Hydrogen Storage
Summary of Annual Merit Review Hydrogen Storage Subprogram

Summary of Reviewer Comments on the Hydrogen Storage Subprogram:

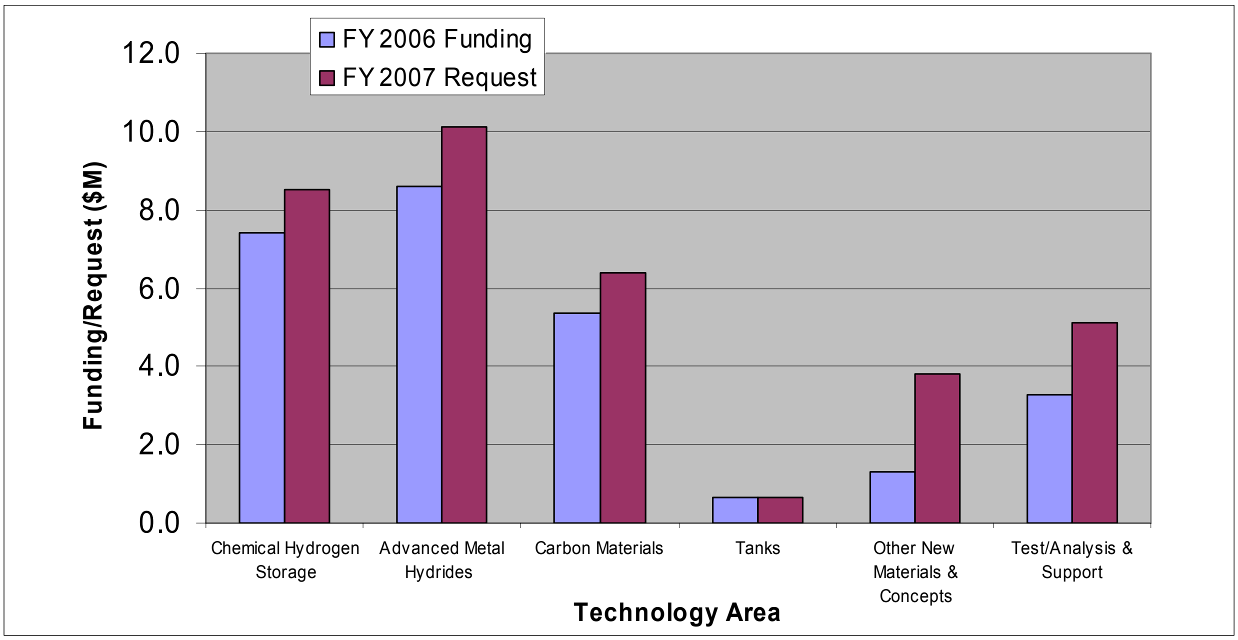
Reviewers consider hydrogen storage to be a critical enabling technology to the hydrogen economy and it remains a significant technical challenge. Overall, the R&D portfolio was judged to be robust, emphasizing key areas and well focused on the DOE targets. According to reviewers, the subprogram "is getting more refined and is constantly evolving in the right direction." Reviewers commented that DOE's "strategy is appropriate, to continue emphasizing a wide net of higher risk-high reward research." Some reviewers commented that the projects have shifted closer towards more basic science and need to keep sight of system and engineering issues. It was also stated that the use of the Centers of Excellence (CoE) "is an appropriate method to manage this diverse portfolio and promote synergy and enhance innovation." However, it was also clear that the flexibility provided by independent projects outside the CoEs is critical as well and that "maintaining independent projects ensures agility." Reviewers emphasized that "storage requires breakthrough discoveries" and that DOE has done an effective job in "developing the proper background and foundation for achieving these discoveries."

Note that although the basic science hydrogen storage projects (funded by the DOE Office of Science, Basic Energy Sciences) were not formally reviewed, FY2006 was the first time both basic science and applied research projects were presented together. This facilitated more interaction between both research communities and increased coordination since the inception of the efforts in FY2005. A "Theory Focus Session" on hydrogen storage materials was also conducted, co-organized by the Office of Science (Basic Energy Sciences) and Office of Energy Efficiency and Renewable Energy (Hydrogen, Fuel cells and Infrastructure Technologies), which included experts from around the world to further help define theoretical research needs in hydrogen storage
(see: http://www1.eere.energy.gov/hydrogenandfuelcells/wkshp_theory_focus.html).

Suggestions and general comments for DOE to address include:
- Provide more information on how the CoEs operate (meetings, openness, duplication of efforts, etc.)
- Ensure that lessons learned are shared among the CoEs. Interaction mechanisms among the CoEs may be valuable (e.g., issues with metal hydrides that are not reversible on-board as part of the Metal Hydride CoE may benefit from progress in the Chemical Hydrogen Storage CoE).
- Continue to remind researchers that targets are system, not material-based targets.
- Expand the discussion of engineering issues including thermal management, system integration, reactor design, and safety/hazard aspects of the materials investigated.
- One area that needs more emphasis is tank systems, which will be used for most solid state/material approaches as well. Research is still needed for cost reduction of high pressure tanks, which will most likely be used in early mobile and stationary applications.
- A recurring concern was the redirection of funds to congressionally-directed projects and the reduction of competitively selected, merit-based projects within the portfolio.

Hydrogen Storage Funding by Technology:

The funding portfolio for hydrogen storage addresses primarily long-term materials R&D to meet 2010 and 2015 targets for on-board applications. The requested EERE FY2007 funding profile (subject to congressional appropriations), which includes the CoEs and independent projects, continues to address the National Academies' report recommendations to "shift…away from some development areas towards more exploratory work" and that "the probability of success is greatly increased by partnering with a broader range of academic and industrial organizations…" Continued support, at a low level, for compressed hydrogen/cryogenic tanks emphasizes cost reduction and novel conformable designs. In addition, it is recognized that materials-based solutions will require low-cost, conformable tanks and would benefit from current R&D in this area. Key milestones for FY2007 will be (1) a system that meets the targets of 1.5 kWh/kg and 1.2 kWh/L and (2) a go/no-go decision on sodium borohydride-based systems ($NaBH_4$). Subject to congressional appropriations, the storage program will also have approximately 3 to 6 new awards from the FY2006 solicitation that will start in FY2007. The chart below illustrates the funding in FY2006 for each major activity along with planned funding in FY2007 based on the Program's budget request.



Majority of Reviewer Comments and Recommendations:

Chemical Hydrogen Storage: The Chemical Hydrogen Storage CoE was commended as well integrated and with excellent collaborations among multi-disciplinary partners. It was felt that the CoE has made good technical progress and produced promising results and that the synergy of the center has enhanced its accomplishments as a whole. However, several critical issues remain, including viability of off-board regeneration, slow discharge kinetics and limitations of systems that require water for on-board hydrolysis. Chemical hydrogen storage researchers were encouraged to focus on regeneration of the spent fuel and continue to pursue high capacity storage materials to enable a viable storage system. Additional recommendations are to start developing down-select criteria to narrow down options and to include cost as a factor in the search for effective catalysts.

Advanced Metal Hydrides: In general, the reviewers agreed that the full set of capabilities established in the Metal Hydride CoE represents an impressive array of tools for the study of hydrogen in metals. It was acknowledged that PIs are demonstrating flexibility and adjusting their materials research, based on early results and viability to meet DOE targets. Both in the Metal Hydride CoE and in independent projects, the utility of theoretical modeling in guiding materials discovery has been demonstrated and is in the process of being expanded. The use of experimental high-throughput synthesis and testing capabilities is accelerating materials discovery and is encouraged by the reviewers. As materials with suitable thermodynamics are identified, the hurdle of improving hydrogen discharge/up-take kinetics is being addressed by utilizing catalysis and reaction engineering. The reviewers acknowledged that the metal hydride work is beginning to address issues common to the Chemical Hydrogen and Carbon CoEs.

The issues of thermal integration for hydrogen re-fill/discharge and material regeneration will benefit from collaborations with the Chemical Hydrogen CoE. Similarly, the work to address kinetics by both catalysis and studying size effects will contribute to the Carbon and Chemical CoEs. The reviewers agreed that going forward with material down-selections and go/no-go decision points will be critical and that these processes should be quantitative and transparent.

Carbon Materials: The reviewers credited the Carbon CoE for expanding its focus beyond single walled nanotubes (SWNTs) to a diverse set of high surface area adsorbent materials. It was also stressed that adsorbent materials have the potential to offer alternatives to metal hydride approaches with reduced re-fill heat rejection requirements and improved hydrogen kinetics. The approach taken by the CoE was found largely sound: theoretical modeling to material synthesis to development. The reviewers were concerned that the CoE was stressing modeling at the expense of "proving" these experiments through synthesis and testing and recommended increased investment in the latter activities. For all adsorbent work in the program, most reviewers stressed that for the vehicular application, adsorption must be addressed to occur at close to ambient temperature rather than solely at cryogenic temperatures (e.g. 77K). As hydrogen binding energies are increased, the reviewers also noted that the issues of hydrogen uptake/discharge kinetics as well as thermal management will need to be addressed. This work will benefit from increased collaborations among the three centers, as noted above. Finally, volumetric capacity is a greater hurdle with these materials compared with gravimetric capacity and should receive priority.

Tanks: Tank projects were not reviewed in FY2006 due to the limited number of projects and the reduced effort on tanks. In lieu, DOE is conducting an independent assessment of cryocompressed tank technologies, with results to be made available at www.hydrogen.energy.gov by early FY2007.

Testing and Analysis: The analysis projects (Argonne National Laboratory (ANL) and TIAX LLC) were considered critical to the program in providing independent assessments of all storage options. Further refinement of assumptions and validation of models are essential. Strong coordination between TIAX and ANL, as well as with relevant storage system developers, was recommended. The independent testing project (SwRI) was not formally reviewed in FY2006; the materials test facility was completed and is available for testing external samples.

Note on Storage Report Structure:

Chemical Hydrogen Storage.
ST-01 to ST-08 and STPs 25, 26 and 27 are partners of the Chemical Hydrogen CoE.
ST-09 is an independent project.

Metal Hydrides.
ST-13 to ST-18 and STPs 03, 04, 05, 6, 7, 8, 9, 10, 12 are partners of the Metal Hydride CoE.
ST-10, ST-11 and STP-02 are independent projects

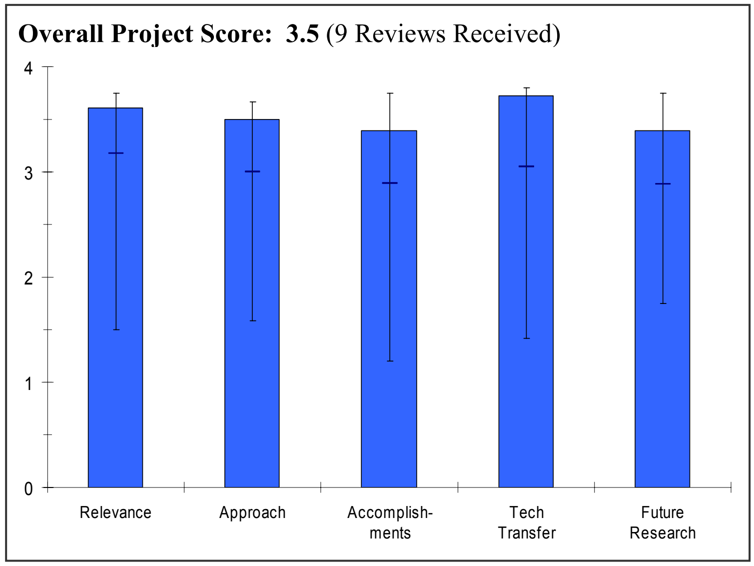
Carbon.
ST-23 to 28 and STPs 15, 16, 17, 18, 19, and 21 are partners of the Carbon CoE.
ST-21 and ST-22 are independent projects

Analysis.
ST-19 and ST-20 are analysis projects

Cross-Cutting,
ST-12, STP-37, and STP-43 are cross cutting projects covering hydrogen storage and fuel cell technologies.

Project # ST-01: DOE Chemical Hydrogen Storage Center of Excellence: Center Overview & Los Alamos National Laboratory Contributions

Bill Tumas; Los Alamos National Laboratory



Brief Summary of Project

[NOTE: This review is on LANL's contributions, not on the entire DOE Chemical Hydrogen Center of Excellence. Each of the partners is evaluated separately.]

