of this project. Should there be a "no-go" decision on NaBH₄?

Strengths and weaknesses

Strengths

- This is a nicely detailed and directed effort on NaBH₄ regeneration. It is much needed.
- The people involved are with industry and are experts on process thermodynamics and economics.
- The process for the down select is clear.
- The presentation suggested very high levels of competence in the project and in the study participants.
- Well-planned and justified series of projects and emphasis for the future.
- Honest conclusions about challenge to these regeneration schemes.
- A strong team with dedicated personnel.
- Appropriate resources to contribute to the hydrogen storage program in an effective way.

Weaknesses

- At the technical level, this project has no obvious weaknesses. R&H is doing all they can to bring borate recycle to a demonstration. They are limited by what the system is capable of in terms of storage capacity, functionality, and cost.
- They need to make some significant progress over the summer in borate to borane conversion to make a convincing case that regeneration can be accomplished at an acceptable cost.
- Processes in which CO₂ is evolved need to be considered with respect to concern about greenhouse gas emissions.
- Intuitively, the difficult thermodynamics of regeneration pose a major challenge. This reviewer has always doubted that this will result in H-storage cheap enough for vehicles. But, by all means, good luck.
- Few actual results were presented.

HYDROGEN STORAGE

- The calculations done seem quite simple, and it's not clear why such a large amount of funding was necessary to produce these results.
- Why are there no collaborations with Suda/Japan?

Specific recommendations and additions or deletions to the work scope

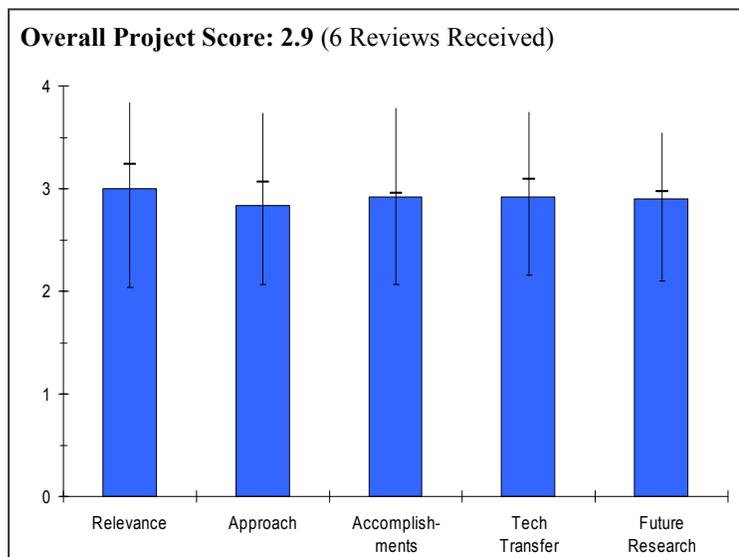
- No significant overall change is recommended.
- Suggest making use of prior thermodynamic and experimental work by Suda on metalothermic reduction; optionally consider establishing collaboration.
- Down select shall be done with the absolute cost/price potential, I hope the figure will be shown with the related analysis.
- None, except possibly more time for the work.

Project # ST-26: Electrochemical Hydrogen Storage Systems*Digby Macdonald; Pennsylvania State University*

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

Two strategies are pursued in this Pennsylvania State University project to advance hydrogen storage technology. In the first case, hydride hydrolysis/regeneration is investigated by exploring the electrochemical reduction of B-O to B-H, while in the second strategy the electrochemistry of various polyhedral boranes is explored to ascertain if electrochemical transformations can be affected between various members that reversibly absorb and release hydrogen and hence could form the basis of a new hydrogen storage technology.

Question 1: Relevance to overall DOE objectives

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

- Consistent with President's HFI.
- Regeneration of sodium borohydride can be done either chemically or electrochemically. PSU is looking at electrochemical routes to regenerate sodium borohydride (borate to borohydride). The project is highly relevant to the mission of the CHS CoE particularly to NaBH₄ regeneration.
- This work fits in with the other NaBH₄ efforts to help determine whether electrochemical regeneration of NaBH₄ is possible.
- Adds to the chemical hydride effort in DOE's Multi-Year RD&D plan by looking at electrochemical methods of NaBH₄ regeneration from spent borates.
- Clearly the regeneration of NaBH₄ is key to this overall process.
- This will determine the future of this (hydrolysis) program.
- The results, if achieved, will ensure the success of the initiative.
- This project is examining a possible spent fuel regeneration route for the NaBH₄ process. A near-term advance in this area could save the day for NaBH₄, which is approaching a go/no-go decision point.
- The main concern here is can the project deliver in time to impact the go/no-go decision.
- Why work on electrochemical regeneration when Rohm & Haas work clearly demonstrates that energetically it is one of the least efficient and most difficult?

Question 2: Approach to performing the research and development

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

- Electrochemical hydrogen storage is a relatively unexplored idea, and hence the present effort is interesting; however, the PIs need to clarify the overall energy balance of such an idea. How much energy input is required in a typical electrochemical process in order to extract the hydrogen?
- One project focus is on electrolytic regeneration of NaBH₄ from the spent borate resulting from hydrolysis. Also covered in part by the Rohm & Haas presentation (ST-25). That is important to the DOE NaBH₄ hydrolysis go/no-go decision DOE must make in FY2007.

HYDROGEN STORAGE

- Project also looks at electrochemical H-storage in the polyboranes, an area that has not been heretofore covered in the DOE program.
- Clear success in either will help toward breaking down H-storage barriers.
- Impressed by the approach.
- Developed a technique for identification of BH_4 in product.
- Addressed the low electrochemical yields and problems of reproducibility.
- Investigator takes a very realistic approach to the studies and the results.
- PI clearly recognizes the problems of this 8e- reduction.
- The approach is based on electrochemical and plasma chemical methods that are clearly promising but at the same time high-risk in nature.
- Success requires winning boron from an anionic moiety – not an easy thing to do, but the PI has ideas that just might work. At least they deserve some feasibility testing.
- The approach is focused on the technical barriers to efficient regeneration.
- The approach could be strengthened by assessing the feasibility of chemically assisting the electrochemical reduction reactions.
- Really trying to work against “Mother Nature” by forcing a negative ion to a negative plate!
- It is difficult to imagine how a system deliberately intended to work against thermodynamics and forces will ever lead to high yields and efficiencies.

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

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

- Some initial success of electrochemical regeneration pathways for NaBH_4 .
- Some experiments give hints of BH_4^- generation, but clear promise is not convincingly shown.
- The development of the needed electrochemical testing techniques is apparently successful and complete.
- The potential for reversible electrochemical H-storage is not yet convincingly shown.
- Achieved the "in situ" method for BH_4 detection.
- Made progress toward understanding the process occurring at the electrode [use of $(\text{Et}_4\text{N})\text{OH}$].
- Obviously the progress made is not very substantial in reaching the goal but the direction is right on-target.
- Given the challenges, he has demonstrated excellent progress.
- The literature has been well reviewed and a variety of electrochemical deposition tests using alternative electrode materials and electrolytes have been performed.
- Reasons for the discrepancies in the literature concerning electrolysis of the borate anion have been sorted out, but attempts to actually produce boron in a reduced state have been only minimally successful.
- A quantitative method to determine borate in aqueous solution was developed during the past year.
- Development of the analytical technique electrochemical reduction of B-O to B-H was demonstrated.
- The electrochemical activity of polyboranes has been investigated.
- Multiple redox transitions were discovered in polyboranes.
- Given the project has been in place for more than two years, progress toward breaking technological barriers is not certain.

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

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

- Good collaborations with Rohm & Haas, Millennium Cell, and the CHCoE.
- Collaboration appears strong between PSU and other center members.
- Good collaboration with several members of the CoE.
- This project is directly supporting the Rohm & Haas NaBH_4 program. It is addressing an issue that seems singularly important to NaBH_4 regeneration at this time.
- Perhaps work on the polyboranes will lead to a new research direction even if NaBH_4 faces a no-go in September.

- The PI is a world class electrochemist. Surely, there are opportunities for applications of his expertise within the other CoEs for H-storage.
- Minimally involved with others, although R&H and LANL are good partners.

Question 5: Approach to and relevance of proposed future research

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

- Need to demonstrate reversibility of electrochemical storage, and also give an indication of the energy efficiency of such an approach.
- Reasonable future effort on B-O to B-H electro-conversion. The problem is the limited time frame until the DOE go/no-go decision point.
- Electrochemical studies will build on the very important "early" results obtained.
- Presentation implied that the investigators are moving slowly, but correctly, towards the goals of the project.
- The proposed ideas about how to electro-reduce borate are deserving of study.
- Focus for 2007 is on overcoming electrostatic repulsion of $B(OH)_4$ from the cathode in the electrolysis cell.
- Another task will look at chemical reduction by means of hydrogen plasma.
- The electrochemical H-storage polyborane half is reasonable.
- The polyborane work might open new windows of opportunity for borate utilization in fuel cells.
- Not exactly sure what his next intended steps are.
- Not clear what will become of this project in light of the upcoming go/no-go decision on $NaBH_4$.

Strengths and weaknesses

Strengths

- Project supports $NaBH_4$ regeneration effort.
- Reversible electrochemical storage successes would offer an exciting new option.
- Competence of the investigators.
- Addressing of the drawbacks of the problem of repulsion of the meta-borate anion by the electrode.
- The PI is an expert in the field of electrochemistry and has a broad range of research experience that could be gainfully employed throughout the HFCIT program.
- The research infrastructure at Penn State is first class for the kind of experimentation required to achieve success in this project.
- Good understanding of the electrochemical pathways to successfully regenerate B-O to B-H.

Weaknesses

- The inherent thermodynamic difficulties of B-O to B-H conversion. Regeneration must be of very low cost (maybe $< \$2/kg$ $NaBH_4$ regenerated) to be applicable to vehicles.
- Difficulty of the electrochemical regeneration.
- Working against thermodynamics!
- The project may be too narrowly focused on the addition of H to B-O. Another possibility is to remove O from B-O.
- The main concern is that there is not much time left to show a truly encouraging result for the borate reduction. Hopefully, the team at Penn State plans to run full bore this coming summer.
- In truth, the chances of success in achieving efficient borohydride regeneration are not great, but it is worth a try.
- Lack of overall progress.

Specific recommendations and additions or deletions to the work scope

- PSU should consider molten salt processing of B-O bonds and/or removal of O from the borates rather than the addition of H.
- Add nuclear power and renewable energy options to the list of electricity sources that complement the electrochemical approach to $NaBH_4$ regeneration.

HYDROGEN STORAGE

- Add a go/no-go decision point in the next year to the effect that at least some reversible electrochemical H-storage must be demonstrated.
- Cease all B-O to B-H regeneration work if DOE decision in FY2007 is no-go.
- At this point, it seems that the investigators will require more time.
- Go full bore on the borate reduction work in the near term.
- The center and PSU should develop a detailed plan that maximizes the amount of information that this approach can bring to the go/no-go decision process.
- Recommend that this work be moved into the BES portfolio.

Project # ST-27: Amineborane Hydrogen Storage

Larry Sneddon; University of Pennsylvania

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are to:

- Develop methods for on-demand, low-temperature hydrogen release from chemical hydrides that can achieve DOE targets.
 - Develop high conversion off-board methods for chemical hydride regeneration.
- Also, in collaboration with center partners the goal of this project is to develop new methods for amineborane hydrogen-release and regeneration reactions that will enable their use for chemical hydrogen storage.

Question 1: Relevance to overall DOE objectives

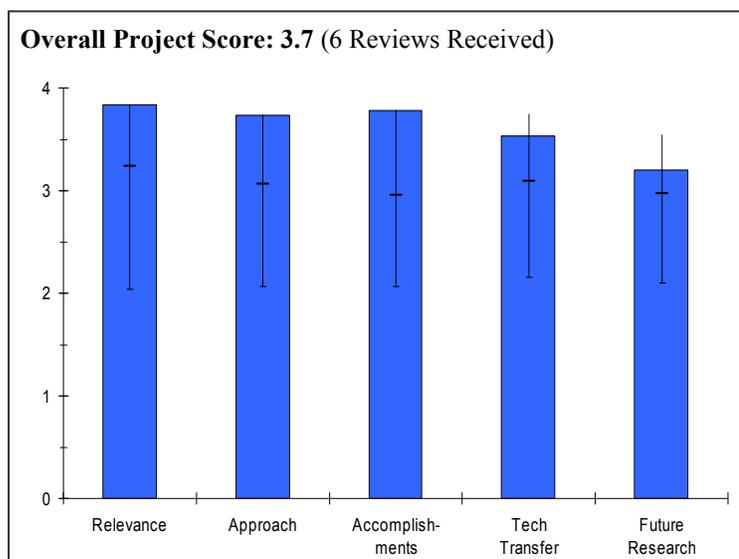
This project earned a score of **3.8** for its relevance to DOE objectives.

- Because of the potentially large theoretical hydrogen capacities of the amineboranes, they are important candidate materials to achieve the 2010 storage targets.
- Program addresses important questions for hydrogen storage in chemical systems that show promise for meeting system goals.
- Use of ionic liquids as a method to both liquefy aminoborane (AB) and improve kinetics and capacity is necessary and novel.
- Work impacts specifically to high capacity storage materials, e.g. amine boranes.
- Project is relevant to DOE objectives.
- As part of the CHCoE U. Penn is studying amine borane chemistry, specifically thermal and catalytic dehydrogenation of AB and the reverse, rehydrogenation. The work aligns well with the DOE program objectives, and is a critical part of the center activities.

Question 2: Approach to performing the research and development

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

- Amine boranes could meet DOE targets. Thermally induced dehydrogenation of AB is known to be very slow at temperatures of interest. Therefore, the approach is focused on discovering a catalyst(s) to increase the extent of hydrogen release at appreciable rates at temperatures of interest, which addresses the DOE weight and volume barriers.
- This project has an excellent focus on the problem areas, and excellent concepts to address the problem areas.
- Liquid amineboranes may be promising new materials approach.
- Hydrogen release from ammonia borane using ionic liquids and metal catalysts is an extremely promising idea.
- Excellent use of ionic liquids with addition of metal hydrides and proton sponges.
- Good approach looking at a number of different chemistries of amine boranes focused on getting the best performance, mainly kinetics.
- Address kinetics and system energy density issues.



HYDROGEN STORAGE

- Have a good understanding of the chemistry, demonstrated by the identification of undesirable side-products formed in the AB-LiH or LiNH₂ systems and their early move from these to strong N-bases to aide the elimination reactions.
- Good self-regulating down select approach. PI does good job at evaluating progress on a given chemical system, and explores alternatives rapidly.
- Have implemented no-go decision on hydrolysis of ammonia triboranes after determining it can't meet 2015 goals.
- Addresses spent fuel regeneration and have developed an approach that bypasses borates, which should lead to lower energy demands for regeneration.
- They are also identifying novel, low-energy methods for regeneration.
- Off-board regeneration of ammonia borane: major problem in the field. Approach proposed is a good starting point for the future work/further development.
- The use of solvents does take a toll on both the gravimetric and the volumetric capacities of the amineboranes.

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

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

- Showed significant improvement in H₂ release from ammonia borane systems
- On a material level, has exceeded 2007 targets for volumetric density and gravimetric density and appears to have met 2010 targets with one system (but need better kinetics).
- Have made significant contributions to understanding of the mechanism of the H₂ elimination reactions in these systems.
- By far, some of the best progress and novel ideas in the entire hydrogen storage program.
- Good progress in looking at various alternatives for getting rapid kinetics at target temperature (85°C). Completed studies of a number of different amineboranes systems.
- In 2007 several additional ionic liquids were found that increased the number of equivalents of H₂ released from around 1 to a little over 2.
- The gravimetric density increased to 7 wt.% at 85°C and the volumetric density to 0.039 kg/L.
- Promoters increased hydrogen release from solid AB to 9.5 wt.% but released NH₃, an undesirable byproduct. Use of proton sponge avoids the formation of NH₃ and is a significant accomplishment.
- Triborane alone has capacity limitations, but may be used in combination.
- Ionic liquids have capacity limitations.
- Chemical promoters (LiNH₂, LiH), mixtures of AB and AT, proton sponge have been studied.
- Excellent experimental work overall.
- Very interesting results on hydrogen release.
- Hydrolysis has been de-emphasized due to the associated regeneration problems.
- Thermolysis still has a significant problem with the rate of hydrogen generation.
- A new regeneration process was developed that avoids the formation of B-O bonds. These are significant accomplishments and represent substantial progress since last year.
- A potentially important new regeneration route for thermolysis reaction products has been identified.
- Have demonstrated a new process for ammonia borane regeneration.
- Regeneration: multi-step process; cost efficiency is low; complexity is high; a good chance that it may be not scalable.

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

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

- Very extensive collaborative efforts to support various aspects of the approach.
- Collaborations with others in the chemical hydrogen storage center are evident.
- Working with all the appropriate partners in the center.
- Good collaborations within CHCoE.
- Appears to be very interactive with center members.

- Collaboration with other research and industrial partners is very good.
- Collaboration and sharing of information is evident across the Center.
- PNNL and LANL will develop engineering assessments of both liquid and solid systems and regeneration processes.
- Rohm and Hass will also perform an engineering assessment and scale-up of the new regeneration process.

Question 5: Approach to and relevance of proposed future research

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

- UPenn will continue to develop and optimize chemical additives to improve hydrogen release rates.
- UPenn will work with center partners to define and optimize the new AB regeneration process.
- Good exploration of alternatives for the amineborane system.
- The plans follow the results of past work in a logical progression.
- Proposed future work appears to be an extension of current work.
- Improving the release rates of the thermolytic aminoboranes is a key issue.
- Regeneration of boron-based materials deserves even more attention.
- Technology transfer issues for the regeneration process of the thermolytic aminoboranes are key issues. Will it be cost and energy efficient?
- Future work is formulated in very general terms.

Strengths and weaknesses

Strengths

- Have a good understanding of the underlying chemistry.
- Good understanding of the chemistry involved.
- Very strong chemistry approach.
- Innovative ideas.
- Have focused on chemistry and systems that can meet the targets.
- Have made significant progress in spent fuel regeneration and in improving kinetics and amount of H₂ release.
- Ability to explore chemical systems fairly rapidly and maintains focus on relevant properties.
- Extensive collaboration.
- Very solid experimental work.
- The project is really focused on achieving the DOE targets. Several materials and processes have been abandoned when it became evident that they did not have the potential to meet the targets.

Weaknesses

- None.
- It is still not quite clear how regeneration of the used ammonia borane could become economically feasible.
- The reduction in release rate after the first equivalent of H₂ is released is an issue.
- Ionic liquids have capacity limitations.
- Regeneration: multi-step process; cost efficiency is low; complexity is high; a good chance that it may be not scalable.

Specific recommendations and additions or deletions to the work scope

- None.
- The engineering component in the center should undertake a conceptual design of the on-board system to establish the acceptable range of materials properties and characteristics.
- Continue as planned.

Project # ST-28: PNNL Research as part of the Chemical Hydrogen CoE

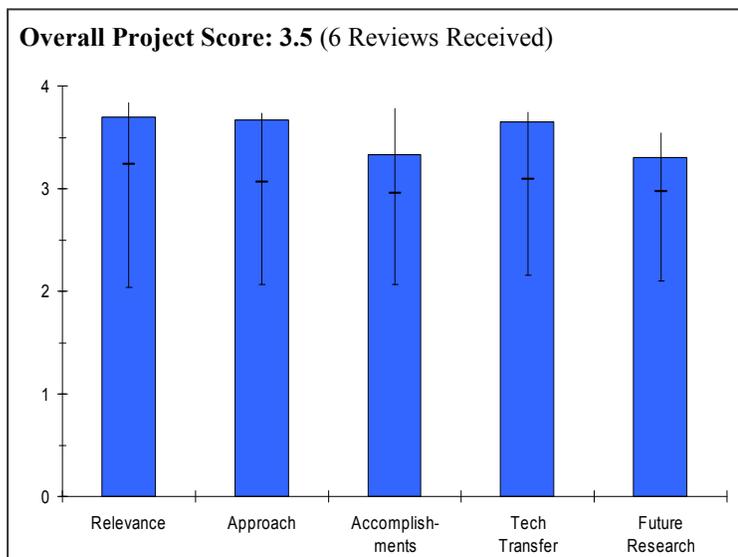
Chris Aardahl; Pacific Northwest National Laboratory (PNNL)

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

This project covers the research and development (R&D) activities being conducted by PNNL as part of the DOE Center of Excellence for Chemical Hydrogen Storage. The objectives for PNNL include identification and investigation of chemical compounds that promise to meet DOE goals for storage density (gravimetric and volumetric), hydrogen release rate, and storage system and fuel costs. The approach includes assisting in evaluation of improved regeneration strategies for sodium borohydride (NaBH₄), examination of other boron systems such as the ammonia boranes (AB), and discovery and development of new chemical systems beyond boron.

Viable bench-scale chemistry from the center will be developed into engineered approaches and demonstrated as a viable storage system.



Question 1: Relevance to overall DOE objectives

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

- The PNNL project directly supports the goals of the President’s Hydrogen Fuel Initiative.
- This project fully supports the goals and objectives of the DOE Hydrogen Program. It is extremely relevant to the other center partners and serves to keep the research of the other center partners focused on developing materials that have the proper characteristics.
- The PNNL effort is a key component in the CHCoE, and the extensive work conducted by PNNL on the ammonia borane systems contributes greatly to the success of the CoE.
- AB is a key player in the chemical hydride effort. The high potential capacities (and relatively low desorption temperatures) of this material make this a potentially viable technology. But, of course, key barriers (capacity, rate, spent fuel regeneration) need to be overcome, and this effort is focused on those issues.
- SNH₃BH₃ has potential to meet the 2010 storage targets.
- Very focused project on a specific storage material with high capacities.

Question 2: Approach to performing the research and development

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

- Excellent mixture of experimental and computational tools. The approach is good, and seems focused on precisely the key barriers for this technology. Would be interesting to see more on the simple analysis of the energy efficiency of the various regeneration strategies.
- The approach for hydrogen release and material regeneration is well thought-out and well-focused. The critical issues and problem areas are being addressed in a careful and thorough way by a first-rate R&D team.
- A wide range of diagnostic tools and capabilities are being used to support the synthesis, testing, and modeling activities. Detailed analysis of this kind is essential for elucidating the mechanistic details and is enabling reasonable decisions to be made concerning future work on this complex system.

- The approach is completely focused on the technical barriers in the CHCoE. The engineering studies being conducted define the physical and chemical parameters that a material must have to ensure system viability. Engineering tools are being used to help direct research activities and to identify challenges.
- Solid work being conducted in parallel with the scientific studies on use of engineering-based tools to examine processes and system requirements.
- Very good approach that is focused at addressing the key issues.
- Stability of NH_3BH_3 is being investigated.
- Initial engineering system considerations are being factored in.
- Looked at additives to enhance kinetics.
- Important work on AB stability at relatively low temperatures e.g., 60°C .
- The most critical issue is still regeneration, and this is being aggressively attacked.
- Enhanced effort this year on regeneration.
- Good use of theory to guide digestion step in regeneration of AB.