The chemical hydrogen storage CoE involves two national laboratories, seven universities, and four industrial companies. The objectives of the CoE 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 2015 goals:

1. Develop materials, catalysts and new concepts to control thermochemistry and reaction pathways
2. Assess concepts and systems using engineering analysis and studies
3. Select most promising chemical systems for engineering development
4. Develop life cycle inventory and demonstrate a 1 kg storage system
5. More efficient borate-to-borohydride (B-OH to B-H) regeneration
6. Alternative boron chemistry to avoid thermodynamic sinks using polyhedral boranes (B_xH_y) or amine-boranes
7. Concepts using coupled endo/exothermic reactions, nanomaterials, heteroatom substitution for thermodynamic control

Question 1: Relevance to overall DOE objectives

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

- Relevance has increased with the diversification into more chemistries. Plan to trim non-productive research – if implemented with vigor – will further improve this criterion.
- Well aligned.
- Need to identify materials with potential to meet DOE targets.
- The CoE is clearly relevant to the President's Hydrogen Fuel initiative; hydrogen storage is identified as the critical need for transportation. Off-board regeneration is the critical step to determine if the chemical hydrides are viable on a round trip basis. Off-board regeneration should have significant on-board advantages (weight or volume efficiency) to make up for the round trip efficiency losses.
- Chemical hydrides are highly relevant towards achieving the DOE goals. This CoE seems to have the best overall appreciation of these goals, and how they guide the research direction.
- Good! Quoted volumetric densities all the time!
- This program strongly supports the Hydrogen initiative and objectives.
- Hydrogen storage is the key enabling technology critical for the success of hydrogen as a transportation fuel. Any work which can further understanding of the basic science of hydrogen storage is vitally relevant to DOE objectives, the President's Hydrogen Initiative and the objectives of the Multi Year R&D Plan. The chemical hydrogen storage CoE is a key research activity which supports all these objectives.
- This research shows very high potential to meet the DOE system goals.
- Work in the CoE is central to hydrogen program storage development. Must have vigorous effort in all approaches to storage, including chemical hydrides.

- LANL work essentially covers full spectrum of work included in the CoE.
- Ammonia-borane holds a clear promise for meeting the DOE targets for hydrogen storage materials. However, it remains questionable whether the serious regeneration and cost issues about this compound and related compounds can be overcome that will allow its practical application to onboard hydrogen storage.

Question 2: Approach to performing the research and development

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

- Good efforts on CoE management.
- Program is well integrated internally. In general the plans are feasible at least in theory. Some questions on the case of electrochemical reversal of BO_2 to BH_4, but new programs are well poised.
- Good understanding of DOE targets; focused on correct technical barriers.
- Good mix of experiment/theory; Good use of computational chemistry.
- The technical barriers are correctly understood. The overall project is designed well. Need further diversification to consider candidates beyond boron-chemistry.
- The CoE is taking a logical, methodical, and thorough results-focused approach to addressing the barriers to a viable hydrogen storage system.
- Good CoE structure; good approach for downselect; CoE has defined down-select procedures and some criteria; flexibility in shifting work
- Good approach.
- CoE appropriately splits efforts in parallel regarding, regeneration, kinetics, etc.
- Regeneration is the key issue with all chemical hydrides. Efforts are being made toward identifying new methods for the electrochemical reduction of $[B(OH)_4]^-$ and regeneration of dehydrogenated ammonia borane. However, the project is too weighted towards improving dehydrogenation kinetics rather than solving the key issue of developing a practical regeneration processes. The organic based systems do not seem to be a very promising approach.
- Would like to see more carbon-based hydrides (not just N & B--assuming no conflict with Carbon CoE).
- Hydride regeneration needs to be considered from day-one on new materials.
- Put "experimental demo of regeneration" above "engineering assessment of H_2 release" in priorities on "funnel" diagram.
- CoE goal of 50% efficiency of recycling seems to be set low; encourage to aim higher.
- Good to expand CoE interest to non-boron chemistries. Need some clearer definition of where to look and what systems seem most promising. Need to articulate some of the downselection criteria reasonably soon as 2007 is drawing close.
- It's good to keep numerous parallel approaches in the first two years of CoE operation but some thought needs to be given for down selection criteria to narrow down the options from among many choices.
- Concentration is appropriately shifting from $NaBH_4/H_20$ systems to amino borane and other liquid carrier systems. Work on B-O regeneration from R&H should be final point for $NaBH_4$ work.
- CoE is demonstrating appropriate balance between modeling and experiment to down select possible materials
- LANL work well integrated with CoE partners

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

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

- The CoE as a whole has made good progress; possibly the best progress of any of the CoEs. Several of the partners have produced results that hold real promise of being able to meet the long term storage targets. LANL's own projects are also promising with positive results from the ammonia borane work. Although lab results have been promising, a more practical solution is needed if ammonia borane is ever to be used in a production vehicular storage system.
- This CoE is providing the most novel ideas and approaches of all CoEs and is actively trying out new materials with some success

- Evidence of good progress from inception of the CoE. It is still a long time to go until the go/no-go decision on sodium borohydride. Last year the CoE was just forming, and this year a number of chemistries for the rehydrogenation step have been identified. It is not clear which one(s) have the most promise, but at least they have been identified.
- I expect this to improve in future, as there is good work underway, but the actual demonstrated progress in the last year is probably best termed between fair and good.
- Many high density materials have been demonstrated although no one material has demonstrated good kinetics, regeneration etc all at once.
- Kinetics still an issue and economical regeneration is unclear at this point.
- Program shows good progress for 1st year.
- LANL made important progress in all areas
- Some promising areas identified for future work
- Need to focus on identifying most promising systems and moving forward.
- The development of a method for the "B-O to B-H" conversion that involves a readily re-generable alkaline hydride rather than the irreversible oxidation of a metal hydride is a truly significant achievement. The development of catalysts for hydrogen release from ammonia borane is nice technical achievement but represents progress on a very secondary front.
- Avoidance of BO bond formation is a good idea.
- Very good that there is significant work on ammonia borane regeneration (w/Penn). This is really the key obstacle for this (and generally for chemical hydride) systems. Have developed a process, albeit a complex one.
- B-OH to B-H work doesn't look terribly inspiring. We will have to wait until next year to see whether any of these pathways actually prove promising. Have a good exit strategy to get out of this game, if things don't prove promising soon.
- Encouraging results on H_2 release.
- Reformation of hydride using formic acid is very significant development.
- Some interesting work on organic hydrides - how does this couple/differ from Air Products work? Why are there so much lower densities than the similar approach from Air Products? It seems like as a base-line, you should be able to build on their ideas? There is a projected theoretical number of >8wt.%, but this is greater than 1 H/C; what is the idea here?
- 5 patents filed; very prolific generation of ideas.

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

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

- LANL is doing an excellent job of CoE coordination. The projects at LANL are well interfaced with multiple collaborations of CoE partners.
- Reasonable mix of partners.
- May need to work to promote interaction between scientists and engineers (chemistry and process design).
- Lots of collaboration and excellent IP arrangement to enable more. Tech transfer is built in with appropriate and strong industry involvement.
- Collaboration between the CoE members appears to be excellent. The university contributions seem to be well integrated into the CoE's portfolio. It appears that the universities can provide some of the basic information on reaction chemistries of interest. It appears that the accomplishments of the CoE as a whole are greater than the accomplishments of the individual members would have been without the benefits of the synergy between the members.
- General comment about dehydriding of AB: there are many separate strategies about this, and new catalysts proposed: what is the coordination between these efforts?
- The CoE has assembled a world class group of partners to work toward the goals of hydrogen storage.
- CoE is collaborating with all the appropriate members and institutions. CoE must be careful about relying too heavily on systems design and assumptions from one partner, other partners in system design should also be pursued.
- Interactions within CoE clear, but not clear with respect to outside of the CoE.

Question 5: Approach to and relevance of proposed future research

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

- Future research plans for both the CoE and LANL appear to be well conceived, thorough and are working toward the go/no go decision points as well as the goals of the program.
- The plans are interesting, innovative and on target. Costs are probably not very well considered, but that is not inappropriate when other goals are far from being met.
- Reasonable goals for next year.
- Go/no-go needs to go forward--regeneration should be prime consideration.
- The CoE has laid out a plan to acquire the knowledge necessary to define the criteria by which to make a go/no-go decision on the borohydride system. However, this decision is not very far away and it is not too early to start laying out the criteria for evaluating the process that will be used to arrive at the decision.
- Will $NaBH_4$ decision rule out other boron routes that go to borate? Since regeneration is critical, that should be part of go/no-go criteria.
- Studies focused on the re-generation of ammonia borane are of key importance and well designed. Work on "non-boron-based 6-7 material wt.%" should be de-emphasized as it seems very unlikely that system based on these materials will meet the DOE goals.
- Need to consider further contingencies in case ammonia-borane does not work out. Further consideration of other regenerative carbon-based hydrides.
- Direct more effort toward regeneration processes on promising candidates since this is a critical aspect of any chemical hydride approach
- Some of the catalyst research for improving aminoborane kinetics seems uncoordinated and/or duplicated. Some more coordination from the CoE is required to fully maximize resources on this issue
- Lean away more from borohydride, concentrate more on the coupled reactions

Strengths and weaknesses

Strengths
- Well organized CoE with strong partners and focused research ideas.
- Strongest CoE.
- Probably have the clearest view of a total system, not just material.
- Good understanding of the fundamental chemistries involved in the boron-nitrogen system. The CoE appears to be up and functioning with excellent collaboration between the partners in evidence. The CoE rightly has cast a wide net in examining various B-N systems because it is too early to downselect to specific paths to regeneration.
- Positive progress with storage technologies in both CoE partners and at LANL.
- Quality of team in this area.
- Technical Expertise.
- Strong leadership from PI. Of the three CoEs, the Chemical CoE has the best grasp on "SYSTEM" and regeneration issues and are either addressing or keeping in consideration all aspects of the system design in their materials discovery path. Amineboranes are demonstrating very high storage densities in terms of volume and gravimetric.
- Strong program management. Excellent collaboration among the CoE members. High degree of technical competence across the entire program. Innovative approach. Using an effective approach on go/no-go decisions. The PIs and management understand the barriers well. Significant accomplishments in the short period.
- Leadership by LANL has been very good. The science has been good too.
- Management Program.
- Progress toward the re-generation of ammonia borane.
- Number of options theoretically meeting 2015 goals.
- Number of new programs.

Weaknesses

- The electrochemical "B-O to B-H" project seems to be approaching a dead end.
- Not sure of capabilities of team for process design/simulation and economic assessments. These efforts need to be started early in concert with experimental work.
- Recycle efficiency goal seems low.
- The overall CoE presentation was a little hard to follow. This probably was a function of the amount of material and information that needed to be presented. That said, however, some fundamental background information to provide a better perspective on how chemical hydrides fit in the overall picture on hydrogen storage would have been helpful. The following talks actually clarified some points from the first presentation.
- It is hard to assess the likelihood of success for $NaBH_4$ regeneration. Data mining did not reveal any favorable pathways, and electrolytic regeneration attempts have not met with success. The only hope appears to be some pathway based on proprietary Rohm and Haas data that was alluded to in the presentation.
- Would like to see more information about the B-O to B-H work at LANL; PI should try to find a way to share more details without compromising IP.
- Recommend that summaries of status be shown in terms of system targets to make it easier to compare progress to the system goals and not to material capabilities.
- One of the initial and key strengths of the CoE is that liquid carriers would allow for cheap and conformable tank systems. The recent shift in material research to solid amino boranes has potentially jeopardizing this strength. Strong efforts should be made to solubilize these materials into free flowing liquids in order to maintain system simplicity. If a compromise in storage density is required to liquefy the materials, It is better to cut the storage density of the fluid in half rather than double the amount of ancillary equipment required to handle the solids. From an OEM perspective, material handling of solid fuels is not preferred.
- The CoE is overly dependent on one partner for system design of liquid based carrier fuels. The CoE should seek additional partners to balance and provide alternative approaches and provide checks and measures to current partner's assumptions and claims.

Specific recommendations and additions or deletions to the work scope

- Stay on all participants to generate data. The main lack is hard data to pour into the evaluation "funnel".
- The CoE should elaborate on their plans for assessing progress on individual projects and the means by which new ideas will be incorporated into the CoE.
- All members of the CoE need to keep the basic requirements for a viable on-board system in mind at all stages of the research. Any concept involving solids handling on vehicles is not desirable.
- The go/no-go decisions and criteria need to be developed.
- The down selection process mechanics need to be articulated.
- Conceptual process design for on-board system using solids.
- As soon as possible, the CoE needs to determine if there is any real value in $NaBH_4$ as a vehicular storage media, and if not, discontinue work on it to focus on more promising developments. There are plenty of chemical alternatives that bear further study to continue work on $NaBH_4$ if it is proven to be of minimal feasibility.
- The potential of the "organic hydrides" is rather marginal and work on these compounds should be deleted.
- Probably should use the lower heating value of hydrogen in burn ratio, HHV [higher heating value] is unlikely to be achieved.
- Go no-go for borate regeneration should be heavily based on outcome of the Rohm and Haas project on identifying economical regeneration routes.

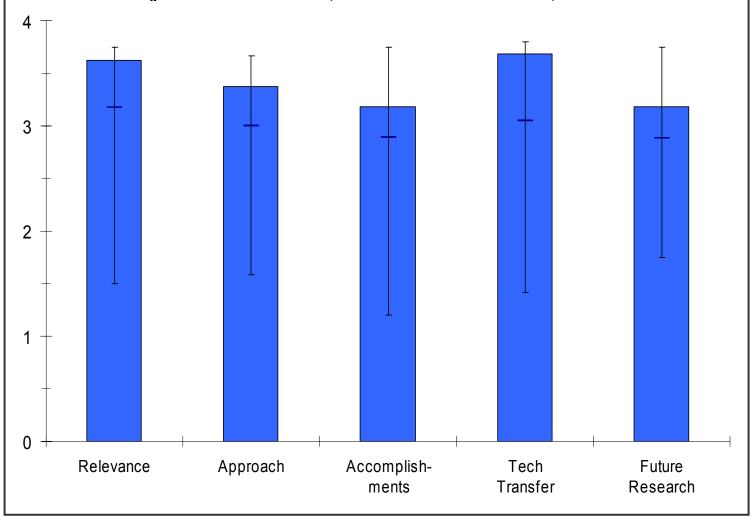
Project # ST-02: DOE Center of Excellence for Chemical Hydrogen Storage: PNNL Progress

Chris Aardahl; Pacific Northwest National Laboratory

[Partner of the DOE Chemical Hydrogen Center of Excellence]

Brief Summary of Project

Overall Project Score: 3.4 (8 Reviews Received)



[NOTE: This project covers the 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 fuel cost. The approach includes assisting in evaluation of improved regeneration strategies for sodium borohydride (SBH), examination of other boron systems such as the ammonia boranes, and discovery and development of new chemical systems beyond boron. Viable bench-scale chemistry from the CoE 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 **3.6** for its relevance to DOE objectives.

- Hydrogen storage is the key enabling technology critical for the success of hydrogen as a transportation fuel. Any work which can further understanding of hydrogen storage is vitally relevant to DOE objectives, the President's Hydrogen Initiative and the objectives of the Multi Year R&D Plan. PNNL in this project supports the chemical hydrogen storage CoE, which is a key research activity supporting all these objectives.
- PNNL's contribution to the chemical hydride CoE is important in two areas related to sodium borohydride: developing models to investigate processing options for higher concentrations of NaBH and extensive literature review of NaBH regeneration schemes. In addition the work on ammonia borane scaffold material is very important to the study of ammonia boron systems.
- Certainly relevant programs.
- Work is completely in line with hydrogen program storage development
- Amino borane materials are showing good promise towards achieving some DOE targets.
- Ammonia-borane holds a clear promise for meeting the DOE targets for hydrogen storage materials. However, it remains questionable whether the serious regeneration and cost issues about this compound and related compounds can be overcome that will allow its practical application to onboard hydrogen storage

Question 2: Approach to performing the research and development

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

- PNNL is taking a logical, methodical, and thorough approach to addressing the barriers to a viable hydrogen storage system.
- Similar to LANL/CoE, the approach here is very good. A nice mix of experiment/theory.
- Combined theory and experiments a good approach.
- PNNL efforts complement the other CoE partner's work, use of engineering tools to direct research activities is particularly noteworthy

- Good understanding of targets, but didn't mention volumetric density (and regeneration) too often; these are some of the most critical issues.
- Accurate determination of the thermochemical parameters of the ammonia borane system is the correct first step in this effort. However, regeneration is the key issue with all chemical hydrides. The project is far too weighted towards improving dehydrogenation kinetics rather than solving the key issue of developing a practical regeneration processes.
- PNNL intends to measure reaction rates for the seeded and unseeded material to determine the status of this technology versus the DOE targets.
- Interesting and simple approach to improve kinetics with seeds but if seeds are simply an intermediate component of the reaction or partially spent fuel-- how stable will they be through several cycles. Will that intermediate sustain an equilibrium concentration?
- Not quite sure how would the system be implemented, seeds are simply an intermediate, scaffolds may be expensive and difficult to regenerate but should be investigated anyway.
- PNNL recognizes the need to minimize the weight and volume of the scaffold material if the concept is to have a chance of success. Unsure if handling solid ammonia borane on board a vehicle is feasible. Probably better to look at solubilizing the AB.
- Active cooling of system (even minimal) may be a concern for system design in order to avoid the thermal runaway situation.
- Don't see value in developing the SBH reactor modeling- avoids the main issues of SBH.

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

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

- Scaffolding approach first reported by PNNL was a significant accomplishment and is being looked at for potential application in the other CoEs
- Seeding with spent ammonia borane to eliminate the delay for the onset of hydrogen release and increasing the dehydrogenation reaction rate appears to be a significant accomplishment.
- Significant progress on ammonia borane programs, however they need to be cautious on setting the induction time such that the material in the tank reacts rapidly after a 600 hr induction time.
- Interesting work on DFT of solid vs. gas-phase ammonia borane dehydrogenation (showed example for cyclic products). How well do these energetics compare with experiment?
- Heat management slide - showed near thermal runaway of pressure at very modest pressure (~50°C)? Isn't this a big concern? This could essentially become a dormancy issue similar to the concern over liquid H_2 - exothermic reaction pressure buildup could cause significant amount of fuel to vent during dormancy? To some extent, this is dependent on the design of the catalyst (i.e., seeding the material with ammonia borane as a catalyst vs. Using a separate heterogeneous catalyst), so this design needs to be more clearly specified.
- Technical accomplishments seem reasonable commensurate with the amount of time and money spent to date. Most of the accomplishments are valuable; however, there is some concern that the accomplishments in heat management (slide 13) indicates there is an exothermic reaction which would require external cooling to avoid run away and the loss of hydrogen after prolonged storage.
- Good progress on seeding- this is a simple and novel approach. More work needs to be done on seeding to determine the cyclic stability of the seeds and the correlation of it's relation to the thermal runaway issues observed.
- Key thermochemical parameters have been established. Very little progress towards development of a method for regeneration.
- Made excellent progress in the areas considered, identified some mechanistic issues, such as induction period in H_2 release from AB, and completed multi-scale model

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

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

- Multiple collaborations with CoE partners and others.
- Well integrated, appropriate transfer to relevant business.

- Development and transfer of engineering reactor model to Millennium Cell is a good sign that collaboration among the members of the CoE is fairly strong. This was evident in some of the following talks as well.
- PNNL is working with the chemical hydrogen storage CoE and with world class partners in the CoE.
- Partnered with CoE.
- good example of collaboration outside of CoE.
- good interactions within CoE.

Question 5: Approach to and relevance of proposed future research

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

- The plan forward is logical and will help resolve the issues in controlling the dehydrogenation process as well as identifying viable pathways to regeneration of the spent AB.
- Future plans are well thought out and logical developments of work conducted so far.
- Builds on this years accomplishments
- Excellent IPHE project proposal on $AB/LiNH_2/MgH_2$ - this seems like a very good idea, and novel results are likely. This seems like an excellent candidate for combinatorial/high-throughput work? Can theory help out here?
- The international collaboration with IPHE could prove to be very promising considering the caliber of partners.
- Future studies should have greater focus on the re-generation of ammonia borane.
- Engineering and regeneration work appropriate.
- Need to work on thermal cooling or ensure that it won't break down in the absence of seeds or catalyst chamber.
- Should really evaluate the tie to reach 10-15 bar as opposed to 500 bar and evaluate if time to thermal runaway becomes increasingly concerning.
- Plans to solve the material handling problems are not clear.
- The prediction of novel B-C-N molecules with good thermodynamics is somewhat less interesting, since their synthesis researchers have also advised that they are likely to be unstable.
- Scaffold work is very intriguing but of questionable value to the development of ammonia borane as a practical hydrogen storage material.

Strengths and weaknesses

Strengths

- The thermochemical parameters of the system have been established.
- High capacity.
- PNNL was able to eliminate the induction period before the onset of hydrogen release from the ammonia borane scaffold material.
- Strong collaboration. High degree of relevancy. High degree of technical competency.
- Strongly leverages basic science.
- Manageable number of projects.
- Very good headway on kinetics - Work on scaffolds to improve H_2 purity is important however cost effective techniques must be stressed in early design of scaffolds. Would aerogels be appropriate for scaffold use?
- Good discussion of "critical issues"

Weaknesses

- Far too little emphasis on development of methods for regeneration.
- The scaffold ammonia borane material has relatively low gravimetric capacity as shown in the table on slide 21. Even the neat solid capacity is not likely to meet DOE targets.
- Handling solids on board a vehicle should be considered only as a last resort if the material capacities and energetics of the reaction are much more favorable than for other materials. Liquid based systems are strongly favored for vehicles.
- Multiscale modeling of reactor systems (transferred to MC) work on SBH with Millennium Cell seems to be of questionable value. Might just be diverting attention from real problem associated with SBH. No real surprising result here, and at least for SBH, this might just be diverting attention from the real problem

associated with SBH. However, this tool could be useful to other chemical hydride systems, and might serve as a model for these other materials when it comes time to build a system out of them. So, this work, if continued, should stay quite general so as to be applicable to a wide variety of chemical hydrides, and not too narrowly specific to SBH.
- The future work does not address the hybridized solutions to take advantage of the seeding versus scaffolding.
- Glad to see that multiscale modeling tool has been handed off to industry.
- Thermal runaway is by far the most troubling aspect of this project. A key strength of these materials is that they operate at lower pressures and could permit the use of conformable tank concepts. Thus the time to reach 10-15 bar should be evaluated to determine if this will become a problem. They should not report time to 500 bar since the plan does not include putting these materials in compressed vessels. This may not change the total time significantly since the induction time seems to dominate the curve.
- Have they addressed H_2 purity?

<u>Specific recommendations and additions or deletions to the work scope</u>

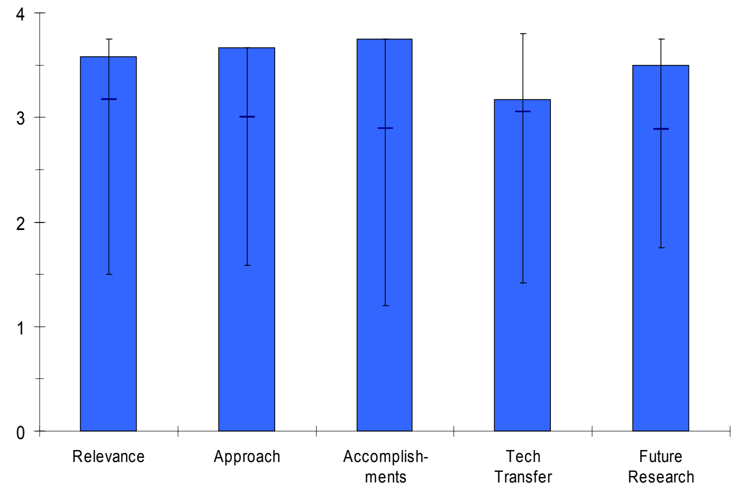
- Add more work on the development of methods for regeneration.
- Need to begin to develop the criteria for selection from the various alternative pathways.
- Heat management slide - showed near thermal runaway of pressure at very modest pressure (~50°C)? Isn't this a big concern? This could essentially become a dormancy issue similar to the concern over liquid H_2 - exothermic reaction pressure buildup could cause significant amount of fuel to vent during dormancy? To some extent, this is dependent on the design of the catalyst (i.e., seeding the material with ammonia borane as a catalyst vs. using a separate heterogeneous catalyst), so this design needs to be more clearly specified.
- The work on alternate scaffolding materials and structure is very important. Also need to address the spontaneous hydrogen release and runaway exothermic.
- Work on SBH multiscale reactor modeling should stay quite general so as to be applicable to a wide variety of chemical hydrides and not too narrowly specific to SBH.