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

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

- Although some questions remain concerning the nature of hydrogen release (e.g., reasons for sluggish second hydrogen equivalent kinetics, possible improvements in release rate with different additives and scaffolds), the PNNL team has done an excellent job of understanding and describing the release process. That aspect seems to be under control.
- Decomposition condition and mechanism of AB have been clarified through this project. This is expected to accelerate designation of a hydrogen generator.
- Very good progress on capacities and kinetics.
- Very nice to see the simple analysis of volumetric capacity.
- Use of new gas burette apparatus has yielded good results aimed at understanding release stages in AB.
- Showed rapid release in AB.
- Has found that surface chemistry controls plays a role in AB desorption in scaffolds, but has not made significant progress in understanding of how scaffolds work and how other scaffold materials might work. Responded to question on this by saying work was in progress.
- The emphasis on understanding and optimizing regeneration processes is a logical next-step that is being addressed in 2007. Excellent work is being done on exploring new strategies and approaches for digestion and disproportionation of spent fuel.
- One of the digestion pathways was demonstrated, although the result may be insufficient for the expectation. Efforts to find better digestion process should be continued.
- Progress on regeneration has been a little slower, but this, of course, is the most difficult issue.
- The engineering effort on hydrogen release from AB has studied the effect of additives on the release rate and their effect on the induction period.
- Stability of solid AB is being studied. Its stability is dependent on the source of the AB indicating that the purity of the material is important.
- Engineering studies have shown the 2015 targets are not attainable with pelleted AB. An ultra-low voidage approach or the release of more H_2 from AB greater than 2 equivalents will be needed. These are significant accomplishments this year and feed important information about materials properties that are necessary to meet the DOE targets that are system based.
- Accomplishments from the current FY are somewhat modest. Most of the ideas, and even preliminary results, were presented last year: nucleation and growth (Avrami) model, effect of additives, DADB mechanism, etc.
- Given the funding level, the results are fairly modest; the expectation for this funding level should definitely be higher.

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

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

HYDROGEN STORAGE

- Well connected within the center; appropriate amount of collaboration with other efforts.
- Perhaps it's not the right place for this discussion, but it would be nice to hear more about the International Partnership for Hydrogen Economy (IPHE) project.
- Strong collaboration within PNNL and across the entire CHCoE.
- Very good integration and use of collaborations.
- Appears to be very collaborative within center.
- Good new project started with IPHE partners outside of the center.
- Good use of capabilities of resources within PNNL that are supported outside of EE program (e.g., work supported by DOE's Office of Basic Energy Sciences).
- Collaboration with other center partners is very good as more promising materials are discovered.
- Theoretical studies by other center partners are guiding the efforts by the engineering team in the development of a regeneration scheme now that some promising regeneration routes are emerging.

Question 5: Approach to and relevance of proposed future research

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

- A logical plan is in place that builds upon the extensive body of work that already exists on this project.
- Testing/optimization of lighter-weight scaffold materials should be an important objective in 2008.
- Future research is well-targeted at the key issues.
- Identified good objectives for future work – increase capacity, increase kinetics, improve efficiency of regeneration, and new proposed regeneration scheme (1 pot).
- Future work on improving the kinetics of the second equivalent will be quite interesting.
- Understanding the reasons for the decreased rate of H₂ release for the second equivalent is important future planned work.
- Understanding the impact of light scaffolds and higher loadings on H₂ release will also be studied in 2007.
- Design of a hydrogen release system from AB is strongly related to dehydrogenation condition of AB. System image and operation condition of hydrogen generator using AB should be clarified even if the image were tentative.
- Establishment of digestion of used AB fuel should be accelerated to complete total regeneration process.
- Even more important work is planned in developing a regeneration process conceptual design in 2007.
- The focus on regeneration is crucial; it could ultimately be the show-stopper for this technology.

Strengths and weaknesses

Strengths

- The material system is a strong candidate for high-efficiency storage and off-board regeneration.
- Excellent basic science work and detailed material characterization supports the overall effort.
- The team has developed an impressive understanding of the hydrogen release process and how hydrogen liberation is facilitated by nucleation and growth processes within the material.
- High hydrogen storage capacity of NH₃BH₃.
- High release rates from the solid NH₃BH₃.
- Very focused on ammonia borane as a storage material and learning how to improve its major properties – kinetics, capacity, stability and regeneration.
- The engineering team appears to have strong capabilities to guide the materials development effort. Equally important is the interaction between the theory focused parts of the center and the engineering team.

Weaknesses

- Efficient regeneration remains a serious concern. Although this is clearly recognized by the PNNL team, it wasn't clear from the presentation if the team is converging on a workable solution.
- Difficulty of regeneration of NH₃BH₃.
- Progress has been a bit slow on the regeneration process development. As feasible chemistries are discovered, progress is expected to pick up.

Specific recommendations and additions or deletions to the work scope

- Recommend that even greater attention be paid to understanding and optimizing the regeneration processes (perhaps at the expense of the systems analysis work).
- Ensure steady feedback to the materials developers regarding materials properties that are required to ensure that a pathway to meeting the 2015 targets exists.
- Some work should be undertaken to identify impurities effects on the fuel and in the H₂ that is released from the fuel.
- None.

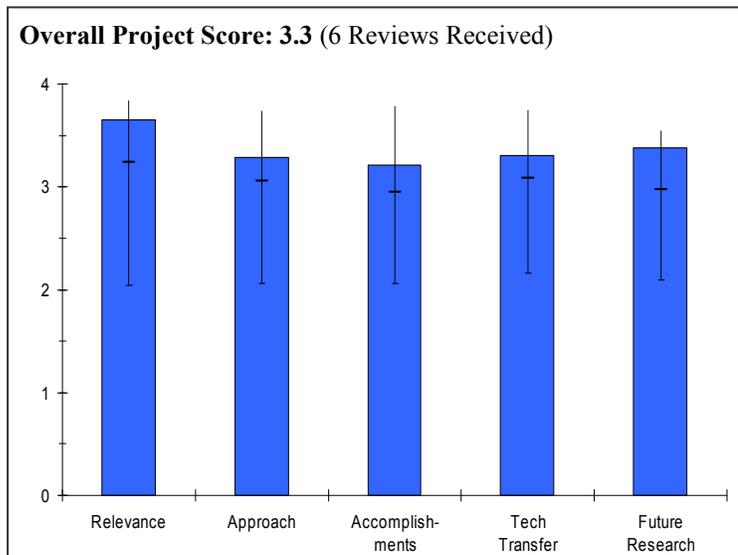
Project # ST-29: LANL Research as part of the Chemical Hydrogen CoE

Tom Baker; Los Alamos National Laboratory (LANL)

[NOTE: This review is for LANL's technical contribution to the CHCoE.]

Brief Summary of Project

The objectives of this project are to 1) provide materials chemistry support for Pennsylvania State University (PSU) work on electrochemical conversion of B-O to B-H; 2) liquefy ammonia-borane (AB) fuel and increase rate and extent of hydrogen release; 3) demonstrate chemistry and conduct engineering assessment for energy efficient AB regeneration processes; 4) continue to identify coupled chemical reactions that release hydrogen with near thermoneutrality; 5) work with International Partnership for the Hydrogen Economy partners to investigate M-B-N-H chemistry to identify potentially reversible storage systems; and 6) increase engineering efforts towards continuous processing.



Question 1: Relevance to overall DOE objectives

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

- The ammonia borane material has potential to meet the 2010 targets.
- Project addresses relevant issues for hydrogen storage in chemical systems that have the potential for meeting the DOE storage goals.
- Work is relevant to CoE for hydrogen release and regeneration.
- Project is relevant to DOE objectives.
- This project is extremely important to the center's work on developing a process based on ammonia boranes.
- The project fully supports the DOE Hydrogen Program RD&D objectives.
- What is the role of the International Partnership for Hydrogen Economy (IPHE) project in the overall effort?

Question 2: Approach to performing the research and development

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

- Very effective approach utilizing members' strengths and being focused on working towards the DOE targets. I compliment the center for cutting research projects, which did not seem promising for hydrogen storage, although they were interesting research topics.
- The approach features several paths in the effort leading to a 4th quarter 2007 down selection to the most favorable routes for H₂ release and regeneration.
- A good combination of theory, experiments, and engineering.
- The liquid ammonia borane approach has engineering advantages over solid ammonia borane.
- Have integrated theory and mechanistic studies.
- Good synergy with other amino-borane projects.
- Homogeneous catalysis work for hydrogen release is preliminary and no clear strategy was described on catalyst selection with respect to organic ligand choice, or other criteria. I would be interested in the criteria driving these choices, and this may be helpful when the transition in research proceeds to heterogeneous catalysts.

- Along that same theme, I am afraid (as is the presenter) that the characteristics suitable for a successful and selective homogeneous catalyst may not be easily reproduced in a heterogeneous catalyst system.
- Have increased focus on what was the main problem with these systems, regeneration.
- Regeneration does not seem to be efficient at the current stage of development. Further progress may require new ideas/approaches.
- Sulfur-based components of the regeneration process may be a problem if hydrogen is supposed to be used in fuel cells (due to the poisoning of the metal catalyst).
- At this time there are still activities underway on numerous fronts that give the appearance of being slightly unfocused. This perception is expected to change next year following the down selection process.
- The relationship between the engineering efforts at LANL and PNNL is unclear.

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

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

- Technical accomplishments have been good the past year. Unpromising work on acid-catalyzed dehydrogenation has been stopped. Significant progress on H₂ was made. A promising S-based regeneration scheme was identified.
- Excellent experimental work overall.
- The liquid amine-borane approach may have significant potential for higher capacities.
- Very good progress with the liquid amine borane systems – this shows that LANL is addressing the wt.% and thermodynamic problems being encountered with other systems.
- The new IPHE materials are very interesting, provided that they have a reasonable reversibility.
- Information given, though limited, shows that M-B-N-H systems could be promising.
- Theory is guiding work on new catalysts to ensure that at least 2.5 H₂ equivalents are released while keeping the products soluble.
- Mechanistic studies have elucidated reaction pathways for hydrogen release from AB.
- Beginning to understand catalytic chemistry needed to obtain desired products.
- It is too soon to assess, but I suspect that catalyst cycling/deactivation could become a big issue for the hydrogen release reaction.
- Progress was slowed somewhat by the effort required to install rapid catalyst screening capability at LANL.
- Considerable work on a regeneration scheme was shown which was not evident last year.
- Potential regeneration routes have been identified.
- Have identified regeneration chemistry and scheme which should be able to exceed regeneration efficiency goal.
- Concerns are from utilization of thiols for the digestion of B₃N₃H₆ as well as ammonia utilization in the BX₃ reduction. NH₃ and S are poisons to fuel cells, anodes, and membrane.
- It is not quite clear how the regenerated material is going to be separated from other products and purified.
- Scalability of the proposed synthetic approaches is to be determined yet.
- I would like to have heard more about work on engineering support for ammonia borane dehydrogenation and regeneration but the presentation was too rushed to cover the amount of information in the time allotted.
- It would have been helpful to include slides providing reference to last year's reviewer comments to help judge progress this year.

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

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

- Good collaborations through the center, particularly with Northern Arizona University and University of Pennsylvania.
- International collaboration on IPHE project.
- Collaborations with other members of the Center are evident.
- Good coordination with other groups, as stated in the presentation.
- Very good apparent utilization of each member's strengths.

HYDROGEN STORAGE

- Collaboration with other research institutions is excellent.
- Collaboration with materials manufacturing industry has room for improvement.
- Collaborations with the other center partners appear to be very good.
- The work at Intematix does appear to be well integrated with the efforts at LANL or with the rest of the center's efforts.

Question 5: Approach to and relevance of proposed future research

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

- Future work appears to be building on the results of the previous year's efforts in a logical progression.
- The plan shows technical consistency and commitment to reaching DOE target.
- The major effort in 2007 should be to work through the down select process to better focus the effort on only the most promising materials.
- All of the key issues are being addressed.
- The new IPHE materials may constitute an important new avenue.
- Catalytic work for increasing H₂ release is on track.
- MBN-H systems appear to have good potential.
- I would like to see more specific plans for catalyst development on hydrogen release, especially with respect to improving selectivity to the borazine route and transforming the lessons learned from homogeneous systems to heterogeneous ones.
- Future work is formulated in very general terms.
- Regeneration of boron-based materials deserves a stronger emphasis.
- Purification of AB after the regeneration deserves more attention.
- Determining if volatile products are in the H₂ stream released from the most promising materials should be part of the work plan for 2007.

Strengths and weaknesses

Strengths

- Ammonia borane materials have potential to meet the 2010 storage targets. The liquid solvent approach may make for easier engineering of storage systems.
- Approach and methodology (such as the new multisampling GC system.)
- Consideration of energy efficiency.
- Extensive collaboration.
- Very solid experimental work.
- Good understanding of the chemistry involved and possible engineering issues.
- The team has strong capabilities and appears to interact well with other center members. There is confidence that effective catalysts for H₂ release will be developed in 2007.

Weaknesses

- Hydrogen capacity levels and hydrogen release rates for AB in solvents are lower than for solid AB.
- Efficient and low cost AB regeneration must still be established.
- Collaboration with materials manufacturing industry has room for improvement.
- I would like to have heard more about work on engineering support for ammonia borane dehydrogenation and regeneration but the presentation was too rushed to cover the amount of information in the time allotted.
- It would have been helpful to include slides providing reference to last year's reviewer comments to help judge progress this year.

Specific recommendations and additions or deletions to the work scope

- Recommend to definitely continue this project.
- Clarify the interaction with Intematix in discovering new catalysts.
- Is the Tier 1 activity still necessary?

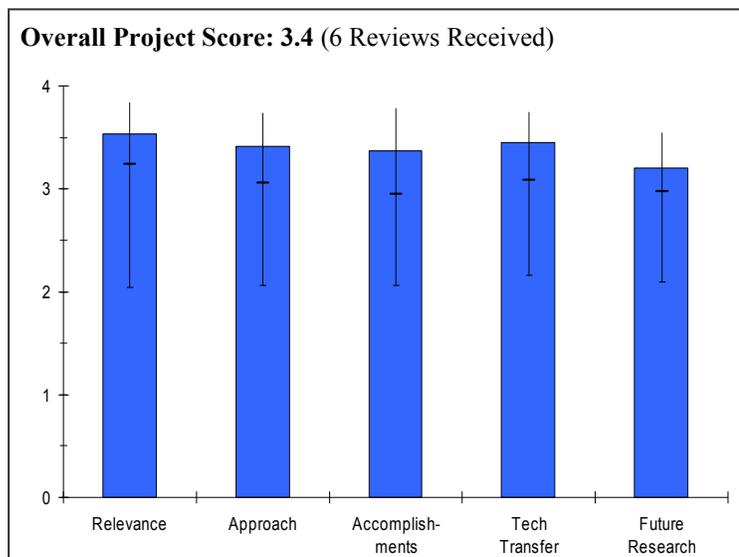
Project # ST-30: Main Group Element and Organic Chemistry for Hydrogen Storage and Activation*David Dixon; University of Alabama*

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are to develop promising approaches to chemical hydrogen storage for future DOE targets:

- Develop new chemistries to enable DOE to meet the technical objective: “By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt.%), 1.5 kWh/L, and \$4/kWh.; by 2015, 3 kWh/kg (9 wt.%), 2.7 kWh/L, and \$2/kWh” by using chemical hydrogen storage systems.
- Focus on organic and main group compounds to enable new chemistries which may be able to perform better for release and regeneration by improving the energy balance. This will provide longer term alternatives.
- Develop and implement imidazolium (carbene) based H₂ activation chemistry.
- Develop and implement systems based on main group elements. Examples: nitrogen and phosphorus.
- Develop and implement cyanocarbon systems for H₂ storage.
- Provide computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE Center of Excellence for Chemical Hydrogen Storage to reduce the time to design and develop new materials that meet the DOE targets.

**Question 1: Relevance to overall DOE objectives**

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

- This project is extremely relevant and supports the DOE objectives through both novel computational and experimental work. Additionally, this research supports and directs the experimental research efforts within the center through computational studies and also seeks to develop and conduct its own independent experimental research.
- The broad-based first principles calculations support many aspects of the Hydrogen Initiative. At a minimum, these calculations should serve to eliminate systems that have no potential to meet DOE RD&D targets for hydrogen storage. In the best case, they may identify classes of materials that do have target-meeting potential.
- This project is making significant and important contributions to the CHCoE.
- The project, developing chemical materials and reaction process for hydrogen storage is an important part of the chemical hydrogen storage CoE, and well aligned with the DOE target.
- Synergy between theory and experiment in understanding energetics, energy barriers, and kinetics is important. The PI is to be congratulated in this regard.
- Direct relevance through experimental developments.
- Computational work supports variety of activities at the CHCoE.
- Work on cyanocarbons offers interesting new possibilities for hydrogen storage capacities in the 10 wt.% range.

Question 2: Approach to performing the research and development

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

HYDROGEN STORAGE

- An ideal combined computational-experimental approach is used to direct the research. In particular, the computational methods are useful for determination of both thermodynamic and kinetic information (as applied to ammonia borane (AB)). These methods, however, seem to utilize gas phase data, which may not be adequate for these solid/melt reactions. Detailed comparisons/corroborations of experimental and computational data are needed to confirm reliability of models. Additional computational efforts have been devoted toward the evaluation of energetics for potential regeneration schemes for ammonia borane, a key barrier to the applicability of this storage material.
- Their independent organic-based work (cyanocarbons, carbenes, etc.) is also unique and implements both computation and experimentation toward optimization of hydrogen storage properties.
- The project provides important kinetic and reaction computational support to the CHCoE. And in addition, there is an experimental in-house effort in the development of new, novel chemical hydrogen storage materials.
- Theoretical approach to determine the accurate enthalpy of B-N-H species, reaction heats, and possible reaction paths is of great importance for exploring promising materials/reactions. It is also fine that these results have been transferred to other experimental team among the CoE.
- Develop new approaches and identify new concepts for improving release and regeneration by improving energy balance and provide theoretical support in the design of new materials.
- Experimental approach of this team does not seem to be linked closely with the theoretical part. The vision for this year is not clear. Their present target C-N-H materials contain 6-11 wt.% H, but it is not realistic that all the H can be used for the dehydrogenation/hydrogenation reaction under reasonable conditions. The expected storage capacity will not meet the 2010 target.
- State-of-the-art AB initio and DFT computational methods are employed in the theory part of the project. Claiming that calculated thermodynamic quantities are correct in the face of non-agreeing experimental data needs to be done judiciously.
- Carbene chemistry methods are used in the materials synthesis task. The focus is on control of the chemistry with respect to hydrogen storage capacity and optimization of dehydrogenation catalysts. Although not stated explicitly, the reviewer assumes that the focus is also on ambient temperature dehydrogenation processes.
- Two components in program – experimental material development and computational modeling. These appear to be quite different in scope and direction

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

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

- A significant amount of work has been done over a short period of time. The computational research on ammonia borane (mechanistic and in particular regeneration) is very useful and seeks to overcome key barriers. The combined computation-experimental approach to material discovery of novel organic molecular and extended storage materials has also progressed with several new and different systems under investigation. Continued evaluation of these newly synthesized materials is encouraged.
- A large number of calculations on a variety of relevant systems were presented. These studies encompassed the dehydrogenation pathways for selected amino-boranes and the spent fuel regeneration energetics. This work is important because it sheds light on the energetics of one of the most promising chemical systems that has a chance of meeting H-storage goals.
- Excellent progress was reported in both computational support activities and the experimental development effort.
- Experiment: Development of oligomerization procedure for making cyanocarbons with high gravimetric density of hydrogen.
- Computational: calculation of accurate thermodynamics and bond energies of $B_xN_xH_y$ compounds; energetics of carbenes, cyanocarbons.
- Modeled regeneration schemes for AB.
- Identified higher energy requirements for release of second hydrogen equivalent.
- Good results in the theoretical part.
- The results for the experimental work are not adequate.
- There is nothing overly exciting coming from the synthesis task (yet). The possibilities and practicalities of a photo-catalyzed, H-exchange approach need to be addressed next year. It isn't obvious to the reviewer that there could be "widespread applicability."

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

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

- Extensive and concrete transfer of knowledge, information, and expertise to a number of CHCoE members is evident. Evaluation of the dehydrogenation pathway of ammonia borane and its potential regeneration routes is particularly useful and relevant to the center activities.
- Collaboration with members of the CHCoE partners has been extensive and has made contributions to overall progress of the center.
- Theoretical results are well transferred to other teams working on amine borane among the CoE.
- The experimental collaboration is not clear.
- Close interaction of computational modeling with many Center partners.
- The computation supports multiple experimental studies by other members of center.
- Experimental program does not appear to have similar level of collaborations.
- Clearly, the computational portion of this project has broad collaboration within the CHCoE. It was not clear how connected the experimental task is to the rest of the CHCoE beyond some connection with LANL.
- The question is, who is defining the Alabama scope of work? Are the systems chosen for study at Alabama selected at the will of the Alabama PIs or are the decisions concerning research directions and specific systems for study made by the CoE in a consensus forming manner?
- Project is well coordinated with experiments.

Question 5: Approach to and relevance of proposed future research

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

- The future experimental research activities on the carbene systems (molecular and extended) are appropriately directed and show promise.
- Theoretical approaches and transfer to collaborator are expected.
- Support center activities by providing theoretical expertise.
- Develop improved reaction mechanisms based on predictions of reaction kinetics.
- Benchmark DFT against quantum chemical approach.
- Study polymerized carbene to increase capacity.
- Also will look at derivatives of cyanocarbons.
- Experimentally – synthesize extended carbene polymers, non-metal catalysts
- Connection between theoretical and experimental teams in this project should be organized in a better way.
- The FY 2008 plans (as presented) are a logical extension of the work done to-date. However, this reviewer has a few suggestions as follows:
 - Focus on compounds that have a chance of delivering at least 10 wt.% hydrogen during system operation. The minimum compensation factor for the effect of balance of system on material capacity requirements is around 1.6. It's likely to be greater than 2.0 for most of the evolving storage materials. That means the 6 wt.% H target for 2010 requires a material that stores 9 to 12 wt.% H.
 - If you plan to pursue the photo catalytic studies, be prepared to say how a photolytic process could be applied in a practical on board system or at a regeneration station.
 - Kinetics issues are as compelling as thermodynamic issues; put more emphasis into that aspect of the FY 2008 plan.

Strengths and weaknesses**Strengths**

- Multi-faceted, computational-experimental approach has been ideal for materials discovery and optimization. A great deal of high-impact research on diverse chemical hydride systems is clearly being explored.
- Activity in the theoretical part.
- Strong collaboration of the theoretical part with other members of the CHCoE.