Project # ST-03: Amineborane Hydrogen Storage: New Methods for Promoting Amineborane Dehydrogenation/Regeneration Reactions

Larry Sneddon; University of Pennsylvania

[Partner of the DOE Chemical Hydrogen Center of Excellence]

Overall Project Score: 3.6 (6 Reviews Received)



Brief Summary of Project

The objectives of this project are to:
1. Develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets
2. Develop high conversion off-board methods for chemical hydride regeneration

Question 1: Relevance to overall DOE objectives

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

- Materials show promising capacities, and hydrogen release is interesting.
- Hydrolysis work focuses on H_2 release, but regeneration is the critical question.
- Because of the high hydrogen capacities of the amine boranes, this work is very relevant.
- Storage is the key to the hydrogen initiative and amineboranes have potential for some of the highest capacities of all approaches.
- The material which they have studied has potential to achieve the DOE target.
- Making a stable and highly water soluble material that won't react without the presence of catalysts dramatically simplifies system design and potentially allows for a membrane single volume tank design.

Question 2: Approach to performing the research and development

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

- The combined approach of hydrolysis and thermolysis of the amine borane materials is excellent.
- They choose two contrasting processes; hydrolytic process which shows better kinetics but relatively lower hydrogen capacity, and thermolytic decomposition which show higher hydrogen capacity but worse kinetics. Those processes are considered to be the most important options for utilization of ammonia-borane as hydrogen storage material.
- Good approach to dissolve $B_3H_7NH_3$ in water and produce a stable liquid fuel. Like the use of ionic liquids as catalysts, solvents etc. would always want some reaction chamber with a catalyst for safety reasons.
- The approaches seem to be appropriate given the volume of results in the span of only one year.
- Really an incredible amount of work and clever ideas for such a small amount of money! This may be the highest return on investment in the entire portfolio!
- Good progress on H_2 release chemistry.
- To be relevant, hydrolysis processes must include release.
- Need to partner with chemical engineering and look at process for regeneration to determine first order economic estimates based on known regeneration chemistry.
- CF_3COOH is fairly exotic for large scale operations.
- Should seek regeneration routes that don't involve electricity to carry out reaction (think that AlH_3 requires electricity).

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

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

- The research seems to have made considerable progress in one year.
- Good progress on new NB candidates for storage.
- This project has achieved some excellent and potentially quite important results, both with the ammonia triborohydride and with the ammonia borane. The catalyst results look very good.
- They characterized $B_3H_7NH_3$ as a hydrogen storage material by hydrolytic and thermolytic process, and reported large hydrogen capacity in a hydrogen evolution process and good kinetics in hydrolytic process. This result shows potential of ammonia-borane as an energy carrier.
- Interesting work on $H_3NB_3H_7$: the simpler, safer synthesis process is a nice discovery.
- Additions of $LiNH_2$ to AB: showed up to 9.6 wt.% at 85°C! This is really very exciting, and should be more fully investigated in the coming year. What are the decomposition products? What is the mechanism by which the second equivalent of hydrogen can be extracted from ammonia borane by adding $LiNH_2$?
- Regeneration of NB products (non-oxides) is encouraging, but need energy and material balance.
- Be careful with reactions which proceed to the formation of B-O bonds and to an energetic well that it will be difficult to get out of. For these systems, really need to prove that regeneration is feasible, or else consider moving onto more interesting activities.
- Need to comment on the solubility of the waste fuel in water. Is it better than $NaBO_2$? If so then, there is a chance to develop a membrane based fuel tank.

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

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

- There appears to be excellent interactions with the other members of the chemical hydrogen storage CoE.
- The PI is affiliated with the appropriate partners. This has become the best coordinated of the three CoEs.
- Improvement of hydrogen evolution kinetics and development of prototype systems with their partners will be expected.
- Should work with engineers to do early stage process design/economics.
- Outside collaborations are not apparent. Perhaps it is too early for many.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.5** for proposed future work.

- The proposed future research paths are excellent. A key aspect will probably be which of the systems, ammonia borane or ammonia triborohydride, has the best potential for regeneration.
- Logical progression from first year's work.
- Good program going forward.
- Research and development of effective technology for production and regeneration for ammonia-borane system is strongly required.
- Some more direction and integration from the CoE is required to ensure that the catalyst work is coordinated well between all partners to avoid duplication.
- Focus on $AB/LiNH_2$ (and related systems): understanding mechanism and regeneration possibilities.
- For reactions involving B-O: try to quickly assess whether regeneration will be feasible; if not, consider dropping these activities in favor of more promising routes.
- Information that needs to be presented next time in order to gauge suitability for simple system design are: mixtures, pH, waste solubility.
- Some mention of regeneration pathways and energy should be made. B-O bonds are formed which could be troubling.

Strengths and weaknesses

Strengths
- Good work on Hydrogen release.
- This project is investigating hydrogen storage materials with high gravimetric and volumetric capacities. A new material system, ammonia triborohydride has been discovered, and this suggests the possibility of discovery of other new hydrogen storage materials.
- Knowledge of the subject and apparent willingness to work hard.
- Experience on ammonia-borane chemistry.
- Ionic liquids serve several beneficial functions, suppress borazaine, serve as catalyst and solvent and could potentially be cheap to make.

Weaknesses
- Too little emphasis on regeneration.
- The incorporation of ammonia-borane into an ionic liquid may reduce the gravimetric and volumetric capacities of the storage system.
- None obvious at this time, but outside collaborations are not apparent. Perhaps it is too early for much outside collaboration yet.
- Knowledge on hydrogen evolution system may be required when they improve performance of their materials. Intimate information exchange with LANL, PNNL, and private companies is expected.
- Ionic liquids are large bulky molecules. This could possiblly reduce the storage capacities of the system depending on how much liquid is required to for solubility, catalytic activity, etc.
- B-O bonds are still a waste product of this system. There may be similar regenerations to $NaBO_2$ - If not, then the PI needs to point this out as an advantage.

Specific recommendations and additions or deletions to the work scope

- Need to define optimum endpoint for dehydrogenation. Is it BN, BHNH, BH_2NH_2?
- For hydrolysis, ammonia poisoning of fuel cell needs to be addressed.
- None.
- None. Look at in six months to a year.
- Please include waste solubility, enthalpy of reaction and system pH values in next presentation.

Project # ST-04: Solutions for Chemical Hydrogen Storage: Hydrogenation/ Dehydrogenation of B-N Bonds

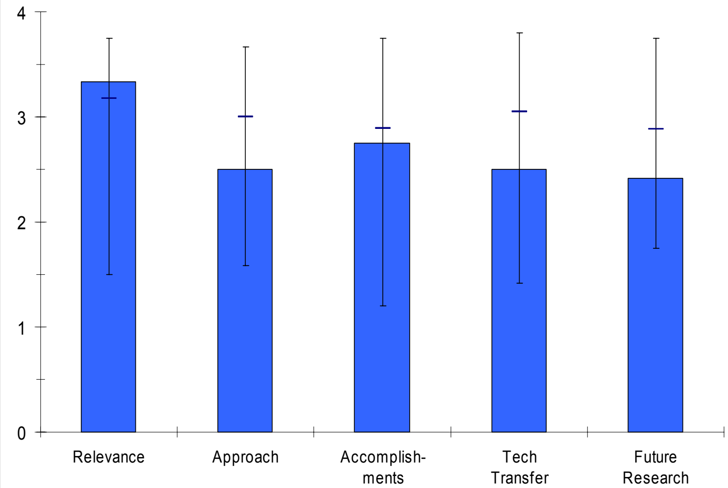
Michael Heinekey; University of Washington

[Partner of the DOE Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are to:
1. Understand the interaction of BN compounds with transition metals
2. Develop platinum group metal (PGM) based catalysts for dehydrogenation and rehydrogenation of BN compounds
3. Determine thermodynamic parameters for hydrogenation/dehydrogenation
4. Develop non PGM catalysts

Overall Project Score: 2.7 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- As part of the chemical hydrogen storage CoE. U. Washington is studying ammonia borane chemistry, specifically thermal and catalytic dehydrogenation of ammonia borane and the reverse, hydrogenation. The work aligns well with the DOE program objectives, and is an important part of the CoE activities.
- Storage is key to the hydrogen initiative and amineboranes have potential for some of the highest capacities of all approaches.
- Effective catalysts for amino borane are required.
- Project has only addressed one of the three barriers claimed in presentation.
- Need to move on to efficiency and regeneration.
- Ammonia-borane holds a clear promise for meeting the DOE targets for hydrogen storage materials. However, it remains questionable whether the serious regeneration and cost issues about this compound and related compounds can be overcome that will allow its practical application to onboard hydrogen storage.

Question 2: Approach to performing the research and development

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

- Good approach on dehydrogenation.
- Thermally induced dehydrogenation of ammonia borane is known to be very slow at temperatures of interest. Therefore, the approach focused on discovering a catalyst(s) to increase the hydrogen release to appreciable rates at temperatures of interest. PGM catalysts were developed. This approach aligns closely with the DOE objectives as well as the CoE's program plan.
- Good thought, but Ir [iridium] is too expensive.
- Focus needs to shift away from Ir based catalysts since world supply of Ir will be a problem.
- Need work on regeneration.
- Not clear how extensive the understanding is of the targets, or hydrogen storage, generally, as a technology.
- There doesn't seem to be a clear strategy to move this project forward.
- Regeneration is the key issue with all chemical hydrides. The project is far too weighted towards improving dehydrogenation kinetics rather than solving the key issue of developing a practical regeneration processes. The practicality of systems involving ammonia borane dissolved in tetrahydrofuran solutions that contain a soluble homogeneous catalyst is questionable as it would seem to be precluded from practicality on the basis of weight, safety, and complication of tank design.

- Program lacks focus, trying too many approaches at once.
- There doesn't seem to be a clear strategy to move this project forward.

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

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

- A very active catalyst for the dehydrogenation of ammonia borane has been identified.
- Effective catalysts containing Ir were found to increase the dehydrogenation reaction rate two orders of magnitude over previously reported data. Further increases are necessary to approach transportation requirements. One hydrogen equivalent of hydrogen is released with this catalyst, and the reaction product is a solid, single cyclic pentamer.
- Good work to isolate unique dehydrogenation product. How long does catalyst last? Need to determine if deactivation is unique to this catalyst or if it's generic.
- They did create an effective catalyst that is reasonably reliable and reactivated under pressure (50 psi may be the limit for non pressurized systems though). However strong emphasis is required to reduce / eliminate precious metals. (multiple)
- If the only accomplishment is an Ir-bearing catalyst; this is not sufficient.
- At the outset, it seemed that a large effort would be focused on regeneration. Somewhat disappointed to see that nearly all the efforts involved trying to improve dehydrogenation kinetics with catalysts, as many others are also doing. The Ir catalyst work shows a remarkable improvement, but how practical is an Ir catalyst towards supporting the DOE goals (i.e., cost)?

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

This project was rated **2.5** for technology transfer and collaboration.

- Good collaborations with PNNL and other CoE partners.
- There is evidence of good collaboration between University of Washington and LANL. It is unclear how much interaction there is between U. Washington and the rest of the CoE members.
- Clarify objective of work with PNNL on the Ir-bearing catalysts?
- This effort needs strong management form the CoE to coordinate catalyst work. This project is at risk for spinning in place and not working toward cheap catalyst production. More collaboration with the CoE partners would be useful.
- Need engineering partner to begin conceptual process design and economics for regeneration. Also need process design for dehydrogenation. What would on-board dehydrogenation reactor look like? How would solid be handled on a vehicle?

Question 5: Approach to and relevance of proposed future research

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

- Future work is laid out but is a little sketchy; e.g., the approach to look at rehydrogenation reactions. It was not clear what role the U. Washington will have in the downselection process being developed by the CoE. A positive aspect of the future work is the investigation of non-PGM catalysts.
- Need to concentrate heavily on identifying less expensive metals.
- Continued work on the Ir-bearing catalyst makes no sense, unless it is used as a surrogate leading to others.
- The practicality of development of solvent based systems is questionable. Studies of the re-generation of ammonia borane should be the highest priority.
- Doesn't appear to be a clear plan or direction for this part of the chemical hydride work.
- Interesting that one of the main future activities is to validate computational work, since the PI appeared to indicate skepticism towards computational work.
- Regeneration is key for this material. It should form the focus of future activities, but currently looks a bit like an afterthought (and not clear that there are any promising ideas here).
- Plans to study regeneration reactions, but no details. Need more info.

Strengths and weaknesses

Strengths
- Good work on dehydrogenation and characterization of catalyst and products.
- Strong background in homogenous catalysis.
- The presentation was clear and well focused. The Ir catalyst was shown to be fairly durable; 50 psi overpressure is enough to maintain catalyst activity indefinitely according to the presentation.
- Knowledge.

Weaknesses
- Less expensive catalysts are needed to demonstrate the viability of the process.
- Solid products of reaction are very difficult to handle on board a vehicle.
- If only one equivalent of hydrogen can be released, the maximum material capacity is only 6.5 wt. % which will fall below even the near-term system level targets.
- Far too little emphasis on development of methods for regeneration (multiple).
- No partners to look into engineering.
- Fixation on a dead-end approach, namely, the Ir-bearing catalysts.
- This presentation was difficult to follow, need to improve explanation of slides.
- Presenter needs to state in one simple bullet point the significance of each slide.

Specific recommendations and additions or deletions to the work scope

- Some effort should be focused on solubilizing the ammonia borane without excessive penalty on capacity or without introducing/producing toxic materials into the process. Investigate means to increase hydrogen equivalents. Has to be at pressure to prevent catalyst deactivation.
- The toxicity of the reactants and products needs to be assessed if there is serious interest in these materials. Also the presence of any volatile nitrogen-containing species needs to be determined. These species will be harmful to fuel cells and very possibly to humans if they are released.
- More work on the development of methods for regeneration. Studies of solvent based systems should be deleted.
- Give regeneration work more priority.
- Partner with engineering expertise.
- Re-orient or discontinue.

Project # ST-05: Chemical Hydrogen Storage Using Polyhedral Borane Anion Salts

Fred Hawthorne; UCLA

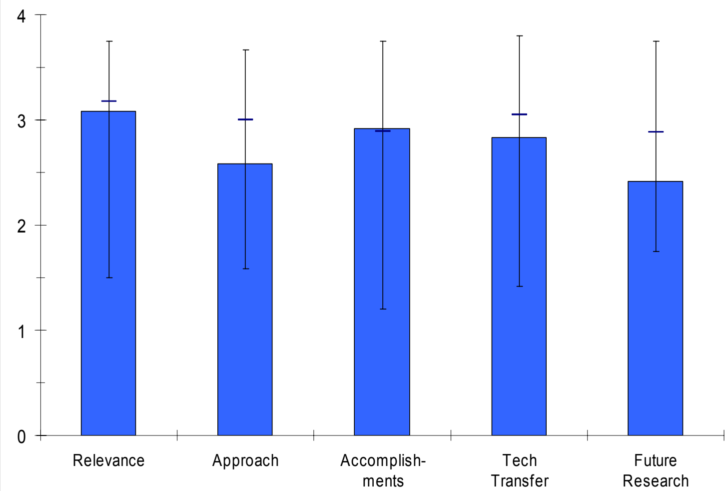
[Partner of the DOE Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are to:

1. Develop heterogeneous catalysts for the controlled release of hydrogen from the hydrolysis of salts of $B_{12}H_{122}$-, $B_{10}H_{102}$- and $B_{11}H_{14}$- ions.
2. Determine the kinetics and mechanisms of these catalyzed polyhedral borane anion hydrolysis reactions to provide design data for large-scale hydrogen storage devices.
3. Optimize existing processes for the conversion of diverse >BH sources to $B_{12}H_{122}$- and $B_{10}H_{102}$- salts for direct use in hydrogen storage without extensive purification.

Overall Project Score: 2.8 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Generally, the area of chemical hydrides is of high relevance to the Hydrogen Fuel Initiative (HFI). Main issues for all chemical hydride approaches are density, kinetics, and (perhaps most importantly) regeneration. Need to keep regeneration at the forefront of the activities, and not treat as an afterthought.
- Mainly relevant to stationary applications. At 5 to 6 wt.% hydrogen based on materials alone, Polyhedral borane (PHB) anions probably won't make it for vehicles. Advantage is that the PHB anions are much more stable in H_2O than BH_4-. The project is mainly focused on catalyst optimization and on H_2 release kinetics.
- Working to stabilize borohydride based materials.
- Storage is key to the hydrogen initiative and polyhedral boranes have potential for some of the highest capacities of all approaches; however, slide 7 indicates they can only approach the 2010 target.
- Polyhedral borane anions are a nice alternative to sodium borohydride and ammonia borane for boron based chemical storage of hydrogen. However, it remains questionable whether the serious regeneration and cost issues about these compounds can be overcome that will allow their practical application to onboard hydrogen storage.
- Hard to see how these low rates would work in a once through reactor that would be needed in a vehicle.
- Hydrolysis of complex boron hydrides appears to be an expensive option for H_2 storage.
- This seems like a good project, but the presentation was too slowl at first and didn't do justice to the results and future plans slides at the end.

Question 2: Approach to performing the research and development

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

- The PI has extensive knowledge of and experience in PHB anion chemistry. The research plan is well thought out, The results so far are encouraging, and the probability of a successful technical development in terms of a demonstrated H delivery capability for perhaps 2010 targets seems high.
- The progress to date seems to indicate approaches are appropriate.
- Good approach to find materials more stable than SBH however the materials identified are almost half the storage density of SBH. Taking a hit on the storage density.

- This approach seems to have many of the same weaknesses of the SBH approach, and the densities are not too high (~6 wt.%). Really need to show why this approach has some advantages over not only sodium borohydride, but the other chemical hydride ideas in the CoE.
- Regeneration is the key issue with all chemical hydrides. The project addresses improving dehydrogenation kinetics rather than solving the key issue of developing a practical regeneration processes.
- A B-O bond is still formed in the waste products and no mention of economical regeneration was presented.
- Needs to look at regeneration as well as H_2 release.
- Until process is demonstrated that doesn't use aqueous solution, state hydrogen capacity including water needed to solvate product.
- The overall economics were not discussed and may in the long run be a show stopper.

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

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

- Interesting compounds that are much more stable than SBH in water. This makes system design simple and avoids the use of excessive NaOH that creates a system of pH 14 and hence makes for difficult material selections. Formation of boric acid is concerning.
- Seemed to have good quality storage and kinetics data. It seems that a significant number of measurements have been made in the first year. Unfortunately the presentation rushed through the most important part of the results.
- A highly effective rhodium hydrolysis catalyst has been developed.
- Good results on H_2 release, Rh catalyst appears to work well for release.
- The research looks like good chemistry, but its unclear how guided this is by the DOE targets, or what the direction of the research is.
- O.K. But, only one catalyst is a bit disappointing, and the 90°C temperature is worrisome.

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

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

- This project is part of a larger integrated program involving Penn State, LANL, and PNNL, overall program planning and integration appears to be proceeding in an orderly fashion.
- The collaborator from Penn State is an excellent electrochemist. That bodes well for a successful outcome with respect to regeneration.
- Partnered with appropriate partners, good collaborations with CoE partners. (multiple reviewer comments)
- Need engineering expertise to consider how chemistry might be implemented.
- Slide 6 indicates that the partners have been identified, but collaborations have not yet begun.

Question 5: Approach to and relevance of proposed future research

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

- Reduction of catalyst cost is a key issue; thus the planned investigations of alternative transition metal catalysts are essential. Future plans should include efforts to develop regeneration process.
- Need regeneration component.
- Seems logical.
- Presentation of the future plans was rushed. They needed more amplification. As presented in the summary slide, all but the last one appear to build on experience to date.
- Future actions should concentrate more heavily on solubility, regeneration schemes, volumetric densities and enthalpy of reactions.
- Need to demonstrate reaction in a plug flow reactor.
- Should calculate target reaction rates.
- Not clear really where the research is going. Doesn't seem to be guided by DOE targets or driving by technological concerns?

Strengths and weaknesses

Strengths
- Good knowledge of BH chemistry.
- Hydrolysis of polyhedral borane anions salts at effective rates has been demonstrated.
- Knowledge of subject.
- The PI is a well recognized inorganic chemist with considerable experience in the field of study of this project.
- The class of chemicals under study has many favorable traits for a safe reliable H delivery system.
- Overall, the project team seems to be a strong one.
- This is a more stable material than SBH at lower pH which should significantly reduce overall system complexity.

Weaknesses
- This approach seems to have many weaknesses of the SBH approach (i.e., placing yourself in a strong exothermic energy well). If this is true, the work likely should be stopped; but if it is not true, need to demonstrate why this approach has (many, significant) positive attributes compared to SBH and other chemical hydride approaches.
- The full system economics associated with borane-based hydrogen storage are still questionable. This talk did not address either economics or the conceptual aspects of the proposed regeneration approach.
- No effort on development of methods for regeneration (multiple reviewer comments).
- Half the weight percentage of SBH/H_20 system.
- None discernible from the presentation.
- The presentation itself could have been much better if time was balanced to cover the information in the back end of the presentation (which happened to include some of the key results).

Specific recommendations and additions or deletions to the work scope

- Focus on non-noble-metal catalysts.
- Other spectroscopies, besides NMR, might add characterization depth to the project. Studies of molecular vibrations should be informative.
- Add solubility and regeneration schemes, volumetric densities and enthalpy of reactions for next presentation.
- Addition of studies aimed at the development of methods for regeneration.
- Continue on in a balanced fashion.
- Include engineering component to make sure work is relevant to onboard storage needs.

Project # ST-06: Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides

Suzanne Linehan; Rohm and Haas, Inc.

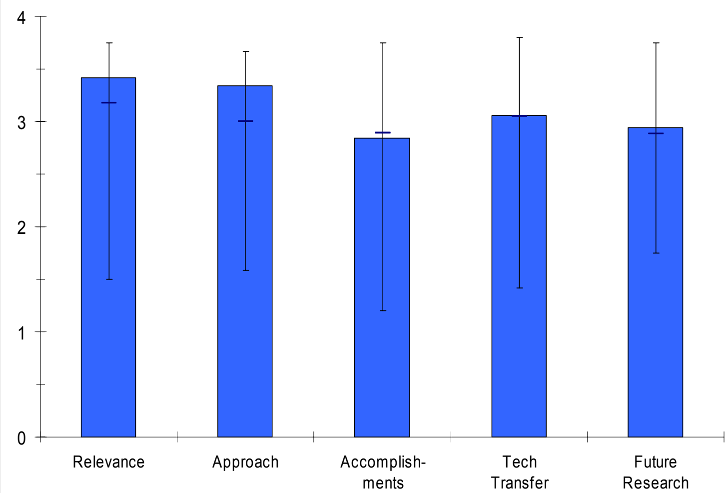
[Partner of the DOE Chemical Hydrogen Center of Excellence]

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.

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

Overall Project Score: 3.1 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- General area of B-OH to B-H, is an important item for regeneration of B-containing hydrolysis reactions. Regeneration is probably the most significant challenge for these systems, yet appears to receive comparatively little attention.
- The high practical potential of chemical storage of hydrogen as borohydrides has been long recognized. However, it remains questionable whether serious regeneration and cost issues can be overcome.
- This project has to succeed if borohydride materials have any chance as H_2 storage media.
- Performance based metrics are a good approach towards identifying best processes. A good support for H_2A tool.
- Storage is key to the hydrogen initiative and regeneration is key to many of the strategies.

Question 2: Approach to performing the research and development

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

- The approach seems like a reasonable one to take; simple modeling to screen out viable regeneration pathways.
- Regeneration is the key issue with all chemical hydrides. This project addresses this issue head-on. The three most promising approaches to conversion of B-O to B-H have been identified and are pursued.
- Engineering approach to metal reductions very good!
- Fast fail concept needs to be applied to more projects when appropriate.
- Need to verify properties of systems researched prior to making decisions or eliminating undesirable options, i.e. identification of leading metals for regeneration. More metrics need to be included prior to screening.
- Starting with an assessment of what is known is a logical approach. But, it is difficult to judge this criteria as so much is proprietary.
- However, this seems like work that should have been done earlier ago before even proposing the SBH idea? Cannot fault this project for this, of course, but it is quite surprising that this is just being done now.

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

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

- Promising new electrolytic processes have been identified.
- Promising results for electrochemistry, but current efficiencies will need to improve greatly.
- Use of metals to achieve reduction would be a very significant development.
- More information is needed on the chemical regeneration routes as little information was provided. No measurable metrics on ongoing regeneration routes discussed or mentioned.
- Seems like a very small amount of progress for the funding amount. The work seems competent and correct, but could have been done with much less time/money expended.
- Significant work to be done.

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

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

- Good collaborations with CoE partners.
- Good work with partners within CoE.
- Slide 10 indicates active contact with partners for information. But, Slide 22 suggests that IP issues may be impeding.

Question 5: Approach to and relevance of proposed future research

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

- If anything is found theoretically, need to concentrate (urgently!) on demonstration of a process. If nothing is found theoretically soon, need to stop.
- The most important aspect of this work is that it could demonstrate clearly that hydrolysis/SBH technologies are not viable.
- Efforts seem well directed but timetable appears to be very tight.
- Ambitious goal for lab evaluation.
- Ammonia borane work looks good.
- Verification of metrics values obtained from literature. More focus on ammonia borane manufacturing routes needed.
- Seems logical.