HYDROGEN STORAGE

- The P.I. interacts well with other researchers in the center providing critical understanding of mechanisms.
- The computational modeling effort is an excellent resource for the center.
- Knowledgeable PI.
- Impressive publication record.
- Strong collaborations in the computational area.
- This is an outstanding project and is an excellent example of how the center concept should work in practice.

Weaknesses

- Experimental data should be compared with computational-based calculations to ensure that these gas-phase models are indeed adequate.
- Perspective of the experimental approaches.
- Connection between the theoretical and experimental teams within this project.
- Experimental portion could benefit from additional collaborations/interactions.
- Some concern about how the scope of work at Alabama is determined. It should be done by CoE wide consensus as mentioned above.
- No noteworthy weaknesses.

Specific recommendations and additions or deletions to the work scope

- Next year, present at a bit slower pace. Some slides went by so fast that it was not possible to grasp the significance of what they reported.
- The FY 2008 plans (as presented) are a logical extension of the work done to-date. However, this reviewer has a few suggestions as follows:
 - Focus on compounds that have a chance of delivering at least 10 wt.% hydrogen during system operation. The minimum compensation factor for the effect of balance of system on material capacity requirements is around 1.6. It's likely to be greater than 2.0 for most of the evolving storage materials. That means the 6 wt.% H target for 2010 requires a material that stores 9 to 12 wt.% H.
 - If you plan to pursue the photo catalytic studies, be prepared to say how a photolytic process could be applied in a practical on board system or at a regeneration station.
 - Kinetics issues are as compelling as thermodynamic issues; put more emphasis into that aspect of the FY 2008 plan.

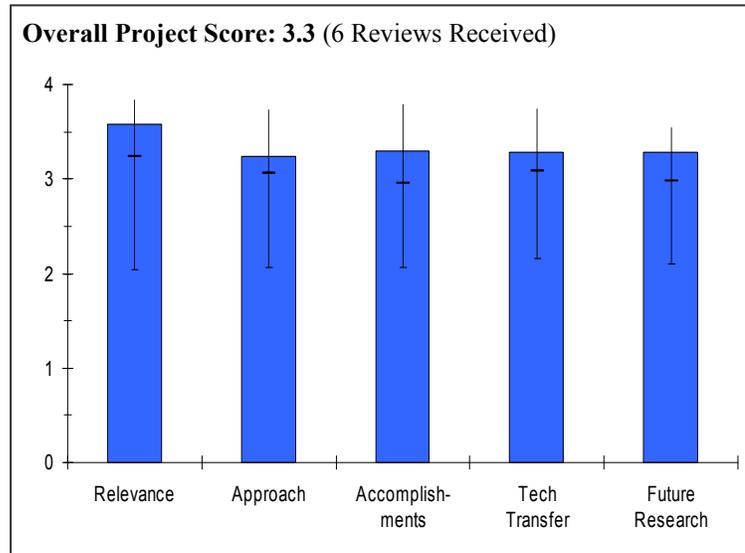
Project # ST-31: System Level Analysis of Hydrogen Storage Options*Rajesh Ahluwalia; Argonne National Laboratory (ANL)*

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

Brief Summary of Project

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

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

**Question 1: Relevance to overall DOE objectives**

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

- This work is exactly what is needed to be able to relate performance targets to the principal contributors to reevaluate their research with respect to the overall DOE goals.
- Project results, when validated, will be key to decisions narrowing-down storage pathways.
- Storage is a major barrier to hydrogen motive applications; therefore supports development of H₂ motive market.
- Appears to be providing a good decision-making tool for DOE.
- Determination of what projects to analyze coming from DOE makes this even more relevant.

Question 2: Approach to performing the research and development

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

- May need to tighten some of assumptions for more realistic/ less optimistic analysis.
- Characterization of the DeH₂ [dehydrogenation hydrogen] reactor is excellent.
- Good technical work but I would like to see other reactor systems, besides trickle beds, considered.
- Generally very well designed and focused.
- Could provide more information on assumptions used – volume, etc.
- Could include sensitivity analysis of effects of changes to design – insulation thicknesses etc – to not overload the scope this could be focused on the models currently developed and should provide useful guidance to the DOE on future requirements to achieve storage targets.
- The approach is rather hard to judge from the presentation, as it would vary for each analysis since the focus for each analysis could be completely different. This is the nature of this type of work, and not a fault.
- The approach to the two analyses reported look reasonable, for the most part, although I question the importance of some of the parameters deemed important for the cryogenic pressurized tank. The hydrogen

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loading for the compressed gas should not be critical here. The tank is designed to overcome this by using liquid hydrogen for long trips.

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

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

- PI accomplished an impressive array of tasks during the year under review.
- System analysis presentation is good.
- Work with LH₂ is excellent and should inform further research in LH₂ and MHC_oE.
- The reverse engineering approach is good.
- Future potential is not clear because the condition of calculation is not clear.
- Very well-managed, particularly with the diverse partnership involved, and appears to be well on-target and to plan.
- Addition of some sensitivity analysis on current designs should provide sufficient depth for assessment of design parameters required in future for storage systems. This may change as other storage options become available (are developed) however.
- I've found some of the presentation graphics hard to follow, especially some of the bar charts showing results and sensitivity analyses.

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

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

- Good breadth of involvement.
- This is rather difficult to judge. Interactions are shown on the overview page, but little was said about it.
- It is assumed that at least there is tech transfer with the projects being analyzed.
- There are five publications noted.
- Some interfacing with TIAX noted in "backup slides".
- It will be critical to project success to ensure close and continuing collaboration with CoEs and other PIs.
- Further early integration will improve accuracy and relevance of analytic results.
- The demonstrated close relationship with the APCI team needs to be replicated with other CoEs.
- It is not clear how the results of this work will become part of the different CoE performance targets and goals. Will this be communicated through DOE or directly from ANL to the CoE or principal contributors?
- Should these results be used to update the Hydrogen Storage targets? For example, should the gravimetric goal also include storage efficiency and hydrogen release conversion? Presumably, these would be specific for chemical storage, metal hydrides, and carbon adsorbents.

Question 5: Approach to and relevance of proposed future research

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

- Appears achievable and well-structured.
- This effort is externally dependent on progress elsewhere in H₂ storage. Provided there is close cooperation and adequate data exchange, it would be unfair to penalize the analysis effort based on go/no-go decisions taken in the centers.
- Care must be taken not to go too far down the analytic path on systems that are still evolving within the CoEs. To do so, risks reaching a negative analytic conclusion on a research strand that has not yet been optimized within the CoE.
- I would like to see the same systems analysis as soon as possible for metal hydrides and carbon adsorbents.
- In addition to this independent study, it would be good to have an outside firm perform a similar analysis to see how closely the results and conclusions agree.
- This looks good, especially looking at some carbon storage.

Strengths and weaknesses**Strengths**

- Good program to guide principal investigators to revise their research to achieve more realistic progress toward meeting DOE goals.
- Strong leadership.
- Breadth of involvement.
- Links with other projects such as TIAX cost analysis.
- Provision of overview of design options and issues to overall DOE projects.
- Good diversity in projects analyzed.
- It combines the physical properties and the volumetric/ gravimetric system performance for the scientist.

Weaknesses

- Even given the pressure of a 20-minute presentation, it would have been beneficial to hear a broader overview of the team's analytic activities.
- It only gives a rough idea of how to improve performance, even through it is a very complicated process.
- If possible, simplify the input parameters for the easy estimation by the chemist/scientist.
- If this is the technical assessment- lack of issue raised to reach the potential, such as using the AL for the outer shell [lacking in identifying issues for reaching potential performance].
- Effect of uncertain design focus due to continuing developments.
- Some presentation materials were hard to follow.
- Perhaps there is the need for a closer look at how a project fits in to the overall HFCIT program rather than just using hard targets.
- While there may be adequate qualifications for ANL to do analyses such as these, I always question situations where National Laboratories (or other organizations for that matter) who have other funded projects within a particular program are asked to perform analyses that may involve comparisons of their own organization's projects with other projects. Independent analyses should be just that. (Note that I am not saying that there *was* anything untoward here; I seriously doubt that there would be. It is better, however, not to have even the possibility of perception.

Specific recommendations and additions or deletions to the work scope

- Some of the underlying assumptions need to be crossed-checked with other stakeholders. For example, how does integrating FC operation to ATO with only 80% hydrogen consumption affect the vehicle? Would OEMs accept this? How about the transient driving cycles vs. buffer tank or battery requirements (i.e. wt.% and vol%).
- Scope appears adequate to present need.
- An extension may be required depending on the timelines of the CoEs.
- Care must be taken not to go too far down the analytic path on systems that are still evolving within the CoEs. To do so, risks reaching a negative analytic conclusion on a research strand that has not yet been optimized within the CoE.
- Addition of some sensitivity analysis on current designs should provide sufficient depth for assessment of design parameters required in future for storage systems.
- Perhaps there is the need for a closer look at how a project fits in to the overall HFCIT program rather than just using hard targets.

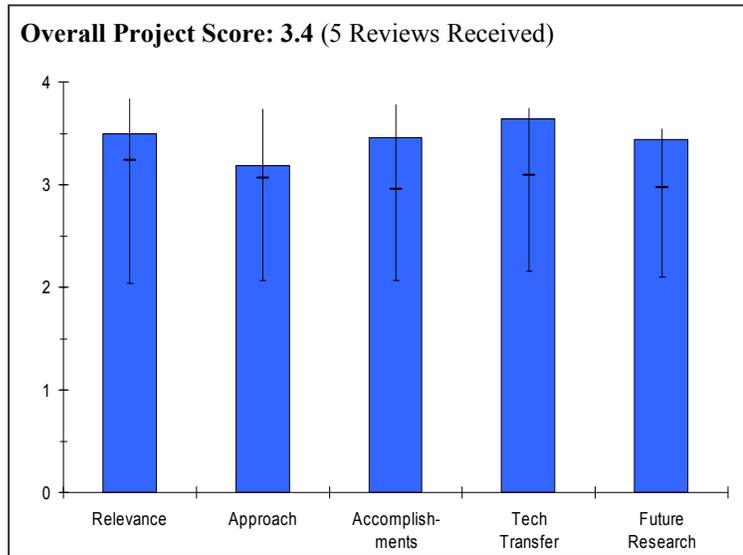
Project # ST-32: Analyses of Hydrogen Storage Materials and On-Board Systems

Stephen Lasher; TIAX LLC

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

Brief Summary of Project

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



Question 1: Relevance to overall DOE objectives

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

- Cost of storage is important and the various pathways and options need both technical and economic evaluation before a valid storage option can be identified and these are key for supporting the introduction of a hydrogen motive market.
- Cost analysis of off-board and on-board hydrogen storage systems and technologies is an important part of the DOE hydrogen program.
- This effort provides valuable trend comparisons of the different types of storage and the factors that make up the total cost.
- This analysis is clearly a success requirement.

Question 2: Approach to performing the research and development

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

- Well structured and clear view of process.
- Excellent design, provided that models are recharged with new data from the CoEs as their efforts evolve.
- Need to cross-examine some of the assumptions to develop more realistic / less optimistic outlook.
- Needs sustained effort to integrate with H2A.
- Issues surrounding the volatility of the data and technology due to the unproven or developmental state of these has been taken in to account – reference factors compensating for safety information – good.
- Good use of sensitivity analysis.
- Flow charts very useful and presentation format showing flow of project and matrix of work undertaken and position of different types of storage very good and clear – appreciate matrix summary in presentation.
- More effort to put analyses on the same basis would be beneficial.
- Safety (sensors, etc.) systems are not included.

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

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

- Good progress on tank and on-board systems. Novel carrier work should progress in parallel with CoE effort.
- TIAX has provided relative costs of different storage systems and technologies. This information will help DOE with go/no-go decisions.
- Project appears to be very well managed.
- Revision to H2A for liquid carrier and recharge could be more fully explained.
- Although at 41% complete, very impressed with volume and quality achievements to date.
- Outstanding barrier that may be difficult to completely overcome is the current fluidity on the ultimate design of the storage devices – outstanding issues such as safety components, etc.

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

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

- TIAX is in close and frequent contact with the hydrogen storage stakeholders and energy providers to ensure appropriate technical and cost assumptions.
- Good to see that all these areas are being communicated with and are part of the partnership.
- Appears that communications are working however would have some concerns about the possibility of missing details because of the number of areas involved.
- Strong collaboration with delivery companies will be required to validate forecourt costs and options.
- Face-to-face meetings might be valuable to save time and validate approaches.

Question 5: Approach to and relevance of proposed future research

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

- Future work is logical – finalizes the preliminary results presented at AMR 2007.
- It will remain important for the PI to stay current with improvements made outside of the CoEs that are related to storage needs, e.g., progress in cryo-tank design for medical use. Progress may come from this extremely competitive industry that could be applicable to this analysis.
- Very interested to see the output- and appears to be achievable.
- Would also like to see greater certainty in some of the cost assumptions but understand the current design situation.

Strengths and weaknesses**Strengths**

- This project has provided very valuable data and is an important part of the entire storage program.
- An excellent start on a key need for the H₂ economy.
- Strong management and structured approach.
- Applicability of output.
- Focused on applicable/possible storage options.
- Clear publication of assumptions is both a requirement and a strength.

Weaknesses

- More work needs to be done to include the total costs to each possible solution in the analysis.
- Some method needs to be found to take out-of-scope cost savings into account. For example, if one were to discover a liquid storage solution, the savings from costs avoided needs to be factored in. Total cost per mile driven is the only real metric.
- Assumptions currently need to be made to allow for costs, through factorization, of some areas, such as safety, due to current uncertainty of the design requirements.

Specific recommendations and additions or deletions to the work scope

- As more cost estimates and GHG emissions data are generated, the developers need to examine the accuracy and cross-check the validity of the original assumptions (e.g., taking into account the commodity cost rise in the past three years or more accurate information on high strength carbon fibers...). On this basis, it is recommended to periodically revisit the previous estimates made in previous years with updated information.
- Substantial effort will be required to validate cost estimates associated with newly emerging chemical storage options.
- It will remain important for the PI to stay current with improvements made outside of the CoEs that are related to storage needs, e.g., progress in cryo-tank design for medical use. Progress may come from this extremely competitive industry that could be applicable to this analysis.
- Strong collaboration with delivery companies will be required to validate forecourt costs and options.
- Some method needs to be found to take out-of-scope cost savings into account. For example, if one were to discover a liquid storage solution, the savings from costs avoided needs to be factored in. Total cost per mile driven is the only real metric.

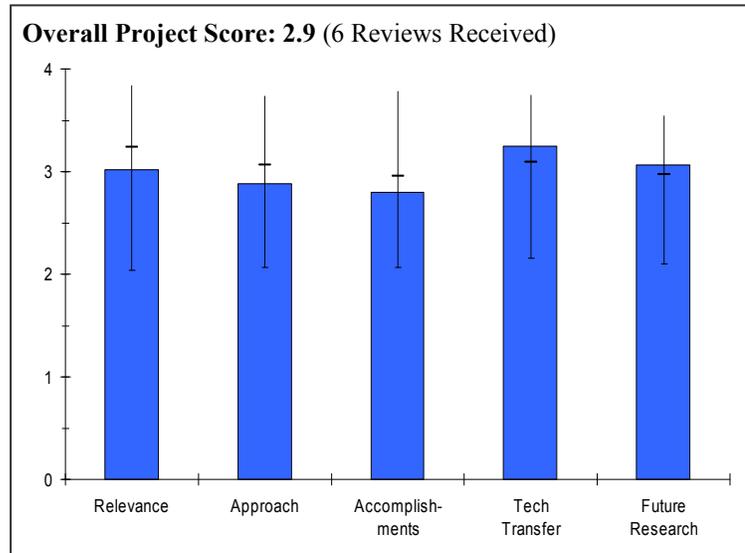
Project # ST-33: International Standardized Testing Protocols for Hydrogen Storage Materials*Karl Gross, HyEnergy*

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

Brief Summary of Project

The objective of this project is to develop and publish a reference document on best practices and limitations in measuring hydrogen storage properties of materials, including kinetics, capacity, thermodynamics and cycle life. The benefits include:

- Transferring the knowledge and experience in making critical performance measurements from experts in this field to the entire hydrogen storage research community.
- Aiding in the establishment of uniform measurement practices and presentation of uniform performance data.
- Providing a published resource to aid those just entering to this rapidly expanding field.
- Improving international communications on these issues among government, university, and industry entities and enabling the reporting of data using standardized measurement techniques.

**Question 1: Relevance to overall DOE objectives**

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

- This is an important project in the DOE RD&D portfolio. It will not provide the breakthrough discovery, but will assist in the establishment of uniform measurement practices and presentation of performance data. This way, it can facilitate the researcher's quest for the material that "could make the difference".
- Standardized testing procedures for candidate hydrogen storage materials would clearly be of value to the advancement of the program.
- This short project indirectly supports the DOE Multiyear RD&D plan. The resultant product will help make the absorption/desorption test procedures consistent among all DOE contractors working to meet storage materials targets.
- If the results can be quickly or fully disseminated, they would be helpful to new researchers entering the field. For senior PIs, this is frankly a limited utility, given work underway elsewhere in the Program.
- Provides support of hydrogen storage projects.

Question 2: Approach to performing the research and development

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

- Quite a straightforward, effective approach, tackling the main issues for conducting critical performance measurements - kinetics, capacity, thermodynamics and cycling life.
- The gathering of information through compiling of literature data and obtaining input from an international group of experts has been excellent. However, it is not clear how, or even if, this information can be assimilated into useful write-ups of generalized, "best practices" procedures.

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- The approach is good. The project will review literature, personal experience, experts' experience and advice, etc., on testing. The overall objective is to develop an open best practices document to cover definitions and procedures.
- The main aim is to reduce errors and improve measurement efficiency.
- It will help train new experts in the field. The reference document will be available to all.
- The project aims to cover the important properties: kinetics, H-capacity, thermodynamic stability, cyclic stability, activation and exit gas impurity measurement, among others.
- Success will be directly dependent on the degree to which the PI is able to secure the cooperation of CoE PIs and others who are actually working in this area.
- The objective is to generate documentation on measurement techniques applicable to hydrogen storage materials development - kinetics, capacity, thermodynamics and cycling behavior.
- Relies mainly on PI's personal experience, but also includes some input from other experts.
- Plans to use post-graduate student for some of the work.
- Documentation should be applicable to all forms of storage materials - hydrides, adsorption materials, chemical hydrides.

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

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

- Appears to be on time and on good track. Task 1 is close to completion and first deliverable is to be released soon. Data and feedback have been supplied by a number of experts in the field.
- No generalized, "best practices" procedure write-ups have been produced.
- Work has only recently begun.
- The kinetics part is about 70% done and should be delivered to DOE in draft form in two weeks.
- Work is well under way on the PCT testing.
- Some of the analysis and writing work is being done by a graduate student from UC Berkeley.
- Too early in the project to provide substantive comment.
- New project, but has initiated some documentation on one of the specific areas, namely kinetics, defined in the project.

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

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

- Experts' involvement is already engaged in this project. Strong interface and interaction also at international level.
- The outcome of this project will be a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials and will be made available to all.
- Input has been obtained from an outstanding group of international experts.
- There are many well-known and experienced collaborators contributing to the project.
- This is part of an international IEA project, including Japan and Australia.
- Outward transfer of information will be key to project success, but it is too early to determine if or how this is occurring.
- External collaborator list appears strong.
- Some collaborations with IEA experts, so has some international input on measurement techniques.

Question 5: Approach to and relevance of proposed future research

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

- Near future plans are reasonable and well drawn, targeting specific barriers.
- The project though could benefit from interactions with the standardised testing facility of the SwRI which at the moment are not obvious.

- A draft of a "best practices" manual is underway. However, there appear to be no plans for the evaluation of the practical utility and subsequent refinement of the document.
- Finish survey work and report as planned.
- Appropriate start.
- Significant effort will be required to stay current with, and gain methodological agreement from PI working with new chemical storage materials.
- Proposed future work is well defined in terms of limited scope of project.

Strengths and weaknesses

Strengths

- Providing a published resource, transferring knowledge and experience particularly to new entrants in this field.
- Getting all interested parties, and particularly experts in field, involved in drawing uniform measurement practices and presentation of performance data.
- The PI is a world class expert in the measurement of the hydrogen storage properties of materials.
- A testing protocol is needed for standardization and error minimization.
- Project is being done over a very short time frame.
- It will get clear after this program is successfully completed.

Weaknesses

- Lack of plans for: 1) the assimilation of gathered information and 2) a method to obtain feedback about the practical utility of the reference document.
- Less "fascinating" topic if compared to material synthesis and development work.
- It may be prove difficult to get acceptance from the whole research community and particularly from laboratories where these measurements are routinely performed for a number of years.
- None.
- Why is data more than one year old being presented at this Review?
- At this moment it is too early to asses the result.
- It is not clear how valuable this project will be to storage program, since essentially all of the program participants are fairly knowledgeable on measurement techniques. New PIs, particularly those within centers have good resources to draw upon for help in either guiding measurements or performing them. Indeed, the examples shown in the presentation were generally drawn from results previously generated within the program.

Specific recommendations and additions or deletions to the work scope

- Liaise with the SwRI standardized testing facility.
- Could also address sample handling conditions and respective protocols integrating feedback from experts.
- Publicize final deliverables/reports in order to gain full acceptance of the quality of the reference document(s) by the research community.
- No changes recommended.

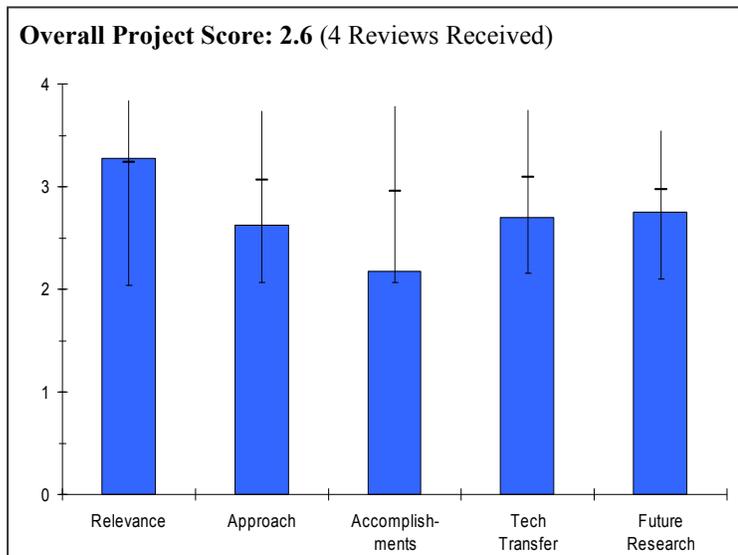
Project # STP-02: Conducting Polymers as New Materials for Hydrogen Storage

Pen-Cheng Wang, presenting; Everaldo C. Venancio, Alan MacDiarmid (Deceased), PI, University of Pennsylvania

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The goal of this project was to identify and further develop the conducting polymer species previously reported to give ~8 wt.% hydrogen storage capacity. The project involves confirming that 8 wt.% hydrogen storage is achievable in doped forms of organic conducting polymers, polyaniline and polypyrrole; determining optimum polymer preparative methods, chemical composition, oxidation state and polymer crystallinity and morphology to give quantitative optimum conditions of hydrogen adsorption and desorption; and investigating hydrogen storage by other known types of organic conducting polymers in their semiconducting and metallic forms.



Question 1: Relevance to overall DOE objectives

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

- Polymeric compounds represent a class of relevant materials to research for hydrogen storage. In particular, these polyaniline species are valuable to investigate as to confirm or dispute varying results which have been previously obtained.
- Generally addresses DOE goals. Success using this approach would represent a potential breakthrough in hydrogen storage.
- Project is aligned with DOE goals for hydrogen storage.
- Relevant confirmation of H₂ storage in polyaniline.
- Developing a better understanding of the nature of H₂ adsorption/desorption in polymeric materials, as well as the preparation methods that optimize H₂ uptake, is critical for developing organic-based H₂ storage materials.
- Understanding why a literature-reported result is not reproducible is valuable in helping to identify experimental shortcomings that may lead others to false conclusions.

Question 2: Approach to performing the research and development

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

- While the general approach to investigate the dependence of heat-treatment on the storage properties is important, it was not clear what specifically was different about the compositions (only two) that were presented. It is presumed that more than two preparation/activation methods have been attempted?
- The work in 2006 focused on identifying and understanding the properties of the polyaniline chemical sub-species undergoing reversible hydrogen sorption. The studies were conducted using combined TGA-mass spectrometry techniques. Although these methods are useful for preliminary assessments, they provide only very qualitative information concerning the amount of hydrogen release and the overall sorption behavior of the material.
- Addresses technical barriers.

- Experimental approach allows for identification of nature of the polyaniline used in the adsorption/desorption studies.
- Approach appears adequate but not comprehensive.
- Use of spectroscopic techniques to characterize the polymer systems should be incorporated into approach. It appears that techniques such as UV-VIS, SEM, NMR were used in previous years. Why were they not included in current approach?

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

This project was rated **2.2** based on accomplishments.

- In general, there seemed to be a limited variety of samples made and testing done. Additionally, this group seems to rely primarily on TGA measurements for hydrogen desorption data. Given, the resources of the sorption CoE, they should also utilize other techniques (i.e. PCT, NMR, IR, etc.) data to fully characterize samples.
- It was shown that a specific form of polyaniline (PANI-a-II) could store up to 2.8% hydrogen. The researchers were unable to replicate the higher capacity result (~6%) reported earlier by other workers. Only very qualitative information was available concerning the amount of hydrogen released upon heating. This made it difficult to evaluate the results in a meaningful way.
- Demonstrated H₂ adsorption of up to 2.8 wt.% on polyaniline.
- Demonstrated effect of thermal treatment on H₂ adsorption in polyaniline.
- Identified potentially critical issues that may invalidate previous studies reporting high H₂ adsorption on polyaniline.
- Minimal results, appears that work at Penn may have suffered as a consequence of the loss of Dr. MacDiarmid.
- Did address previous reviewer's comments by providing TGA and H₂ uptake measurements.

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

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

- The group seems to be leveraging some measurement techniques internal to their university as well as other institutions, however, it was not evident that a great deal of collaboration within the sorption CoE was made.
- There is a collaboration between workers at Penn, U of Houston, and U of Texas-Dallas. However, only a marginal connection with other partners in the HSCoE is evident.
- Collaborations with NREL and the University of Houston appear to be fruitful.
- The only role of collaborators at U of Texas-Dallas and U of Houston seem to be to provide results from characterization studies. Collaborators do not seem to be actively involved in the research aimed at improving the technology.

Question 5: Approach to and relevance of proposed future research

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

- The future work is appropriate and relevant to the objectives of the project. In particular, additional characterization of the materials and hydrogen adsorption sites is important. PCT investigation would also highly supplement the TGA and TPD measurements that have been done thus far.
- Consideration of other new polymeric compounds for hydrogen storage would also be beneficial.
- Future research plans were not adequately motivated or described (i.e., What specific problem/issue is being addressed? What is the impact?).
- It is not clear whether the proposed plans will provide much meaningful insight into either the mechanism or optimization of the material for hydrogen storage applications.
- Proposed NMR and neutron diffraction studies should be quite useful in proof of adsorption- decorated polyaniline may lead to higher H₂ uptake.
- Neutron scattering measurements could provide valuable insight on H₂ adsorption sites.

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- Introducing trace metals may improve H₂ uptake.
- Critical assumptions and issues should be incorporated into future research and addressed.

Strengths and weaknesses

Strengths

- Relevant work and extremely competent team.
- A novel hydrogen storage material system is being investigated by a research group that is internationally recognized in the field of conducting polymers.
- Careful sample preparation and identification.
- Team has done a good job to show that literature-reported H₂ uptake by polyaniline is probably not correct and that the maximum H₂ uptake appears to be 3 wt.%.
- Good work from previous years to improve our understanding of oxidation states of polyaniline.

Weaknesses

- The pace and degree of exploration seem limited.
- The idea and potential motivation for the project are interesting, and the work should be pursued. However, the overall project plan is very sketchy and the description of future work is unclear.
- The team should work more closely with other partners in the HSCoE to provide a more quantitative description of the amount of hydrogen absorption and release.
- Need to identify a project leader to replace Dr. MacDiarmid. This is critical if the project is to progress.
- Should consider broadening effort to investigate other conductive polymers now that literature-reported 6 wt.% H₂ loading on polyaniline does not appear to be achievable.

Specific recommendations and additions or deletions to the work scope

- Focus on quantitative measurements of hydrogen uptake/release.
- Focus on providing a more detailed description of hydrogen sorption in polyaniline and why certain sub-forms of the polymer will be more active.
- Provide a description of anticipated performance of an optimized PANI at realistic hydrogen delivery temperature in on-board fuel cell applications.
- "Go/no-go" type decision should be made on polyaniline and approach. Should approach be radically changed or redirected?

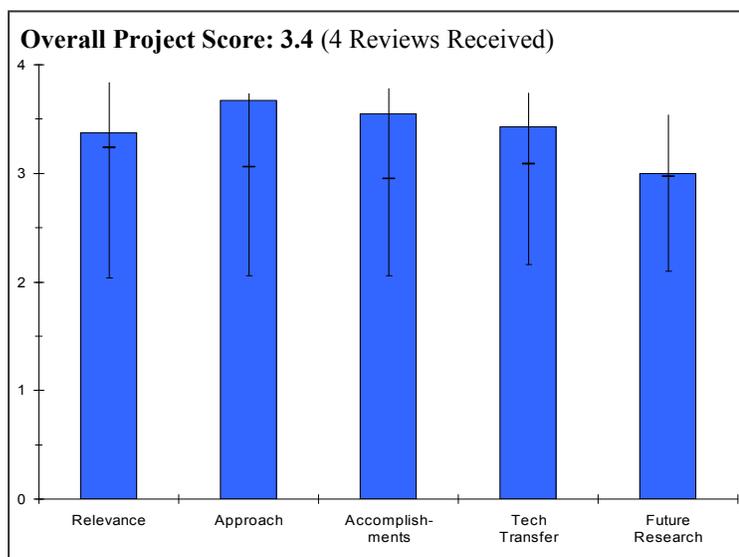
Project # STP-03: Characterization of Hydrogen Adsorption by NMR

Yue Wu (PI), Alfred Kleinhammes, Co-PI, University of North Carolina

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The University of North Carolina is using NMR techniques to support team members of the DOE Hydrogen Sorption Center of Excellence in developing reversible materials with 7 wt.% (material) gravimetric capacity, with potential to meet DOE 2010 system-level targets. In 2007, the objectives of this project include 1) expanding the capability of the NMR adsorption system to low temperatures (77K) along with the high pressure capability (100 atm); 2) carrying out adsorption studies of single-walled carbon nanohorns; 3) understanding the effectiveness of B-doping in enhancing binding energy in graphitic carbon; and 4) analyzing the structure of B-doped carbon using NMR.

**Question 1: Relevance to overall DOE objectives**

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

- Detailed and reliable characterization methods which can monitor the hydrogen adsorption/desorption process in-situ are highly valuable and critically support the sorption CoE (whose materials are often amorphous and thus more challenging to characterize). Quantification of hydrogen binding energies and hydrogen capacity are essential to this center's efforts and should be increasingly exploited. It should also be reiterated that it would be of additional value to corroborate these NMR-based measurement values with other techniques.
- Sorbents have long been one of the most promising but also the most controversial class of materials in the DOE portfolio of potential, high performance hydrogen storage materials. Resolving the long standing disputes relating to the hydrogen storage capacities and hydrogen binding energies of many members of this class of materials is a key barrier to their development.
- This work provides valuable information on amounts of hydrogen adsorbed and locations of adsorption sites. Such information is important to the development of hydrogen sorbents.
- This project proposes a powerful tool to characterize the sorption properties of hydrogen in materials.

Question 2: Approach to performing the research and development

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

- The techniques used appropriately focus on evaluation of hydrogen capacity and binding energy, and instrument capabilities are broadly able to examine both low temperature (to LN₂) and high pressure conditions. The only apparent gap in measurement protocol is to validate NMR-based data with data from other techniques (experimentally conducted at same pressure/temperature). Although slight differences in values are expected due to sample variation and/or instrumental errors, in general, there should be correlation.
- Solid state NMR spectroscopy provides a means for the reliable determination of the hydrogen storage capacities and hydrogen binding energies associated with this class of materials.
- The development of 77K capability is very good.
- NMR capabilities are very good.

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- NMR is an important tool to identify the nature of hydrogen binding in sorbents that can be used in virtually all the sorption projects.

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

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

- It is good to see increased collaboration with other projects in the sorption CoE (NREL and ORNL measurements in progress) and evaluation of a few materials under different pressure-temperature conditions. Given the demonstrated capabilities of this method, increased utilization of this tool for other systems in the HSCoE, such as the cross-linked SWNT (Rice) and Pt-spillover MOFs (Michigan), etc., is encouraged.
- Methods and hardware have been developed that allow the reliable measurement of storage capacities and binding energies associated with physisorbed and chemisorbed hydrogen. Notably, the investigators have, for the first time, determined the hydrogen capacity and binding energies of boron doped graphite through NMR techniques.
- It would have been useful to have established a calibration of the NMR hydrogen capacity measurements earlier in the project. Materials should be tested that have been corroborated by measurements at SwRI.
- Measured the binding energy of hydrogen in B doped materials (11.2 kJ/mol). Can estimate the relative contribution of adsorption sites to overall hydrogen uptake.

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

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

- This project's impact is highly dependant on the amount of collaboration that occurs with other sorption CoE projects (and other CoEs in general). Transfer of samples/data between partners seems established for NREL and ORNL and should continue to expand to others in the center.
- Good collaborations with the synthetic groups within the HSCoE. Further collaboration with groups specializing in the synthesis of MOFs is recommended.
- The project has many collaborations and the more studies that this project can perform on materials with significant potential, the better. Collaborations to run MOF materials are especially encouraged.

Question 5: Approach to and relevance of proposed future research

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

- Proposed plans are sound and are based on continuation of present studies (of SWNHs and B-doped graphite). As mentioned in the future work section, more focus should be placed on exploring other new sorbent materials in the center (i.e. Pt-spillover MOFs and cross-linked SWNTs). Additionally, it would also be beneficial to continue to fully evaluate each sample under a variety of conditions, both at low (~77K) and room temperature and during hydrogen desorption and adsorption.
- Future plans are too focused on materials which do not seem likely to reach the DOE targets.
- Can this project provide any useful insights into the mechanisms of hydrogen spillover at room temperature? NMR characterizations on unpromising materials should be kept to a minimum.
- Logical next steps.

Strengths and weaknesses

Strengths

- Valuable tool developed and proven for evaluation of hydrogen binding energy and capacity for physisorptive materials. This project highly compliments and supports the sorption CoE.
- NMR methods have been developed that allow the reliable determination of the hydrogen capacities and binding energies of sorbant materials.
- Technique for measuring both hydrogen content and hydrogen location in sorbent materials.
- Very important tool to advance the comprehension of the sorption process in materials.

Weaknesses

- The ultimate success and impact of this project is dependent on collaboration with its partners. Therefore, this technique should be integrated as a tool accessible to all sorption CoE partners and samples should try to be filtered through UNC as part of standard testing.
- Additional validation of NMR-based data with other techniques should be performed regularly on new samples.
- Project is concentrated on materials that are unlikely to meet the DOE targets.
- Hydrogen content measurement values need better calibration.

Specific recommendations and additions or deletions to the work scope

- Investigation of cross-linked SWNTs (Rice) and Pt-spillover MOFs (Univ. of Michigan).
- Scope of project should include the study of more advanced MOF materials.
- Studies of hydrogen spillover mechanisms should be included.
- NMR to characterize spillover (spilled-over H atoms physisorbed or chemisorbed)?

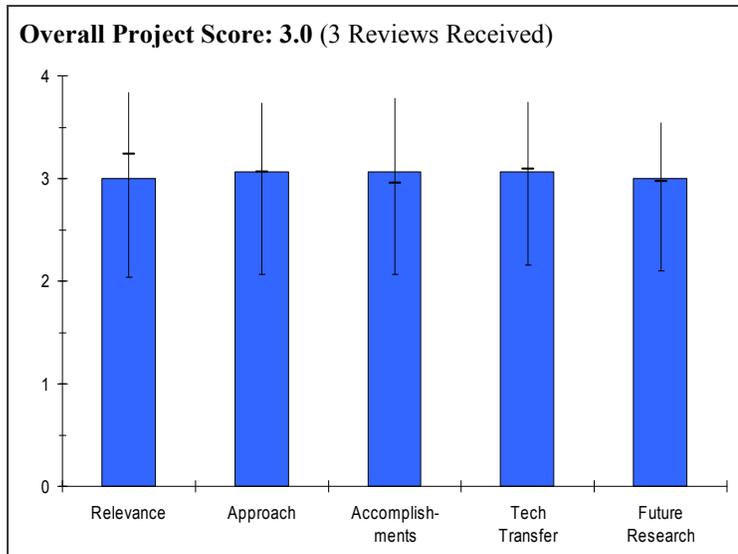
Project # STP-04: Synthesis of Small Diameter Carbon Nanotubes and Microporous Carbon Materials for Hydrogen Storage

Jie Liu; Duke University

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

Goals of this project include demonstrating the storage potential of small diameter single walled carbon nanotubes and mesoporous carbon materials with metal loading to meet or exceed the DOE 2010 goal for both gravimetric and volumetric capacity. Work is underway to understand the effect of diameters of nanotubes on their hydrogen storage properties; develop a method to precisely control the diameter of the produced nanotubes; understand and demonstrate the effect of metal loading on nanotubes on the hydrogen storage properties; synthesize mesoporous carbon materials with high surface area; and study the effect of metal loading on mesoporous carbon on the hydrogen storage properties.



Question 1: Relevance to overall DOE objectives

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

- The project serves to a certain extent the DOE objectives and supports the Hydrogen Program.
- Project on growth methods and conditions for nanotubes as well as SWNT purification is not completely novel but mostly incremental. Work on porous carbon generation from micelles precursor is a new direction and seems very promising in terms of meeting the DOE's goals regarding production scale-up and cost.
- This is one of several projects with new materials that could be important if there is a breakthrough in storage capacity.

Question 2: Approach to performing the research and development

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

- Following the No-Go decision on pure SWNTs, the project strategy has been redesigned, transferring existing knowledge on the pore size control of SWNT to the microporous carbon materials. Investigation of the effect of pore size and volume control on the binding energy of microporous carbons by using templates and its impact on their storage capacity.
- The porous carbon materials also offer an ideal template to study many physical phenomena including doping, spillover and pore size effect on carbon structure. The porous carbon production method is promising with regards to cost, scale-up and particle addition to the substrate. Very flexible system for control of many of the parameters.
- Research approach is narrow but focused. However, this is appropriate for a project funded at \$100K.

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

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

- It is difficult to distinguish what was accomplished earlier and what are the specific achievements of the reporting period particularly with respect to the CNT diameter control. With respect to targets, an incremental improvement in specific energy has been achieved compared to 2006.
- The proposed method to generate porous carbon exists in other fields but to implement it in the context of hydrogen storage is definitely an advance that could impact the field. Work on size control for nanotubes is not completely new but completes contributions from Endo and other people working on nanotubes.
- Excellent work on material development but well short of DOE gravimetric goal. Next year, I would like to see progress on other DOE goals including volumetric capacity, adsorption, desorption, and cycle life.

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

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

- A fair degree of collaboration established within the Sorption CoE.
- Good collaboration with many group members and production of samples that can be measured by other collaborators. Expertise as a chemist is a good asset to the other team members while the PI can take advantage of other members' facilities to characterize his samples.
- Project makes good use of modeling work performed and material characterization at other institutions.
- This work is subject to crosscutting issues and may be receiving funding from other sources.

Question 5: Approach to and relevance of proposed future research

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

- Sensible future plans, yet a high risk area that may not deliver.
- Aggressive pursuit of the micelles based synthesis of porous carbon is the right option for future research considering the originality and promising future of the work that has been initiated.

Strengths and weaknesses

Strengths

- Long experience in SWNTs and controlling of their structure - can be the building block for the current work and could assist partners in the Sorption CoE.
- Did a lot of high quality work with very little money.
- The report is nicely presented and makes the reviewing process easy.
- The group is focusing future work on the most promising aspect of the research.
- He seems to have very strong command of his research project and where he was leading.
- Low budget cost with a possible high return.
- Good balance between fundamental and applied science.

Weaknesses

- Project presentation and clarity of ideas.
- Stability issues with materials.

Specific recommendations and additions or deletions to the work scope

- Introduce intermediate decision points/milestones for tracking down progress and fine-tuning work.
- Establish stronger collaborations and benchmark your approach against other labs' within the Sorption CoE.
- Considering the quality and quantity of the work that was done, this program should receive a funding increment.

Project # STP-06: Single Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

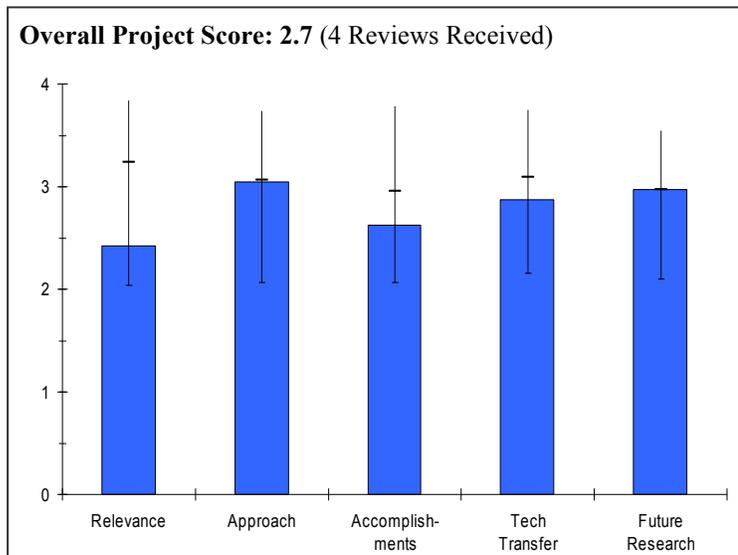
David Geohegan; Oak Ridge National Laboratory (ORNL)

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The overall objective of this project is to control the synthesis and processing of a novel form of carbon – single walled carbon nanohorns (SWNHs) – as a medium with tunable porosity for optimizing hydrogen storage. Specific objectives for FY 2007 include:

- Coordinate synthesis and processing treatments to tune the surface area and porosity of SWNHs, and decorate them with metal clusters;
- Vary pore size and metal decoration; work interactively with center members to clarify the dominant mechanisms of hydrogen storage in metal-decorated nanohorns to address gravimetric and volumetric DOE targets, investigate spillover, supercritical adsorption and dopant-induced charging.



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.4** for its relevance to DOE objectives.

- Projects explore new materials and important mechanisms that have yet to be fully understood such as the effects of spillover, dopants and supercritical absorption. Study of important hurdles that are often neglected from a systems point of view such as heat management. Emphasis on increasing enthalpy of formation and storage capacity is also important. Best results for absorption still remain very far from what is needed according to DOE and the potential to improve enough to reach targets is not clearly demonstrated. Investigation of new ideas such as introducing polarizing molecules inside nanohorns to improve sorption properties.
- The project only partially supports the DOE R&D objectives. This is an issue that should also be viewed in relevance to the recently taken No-Go decision on [pure, undoped] CNTs.
- It is difficult to understand how these molecules will be able to satisfy the DOE goals for gravimetric and volumetric capacity at non-cryogenic temperatures and at a cost that is consistent with large-scale commercialization.
- This is one of several projects with new materials that could be important if there is a breakthrough in storage capacity.

Question 2: Approach to performing the research and development

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

- Experiments are well designed to study the impacts of spillover, doping and structural treatments on the sorption properties of nanohorns. Interplay between theoretical modeling and experiment is apparent in the case of charge introduction within the nanohorns. It is not clear that either the nanohorns or charged structures can reach DOE's goals. This is why contributions should really focus on quantitative understanding of the described mechanisms instead of qualitative description of the improved properties, and they are planning to do this. Approach is thorough with many methods, techniques, characterization tools and collaborators. Good coupling with experimentation and theory.

- The approach seems diffuse. The investigators should focus more clearly on specific barriers and targets. 'New Directions' are proposed without clear relations to the ongoing work.
- Laser vaporization is an interesting and versatile approach for fabricating nanoscale hydrogen storage media with tunable pore size. Enhanced hydrogen adsorption on these materials requires the addition of reactive metal atoms that are incorporated in a separate processing step. Achieving hydrogen storage capacity at $T > 77\text{K}$ is extremely challenging. These are intriguing molecules for studying basic surface reaction phenomena and for exploring the details of hydrogen sorption processes in metal-containing carbon nanostructures. However, it is not clear how adjusting the nanostructure and composition will facilitate storage at capacities and temperatures consistent with DOE goals. There is a huge gap between current observations and DOE requirements.
- I was impressed with the creative strategies and future plans. During my discussion with them, they indicated that receiving hydrogen uptake results from other institutions can sometimes be a rate limiting step for them. Thus, I support their plan to measure hydrogen uptake in house. I should have asked during my discussion with them, but I now wonder why they use only $\text{H}_2\text{PtC}_{16}$ to decorate with Pt. Is it possible, or have they considered, other forms of Pt with organic ligands?