Strengths and weaknesses

Strengths
- This is a key project as the practical viability of all boron based chemical hydride, hydrogen storage systems would seem to depend on the development of an economical method for production of borohydrides from borates.
- Good fundamental approach. Only project in CoE to be looking hard at life cycle issues.
- Collaboration with different members.
- In-depth knowledge of field with industrial perspective as to what is viable.

Weaknesses
- Economically viable methods for the conversion of borates to borohydride have yet to be identified.
- Data verification.
- None apparent, except maybe the extent of the study and potential IP issues.

Specific recommendations and additions or deletions to the work scope

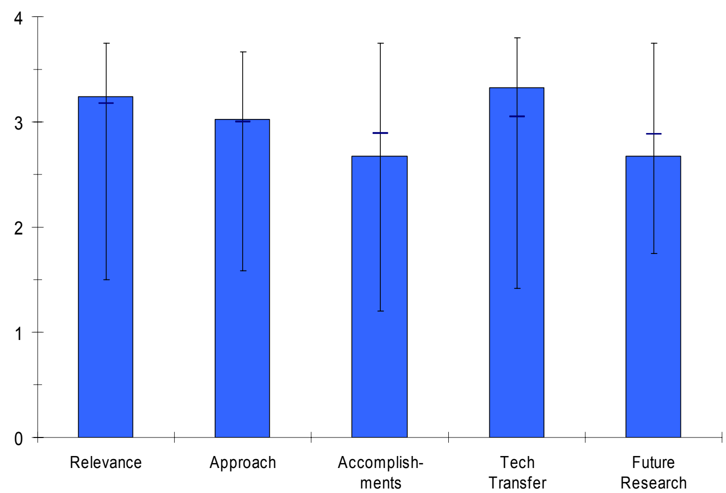
- Coordinate with delivery or production teams since regeneration costs will be relevant to these teams.
- Use grid mix rather than hydroelectricity when doing life cycle analysis.
- Verification of results reported in literature prior to making any final judgments is needed for the project results to be of use and value.
- Continue, but look to see if anything can or needs to be done about the IP issues impeding the collaborations and information exchanges.

Project # ST-07: Development of Advanced Chemical Hydrogen Storage and Generation System

Ying Wu; Millennium Cell, Inc.

[Partner of the DOE Chemical Hydrogen Center of Excellence]

Overall Project Score: 2.9 (7 Reviews Received)



Brief Summary of Project

The objectives of this project are to:
1. Improve capability to store and release H_2 from chemical hydride
2. Meet the DOE 2007 target and beyond: 1.2 kWh/L (36 g H_2/L) and 1.5 kWh/kg (45 g H_2/kg)
3. Leverage Millennium Cell engineering expertise and guide chemical hydrogen storage CoE research

Question 1: Relevance to overall DOE objectives

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

- Borohydride represents the most viable, near-term chemical hydrogen storage system; however it may be difficult to meet longer-term DOE targets.
- Control of hydrogen evolution rate and stable operation for a commercial system is one of key issues for practical use.
- Storage is key to the hydrogen initiative.
- Good project to bring hydrogen goals to fruition.
- This project appears to be the only partner in the CoE that has demonstrated systems experience. Assumptions and system projections must be scrutinized heavily by reviewers or users.

Question 2: Approach to performing the research and development

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

- The approach is reasonable and appropriate.
- The use of modeling capabilities to identify areas for performance improvements is very useful.
- The approach takes advantage of Millennium Cell's extensive experience in borohydride storage technology.
- Development of the simulation software suitable for the $NaBH_4$-hydrolysis system is the key issue to design an effective construction for hydrogen evolution.
- Someone has to do the system work, and they seem to be doing it properly.
- Even though the number of project variables provide a challenge, the project team has done a good job in addressing them.
- Millennium Cell appears to not focus on the true issues of regeneration efficiency and is creating a simple compact system. The reactor chamber represents less than 5% of the weight of the system and currently works well (has worked well since 2003) it does not require as much attention as the other areas.
- Need to address the materials properties issues instead of focusing on engineering optimization, for example enhance wt.% of borohydrides in solution. What about wetting solid borohydrides with water studies?

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

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

- Progress has been based primarily on use of modeling to identify areas for potential performance improvement.

- Model validation experimental activities are important - however presentation of validation results were confusing and not clear.
- Future work is strongly tied to the accuracy of the model and parametric inputs. Apparently validation measurements are made only at the exit of the reactor - data at other locations would be very useful in the validation process.
- Enhancement of borohydride wt.% in solution is a key item to improve H_2 wt.% efficiency, reaction mechanisms and kinetics studies need to be addressed and thoroughly studied prior to any engineering optimization studies.
- Development of the simulation software suitable for the $NaBH_4$-hydrolysis system has been completed, and effectiveness of the software has been shown.
- They are almost to the DOE 2007 target now. But, they have been at it for a long time.
- Good job so far.
- Need to support with data the claim for a system capacity over the previous state of the art of 1.8%.
- It appears unlikely that they truly has a system that has exceed the previous state of the art of 1.8%. They do not have a bladder system. According to previous additional studies, the bladder system failed due to material compatibility with high pH (14) and temp (160°C) of waste fluids. Heat transfer from waste to fuel causing premature evolution and crystallized fuel would tear any membrane. A bladder system (if it could be built) would not nearly double the system weight density (it would only reduce by 30-40 lbs the 200 lbs necessary), 30% fuel will create a semi crystallized waste fuel in the system and waste tanks.

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

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

- Collaboration with PNNL in the modeling activities are very significant.
- Additional collaborations with Rohm and Haas, PSU [Penn State] and LANL were mentioned but the nature of these collaborations was not clear.
- Seem to be working well with others especially PNNL.
- The project team has functioned well and has been productive.
- Partnered with the right partners as part of the CoE.

Question 5: Approach to and relevance of proposed future research

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

- Future plans were not discussed in oral presentation because time ran out. Future work should focus on ability of approach to meet 6 wt-% and other DOE performance targets.
- Plan needs modification to be able to meet DOE targets.
- This developed software is expected to be useful to design a hydrogen evolution system.
- Logical. Close to 2007 targets now.
- The successful completion of this project, when it occurs, will contribute to the commercialization of hydrogen.
- Future work on the catalyst chamber is not the issue. Regeneration and finding alternative ways to stabilize SBH without NaOH should be their primary goals; increasing solubility in a liquid medium is also important. [DOE note: Regeneration is investigated under a separate DOE project with Millennium Cell]

Strengths and weaknesses

Strengths
- Overall view is very clear.
- Strong background capability in this approach based on prior Millennium Cell experience and accomplishments.
- PNNL modeling contribution to this approach is very significant and future performance improvement will likely result from the utility of the PNNL model.
- System engineering know-how.

- Knowledge of design, modeling, and integration of hydrogen evolution systems with knowledge of hydrolysis of $NaBH_4$.
- Extensive knowledge with industrial perspective.
- Good team, solid performance.
- Only system supplier in the CoE.

Weaknesses
- System image for the evaluation in not clear.
- Apparent, inherent limitations of this approach to meet long-term system performance targets.
- It is not clear that proposed future work (reducing fuel and BOP volume and increasing fuel concentration) has a reasonable probability of meeting 6.0 wt.% system target.
- Need more focus on reaction kinetics studies prior to any reactor optimization efforts.
- None apparent form presentation.
- None noted.
- Regeneration of fuel and NaOH causing a pH of 14 makes economical material selection very difficult.

Specific recommendations and additions or deletions to the work scope

- System image is a little bit difficult to reach to the researcher. It is recommended that the PI explain the basic mechanisms, at the least. For the evaluation of the system image, it is recommended that the PI listen to CRA OEM's system engineer's opinions. For example, use of water for the hydrogenation shall include the antifreeze and condenser.
- The fourth quarter, 2007, go/no-go decision point is appropriate for this borohydride approach - all effort in the interim should be strongly focused on demonstrating the ability of the approach to meet required performance targets that will be the basis for the decision determination.
- What about wetting of borohydrides with water kinetics studies, basically avoid solutions? Reactor optimization is not needed. Using systems likely not to meet targets; modification of the project's focus is recommended.
- Continue as planned.
- None at this time.

Project # ST-08: Combinatorial Synthesis and High Throughput Screening of Effective Catalysts for Chemical Hydrides

Xiao-Dong Xiang; Intematix Corporation

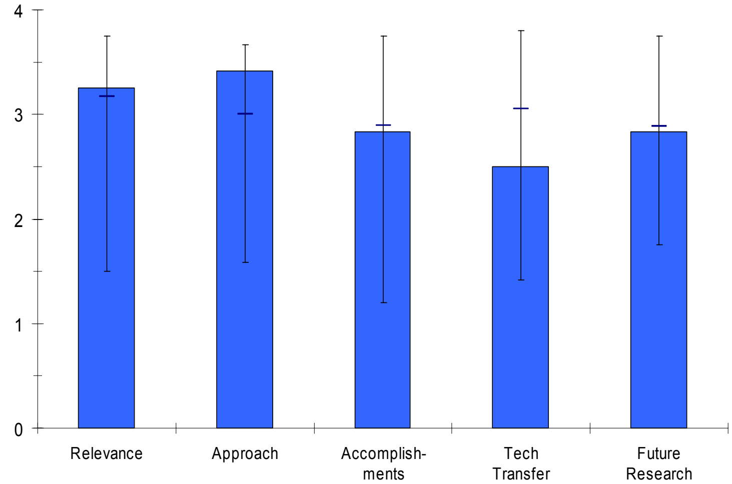
[Partner of the DOE Chemical Hydrogen Center of Excellence]

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 2006 include:

1. Validate scale-up of catalyst from microgram to gram scale
2. Screen catalyst libraries for H_2 release from ammonia borane
3. Screen catalyst libraries for H_2 release from polyhedral boranes

Overall Project Score: 3.0 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Any fast throughput technique for catalyst discovery is welcome because catalysis is not an exact science. Fast synthesis is the only method to truly investigate a reasonable amount of possible candidates.
- Development of technique to search catalysts widely and quickly is important to develop hydrogen evolution system with higher rate for chemical hydrides.
- Should accelerate developments.
- Storage is key to the hydrogen initiative and catalysts are key to both hydrogenation and dehydrogenation at acceptable and cost-effective rates.
- Scope of the catalyst search is limited to only well known chemical hydride systems with well known limitations that limits overall probability of success of the project.
- PI doesn't seem to be too concerned with hydrogen storage and targets. The approach seems to be to just take materials and systems from their collaborators, and search for catalysts. I don't think that this is necessarily bad, but just need to ensure that their collaborators are always giving them the right things to work on.

Question 2: Approach to performing the research and development

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

- Any fast throughput technique for catalyst discovery is welcome because catalysis is not an exact science. Fast synthesis is the only method to truly investigate a reasonable amount of possible candidates.
- Very interesting approach to catalyst discovery (largely a “black art”). High-throughput seems like the perfect tool to apply to this problem.
- How high is the throughput? Are these "continuous" libraries of samples, or physically-separate samples? It would be appreciated if Intematix could be a bit more open about their experimental approach, and describe in a bit more detail.
- Should focus a bit more strongly on regeneration catalysts.
- They contribute to this chemical hydride storage CoE based on their high potential for combinatorial technology.

- Solid combinatorial approach.
- Screens appear to work.
- Proven. Seems to work.
- Not sure what "proprietary screening of libraries for catalytic activities" means on slide 10-- Are these libraries that are being developed from this testing or from their own previous work? Should some of this info be accessible to the researchers sending samples?
- Experimental design is good within the scope.

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

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

- Most of their targets have been achieved.
- Good discoveries of cheaper catalysts.
- Lots done in one year.
- Not completely clear how catalyst results are scaled from high-throughput scale, to larger scale? Are the ones identified via high-throughput the same ones that show good behavior in the larger-scale bulk testing?
- Showed data for screening of catalysts, but it's unclear exactly did they find anything that was really good? This is something they need to be demonstrating very soon (or the chemical CoE needs to demand this soon)!
- Minimal results were presented and even then they were difficult to understand. No attempt to quantify or explain the results were made. PI should take a more active role in developing the catalysts rather than just providing a service to the CoE.
- The CoE is not working on hydrogen release from $NaBH_4$. Not clear why the high throughput experimentation is being done in this area.

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

This project was rated **2.5** for technology transfer and collaboration.

- They collaborate well with PNNL and LANL on reaction mechanism.
- Effectiveness depends on CoE arrangements to share IP coming out of combinatorial work.
- Working through PNNL and LANL to get to Rohm & Haas and Millennium Cell; probably because of IP concerns.
- They are sufficiently collaborating with the appropriate partners due to their association with the CoE however they need to produce more results and take a more active role in the development and understanding of these catalysts.
- Only three collaborators within the CoE have been mentioned. Not a great deal on collaboration.