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

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

- Authors are creative in finding ways to improve sorption properties of nanostructures even if observed results still fall short of DOE's goals at this point. Progress in increasing enthalpy of formation and improving heat transfer properties show promising concepts. Given the weak storage capacity of nanohorns even with modified nanostructures and doping, it is appropriate for them to consider investing their time on aspects of the research that have a broader reach – which they are doing through study of spillover, materials modifications, and the study of metal additions. Technical accomplishments are very substantial. Through collaboration and extensive experimental characterization, their work has advanced the field. Important issues such as heat management are investigated.
- Progress so far is modest. Work in pure nanohorns should be viewed in comparison with the recent go/no-go decision. First results from metal decorated nanohorns show decreased uptake. An accelerated rate of progress is needed.
- There is good progress on synthesizing nanostructures with tailored pore size and tunable morphology using controlled oxidative processing in CO_2 . Attachment of reactive metal atoms and clusters (Pt, Pd) was successfully demonstrated and shown to promote enhanced H-adsorption. Results are consistent with a spillover mechanism. Only modest hydrogen adsorption/confinement demonstrated at room temperature. Pathway to achieving higher capacities is not clear. These are interesting materials that can be used for exploring basic surface reaction phenomena. For example, they provide a good framework for studying the details of the spillover process. However, it is highly questionable whether the adsorption mechanisms operative in these materials can result in high capacity confinement of hydrogen at non-cryogenic operating temperatures.
- Excellent work on material development but well short of DOE gravimetric goal. Next year, I would like to see progress on other DOE goals including volumetric capacity, adsorption, desorption, and cycle life.

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

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

- The team seeks the help and expertise of collaborators to perform experiments and characterize samples. The team adjusted well to last year's review regarding the lack of collaboration. More collaboration on the theoretical side leading to fundamental understanding would be of interest. No publications of past and current results are available at this point.
- Some collaboration exists but it can be significantly improved.
- Collaborations with numerous investigators within the HSCoE greatly enhance the synthetic capabilities that exist in the ORNL effort. The ORNL team has done an excellent job of providing nanostructured samples to other partners in the HSCoE.

Question 5: Approach to and relevance of proposed future research

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

- Orientating the project towards using polarization as a method for increasing hydrogen storage capacity is a good idea and should be pursued. A lot of their research for the future is aimed at understanding the fundamental physics behind the improved results that were obtained in '06-'07. They are building on Iijima's work on nanohorns, opened nanohorns and decorated nanohorns. It is appropriate for them to emphasize projects that can lead to a potential breakthrough (such as understanding of spillover and supercritical absorption mechanisms).
- Plans for future research lack focus. More specific actions must be reported with regard to specific barriers (gravimetric capacity, room temp. performance...).
- Charging nanostructures is a proposed new direction that is suggested to increase the hydrogen binding energy. This concept is highly speculative and seems difficult to implement. Although it is an interesting idea, it is a serious long shot. It will be challenging to formulate a straightforward experiment that definitively demonstrates and validates this approach. There appears to be no clear pathway for increasing the storage density beyond the 0.2 - 0.8% level measured at room temperature using the spillover process.
- Future work plan looks like it will address the appropriate issues.

Strengths and weaknesses

Strengths

- The team is diverse and provides a diversified set of tools to study the proposed nanostructures.
- The team has shown that it can build on its prior findings to advance its understanding.
- Good control over designing the nanostructures in terms of size distribution and morphology.
- The team proposes interesting ways to improve sorption properties through metal introduction in the nanohorns.
- Good balance of fundamental and applied research.
- The ORNL team has significant expertise and background in the synthesis and characterization of carbon nanostructures such as nanohorns using laser-based approaches. The ability to tailor the properties of the nanostructures is a big advantage over many other synthetic routes.
- Creative and novel research.

Weaknesses

- Given the resources and two years of effort, the team would be expected to have some significant publications.
- Approach and plans for future research lack focus.
- The overall work program is not coherent enough.
- The future directions should be more closely related to current activities.
- Although nanohorns provide a good platform for studying basic sorption processes in nanostructured materials, I have serious concern as to whether these materials could ever be used in a storage system that meets DOE goals for gravimetric and volumetric capacity at elevated temperatures.
- Large gap between current gravimetric results and DOE target.

Specific recommendations and additions or deletions to the work scope

- Put emphasis on quantitative description and understanding of the spillover, effect of pore size, and supercritical absorption in the second part of this project.
- Work on explaining and predicting the enthalpy increase that is observed in metal doped structures.
- Identify what major roadblocks stand in the way of achieving high capacity storage at non-cryogenic temperatures. Provide a candid and detailed assessment of the ability of this approach to overcome those problems.

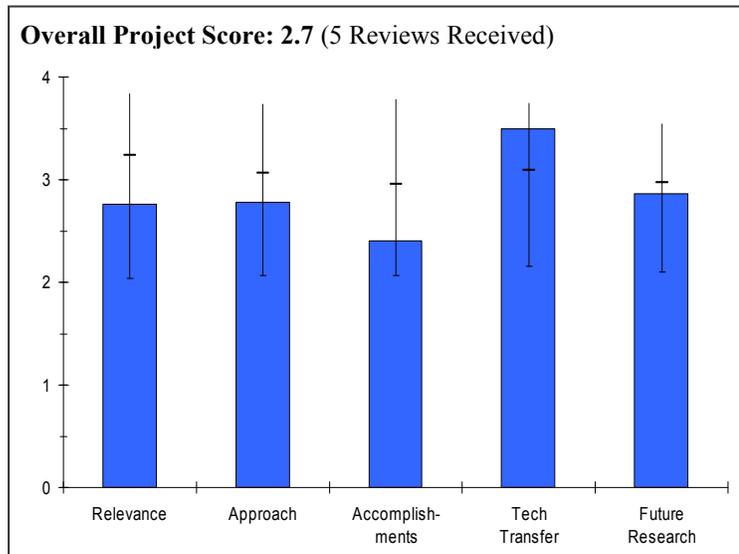
Project # STP-07: Enhanced Hydrogen Dipole Physisorption*Channing Ahn; California Institute of Technology (CalTech)*

[Member of the Hydrogen Sorption Center of Excellence]

Brief Summary of Project

The goal of this CalTech project is synthesis of high surface area physisorbents (in order to achieve gravimetric densities of 7.7 wt.%) with tailored pore size (to reach volumetric densities of 58 gm/liter) and high adsorption enthalpies (ambient temperature operation). Specific objectives include:

- Further enhancement of surface area needs to be accomplished in order to improve gravimetric density (from our work, presently at 5.4 wt.% at 77K for a 2447 m²/gm surface area activated carbon).
- Tailoring pore size needs to be addressed to maximize volumetric density (presently ~38gm/liter at 77K). Optimal pore size should be ~1.1 nm in order to maximize volumetric density.
- Sorption enthalpies beyond the 4 to 8 kJ/mole range typical of current materials needs to be increased so that sorbents can work at ambient temperatures.

**Question 1: Relevance to overall DOE objectives**

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

- Several project aspects and activities are in line with the program objectives. These include detailed H-uptake measurements, metal decoration of aerogels, testing of MIL materials, and thermodynamic analysis.
- Project seems mostly incremental even if results from aerogel absorption are impressive. The idea that particles can influence the sorption is a good idea but the actual results thus far are not so satisfying.
- The project includes activities that align with the programmatic vision and objectives. Nevertheless attention is needed to ensure that the relevance is kept for all its aspects.
- Developing new materials with high hydrogen capacity is in line with the DOE objectives.
- The project is concerned with carbon aerogels.

Question 2: Approach to performing the research and development

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

- The poster is not by itself sufficient to judge thoroughly the approach. The collaborations stated in the poster suggest good integration with other R&D. The group's work on metal decorated aerogels, MILs, and the use of its facilities and long experience on H-uptake measurements contribute to overcoming some barriers.
- Ni catalyst addition was not shown to improve sorption properties. Ideas and methodology are good. Better study of dopants on storage capacity could be obtained at room temperature where the aerogel is not already saturated because of the low temperature. The PI works on a wide range of interesting topics including aerogels, MOFs and KC24 and the comparative behaviors of these materials are potentially very interesting.
- Exploring high surface materials is a reasonable approach for finding high-capacity materials. Approaches for improving binding (sorption) energy are not presented clearly.
- So far, there has been no work at temperatures between 77K and 298K.

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

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

- The progress so far is modest. The relevant rate can be definitely improved. It seems that in many aspects, the project is simply offering high-level services to other groups (with regard to detailed uptake and thermodynamic measurements). 5.5 wt.% at 77K is claimed for a certain type of material and further improvements are expected according to the investigation.
- Interesting results on enthalpy of formation increase due to use of dopants. Good effort in order to improve the storage capacity of aerogel beyond the Chahine rule. Good ideas with the Ni nanoparticles but no results and no follow through. Good hydrogen uptake at 77K for carbon aerogels. No publications yet. Good results on carbon aerogel capacity with Baumann [LLNL].
- The progress so far is rather modest. Although the investigators expect to improve their current 5-6% , they need to better explain how they will achieve such improvement.
- High surface area materials are successfully prepared and about 5 wt.% of adsorption capacity is achieved at 77K. More detailed characterization is expected for the promising material.
- H-uptakes shown are too low to meet DOE targets. Work with Ni does not logically follow from work with pure aerogels (surface areas are different??). It is unclear how much MIL materials will be able to meet DOE targets.

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

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

- There is good collaboration and sufficient coordination with other groups (e.g., for the carbon aerogel work).
- Good collaboration with other members of the group and good exchange of ideas and materials. Many sample exchanges with other members of the group to maximize the use of the characterization tools available to the team.
- A close cooperation with other groups exists.
- Good collaboration with partners.
- Very strong collaborations with LLNL and Material Institute of Lavoisier.

Question 5: Approach to and relevance of proposed future research

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

- Plans focus on aerogels / need decoration, continuation of MILs testing. They build [on] past progress but need to address more closely how barriers will be overcome, especially at room temperature conditions.
- Incremental but good follow through with the current results. Future research is definitely building on past results and could prove interesting if successful.
- The proposed future research focuses on metal decorated carbon aerogels and MILs. There is a clear need for further elaboration on how barriers will be overcome, especially with regard to room temperature performance.
- Some new materials such as carbon aerogel are promising. Critical vision for improving materials other than by increasing the surface area is not shown.
- No clear path forward with catalytic activation of aerogels.

Strengths and weaknesses

Strengths

- Extended facilities, long experience of the group in H-uptake measurements.
- Existing coordination/cooperation with other groups.
- The research results on aerogels are promising with the high surface area density and the above 5% storage capacity at 77K.
- The group is using collaboration well to maximize the contributions that it did with very little money.
- Adequate experience with characterization of sorbent materials.

- Systematic approach to aerogels.
- Combination of experimental techniques (PCT - microscopy).

Weaknesses

- Focus on improvements with regard to room temperature operation is needed.
- The project would benefit from additional collaboration with a theorist and a better interplay between fundamental and applied science.
- More detailed future research plans are necessary.
- The issue of performance at room temperature must be addressed in more detail.
- Low sorption enthalpy needs low temperature to keep hydrogen in the material. Vision for how to increase the sorption enthalpy is not clear.
- Future plans are not detailed enough (which catalysts, why, method by which they will be dispensed).
- Too little data were presented, or maybe, not enough experiments were carried out.

Specific recommendations and additions or deletions to the work scope

- The team is currently investigating on many fronts at the same time but results are rather incremental. But through collaboration they obtained good results for the high surface area carbon aerogel storage capacity.
- The team might benefit from choosing the direction that it considers the most promising (possibly high surface area aerogels) and pursue it more aggressively.
- The project would benefit from additional collaboration with a theorist.
- The support level should be at least 50K for one investigator.
- Surface area is apparently one of the key properties determining storage capacity. However, some other properties regarding nanostructure are possibly related to storage properties. Discussion should not be limited to surface area.
- If the project is to be a success, experimental work must be intensified (more materials, different temperatures).

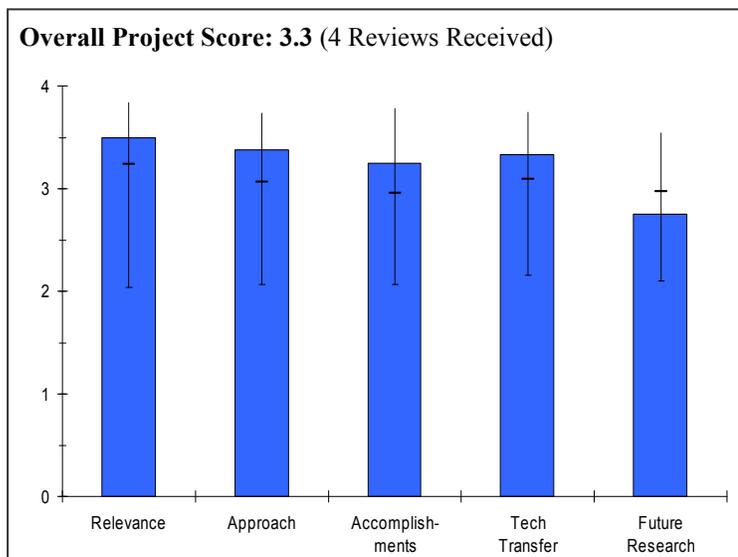
Project # STP-10: Solutions for Chemical Hydrogen Storage: Hydrogenation/ Dehydrogenation of B-N Bonds
Karen Goldberg; University of Washington

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are to:

- Identify materials/systems to meet DOE targets for gravimetric and volumetric density of H₂, focusing on amineboranes and other BN compounds with potential for high H₂ storage capacities;
- Develop catalysts to meet DOE target goals for H₂ charging/discharging rates from BN materials – thermal H₂ release from BN materials is slow and inefficient. Effective catalysts for dehydrogenation/rehydrogenation will be needed;
- Optimize and develop cost-effective catalysts – scale of project requires inexpensive and widely available system components;
- Optimize BN materials for potential in effective regeneration processes – efficient regeneration of spent BN materials is critical.



Question 1: Relevance to overall DOE objectives

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

- Addresses DOE goals for hydrogen storage—addresses key issues for aminoborane systems.
- The project is closely related to DOE H₂ initiatives.
- The objectives of the project are aligned with DOE RD&D objectives.
- Finding effective and inexpensive catalysts to achieve maximum equivalence at lower temperatures with aminoborane is key to the success of this material for automotive consideration.
- Aminoborane has the potential to meet many of the DOE storage targets. However, this project does not address the very difficult cost and energy issues that are the barriers to the practical application of this material and is totally focused on the much “softer” issue of dehydrogenation kinetics.

Question 2: Approach to performing the research and development

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

- The approach is sharply focused on cost and reversibility.
- The PI needs to consider the reaction rate, efficiency, and selectivity when searching for a cheaper catalyst.
- BN compounds have potential as hydrogen storage materials which may meet DOE targets.
- Started with expensive materials and moving towards cheaper transition metal materials – typical approach, needs to be investigated though.
- Work to modify AB to make it reversible and slightly endothermic seems doubtful. What effect will these organic linkers, etc. have on storage capacity and hydrogen purity?
- The approach that has been taken is perfectly on target to overcome the barrier to achieving acceptable dehydrogenation kinetics. However, as good as this project may be, it will have little impact on overcoming the key barriers to the practical application of aminoborane.

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

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

- Demonstrated the best catalyst reported to date.
- Currently, the PI has one of the most effective catalysts for aminoborane.
- Identified catalyst for AB system that provides one equivalent of H₂ in a matter of a few minutes.
- Have identified a non-PGM catalyst which should lower cost.
- Have identified one of the problems limiting hydrogen release to first equivalent of hydrogen; however, the reaction leading to soluble product still appears to be limited to first elimination reaction (one equivalent of H₂).
- Catalysts studied appear to be limited to one equivalent of H₂ – need a system that will catalyze second elimination.
- Determined thermodynamic data for the potential of regeneration of BN compound.
- This project provides an excellent example of how fundamental studies can quickly and effectively provide guidance to the development of a practical system. Unfortunately, the value of what has been achieved can not be harnessed unless the more difficult barriers relating to re-hydrogenation can be overcome.
- Work on modifying thermodynamics of AB has just started but little details or method was offered as to how that task will be accomplished – please provide more insight.

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

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

- An excellent collaboration has been established with PNNL. Better collaboration with the investigators working on the re-hydrogenation side of the problem is critical to overall success of the effort for the practical development of this material.
- Appears to have good collaboration with other center members. All have picked up on U of Arizona's work with ammonia borane-methyl ammonia borane mixtures.
- Demonstrated close coordination with other institutions.
- Working well within the center and all appropriate partners are utilized.

Question 5: Approach to and relevance of proposed future research

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

- Effort for the development of catalysts based on non-precious metals needs greater emphasis. Thermodynamic constraints prohibit studies of this system from having any relevance toward the elimination of the significant barriers.
- Catalyst development work attempting to build on knowledge gained from precious metal catalyst.
- Some modeling work may be beneficial.
- Plans are built on past progress and focused on overcoming the barriers.
- The catalyst development for the dehydrogenation of liquid "solvent-free" BN system is critical.
- Continue work on cheaper catalysts – crucial.
- Continue work on reducing exothermic thermodynamics of system – although success seems unlikely, it's worth a shot. This center has surprised us pleasantly before.

Strengths and weaknesses**Strengths**

- The PIs are world class experts in the study of organometallic mechanisms and homogeneous catalysis. They have demonstrated the ability to quickly utilize the findings of their fundamental studies of a catalytic system to the development of a system showing significantly improved practical performance.
- Have obtained very good kinetics for the release of the first equivalent of hydrogen.
- The project has a well defined and focused research approach.

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- The outcomes can be used for both on-board and off-board purposes.
- Great catalysts.
- Good center support.

Weaknesses

- Thermodynamic constraints prohibit utilization of the catalytic system to the key problem of re-hydrogenation.
- Catalysts used appear to only affect first elimination reaction.
- The PIs need to lay out a strategy to balance the cost, efficiency, and selectivity issues in developing the alternative catalyst.
- Unclear plan for reducing thermodynamics of system.

Specific recommendations and additions or deletions to the work scope

- Some modeling work may help guide catalyst search.
- Please provide plans for reducing the thermodynamics of the system.

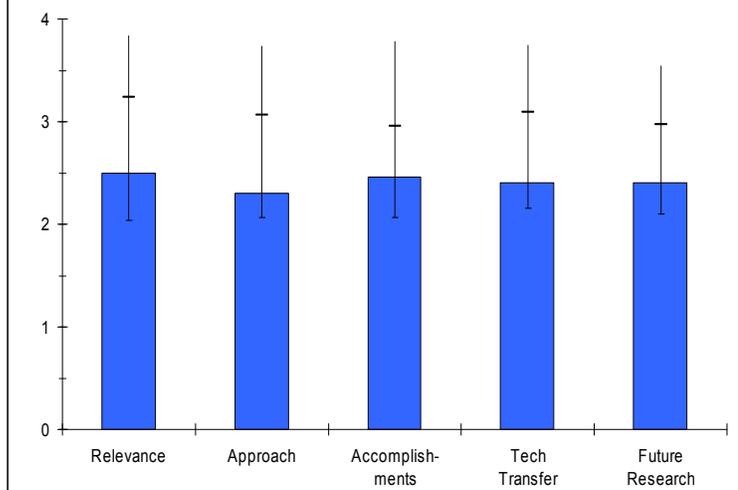
Project # STP-11: Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts*Fred Hawthorne; University of Missouri*

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are to:

- Develop heterogeneous catalysts for the controlled release of hydrogen from the hydrolysis of salts of $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{11}H_{14}^-$ ions.
- Determine the kinetics and mechanisms of these catalyzed polyhedral borane anion hydrolysis reactions to provide design data for large-scale hydrogen storage devices.
- Optimize existing processes for the conversion of diverse BH sources to $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ salts for direct use in hydrogen storage without extensive purification.
- Develop BO to BH regeneration process.

Overall Project Score: 2.4 (5 Reviews Received)**Question 1: Relevance to overall DOE objectives**

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

- Mixtures of polyhedral borane anions and $NaBH_4$ have the potential to meet many of the DOE storage targets. However, this project does little to address the very difficult cost and energy issues that are the barriers to the practical application of this material. It is instead focused on the much “softer” issue of dehydrogenation kinetics.
- The gravimetric capacities of this approach are somewhat marginal to meet the 2010 system target of 6 wt%.
- Relevant to stationary but likely not transportation, so aligned with some but not all program goals. Capacity is not too bad, but they don’t know if they are on target for cost or efficiency goals.
- The stability of these types of materials is a definite plus.
- Cost of regeneration is a central issue.
- Polyhedral boranes have many of the same issues as sodium borohydride in terms of creating B-O bonds and only marginally better solubility characteristics in water.
- It seems quite likely that they will experience many of the same difficulties as $NaBH_4$ hydrolysis technologies do.
- Hydrolysis of polyhedral boranes has limited application to on-board storage.
- The main attributes of the system lie in the long term, stable storage of hydrogen.
- Good kinetics of release, but only effective catalyst is expensive (Rh).

Question 2: Approach to performing the research and development

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

- The approaches taken for developing cost effective catalysts that can effect acceptable dehydrogenation kinetics are on target. However, there is no clear approach to overcoming the key barrier of developing a practical method of BO to BH regeneration.
- Is 6 wt% the top end for these types of materials? Can the project identify any higher hydrogen gravimetric anions?

HYDROGEN STORAGE

- A hydrolysis rate improvement program for polyhedral boranes, this is certainly crucial, but they are not investigating or aware of the energy lost in reaction, nor the energy of recycle, so the approach is not realistic.
- Focused on kinetics of hydrogen release by hydrolysis of alkali metal boranes, such as $K_2B_{10}H_{10}$. These have limited capacity, require expensive catalyst (at this time) and require regeneration from BO to BH, the same as the $NaBH_4$ system.
- No regeneration work. Relies on CoE partners (Penn State, Rohm and Haas, Millennium Cell).

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

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

- Excellent progress has been made in the development of rhodium-based dehydrogenation catalysts. However, little has been done toward the development of more economically viable catalysts. Moreover, the value of what has been achieved can not be harnessed unless the more difficult barriers relating to re-hydrogenation can be overcome.
- Best initial catalyst was determined.
- Hydrogen generation rates were determined.
- Did a good deal of work but they still requires an Rh catalyst, which will be prohibitively expensive. Also looked at multiple boranes and looked at rate data. No real action on any of last year's inputs.
- Good kinetic results obtained with Rh catalysts, requiring about 1.8 liter reactor to supply 80 kW FC (at initial rate).
- Studied a number of other catalysts, but found all but Rh to be inactive.
- Measured capacities of various polyboranes ranging from about ~6 to ~6.5 wt%.

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

This project was rated **2.4** for technology transfer and collaboration.

- Better collaboration with the investigators working on the regeneration side of the problem is critical to the practical development of this material.
- Need more interactions related to regeneration of the materials that are being produced.
- Collaborations might be useful to identify other types of higher gravimetric types of anions.
- Collaborations might be useful to identify alternative catalysts to rhodium.
- They are more dependent on partners than collaborating.
- Limited collaborations. Only with a few CoE partners that are working on regeneration of BO to BH.

Question 5: Approach to and relevance of proposed future research

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

- Plans for the development of catalysts based on non-precious metals are on target. Unfortunately, no studies are planned that might be of value to solving the key, BO to BH recharging problem.
- Need to start addressing the regeneration issue, even if just on a collaborative basis.
- What about exploration for higher wt% materials?
- It would be desirable to try to identify a cheaper catalyst material than rhodium.
- Plans are suitable but they do not appear to understand the full picture enough to say if the work is worth pursuing.
- Future work described in the presentation appears limited to increasing the hydrogen generation rate and finding an alternative catalyst.

Strengths and weaknesses

Strengths

- The PI is a world class expert in the study of the reactions of boron hydrides.

- High stability of hydrogen storage materials.
- Liquid material morphology.
- High generation rates.
- PI has demonstrated good scientific capabilities and has made progress toward rapid hydrogen release from polyhedral boranes.

Weaknesses

- The value of this project to achieving the objectives of the program is tied to the “shaky” premise that a practical system can be found for the regeneration of BH from BO.
- Marginal wt% levels.
- High cost of catalyst.
- Regeneration issues.
- Even if the the gravimetrics are acceptable for stationary applications, the volumetrics are not because water has to be shipped.
- Limited scope.
- Effort is focused on materials that do not appear to have the relevant properties for achieving better on-board storage systems. However, they may have application to portable devices or long-term storage applications, so finding a low-cost catalyst could have some value.

Specific recommendations and additions or deletions to the work scope

- Project should include a task that explores some aspect of the BO to BH regeneration problem.
- None.
- More incorporation into other CoE activities would provide benefits to both the PI and the center.

Project # STP-12: Development of Advanced Chemical Hydrogen Storage and Generation System

Oscar Moreno; Millennium Cell

[Member of the Chemical Hydrogen Center of Excellence]

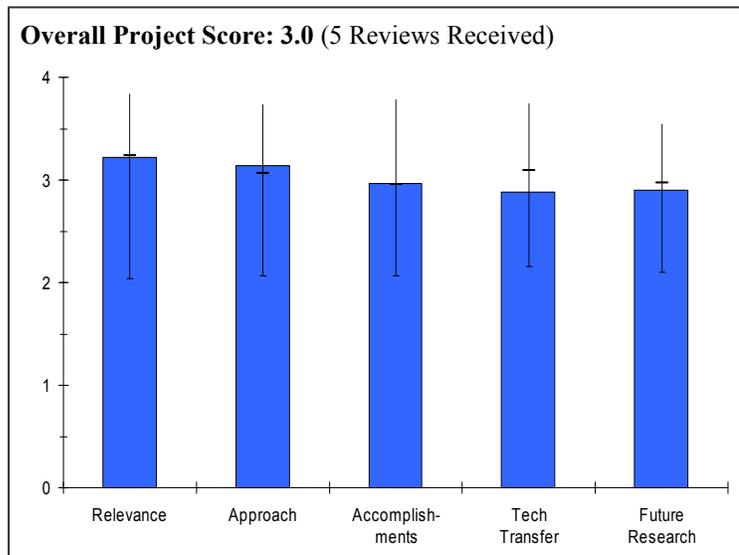
Brief Summary of Project

The objectives of this project are to:

- Improve storage and release of H₂ from chemical hydrides;
- Meet the DOE 2007 target and beyond: 1.2 kWh/L (36 g H₂/L) and 1.5 kWh/kg (45 g H₂/kg);
- Leverage Millennium Cell’s engineering expertise and help guide Chemical Hydrogen Storage Center research.

Question 1: Relevance to overall DOE objectives

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



- Important systems work that directly supports DOE goals. This project offers a unique opportunity to demonstrate an entire "end-to-end" hydrogen storage system.
- The sodium borohydride system, as developed by Millenium Cell, is essentially the only chemical hydride system that has been operated on-board a vehicle. Analysis of this system and the development of engineering tools should be of value to future on-board storage systems based on chemical hydride materials.
- This project is an integral part of the DOE Hydrogen effort to develop a hydrogen storage system based on NaBH₄ (SBH). These are the kinds of projects that will ultimately lead to successful demonstrations of on board hydrogen storage.
- The Millennium Cell project aligns very well with the DOE RD&D objectives.
- BO to BH regeneration remains a problem on chemical hydrogen storage systems based on hydrolysis reactions for releasing stored hydrogen.
- Successful completion of the design program is critical to a positive go/no-go decision on the viability of the sodium borohydride fueling solution.

Question 2: Approach to performing the research and development

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

- Experimental validation of modeling results is a critical step in acquiring all of the data needed for a go/no-go evaluation in September 2007. The scope of the individual project tasks is appropriate to provide the information needed for that decision.
- The current program is focused on the engineering aspects of an on-board system based on the Millenium Cell approach. This could provide useful information for later research on chemical hydride systems.
- Good partnership with PNNL in the development of a reactor modeling tool.
- Major issues with the material system are not addressed in the current work.
- Development of engineering toolkit may be of value to other system development work.
- The overall approach is what one would expect for such a project--modeling, data gathering, experimental validations where needed, conceptual design, construction, and testing. The problem is that the project is "saddled" with a storage material (SBH) that has no real chance of meeting 2015 or even 2010 hydrogen capacity targets.

- Nonetheless, the work on this project through completion will serve as a valuable system development model for the rest of the DOE Hydrogen Program.
- The approach builds on the catalyst and reactor modeling effort over the last two years leading up to a conceptual onboard system design that is to be completed in time to allow for a preliminary cost estimate to be completed in time for the September 2007 go/no-go decision on the sodium borohydride system.
- Small-scale experiments provide data for model validation and for optimization of the reactor geometry, catalyst porosity, and pressure and temperature control strategy.

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

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

- Good progress on development of reactor modeling—results are important to predict ultimate system performance and to provide information needed for making "mid-course" design corrections.
- Useful results obtained on defining reactor geometry and on identifying critical materials issues that could alter system performance (e.g. proper catalyst dispersion and porosity).
- Some progress made in validating reactor modeling tool. This work is continuing.
- Some effort devoted toward completing a report on all data and tools developed through this project and on pending go/no-go decision later this year.
- On-board system design improved over earlier versions. Drawing of system shows individual components and overall dimensions well, but hydrogen capacity was not stated.
- Not clear how to relate the stated hydrogen volume density value to the system depicted in the presentation. If one estimates the total volume of the individual components, the stated energy density would correspond to about a 10 kg H₂ system capacity. But if the overall dimensions are considered, the energy density is significantly lower. In any case, it isn't clear where the density numbers came from.
- It appears that enough modeling work has been done to provide a sufficient characterization of the SBH-based system for the scheduled go/no-go decision point in September 2007.
- Several key system development issues have been resolved but a few still remain unresolved.
- The key accomplishment in 2007 is the completion of the onboard hydrogen release system design. The fuel concentration was increased to 30%. The catalyst was improved to handle the more concentrated fuel and the balance of plant volume was reduced.

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

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

- Collaboration with PNNL seems to have been highly valuable to the project.
- PNNL and Rohm and Haas are the two center members with the most collaboration with Millenium Cell.
- Collaboration with PNNL is an important element of this project. Involvement with other partners in the CHS CoE seems to be limited.
- Very little collaboration, except for work with PNNL on reactor model.

Question 5: Approach to and relevance of proposed future research

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

- The future of this project depends on the results of the go/no-go decision in September. Detailed future plans will presumably emerge from that review. Only very limited future plans given in existing presentation.
- Scope of future work limited, but probably about right for present state of the project
- The path forward hinges on the outcome of the go/no-go decision this coming September.
- Some work still needs to be completed to get fully ready for that decision, i.e., details of reactor features, balance of plant considerations, and a safety review.
- A key question for DOE is whether or not there is value in going forward with the completion of this project when the projected hydrogen system capacity performance of SBH barely meets 2007 capacity targets.

HYDROGEN STORAGE

- For the remainder of FY2007 a report that compiles all the data and tools developed under this project will be generated.

Strengths and weaknesses

Strengths

- This is an important project for demonstrating and validating a fully operational hydrogen storage system.
- Success in this project could significantly impact the ultimate commercialization and utilization of hydrogen storage systems for transportation applications.
- Extensive systems experience of Millennium Cell makes that organization an ideal candidate to conduct this demonstration study.
- Strong engineering experience of Millenium Cell is being applied to increase on-board system design capabilities of the center.
- Work to date seems to have been done in a thorough and scholarly manner. The engineering looks good. The prospects for a successful demonstration of an operating SBH system seem encouraging. Unfortunately, the demo will take place no earlier than 2008 but the system will barely be able to meet 2007 metrics for overall performance. (Note: the demonstration is not until phase II of the project and will depend on the outcome of DOE's SBH go/no-go decision)
- The preliminary design indicates that the on-board system will achieve 1.2 kWh/L and 4.5 wt.% which meets the near term DOE targets.

Weaknesses

- Demonstration system only—unlikely to meet longer-term storage objectives; degradation of catalyst properties and stability during operation can occur. This would seriously limit system performance.
- Engineering a system utilizing a material which has inherent problems with hydrogen wt.% and thermal efficiency (regeneration of the fuel) could be very difficult to optimize in an attempt to reach DOE's goals.
- The SBH demo project as a whole needs to be a bit further along to make a compelling case for being allowed to go to completion if the decision is really to be made in September of 2007.
- It is not clear that the system can meet the 2015 targets, at least a clear path to the goal is not evident.
- The current design has not yet been costed so it is uncertain if the on-board system can meet the storage system cost goal for the go/no-go decision.

Specific recommendations and additions or deletions to the work scope

- None (future work pending go/no-go decision).
- System modeling and engineering is recommended to be refocused on more promising materials.
- Devise a compelling rationale for why the project should be allowed to go to completion even though the SBH storage capacity is below target. It seems the entire Hydrogen Program will gain a great deal of valuable insight into what will be required to bring such systems to life. The list of lessons learned will be long for sure.
- Consider whether the system now on the drawing board could accommodate other types of related hydrogen storage materials.

Project # STP-13: Combinatorial Synthesis and High Throughput Screening of Effective Catalysts for Chemical Hydrides

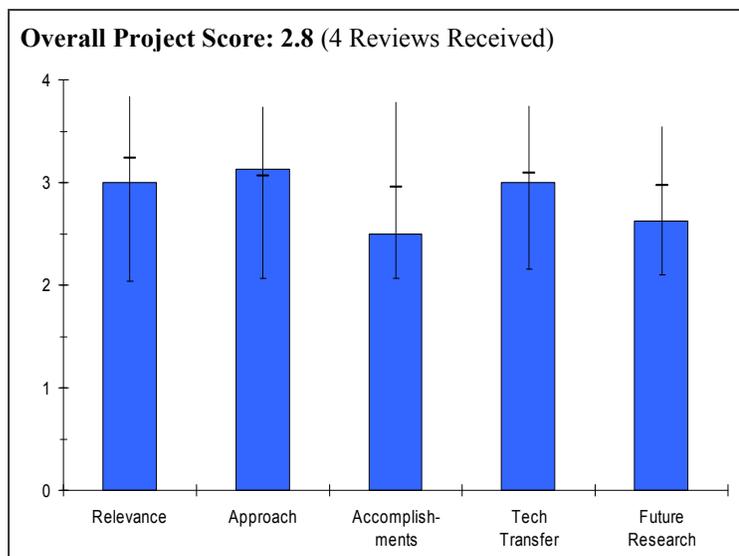
Jonathan Melman; Intematix

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are to discover cost-effective catalysts for release of hydrogen from chemical hydrogen storage systems to enable deployment of on-board automotive hydrogen systems; and discover cost-effective catalysts for the regeneration of spent chemical hydrogen storage materials. The specific objectives for 2007 include:

- Synthesis and screening of hydrogen-release catalyst libraries (in nano-particle and thin-film forms) to identify catalyst leads;
- Bulk tests of catalyst leads on gram scale to confirm scale-up;
- Bulk production of chosen catalyst leads for further study among center partners.



Question 1: Relevance to overall DOE objectives

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

- This project provides important support to other partners in the CHCoE by using novel high throughput/combinatorial analysis of catalysts for the synthesis of chemical hydrogen storage materials.
- The project is very relevant to the CHCoE objectives and has the potential to be a significant contributor to the effort.

Question 2: Approach to performing the research and development

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

- Combinatorial screening of dehydrogenation and hydrogenation catalysts is a very effective means of discovering the most efficient catalysts in a short amount of time.
- The approach is focused on the analysis of candidate storage materials and provides important guidance and technical direction to other CoE partners.
- There does not appear to be a significant contribution to the effort from the theorists in the Center. The rationale for the selection of the catalyst library was not presented.

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

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

- Significant progress has been made in developing and applying analytical techniques to accessing potential chemical hydrogen storage materials.
- Intematix developed a few leads for suitable dehydrogenation catalysts for the center members.
- A reviewer comment from 2006 suggested that Intematix increase effort on hydrogenation catalysts; no work was reported in this area.

HYDROGEN STORAGE

- It is difficult to assess progress when so few details were presented.
- There does not appear to be much progress.

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

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

- This project is basically a support activity for other partners in the CoE and, as such, they have worked closely with most of the CoE partners. Their achievements have improved the efficiency and productivity of the center as a whole.
- Intematix collaborates with PNNL, LANL, U. Penn, and Northern Arizona University on amineboranes (AB). Collaboration appears to be good.

Question 5: Approach to and relevance of proposed future research

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

- Future plans build on the past progress and established collaborations with other center partners. Future plans also include important work on catalyst development important for regeneration of candidate hydrogen storage materials.
- Future research includes development of dehydrogenation catalysts from solution phase systems such as AB, and polyhedral boranes. The work will likely benefit from previous efforts in this area.
- Hydrogenation catalysts will also be developed but no time schedule was presented.

Strengths and weaknesses

Strengths

- This project makes important and outstanding contributions to the CHCoE.

Weaknesses

- Project scope is limited to ammonia borane systems including current and future research.
- Intematix did not provide any description of the catalyst libraries that were studied.

Specific recommendations and additions or deletions to the work scope

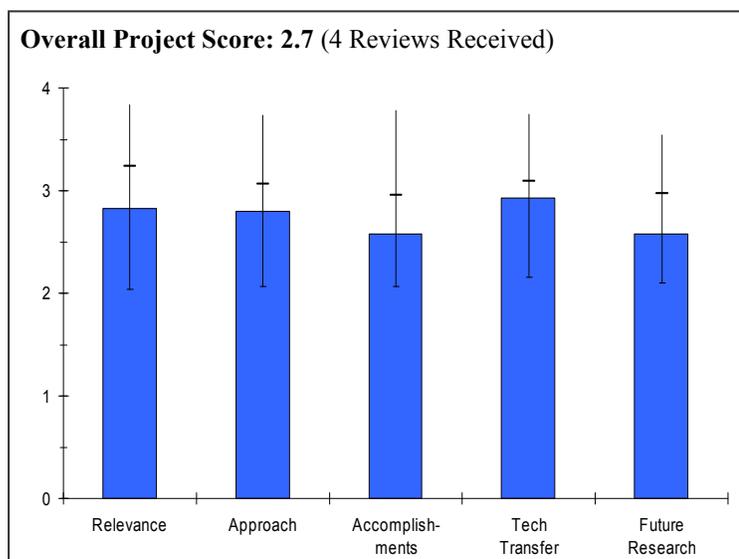
- Expand the scope to catalyst screening for other chemical hydrogen storage systems such as liquid hydrogen carriers.

Project # STP-14: Chemical Hydrogen Storage using Ultra-High Surface Area Main Group Elements*Susan Kauzlarich; University of California-Davis*

[Member of the Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The goal of this project is to increase the understanding of synthetic approaches and physical properties of main group element clusters, such as Si, B, Al, and alloys thereof, BP and BN compounds and identify hydrogen storage materials with potential to meet DOE targets. Over the past year, efforts have been directed towards designing simple routes to such compounds using mild conditions and studying weight and volume capacities of the synthesized materials as well as the reversibility of hydrogen uptake. An objective is also to provide new materials, compounds, and support for chemical regeneration of amine-boranes or boron amides from B--X (X= halide or oxide) compounds.

**Question 1: Relevance to overall DOE objectives**

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

- The work in this project is directed at the development of hydrogen storage materials and supports the DOE objectives.

Question 2: Approach to performing the research and development

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

- Revised plan uses the scientific capabilities of the UC Davis group to help on a specific aspect of AB regeneration. This is a nice example of effective collaboration within a center.
- Revised work plan is an improvement toward contributing to the overall CoE needs.
- Good combination of chemical synthesis and characterization of materials with spectroscopic techniques.
- Continuation of the work on high surface area materials appears to be less promising and could be redirected toward more activities in support of the CoE development efforts.

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

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

- Good progress toward synthesizing amide, hydride and formate derivatives.
- Determined quantitative yield in hydride, amide conversion to formate. Not much progress apparent on high surface area storage materials in terms of weight capacity for hydrogen.
- High surface area materials also appear to have relatively high binding energies for hydrogen, with no clear pathway indicated toward improving this parameter.

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

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

- Apparent collaboration with PNNL and LANL.
- Good collaborations and interactions within the Center.

Question 5: Approach to and relevance of proposed future research

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

- Stated future work indicates looking at regeneration of high surface area particles. But since the materials to date do not exhibit good storage properties, it's not clear why one would spend effort on regenerating them.

Strengths and weaknesses

Strengths

- Utilization of synthetic chemical routes, preparation of nano particles.
- Excellent scientific capabilities in nanoparticle synthesis and characterization. This could lead to efficient regeneration processes for ammonia borane.

Weaknesses

- The use of non-reversible, high surface area materials for hydrogen storage appears to combine the negative properties of adsorbents (low volumetric hydrogen density), hydrides (low weight density and strong binding energy) and chemical hydrides (potentially complex off-board regeneration).

Specific recommendations and additions or deletions to the work scope

- Recommend to definitely continue this project.
- More focus on bimetallic Si compounds.
- Suggest future utilization of LANL's new GC screening system.
- The use of non-reversible, high surface area materials for hydrogen storage appears to combine the negative properties of adsorbents (low volumetric hydrogen density), hydrides (low weight density and strong binding energy) and chemical hydrides (potentially complex off-board regeneration). Perhaps this effort should be reduced further and future work should be focused more on materials development for regeneration pathways for ammonia borane, or other materials of interest to the CoE.

Project # STP-17: Hydrogen Fuel Cells and Storage Technology Project at UNLV

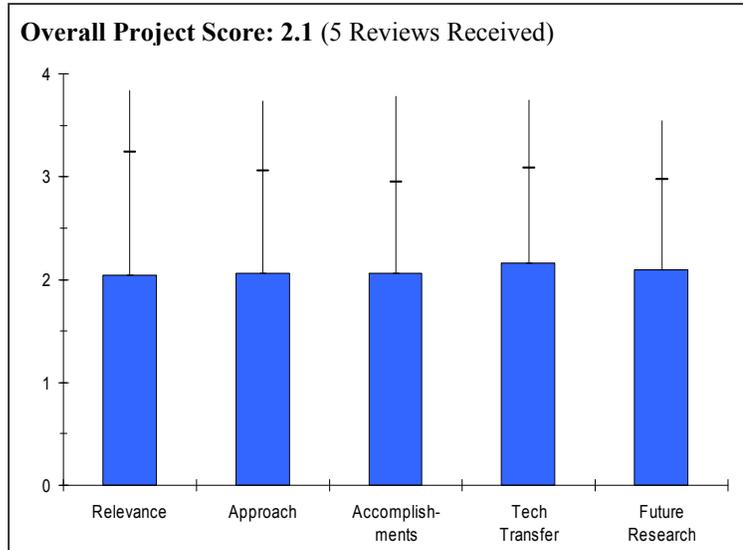
Clemens Heske, Balakrishnan Naduvalath (Co-PIs); Robert Perret, Project Manager, University of Nevada – Las Vegas

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

Brief Summary of Project

The objective of this project is to create a framework for interdisciplinary academic research that combines theory and experiment to address specific fundamental aspects of hydrogen storage and utilization. This will be done by establishing new infrastructure (computer cluster, experimental stations, etc.) to perform integrated interdisciplinary studies on hydrogen storage, and to perform closely-coupled theoretical and experimental investigations of:

- hydrogen adsorption/desorption in various matrices to establish a solid fundamental base for optimal storage concepts;
- the electronic structure of metal hydrides, nanomaterials (C, B, N), metal adatoms, and adsorbed hydrogen molecules/atoms;
- fuel cell membranes and catalytic materials;
- Collaborate closely with external partners.

**Question 1: Relevance to overall DOE objectives**

This project earned a score of **2.0** for its relevance to DOE objectives.

- This project seems to be aimed at storage materials that have [been] largely explored (and to some extent eliminated from further consideration) by other hydrogen storage material researchers. The possibility of new, important advancement of the storage material state-of-the-art seems highly unlikely.
- Much of the work is basic and focuses on systems that will not likely meet DOE goals. Thus far, the emphasis has been on the development of basic research capabilities that will form the foundation for future work at UNLV in the field of hydrogen storage.
- The project could support the hydrogen vision, but should align to work underway in Storage Centers of Excellence as it is working in common areas.
- A diverse project that is not fully organized toward a single track of technology. Some parts better aligned than others.

Question 2: Approach to performing the research and development

This project was rated **2.1** on its approach.

- The approach appears to be primarily a basic theoretical study complemented by experimental verification. It is not clear that new materials and their hydrogen storage capacity measurement will result from the proposed approach. This project was billed as "cross-cutting" between hydrogen storage and fuel cell enhancements, but the presenters stated that they were directed not to present their fuel cell results.
- It appears there is a lot of duplicated work which is already covered by at least one or more projects. It is not clear what strategy the PIs are developing to meet the DOE storage targets.

HYDROGEN STORAGE

- Since last year, the UNLV team has done a good job of focusing its research efforts on a few specific areas. The initial effort was very delocalized. This was a serious concern that the UNLV team has obviously worked hard to address. The three tasks in the hydrogen storage area (two other fuel cell-related tasks) address useful topics. However, the work is very basic, and it is unclear whether the results of this work will have any impact on the development of a hydrogen storage material in the time frame established by the EERE program. Recommend close communication with CoE leads (esp. HSCoE-NREL in Task 1) to develop approaches and project emphasis that is complementary to on-going CoE efforts.
- Since the Carbon (Sorbent) CoE has made a "No-Go" decision with respect to pure, undoped single walled carbon nanotubes, it is not clear why work is still underway in this project.
- Some of the work is much improved from last year, the idea of probing the field on individual, identified chirality, decorated nanotubes does contribute to theory in several areas. The theory work could be useful too. Approach is not very coordinated/integrated though.

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

This project was rated **2.1** based on accomplishments.