Question 5: Approach to and relevance of proposed future research

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

- Future work should focus more strongly on regeneration catalysts. Right now, it seems like an afterthought. Not sure that the SBH work is really adding much value.
- Extension to regeneration is a good direction if screens can be developed.
- More of same, but logical.
- Work should be dropped on $NaBH_4$ catalysts unless they will be useful for other materials.

Strengths and weaknesses

Strengths
- Technique to search catalysts widely and quickly. Their contribution is very effective for the CoE.
- Combinatorial approach.
- Knowledge of their approach.

- Fast throughput method is key; appropriate equipment for the job.
- Applications of heterogeneous catalysts to improve dehydrogenation of chemical hydrides as well as attempts to prepare nano-particles to improve kinetics are promising.

Weaknesses
- None really apparent from presentation, but concerned about transferability of results due to proprietary nature of approach.
- Lack of understanding of the catalyst and poor presentation and explanation of the results obtained.
- Not clear why $NaBH_4$ and NH_3BH_3 were selected. Not clear now heterogeneous catalyst can be separated from spent system that may contain solid products. Catalyst regeneration options are not addressed. In case of ammonia borane, product composition issues (hydrogen purity) were not addressed.

Specific recommendations and additions or deletions to the work scope

- Future work should focus more strongly on regeneration catalysts.
- Create mechanism for other CoE partners to send early leads to combinatorial effort so that combinatorial efforts could take leads and fully explore them.
- Continue, but watch lack of interaction with R&H and Millennium Cell to see if anything can or needs to be done to foster more interactions.
- Shift focus towards ammonia borane and other more promising chemical systems. Suggest abandoning sodium borohydride dehydrogenation work as irrelevant to the chemical hydrogen storage CoE.

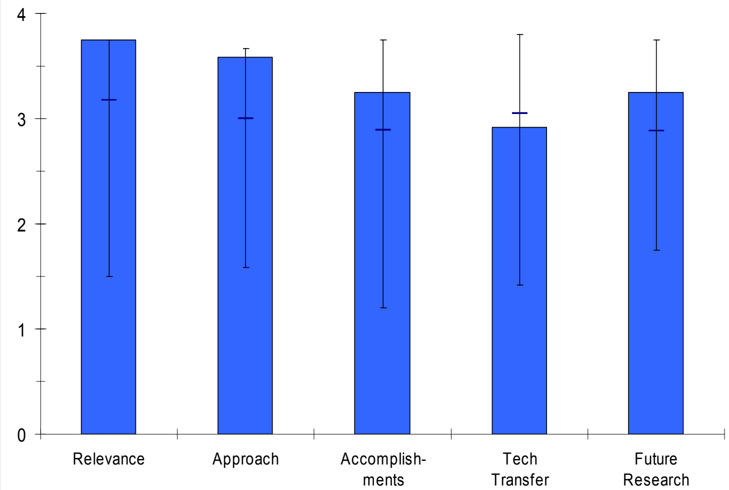
Project # ST-09: Hydrogen Storage by Reversible Hydrogenation of Liquid-phase Hydrogen Carriers

Alan Cooper; Air Products & Chemicals, Inc.

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 H_2-powered vehicles. The overall objective is the development of liquid-phase hydrogen storage materials with capacities of >7 wt.% and >60 g H_2/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.

Overall Project Score: 3.4 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Focused on exploration of heterocyclic chemicals that can give >7 wt.% and >60 g/L reversibly.
- A total system approach is being taken.
- The materials are expected to meet the 2010 target.
- Very promising approach
- No materials that meet DOE targets yet
- Liquid approach has definite benefits that no other approach has. Don't necessarily need high-pressure storage, so it is possible that tank could be conformable.
- Only proposed endothermic release reaction that is proposed to be regenerated (exothermic) off-board. This gives some energy efficiency advantage (energy released during recharge is partially recovered).(but couldn't all of the endothermic reactions adopt this approach? Should some of the concepts in the metal hydride CoE explore this idea?)
- This project is perhaps one of the most promising of Chemical hydride approaches. This concept potentially may achieve the best well to wheel efficiency and onboard safety and cost.

Question 2: Approach to performing the research and development

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

- One of the best examples of how computational modeling has led experimentalists to a proved-out promising hydrogen storage reaction. Serves as the model for this type of approach.
- Excellent use of theory to guide experiment
- Their approach is considered to be appropriate to develop organic chemical hydrides.
- The approach that Air Products is taking seems to be very effective. Solutions to key technical barriers are being emphasized in the research.
- The testing is sufficiently combinatorial in nature that over 100 candidate molecules were tested in the past year.

- This project is perhaps one of the most promising of chemical hydride approaches. This concept potentially may achieve the best well to weal efficiency and onboard safety and cost.
- Could perhaps some small amount of ionic fluids be used to catalyze the reaction and keep it liquefied at all times?

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

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

- Conformer results are interesting and suggest potential new routes to lower temperatures
- The finding that molecular conformation is important provides seminal insight about the types of molecular structures to most beneficially explore.
- New materials from last year have better capacity
- Lower temperature for initial step
- Incremental but necessary improvements were made this year ~ 1% g.d but no mention of volumetric or viscosity improvements were made.
- They have developed promising organic hydrides for hydrogen storage. Some of them exceed 6 wt.% and release hydrogen around 200^oC. Especially, N-ethylcarbazole releases hydrogen about 100^oC, although the hydrogen capacity of the compound is slightly lower than 6 wt.%. Active research and development on chemical hydrides are outstanding.
- Significant progress has been made in the past year. New, higher capacity compounds have been identified.
- Showed some new results on novel molecules, catalysts, etc. The results are good, but this is a large project, and so expectations are quite high; A stunning amount of progress in last year's meeting, but this year, the progress wasn't as substantial(?) Hopefully, this is not standard.

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

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

- In response to prior year comments about lack of coordination with other institutions, four new collaborations are either underway or being formulated.
- Not as significant since this is independent project and APCI has skill sets needed for project
- They have submitted some papers important in the field of organic hydrides, although interaction with other institutes and projects is not described.
- Not really applicable in this case since this program and material is unlike any other in the CoE. Air Products has all the expertise that they need but could perhaps benefit from organometallic chemists and ionic fluid chemists to investigate further options.
- Perhaps Air Products can team up with some fuel systems suppliers or polymer suppliers to work on single volume exchange tank design.

Question 5: Approach to and relevance of proposed future research

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

- Main two things that this project needs to focus on are (a) bringing the temperature of desorption down even further, and (b) trying to figure out a way to exceed the ratio of 1 H:C. So, their focus for next year is very good, but with the funding amount, substantial progress will be expected.
- A bit more clarity on what the ideas are to exceed 1 H:C would be valuable. What are the theoretical upper bounds, and what temperatures are really thought to be practical for extracting a second mole of hydrogen from these carriers?
- It seems as though the options of materials to choose to fit the appropriate window are becoming more limited which may be disturbing. Would be interesting next year to investigate options such as blending other H_2 storage fluids that are exothermic in release to tune the enthalpy of the system. Or to try ionic fluids for viscosity / catalytic effects.
- Needs to explain how they will improve on more than 1 H per carbon/molecule and also explain a bit about how to liquefy the system.

- Future plans look good
- Challenge of going to higher degrees of unsaturation is a good stretch target
- Need to address melting point issues
- Development of regeneration technology and accumulation of toxicity of organic hydrides should also be emphasized.
- The future work plan is indeed focused on resolving technical barriers in a relatively short time to maintain pace with project schedule.

Strengths and weaknesses

Strengths
- Strong approach
- Good continuing accomplishments
- Approach can use existing infrastructure
- Ability on organic synthesis and knowledge on organic compounds and catalysts are outstanding.
- The PI did an excellent job of presenting the program. That helps shape opinion but it also lends confidence that the planning and execution are being done thoughtfully and thoroughly.
- The class of molecules being investigated is one that could at some level provide adequate on-board storage, delivery, and regeneration capabilities suitable for implementation in a prototype vehicle in the not too distant future.
- The fact that this material will not react without a catalyst greatly improves their chances to build a safe system and incorporate a bladder tank system that won't evolve H_2 prematurely due to heat conductivity form waste fuel across membrane to the fresh fuel. The material is not corrosive or abrasive as compared to SBH which also greatly improves their chances; good understanding of overall system.
- The approach of liquid hydrogen carriers is advantageous to most of the other approached since it covers transportation, delivery as well as on-board and off-board storage.

Weaknesses
- System integration for hydrogen evolution.
- Achieving 2015 wt.% H and g H/L targets might be out of the question for these materials.
- Future Material selection may be limited. Most materials selected are limited to the 7% range which may be too low to build an adequate system around. This is why it is crucial that they explain how they can break this barrier in order for this program to remain relevant and promising.
- Useable hydrogen capacity is not considered (that is measured capacity minus hydrogen equivalent of the energy requirement to maintain the system at required operating conditions).

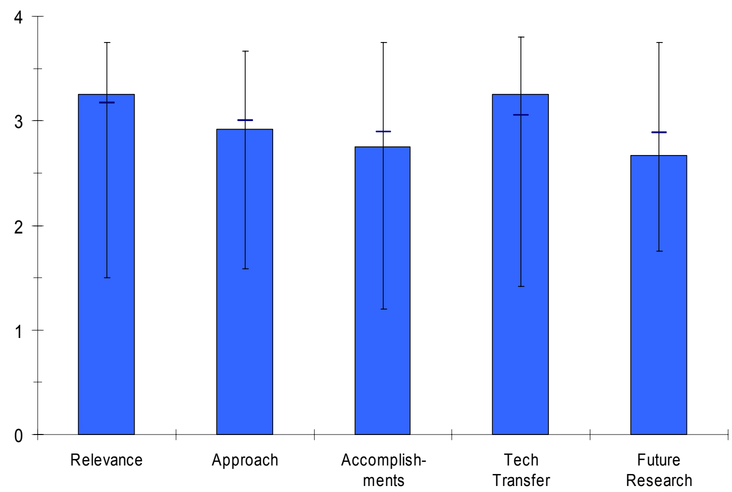
Specific recommendations and additions or deletions to the work scope

- Discuss/address effect of catalyst on confomer mix. Probably have already, but would be interesting to hear.
- Address what calculations say about hydrogenolysis.
- The pace of collaboration development needs to be stepped up to start getting benefit from other institutions in selected problem areas. Stronger collaboration with appropriate members of the chemical hydrogen storage CoE is recommended.
- Continue efforts to reduce or eliminate platinum.
- Would be interesting next year to investigate options such as blending other H_2 storage fluids that are exothermic in release to tune the enthalpy of the system. Or to try ionic fluids for viscosity / catalytic effects.
- Needs to explain how they will improve on more than 1 H per carbon/molecule and also explain a bit about how to liquefy the system.
- Conduct systematic research on catalyst development in conjunction with the liquid carrier development to include both the factors simultaneously in the experimental design (statistical, combinatorial). Pay more attention to regeneration of hydrogen carriers (hydrogenation step) as hydrotreating reactions may occur. In addition, a broader collaboration in the area of catalyst development is highly recommended.
- The system development for the Air Products' materials is currently unfunded. The two Air Products' projects depend on each other and it would represent the only other true system work being done aside from Millennium Cell.

Project # ST-10: Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

Dan Moser (PI); Susanne Opalka (co-PI, presenting); United Technologies Research Center

Overall Project Score: 2.9 (6 Reviews Received)



Brief Summary of Project

United Technologies Research Center (UTRC) and the project team are developing new complex hydride compounds capable of achieving hydrogen capacity greater than 7.5 wt.% H_2 and 0.05 kg H_2/L, and discharge rates greater than 0.02 g/s/kW. The focus is on fully hydrided phases with the formula: $Ak_wAe_xM_{+iy}(P_{\pm j}H_z)(w+2x+iy)$ where $z = | 1 \pm j |$, formed in the multi-dimensional phase spaces between alkali (Ak) and/or alkaline earth (Ae) hydrides, d-metals (M), p-metal hydrides (alane, borane, or ammonia) (P), and molecular hydrogen (H_2). The project team is using first principles modeling to guide and accelerate the discovery of new complex hydride compounds with solid-state, molten-state, and solution-based processing methods. The project activities include: conducting performance evaluations to select compositions for further development; optimizing dehydrogenation and hydrogenation catalysis with spectroscopic mechanistic studies and first-principles screening simulations; evaluating safety and compatibility; and outlining plans for synthesis scale-up and business case development for commercialization of hydrogen storage systems integrated with fuel cell power plants.