- Some progress was reported on the study of electronic structure of candidate storage materials – applicability to DOE storage material targets and objectives is questionable although the work might contribute to basic understanding of the electronic properties of the materials under study.
- It is difficult to gauge the actual progress. The slide on technical accomplishment does not address the actual numeric results the project has achieved vs. the targets.
- The UNLV team is "coming up to speed" in areas of theory and experiment that relate to hydrogen storage. Some interesting initial progress has been made on characterizing nanostructures for enhanced hydrogen sorption and on developing new candidate metal hydride materials. It would be helpful if the results obtained in the three tasks were described in the context of previous work—i.e., What is new here? Why is it important? What are the critical issues going forward? How does it impact the selection of materials that are relevant to DOE goals? In Task 1: It is well known that Ti is a getter for oxygen, so it is not surprising that reactions with oxygen will limit hydrogen uptake in SWNTs containing Ti substituents. Also, high capacity (>9 wt.%) uptake in metal-containing organic systems is predicted. What is the predicted performance at non-cryogenic temperatures? Discussions with partners in the HSCoE could help to guide future work. In Task 2 (complex hydrides): Considerable work has been done by others. Again, a description of how the UNLV effort differs from that work and what new questions will be answered is needed. In Task 3 (PANI): Actual hydrogen uptake/release characteristics are needed (work planned). At this stage, it's not at all apparent why this approach will be superior to others employing conductive polymers.
- Lots of work going on, but not clear what has been accomplished with respect to overcoming the technical barriers of the hydrogen vision.
- Lab work has been pretty slow, especially given the large budget. Almost all results are calculations. This is the second year that we have been told they were "waiting for equipment". There is evidence that they have had a slow learning curve on using it too, and that buying equipment was put off until far later than good planning would suggest (e.g., hydrogen sorption equipment for polymers). A large bank of polymers was made and the nanotube tests are starting and the Raman mapping is starting. Several theoretical predictions were made and they constitute the bulk of the progress. More would be expected for the budget received. I am more confident than ever before though that progress in storage may emerge from this project.

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

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

- Although a number of collaborations were claimed, the nature of the collaborations and their specific contributions to the project were not clear.
- Strong collaboration exists among the members of the UNLV team (theorists and experimentalists); numerous informal external collaborations have been established. Input from other workers in the field of hydrogen storage would be useful to ensure that the topics most relevant to DOE needs are selected for future work.
- Though many collaborators identified, most work is within UNLV.
- Collaborations are present but the work still seems isolated.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.1** for proposed future work.

- Future plans appear to continue the work in progress. The project is reported to be 75% complete, thus the opportunity for additional work is limited.
- The Ti-SWNTs have been shown to be extremely good getters for oxygen. Since they can be so easily poisoned by oxygen, that greatly reduces their desirability as a candidate for future study. Work on functionalized BCN nanostructures and PANI is interesting and potentially important. Initial work should focus immediately on measurements of hydrogen uptake/release.
- Re-focus future work to support DOE technical targets complementing CoE work.
- This is much improved, but needs to move forward more toward the cutting edge of research that will get to the goals of the program.

Strengths and weaknessesStrengths

- Enthusiastic interdisciplinary research team with broad and varied background in areas relevant to hydrogen storage research; good experimental and computational capabilities.
- The UNLV team has potential to make important contributions to the DOE program.
- Well funded.

Weaknesses

- The main focus of this work is on basic science and the researchers have only done very initial studies. It is questionable whether this approach can yield materials that are viable candidates for hydrogen storage in a time-frame that is consistent with DOE/EERE Program goals.
- NaBH₄ and SWNT work has been well investigated in the past, this project appears to be repeating some of that work.

Specific recommendations and additions or deletions to the work scope

- Restructure the project to be responsive to DOE targets and goals. Focus activities on the PANI/Pd composite material and assess the potential hydrogen storage capacity.
- Candidate materials should be identified and tested for hydrogen storage capacity as soon as possible in this project. Until a good candidate material has at least been tested initially, there is concern that this project will produce an in-depth investigation of materials and processes that aren't particularly relevant to the overall DOE hydrogen storage program.
- Recommend that UNLV lead investigators engage in discussions with CoE leads concerning candidate systems and focus topics.
- Consider aligning project to a Storage CoE.

Project # STP-24: Complex Hydrides for Hydrogen Storage Studies of the Al(BH₄)₃ System

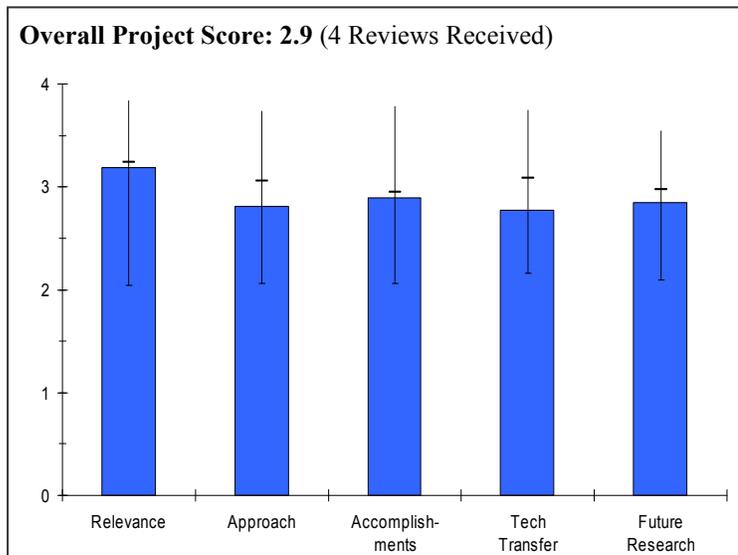
Gilbert Brown; Oak Ridge National Laboratory (ORNL)

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The objective of the project is to develop the chemistry for a hydrogen storage system based on complex hydrides, chosen from the borohydrides, amides/imides, alane, or the alanates of the light elements in the periodic table. ORNL is developing new materials and methods for synthesis of new and known materials. The ORNL goal is to employ solvent-based procedures appropriate for scale-up to production and practical application. There are two general tasks:

1. The discovery and characterization of new materials and processes.
2. The development of synthetic methods and processes in support of MHCoe collaborators.



Question 1: Relevance to overall DOE objectives

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

- The objectives of the proposal are relevant to DOE's overall objectives in pursuing the Hydrogen Fuel Initiative.
- Project fits into the President's HFI.
- Project now focuses on very high wt.% materials, clearly capable of meeting the 2010 and 2015 targets of the DOE HFCIT Multi-Year RD&D plan, if successful.
- The project is in support of DOE H₂ initiative and overall R&D objectives.
- The development of new materials and synthesis method for complex hydrides is critical to DOE targets.
- Exploring materials with a high storage capacity is oriented to the DOE objective for hydrogen storage.

Question 2: Approach to performing the research and development

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

- The PI is aware of the technical barriers and designed the project accordingly.
- Recent redirection of efforts has correctly moved from alanates to very high [capacity] novel borohydrides, e.g., Al(BH₄)₃, theoretical 16.8 wt.% H.
- Although such materials are difficult to handle and utilize in the liquid and gas states, this project's approach is of interest. Although very high risk, such activities offer potentially very high rewards.
- The work and its philosophy fit well into the MHCoe.
- The covalent borohydrides may contribute to overcoming barriers.
- The strategy of technical approach is not well defined in the poster.
- The main target material of this year is Al(BH₄)₃. This material is highly volatile and the decomposition reaction includes B₂H₆ emission with a high concentration. These two properties would be serious disadvantages for a storage material. However, any idea for solution is not shown clearly.

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

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

- Work has made progress against the weight barrier.
- A good understanding of the decomposition mechanism of $\text{Al}(\text{BH}_4)_3$ has been developed. The B_2H_6 intermediate poses some practical challenges vis a vis H_2 purity and practicalities.
- Up to 15 wt.% H has been measured at relatively high desorption temperature (350°C).
- Demonstrated a substantial amount of H_2 can be obtained through the pyrolysis of $\text{Al}(\text{BH}_4)_3$.
- Achieved some fundamental understanding of the $\text{Al}(\text{BH}_4)_3$ pyrolysis mechanism.
- The PI needs to validate some experimental results.
- Characterization of $\text{Al}(\text{BH}_4)_3$ and its decomposition reaction is not accomplished enough.
- Most indications shown in the presentation (structures of $\text{Al}(\text{BH}_4)_3$ and the intermediate, reactions of B_2H_6) are not what they confirmed by themselves but what is suggested from the results already known.
- The anomalies described in accomplishments are good, which also suggests that the project needs change in direction to be fruitful.

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 partners.
- Good collaborations within the MHCoe are evident: GE, SNL and JPL.
- A few more collaborations might be encouraged.
- Certain coordinations exist.
- The PI needs to communicate with the theory group to obtain some theoretical understanding of the system.
- Collaboration on several characterization methods is ongoing.

Question 5: Approach to and relevance of proposed future research

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

- Looks good to address new materials.
- Proposed continuation of efforts on the complex borohydrides and other Al complex hydrides is encouraged.
- Plans are built on past progress and may lead to some improvement.
- The PI needs to layout some strategy in determining the future research direction.
- Exploring other kinds of TM-borohydrides have been already reported by some groups. It is not clear what is the unique vision or approach of this project.

Strengths and weaknessesStrengths

- The PI has a good group.
- Project involves unusual borohydrides with very high gravimetric capacities.
- Strong solution-based synthetic capabilities for oxygen and water sensitive materials.
- Background and experience of chemistry.

Weaknesses

- Continuation of investigation of $\text{Al}(\text{BH}_4)_3$ with problems indicated.
- Effort is very high risk. Liquid/gaseous hydrides such as these (and their intermediate borane products) will have practical handling and safety problems.
- A clear research strategy/pathway needs to be defined in this work.
- No clear perspective for exploring materials or improving the properties.

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Specific recommendations and additions or deletions to the work scope

- Suggest setting a go/no-go point in the next year or so, one based on some measure of practical hope for such unusual and difficult systems.
- Highly volatile materials are not suitable for hydrogen storage because the released hydrogen should contain the vapor of the material.
- Toxicity of B_2H_6 should be addressed. This problem should be considered more seriously.

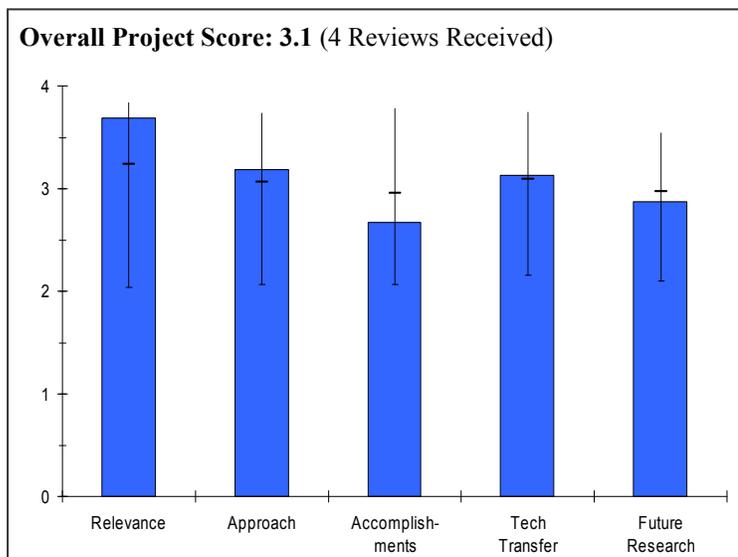
Project # STP-25: High Throughput Combinatorial Chemistry Development of Complex Hydrides*Darshan Kundaliya; Intematix*

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The overall objectives of this project are to identify and synthesize novel metal hydride systems using high-throughput combinatorial techniques and to identify catalysts to achieve fast reaction kinetics for metal hydride systems and thus support DOE's 2010 targets for start time (4 s), flow rate (0.02 (g H₂/s)/kW) and refill time (3 min). Specific objectives for 2007 include:

- Synthesize and characterize novel complex hydride materials in thin film format;
- Continue catalyst screening on LiBH₄ + MgH₂ system based on leads obtained in 2006;
- Screen catalysts for various other partners/systems (GROUP A and GROUP B of MHCoe).

**Question 1: Relevance to overall DOE objectives**

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

- The objectives of the proposal are relevant to DOE's overall goal in pursuing the Hydrogen Fuel Initiative.
- This project provides important support to other partners in the Metal Hydride CoE by using novel high throughput/combinatorial analysis of the synthesis of metal hydride storage materials including analysis of potential catalysts to enhance the performance of metal hydrides as storage media. In addition, the project includes independent analysis of metal hydride materials and potential catalysts to enhance material performance.
- High relevance, allows fast screening for new materials or catalysts.

Question 2: Approach to performing the research and development

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

- The approach is focused on the analysis of candidate storage materials and provides important guidance and technical direction to other CoE partners.
- Good approach for a rough screening of catalysts. Not so suitable for anything more subtle than H₂ is moved in and out or not. Possible false positive if the expected color change is masked.
- The project is not designed well.

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

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

- Accomplishments are fair.
- Significant progress has been made in developing and applying analytical techniques to accessing potential metal hydride storage materials.

HYDROGEN STORAGE

- Suitable accomplishment pace but not clear they are really getting high throughput, not well described.
- Could be improved with help [from] analysis.

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

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

- This project has supported partners in the CoE; they have worked closely with HRL and SNL. Further collaborations are planned with other CoE partners. Their achievements have improved the efficiency and productivity of the center as a whole.
- Two patent applications have been filed.
- Reasonably well connected.
- The PI needs more collaboration.
- Collaborations need to be expanded, especially in area of data analysis.

Question 5: Approach to and relevance of proposed future research

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

- The PI needs to address some fundamental problems related to his objectives. Using a thin film over a storage material, does not give you a good [indication] of catalysts by optical screening.
- Future plans build on the past progress and established collaborations with other center partners.
- Suitable, I hope; not too clear yet.
- Need to increase throughput.

Strengths and weaknesses

Strengths

- Handles large number of samples.
- This project makes important and outstanding contributions to the Metal Hydride CoE.
- Fast method to screen binary and ternary systems based on Mg and Li. Good experimental and theory based effort.

Weaknesses

- Basic understanding is lacking.
- More data is generated than can be analyzed. Data mining is a “choke point” that needs to be corrected. Sample geometry is cumbersome. Need to consider a single sample geometry where composition of alloys can be controlled from thin to thick prior to annealing. One sample rather than a wafer with six or more would be easier. Also, a faster screening tool such as fast IR would expedite analysis for H₂ active areas.

Specific recommendations and additions or deletions to the work scope

- Data mining is a “choke point” for this type of work - need to find an alternative path to increasing data mining. Consider university partnership.
- More data is generated than can be analyzed. Data mining is a “choke point” that needs to be corrected. Sample geometry is cumbersome. Need to consider a single sample geometry where composition of alloys can be controlled from thin to thick prior to annealing. One sample rather than a wafer with six or more would be easier. Also, a faster screening tool such as fast IR would expedite analysis for H₂ active areas.

Project # STP-26: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

Bruce Clemens; Stanford University

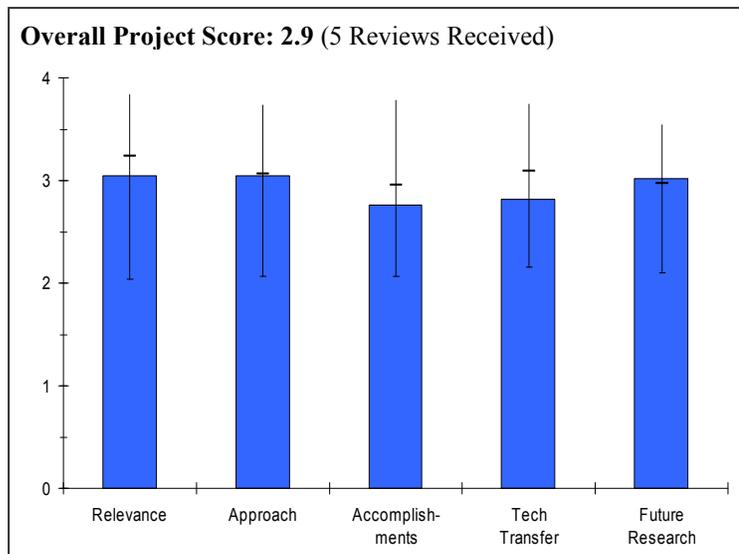
[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The objectives of this project include developing a fundamental understanding of metal hydride reaction kinetics. Kinetics limit practicality and reversibility of many promising metal hydride material systems. This work will focus on systems such as: Mg, Mg₂Si, Li₄Si, NaAlH₄, LiBH₄+MgH₂. Initial work on Mg₂Si showed that kinetic issues prevented the system from achieving reversibility. Catalyst additions have shown some success in improving kinetics for some systems (ie. Ti in NaAlH₄), but little is known about the nature of these effects.

Little is also known about the kinetic mechanisms present in these systems, and in order to improve the kinetics for these metal hydride systems, a sound understanding must be developed.

Another project objective is to develop an understanding of metal hydride structures during phase change. Material structure can play 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 **3.0** for its relevance to DOE objectives.

- The objectives of the proposal are relevant to DOE's overall goal in pursuing the Hydrogen Fuel Initiative.
- Aligned with DOE Hydrogen Storage Program goals.
- The project is closely related to DOE H₂ initiatives and overall R&D objectives.
- Fundamental understanding of the reaction kinetics is critical in new material development.
- Much of the work to date, although good scientific research, has not been demonstrated to have relevance to many of the activities in the Metal Hydride CoE.
- Project is in agreement with DOE objectives.
- A basic research component is much stronger than those related to the applications.

Question 2: Approach to performing the research and development

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

- The project is well designed to address basic understanding of structure and kinetics of hydrogen storage material.
- Thin film approach allows for a controlled system with known structures.
- Study of kinetics in thin films should provide better understanding.
- Thin film model system and in-situ structural characterization is a good approach to get a fundamental understanding of the system.
- The approach is sharply focused on understanding the reaction kinetics.

HYDROGEN STORAGE

- The Mg system should only be used as a starting point for ground work.
- The approaches should include other materials/systems.
- The argument that studying the hydriding behavior of thin films of Mg will help us understand the behavior of other hydrides prepared by bulk or nanoparticle methods is not convincing. For example, the results presented on Mg show how epitaxy can be a complicating factor in thin films compared to particles. Are the results (e.g., planar, interfacial growth rather than nucleation and growth) specific to thin films only?
- Stanford's approach is in a good agreement with the project's goals and objectives.
- Major focus: fundamental understanding of hydriding-dehydriding processes in hydrogen storage materials.

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

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

- Technical accomplishments are fair.
- This study has provided insight into mechanism, suggesting it is a moving interface growth and diffusion limited kinetics for Mg films with much faster uptake kinetics for Ti doped films.
- Cycling experiments show rapid loss of texture-leading to slower kinetics – show directions needed for further studies.
- Developed an understanding of Mg/MgH₂ phase change kinetics.
- Demonstrated using neutron reflectivity to gain insight information about kinetic mechanisms.
- Most of the results to date are on the thin film Mg system. It is understandable to begin this project by examining a single element, well studied hydride system, but it could be argued that this initial phase could have been shortened and work extended to relevant materials. It remains to be seen if new information will be obtained with this technique when applied to more complex hydride systems and studying Mg more won't contribute to answering this question.
- It is not quite clear whether data collected may be really used for material design.
- No major breakthroughs have been demonstrated so far.

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

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

- It will help to have more technical collaborations.
- Collaboration with NIST should be very valuable.
- The PI demonstrated certain coordination with other institutions.
- The PI needs to communicate with theory groups to incorporate the experimental findings into their future studies.
- Some collaborations with center partners.
- As work progresses towards other complex systems, closer collaborations will be of value.
- Collaboration and tech transfer have room for improvement.

Question 5: Approach to and relevance of proposed future research

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

- Looks good.
- Planned work with quartz microbalance for thin films and nanoparticles will help bridge thin film studies to real particulates.
- Plans are built on past progress.
- The approach should be expanded to study a more promising system rather than Mg.
- Future plans are well formulated to address some of the issues discussed above – developing nanoparticle synthesis capability, direct H uptake measurement capability, and beginning a study of the Li borohydride/Mg hydride system.
- Future work looks not very convincing.

- There is a high probability that metal hydride films would quickly deteriorate during operation.
- It is not quite clear whether Mg nano-particles will "survive" handling even in a glove box.

Strengths and weaknesses

Strengths

- Good fundamental approach to understanding.
- Well defined systems to study. This leads to a better understanding of processes.
- Collaboration with NIST should allow for an even better understanding of what is occurring at the interface between the metal and metal hydride phases.
- Thin film model system and in-situ structural characterization enable a fundamental understanding of the reaction kinetics that is critical in the new material development.
- Could be a powerful tool to studying interfacial reactions in complex hydride systems.
- Much cleaner material systems can be fabricated using the techniques described here compared to other synthesis approaches. This could reveal material interactions and behavior related to the pure materials that may not be observed using other approaches.
- Good understanding of advantages and limitations of the approach used.

Weaknesses

- Limited to thin film.
- Some differences between thin films and bulk or particulates.
- The research scope needs to be expanded to include other promising materials besides Mg.
- Need to transfer the knowledge gained from this study to theory groups for their future study.
- Uncertainties remain concerning the validity of the approach as applied to more complex systems and whether or not these results will benefit other studies.
- Despite the high percent completion (40%), the project is still at a very early stage of development.
- Applicability of the results obtained is to be demonstrated.
- Unfortunately, experimental data collected for thin films may not be applicable to the bulk materials.

Specific recommendations and additions or deletions to the work scope

- Move on to other material systems.
- The research scope needs to be expanded to include other promising materials besides Mg.
- Need to transfer the knowledge gained from this study to theory groups for their future study.

Project # STP-27: Alane Electrochemical Recharging

Ragay Zidan; Savannah River National Laboratory (SRNL)

[Member of the Metal Hydride Center of Excellence]

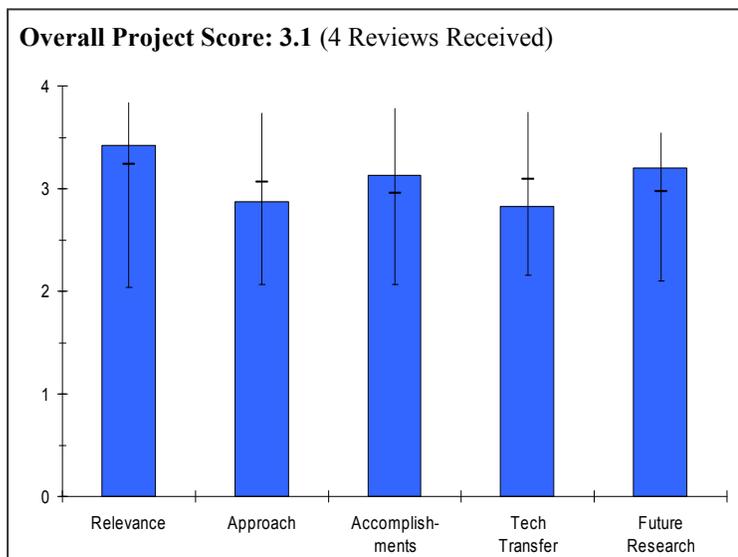
Brief Summary of Project

Alane has the potential to meet the DOE’s 2010 gravimetric and volumetric system targets, but regeneration of spent material is a critical issue. The objective of this project is to directly charge and recharge alane by developing a low-cost/high-yield electrochemical method for forming this material.

Question 1: Relevance to overall DOE objectives

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

- Alane has the potential to meet DOE 2010 gravimetric and volumetric storage capacities. Energy efficient and cost-effective methods for recharging spent alane are critical.
- (Off-board) recharging of alane is seen as a major hurdle to use of on-board chemical hydrogen storage. This project presents an alternate to chemical recharging.
- The general technical area, on-board hydrogen storage, is very important to the DOE goals.
- Success would provide another option for recharging chemical hydrides.
- Study of a high capacity storage material is in line with the DOE target.



Question 2: Approach to performing the research and development

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

- The hydrogenation of Al is the most serious issue for using AlH₃. To apply an electrochemical method is one of good approaches.
- Use of non-aqueous environment to suppress oxidation of Al is an interesting approach.
- Development of high pressure, non-aqueous electrochemical cell is a move in the right direction.
- Should include characterization studies in the approach to confirm AlH₃ formation.
- Assuming a “GO” decision, will need to consider electrode durability studies.
- Significant technical risks are evident such as operating conditions and continuous operation.
- Technical hurdles are recognized and will be addressed.

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

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

- They designed the reaction cell and successfully demonstrated the formation of alane. This shows possibility of off-board regeneration.
- Good decision to abandon aqueous-based process.
- Good process on development of non-aqueous high pressure based process.
- Initial results to produce AlH₃ look encouraging. Need to begin optimizing yields and measuring rates.
- Considering the October 2006 start date, significant progress has been made.
- The technical feasibility of the approach has been demonstrated.

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 BNL and U of Hawaii on rehydrogenation of Al.
- Other collaboration on characterization of the product is also fine.
- Responded to FY06 reviewer's comment and increased interaction with partners BNL and U of Hawaii.
- Good interactions – use of BNL thermodynamic data to guide electrochemical cell operations.
- There is no industrial participant.

Question 5: Approach to and relevance of proposed future research

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

- The proposed future plans are appropriate.
- Proposed future work should provide information necessary to make the go/no-go decision.
- Work to quantify yield and determine process efficiency should take top priority.
- Assuming energy efficiencies are favorable, optimizing cell performance and addressing durability issues should take second priority.
- Future work addresses questions which have arisen to date.
- Yield, efficiency, and cost need to be addressed, at least qualitatively – planned for future.
- Future work also addresses logical next steps.

Strengths and weaknessesStrengths

- The PI has adequate experience in the field of hydrogen storage materials.
- Non-traditional approach to rehydrating metal hydride carriers.
- Development of high pressure, high temperature electrochemical cells.

Weaknesses

- Criteria for go/no-go decision are not clearly presented.
- Need to address process energy efficiency for recharging aluminum - not clear how energy cost comparing wet and electrochemical synthesis addresses this issue. A quick "high level" electrochemical energy balance - theoretical energy compared to actual energy - would be a good starting point. More detailed balances will need to consider thermal energy required to maintain cell temperature, electric power generation inefficiencies, and other process energy inputs in calculation.
- Need to develop a better approach for dealing with passive oxide layer that forms on aluminum particles.

Specific recommendations and additions or deletions to the work scope

- Feasibility of scaling up and handling should be considered.
- Characterization of the product is recommended.
- Assuming a "GO", electrode durability and possibility of Pt loss due to dissolution or other processes should be addressed.
- Although premature, should begin considering cycling experiments measuring rate of hydrogen discharge coupled with electrochemical hydrogen recharge to confirm the electrochemical process does not degrade hydrogen storage capacity.
- Need to address process energy efficiency for recharging aluminum - not clear how energy cost comparing wet and electrochemical synthesis addresses this issue. A quick "high level" electrochemical energy balance - theoretical energy compared to actual energy - would be a good starting point. More detailed balances will need to consider thermal energy required to maintain cell temperature, electric power generation inefficiencies, and other process energy inputs in calculation.

Project # STP-28: Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

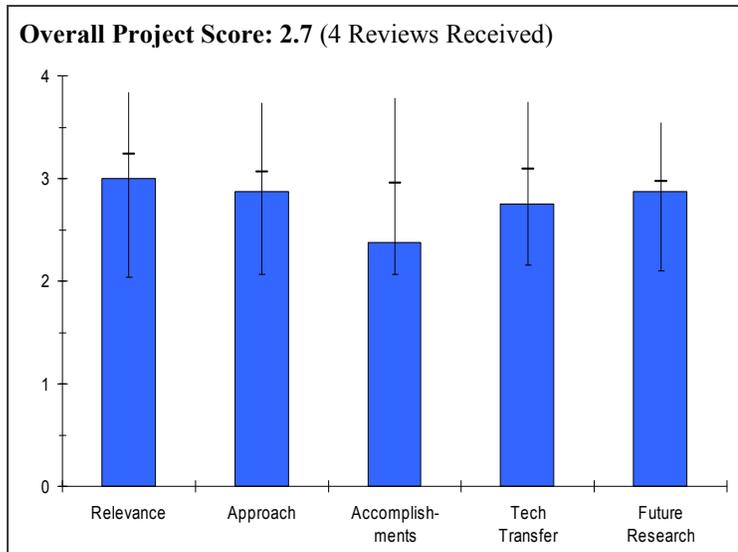
Channing Ahn; California Institute of Technology (CalTech)

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The objectives of this project are:

- To understand whether thermodynamically tunable reactions based on hydride destabilization, such as $Mg_2Si + 2H_2 \rightleftharpoons 2MgH_2 + Si$ that should be reversible but appear not to be, are kinetically limited;
- To address short hydrogenation times associated with refueling, that will require short solid-state and gas-solid diffusion path lengths;
- To 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. Systems of interest determined through “theoretical screening” by center partner members;
- To understand issues related to grain growth and surface/interface energies, vital in order to optimize the kinetics of hydrogenation/dehydrogenation reactions;
- To follow up on previously studied reactions with phase identification via X-ray diffraction, NMR and transmission electron microscopy.



Question 1: Relevance to overall DOE objectives

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

- Discovery of novel, high-capacity, reversible reactions is the ultimate goal of many in this field. This project is directed at this goal.
- Most of the project objectives are aligned with DOE R&D objectives.
- Synthesis of destabilized hydride systems and analysis of reaction kinetics is critical in meeting DOE targets.
- This project is reasonably well aligned with the goals of the Metal Hydride CoE. The selection of materials is guided by computational work done in other parts of the CoE, so the outcomes are determined in part by how fruitful the recommendations turn out to be.
- The findings of this project, whether favorable or not, are of value in that they elucidate performance limiting effects the calculations don't address.

Question 2: Approach to performing the research and development

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

- Destabilized metal hydrides are synthesized and characterized.
- Physicochemical hydrogenation measurements are coupled with appropriate materials characterization methods to sort out the relationship between predicted behavior and experimental observations.
- Nice to see this group quickly testing theoretical predictions in the lab. Experimental efforts seem to be carefully done, reliable, and reproducible.

- Looking at systems which are irreversible (and possibly kinetically limited) may be academically interesting but information being obtained is not helping advance systems toward obtaining H₂ storage goals.
- Studying systems which will not meet cost targets.
- The "theoretical screening" approach is very efficient.
- The experimental findings do not necessarily agree with the theoretical prediction; the PIs need to address this issue in their approach.

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

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

- Tested several theoretically-predicted reactions. Unfortunately, most results were negative.
- ScH₂-LiBH₄ system appears to be non-reversible, products observed in NMR and X-ray do not correlate with those predicted.
- NMR studies of value in following reactions.
- First direct mechano-synthesis of Ca(AIH₄)₂-LiBH₄ system.
- Demonstrated a low reaction enthalpy system.
- Need some fundamental understanding of Ca(AIH₄)₂ + 2LiBH₄ system.
- Need to validate the reaction mechanism.
- Several "theory recommended" systems were investigated.
- Experimentally determined desorption temperatures were higher than predicted. Kinetic limitations seemed to be the reason.
- Some informative materials characterization work was completed.

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

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

- Very nice to see this experimental group quickly testing theoretically predicted reactions (despite the largely negative results); would be nice for the Sorbent CoE to emulate this model.
- Collaborations not clear.
- The PI demonstrated certain coordination with other institutions.
- The PI need communicate with theory groups to incorporate some of the experimental findings into their future study.
- The project is guided in part by recommended systems for study determined in other parts of the CoE. It's good to have a few projects like this to explore the predictions of the theory component of the CoE.

Question 5: Approach to and relevance of proposed future research

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

- Proposed future research seems like a reasonable direction, particular the aerogel work and the determination of whether this affects thermodynamics or kinetics.
- Much of the proposed future work relies on aerogel scaffolds, scaffold work has run into some problems in the chemical hydrogen storage center, decrerasing effectiveness at higher loadings.
- NMR studies could provide very useful information.
- Plans are built on past progress.
- When setting a future research direction based on some of the literature results, the PI needs to validate some of the claims first in order to efficiently direct the available resources.
- The future plans are in part a logical extension of prior work. But, there are eight or nine task areas, which seems like too many for a project of this size.
- It might be better to interact with the planning component of the Metal Hydride CoE to determine which tasks deserve the highest priority and to focus on those tasks.

Strengths and weaknesses

Strengths

- NMR studies.
- "Theoretically screened" approach is very efficient.
- Good collaboration effort with different groups.
- An enthusiastic PI and a hard working group of students.

Weaknesses

- Have been investigating systems which are not likely to meet targets (cost, reversibility).
- The experimental finding that is different from theory prediction needs to filter through to the theory group and be incorporated into future theory prediction.
- If this project is going to continue to be guided by the recommendations/results from other parts of the CoE, the results of their work may continue to be uninspiring albeit useful and interesting.

Specific recommendations and additions or deletions to the work scope

- Refinement of the future plans is recommended with input from the CoE.
- The future plans are in part a logical extension of prior work. But, there are eight or nine task areas, which seems like too many for a project of this size.
- It might be better to interact with the planning component of the Metal Hydride CoE to determine which tasks deserve the highest priority and to focus on those tasks.

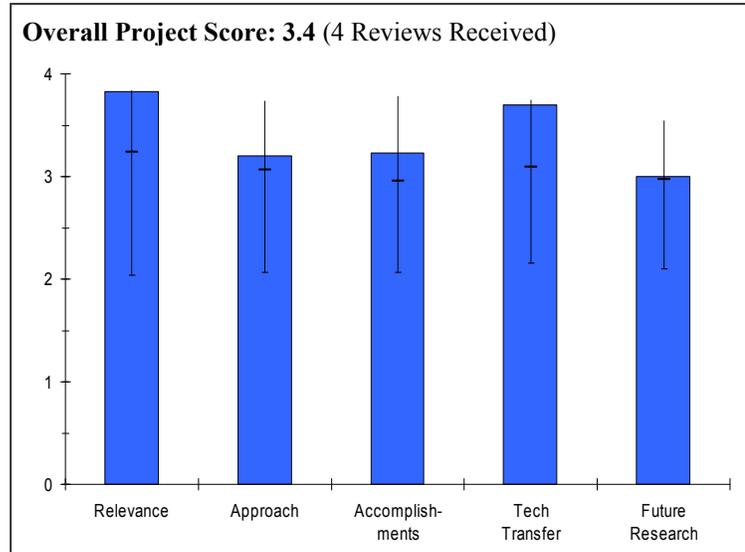
Project # STP-29: Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

Dhanesh Chandra; University of Nevada, Reno

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The primary objective of this project is to determine the effects of gaseous impurities (ppm levels of O₂, CO, H₂O etc.) in the H₂ on long-term hydriding/dehydriding of complex hydrides, and a related secondary objective is to determine the mechanisms of degradation. Accelerated laboratory tests designed at UNR can simulate these conditions providing insights into the long term reliability of complex hydrides and their precursors. Research in 2007 focused on effects of using industrial hydrogen for 1100 cycles in a Li₂NH-LiNH₂ system. Pressure cycling (~500 cycles) using 100 ppm level O₂ impurity in ultra-high purity (UHP) H₂ as well as thermal aging (CO impurity) of mixed phase Li₃AlH₆-LiNH₂ have been completed.



Question 1: Relevance to overall DOE objectives

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

- This project plays an important supporting role toward the DOE's RD&D plan in evaluating and characterizing promising compositions and their response to impurities and cycling.
- Determination of the effect of impurities on hydrogen storage characteristics and stability is a critical part of the hydrogen and fuel cells for transportation program.
- Fundamental understanding of hydride hydrogen storage capacity and physical stability are crucial to meeting DOE durability targets.
- Addressing an important area – role of impurities.
- Component relevant to fundamental understanding: phase transitioning.
- Studying vaporization thermodynamics, which is often overlooked.

Question 2: Approach to performing the research and development

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

- The approach and techniques used are very useful and appropriate toward evaluation of aging and impurities. All of the necessary instrumentation and experimental protocol seems to be well-developed and useful in testing materials. These studies, however, could be a bit more focused and thorough. For example, a variety of different 'exposure' conditions and impurity levels should be tested (including reference data) for each composition.
- This project appears to be covering many areas and should be rethought and refocused on the relevant issues at hand.
- Good analysis tools.
- It is not clear how and if the fundamental mechanistic studies will be generalized from the specific hydride systems being studied to other systems.

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- Will general conclusions on effects of impurities be drawn from the impurity empirical work? What are the general mechanisms of the impurity effects?
- Needs more theory.
- Use of an array of techniques: Sieverts, in-situ diffraction, microbalance.

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

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

- A variety of hydrogen storage compositions (fed from the MHCoe) have been preliminarily investigated using a variety of measurement and characterization techniques. The most relevant compositions from the metal hydride CoE seem to be rapidly transferred to this partner for evaluation and the testing thoroughly and efficiently performed. While, these studies are vital to the eventual application of a suitable hydrogen storage material, their impact could be maximized with a more detailed experimental focus on each composition rather than a rough survey of many compositions.
- Most of the technical accomplishment appear not impactful to state of the art. The relevance of the approach should be considered.
- The effect of CO on hydride behavior is interesting and encouraging. Is the same behavior expected on other hydrides?
- The mechanistic studies are extensive but the relevance gets lost in the data. How do the results affect the direction of metal hydride research?
- Studied numerous systems: alanate-amide, amide-imide, BH₄-based.

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

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

- Impressive communication between experimental partners and this project. Very effective materials selection and communication lines are in place which drive the current and future success of this project. It would also be nice to see promising materials from other CoEs fed to this project.
- A hydrogen producer would strengthen the team.
- Very good collaborations, which are continuously expanding.

Question 5: Approach to and relevance of proposed future research

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

- Strengthen focus on individual compositions under a variety of different impurity and cycling conditions in order to fully characterize the durability and impurity tolerances (and resulting failure modes). Likewise, it is important to include reference/control data for each experiment.
- Needs to be focused.
- Important future work includes more interaction with the theory efforts of the MHCoe.
- Experimental future work follows logically.
- Clear path forward.

Strengths and weaknesses

Strengths

- Experimental capabilities are impressive. Focus on evaluating materials in a potential 'on-board' environment is highly valuable.
- Impurity analysis-critical study. Should be expanded to include other trace gases that metal hydride could be exposed to.
- Integrated use of different techniques.
- Strong collaborations with other partners in the Center.

- Strong international collaborations.
- Addressing rarely thought about issues (vaporization of metals in the alanates and BH_4).

Weaknesses

- Needs boundaries of investigation. For example, material cycling and response to impurity are the assigned studies. However, there seems to be a gray area as to the degree to which this project is being used for fundamental measurements and characterization which should be performed elsewhere.
- Research appears defocused. Impurity effects important enough to be entire study. Linkage to center of excellence not well explained.
- Recommend more feedback from theory.

Specific recommendations and additions or deletions to the work scope

- Make impurity effects focus of study.
- A single page with one-line bullets of high-level accomplishments would help the reviewers understand what has been done and the significance.
- Too much data if that's possible. The conclusions/message get lost in the charts for someone who doesn't "live" with the analysis techniques and their output graphs.
- Recommend more feedback from theory.
- None.

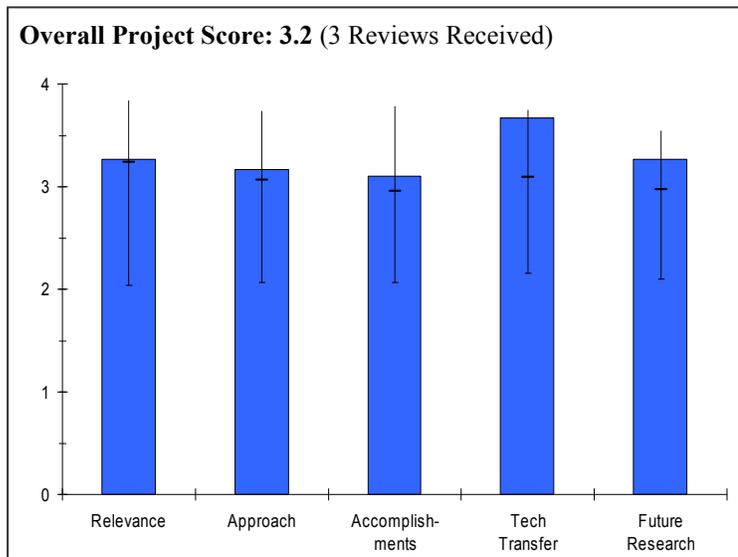
Project # STP-31: Metal Hydride-Based Hydrogen Storage

Ian Robertson (PI), presenting; Duane Johnson (Co-PI); University of Illinois Urbana-Champaign

[Member of the Metal Hydride Center of Excellence]

Brief Summary of Project

The overall objectives of this project are to support and guide development of complex metal hydrides to meet systems requirements by providing center partners with structural and chemical insight of candidate systems and providing experimentally-based and validated theoretical modeling. Specific objectives in FY 2007 are to provide modeling to guide materials development, provide understanding of the role of catalysts, and determine nature, state and effect of surface contaminants on hydrogen uptake and release.



Question 1: Relevance to overall DOE objectives

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

- This MHCoe support project is clearly contributing to the President's Hydrogen Fuel Initiative.
- Project focus is on high-capacity hydrides that need to be optimized to meet DOE targets listed in the Hydrogen Fuel Cell and Infrastructure Technologies' Multi-Year RD&D plan.
- This project provides direct support of materials development in the metal hydride CoE.
- Project is in a good agreement with DOE objectives.

Question 2: Approach to performing the research and development

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

- The effort serves as a miscellaneous support and service vehicle to the MHCoe and thus indirectly helps the "assault" on the many technical barriers to vehicular hydrogen storage.
- PI and his students make important contributions to the MHCoe partners in the form of structural studies, surface chemistry and theoretical modeling.
- It is more a support effort than a lead effort. In that sense, it provides scientific objectivity over competition for a new and revolutionary material.
- This project consists of two relatively independent parts. One is experimental and provides structural and chemical information on metal hydrides. The other part is theoretical, using first principle calculations to determine thermodynamic properties of hydride structures. Both parts interact closely, providing information to each other as well as to the center partners that they are collaborating with.
- This project is not involved in the development of a specific hydride material or system. Both parts provide support to the material development efforts within the CoE.
- Development and maintenance of a structural database is an important contribution to all modeling activities in this center and could be used by other centers.
- University of Illinois's approach is in good agreement with the goals and objectives of the MHCoe and the funding.

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

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

- The project is fairly new, but has made several contributions in the first year or so.
- Work has focused on high-capacity materials such as $\text{Ca}(\text{BH}_4)_2$ and LiBH_4 .
- Progress has been made in understanding surface contamination; this has led to suggestions for improving kinetics and reversibility.
- Ab initio calculations have confirmed (or not) other calculational approaches within the CoE and other DOE projects.
- A very useful structural database has been created.
- Experimental efforts were focused on borohydrides, including (1) examining rehydriding of Ca borohydride on a microstructural scale; (2) determining non-uniform dispersion of Pt catalysts on Ca borohydride; (3) found uneven distribution of different catalysts on Mg borohydride. These results indicate the complexities involved in determining the optimal fabrication techniques for enhancing hydride kinetics, rehydriding yield, etc.
- Theoretical modeling was mainly directed on Li borohydride: (1) Molecular Dynamics study that determined the high temperature structure and transition enthalpies; (2) DFT calculations that predicted formation enthalpy and P-T curves. Other work examined the reaction of oxygen with LiH as a possible poisoning reaction preventing re-hydriding of Li alanate.
- The approach used has been tested using relatively simple test system - LiBH_4 . Whether it would work for more complex ones remains to be seen.
- Chemistry of alanates, borohydrides and metal hydrides is well established. An additional literature search or collaboration with chemists may benefit the project.

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

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

- The project has many useful collaborations within the MHCoe.
- This effort is a very important scientific support contribution to the CoE and could be even more used in DOE projects outside the CoE.
- Excellent collaboration with center partners.
- Collaboration and tech transfer are quite impressive.

Question 5: Approach to and relevance of proposed future research

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

- The future work is fine. Continue as planned.
- Future work appears to be mainly to continue on the current path by supporting the development of hydride materials by center partners.
- New areas include experimental work examining structure/chemistry of contaminant layers and their role in inhibiting rehydriding, modeling work on kinetics and poisoning issues associated with O^+ and OH^- .
- Future work looks good.
- A collaboration with chemists may bring additional benefits.

Strengths and weaknesses**Strengths**

- The project provides an excellent spectrum of tools to aid the MHCoe partners.
- The modeling activities provide a reality check to other modeling activities within the MHCoe.
- Excellent experimental capabilities in microstructural analysis.
- Excellent theoretical modeling capabilities.

HYDROGEN STORAGE

- A good combination of advanced characterization techniques with first-principles electronic and thermodynamic calculations.
- Understanding of advantages and limitations of the approach(es) used.

Weaknesses

- No significant weaknesses.
- A significant part of the future work is "work for others", which may have a negative impact on the final outcome of the project.
- A careful screening of the literature on chemical behavior of light metal hydrides can be advised.

Specific recommendations and additions or deletions to the work scope

- Consider broadening this support activity beyond the MHCoE to other CoEs and non-CoE DOE projects.
- The experimental capabilities of UIUC could be expanded to include more detailed surface science studies of impurity and oxidation effects in complex hydrides and their possible role in inhibiting kinetics and rehydriding. Related work already appears to be in future plans for the modeling effort.
- In-situ studies of microstructural changes during reactions of complex, mixed hydride systems could shed some light on kinetics and intermediate reaction paths.
- A collaboration with chemists may bring additional benefits.
- A careful screening of the literature on chemical behavior of light metal hydrides can be advised.