Question 1: Relevance to overall DOE objectives

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

- The project is fully focused on hydrogen storage, a critically important component of achieving the President's H_2 Initiative and RD&D plan.
- In principle, this project has the features of relevance that support the goals of the HFCIT Program. The problem is that they have only a few months left to make the project come to fruition and they have several challenging technical barriers to circumvent.
- The project mainly concentrates on hydrogen storage capacity with no attention to operability.
- The project supports the gravimetric and volumetric density according to the DOE RD&D plan, but does not support the discharging rate.
- Addresses 2007 targets, but not later targets.

Question 2: Approach to performing the research and development

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

- This project has set up a very nice approach combining computational approaches to screen out viable candidates and pass them along to experimentalists. However, though the approach looks nice in principle, the current year's results show only three exothermic reactions (i.e., reactions with precisely the wrong thermodynamics). It looks like the approach broke down somehow? Molten state processing is one of the few things this project has that others do not. (Others have first-principles modeling; others have solid-state and solution-based processing.) CALPHAD modeling is an interesting tool (and perhaps unique), but what is it used for in terms of materials discovery?
- The project is well focused on the key technical barrier of hydrogen density. The approach is well organized and balanced to integrate theoretical and experimental activities. The technical feasibility is experimentally

supported. The project has limited time to consolidate the results and make a conscious choice, because the time left and the concentration only on hydrogen capacity allow a partial evaluation of the investigated materials.
- The approach, as portrayed on several consecutive slides, is multifaceted and complex. There is certainly room for improvement in a number of areas, but on the whole the R&D strategy is generally well planned and executed. There is so much going on; it is hard to understand why more progress on the reversibility issues has not been made. Perhaps the problem is intractable for the particular class of compounds being investigated.
- Good combination of synthesis techniques. Ordered approach to exploring most promising areas of phase space. Appropriate use of various levels of theory to guide work.
- Project has nicely focused on DOE gravimetric and volumetric storage targets, with reasonable consideration of thermodynamic needs. Combined modeling (various techniques) and experimental work constitutes an excellent approach. Strong focus on alanates and amides could be questioned.
- Densification efficiency and macrokinetics may depend on sample scale; would be good to investigate scaling effects in the next stages of the project.

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

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

- Don't understand why they are looking at decomposition reactions that are significantly above the lowest-energy pathway? For instance, they claim in the talk that they might be able to get more than 8 wt.% out of the Li/Mg alanate, but that's only from a non-preferred pathway. The preferred pathway (as they point out) is exothermic/non-reversible decomposition, with a much lower weight percent. Why do they think that these non-preferred reactions are interesting? Had a very good layout for an approach to tune thermodynamics: but how did they come up with three exothermic reactions? How did they find System A and System B? Did their modeling approach really lead them to these discoveries or were they serendipitous? Seems like flawed logic is being used in adding compounds to the hydrided side of the reaction in order to improve the thermodynamics. These reactions have been demonstrated to have exothermic decomposition paths, and so adding compounds cannot really raise the energy of the decomposition.
- The progress is good on storage capacity. The technical progress on capacity is made by significantly increasing the desorption temperature. The PI does not present ideas to overcome and reduce the temperature within the fixed target.
- Clearly lots of work has been done in the past year and the project team deserves credit for that. But, other than the claim of some improvement in volumetric storage density, it is not obvious that enough progress has been made to allow the team to meet the coming November deadline. The results with co-reactants offer some hope but the team is still not where it needs to be on, e.g., the reversibility problem.
- New LiMgAl phase formation good result--dehydrogenation results good. How about hydrogenation? MBNH systems look interesting as well, but no rehydriding info.
- Good progress has been made, but limited hope for reversibility (perhaps not quite as critical a requirement anymore). The dual computational + experimental approach has been shown to be valuable.
- Would be good to use total exergy balance of cycles for hydrogenation - dehydrogenation at final system(s) selection (second law analysis of efficiency).

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

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

- The network of collaboration is well established and effective.
- The presenter did not elaborate on how the five collaborating organizations work together. One can only assume that each organization is effectively coordinated with and contributing to the aggregate activity. Collaborations beyond those among the five team members don't seem to be an important part of the project.
- Good partners.
- A nice collection of collaborations.
- Would be good to expand collaboration with leading laboratories of IPHE countries (Russia, China, India, etc).

Question 5: Approach to and relevance of proposed future research

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

- Approach to stabilize dehydrogenation seems unlikely to work, even in principle. More information about these ideas would be helpful in evaluating their validity. The methodology to screen and predict new reactions seems like it has generally failed this year; why is it likely to work in the future? System/material "scale-up" seems a bit premature, if promising materials have not yet been found. What is the plan here?
- The future steps are reasonable for the limited time available to the project completion. The PI must identify better final criteria for selecting the most promising candidates. The operability of the selected materials is not addressed in the final experimental work.
- The presentation did lay out what needs to be done to meet end-of-project goals. However, the barriers to meeting system gravimetric targets, hydrogen delivery requirements, and reversibility expectations may turn out to be insurmountable for the particular classes of metal hydrides being explored.
- Reversibility key for materials. Needs to be emphasized.
- This project should continue, but the PI is a bit vague on the future plans. It is far from clear how PI plans to accomplish reversibility. Will work continue mostly on the alanates and amides? Will the focus migrate to all-new systems?
- Designed reversible reactions are the most important part of the future plants. Would be rational use of 2006 budget for solving that problem.

Strengths and weaknesses

Strengths
- The project has developed a highly effective approach of theoretical and experimental work suitable for fast screening and analysis of novel materials. The network of collaborations and participating organizations is of value and able to maximize scientific development and technology transfer.
- Reported potentially achievable storage capacities are approaching 9 wt.% H and 90 g H/L.
- A very nice combination of multiple modeling and experimental verification.
- Well designed project; high level of theoretical and experimental research.

Weaknesses
- The project has progressed too slowly, because it has not been able to apply the developed approach in a timely manner.
- This team does not appear to be close to solving the reversibility problem. Reducing the exothermicity should remain the top priority task, even at the expense of storage capacity. The project team puts considerable stock in what the theoretical results indicate. There is no substitute for definitive experimental data.
- Alanates seem to be suffering from very low volumetric densities. There is a growing body of experimental evidence that the amides will never produce NH_3-free H_2 (in spite of project results suggesting the contrary).
- Not substantial.

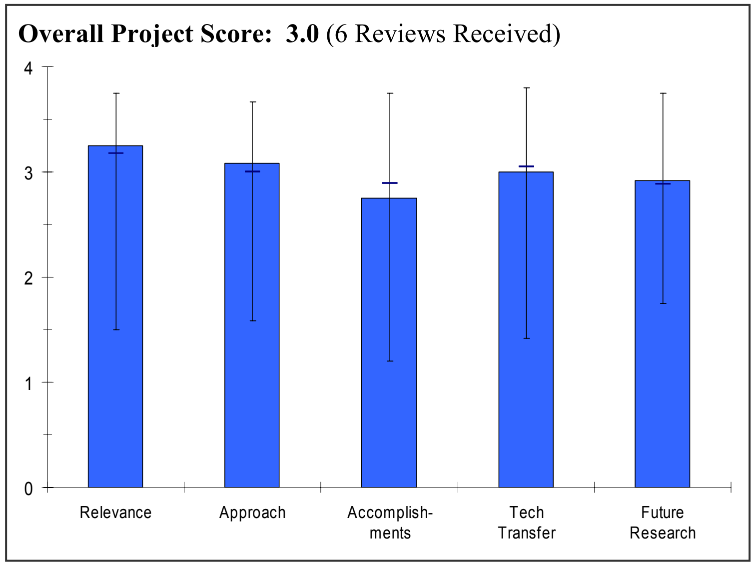
Specific recommendations and additions or deletions to the work scope

- The project has to include in the list of last period objectives the operability aspects.
- There is little time left to solve the remaining unresolved issues. Pushing forward with the composition(s) that come closest to meeting performance targets may be the best plan forward for the remainder of the project. Is an extension of the contract period appropriate or even possible?
- Does compaction of powder affect gas phase flow and mass transfer in bed?
- If possible, try to move away from the alanates and amides, both of which have their limitations. It may be that emphasis on requiring onboard reversibility may not be so necessary (i.e., the recharging heat problem). Consider extending this approach to the chemical (not-easily-reversed) hydrides. Give cost a higher weight in the project: cost of synthesis and/or off-board regeneration.
- Would be good to continue investigations and add project scope to problems connected with reactor discharging rate, sample-scaling effects on co-reactant segregation, heat and mass transfer, reactor design optimization etc.

Project # ST-11: Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

David Lesch (PI); Greg Lewis presenting; UOP

Brief Summary of Project



The objective of this project is to discover novel complex metal hydrides to enable a hydrogen storage system that can reversibly desorb 6 wt.% or more of hydrogen between -30 and 100ºC. UOP is applying methods of combinatorial chemistry and molecular modeling to discover materials with optimum thermodynamics and kinetics for on-board hydrogen storage. Virtual high-throughput screening will be used to screen complex hydrides to find materials which could meet the DOE system requirements and focus the synthesis effort on making the most promising materials. Even more importantly, the coupling of combinatorial experiments with molecular modeling of structural and thermodynamic properties will provide insights into the underlying mechanisms of action in these complex materials, permitting the design of hydrogen storage materials which would never have been envisioned otherwise.

Question 1: Relevance to overall DOE objectives

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

- Project properly aimed at solving the storage problem, an extremely important component of the President's Initiative and RD&D plan.
- Project fully supports multi-year RD&D DOE plan.
- This project is working on classes of materials that appear to be “dead ended” as far as DOE H-storage targets are concerned. They have given up on pure alanates (a wise decision) but do not seem to move towards storage material compositions that have a reasonable chance of meeting storage targets for 2015 or perhaps even 2010. The stated objective is 2010 goals.
- The materials sought would enable 2010 goals in theory.
- Conclusion regarding the end of testing of the alanate system is very relevant to the Hydrogen Fuel Initiative. It reinforces the sense of the community that this system cannot meet the DOE targets.

Question 2: Approach to performing the research and development

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

- The combinatorial approach is being implemented effectively and represents a valuable resource to the HFCIT Program as a whole. Even if one questions the choices of materials to measure that are being made in this project, there is much to appreciate about the measurement capability in place and under assembly.
- Definitely well designed.
- The ability to rapidly synthesize and screen compositions of metal hydrides is a valuable tool with which promising materials can be investigated throughout the material phase space. The approach to expand the investigation beyond the $LiNH_2$-MgH_2-$LiBH_4$ system does not appear well thought out or defined.
- The concept of combining first principle calculation and combinatorial experimentation is a good one. Project leaders seem to have chosen a ternary system derived from the literature ($LiNH_2$-MgH_2-$LiBH_4$), rather than an entirely new approach. A quick overview of the alanate limitations was useful.

- H_2 purities problem and thermal problem (heat of formation and effective thermal conductivity) are interconnected. Is it possible to extend model for that analysis?

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

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

- Nearly 1000 compositions screened and only one new mixed phase identified that has promise. Unfortunately, the gravimetric storage capacities being measured are all significantly below target values. The team deserves high marks for the amount of screening data accumulated but they just aren't finding promising performers.
- Recent MgH_2, $LiBH_4$, $LiNH_2$ work is most interesting result to date. New materials are always a triumph. While still not at the goals, it shows the power of the process and identifies new areas to concentrate on.
- The development of both model-based virtual high throughput screening in addition to combinatorial synthesis and screening capabilities are the most significant accomplishments in this project. However, it is well into the life of the project and the equipment is not yet in place and/or functional. Results have confirmed what others in the storage community have felt for some time; namely, that the alanates can not meet the DOE capacity targets. These tools can lead to greatly increased capacity to investigate promising materials.
- For two years of effort, the project seems to have started rather slowly. Some of the high throughput equipment is still not in place. To the project's credit, a final definitive closing of the alanates' door was helpful. The exercise on the ternary system was also interesting in proving the approach, but does not seem to be leading us toward a practical (low desorption temperature) end. There are complicated cyclic stability "composition equilibrium" problems.
- Is the 2nd cycle representative?
- Although the result of screening of alanate systems is negative, these findings are very important for future research (e.g., for those who are still working on alanates for on-board storage).

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

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

- The presenter did not elaborate on how the five partners work together. One gets the sense that most of the work is being done at UOP. Considering the amount of data generated in the past year, the team deserves the benefit of any doubt about how they function collectively.
- Good.
- There was little indication in the presentation that there is extensive and/or effective collaboration among the partners. Their contributions were not evident. Likewise there was no mention on how the tools will be disseminated to the community of researchers in these systems. There is no discussion in the presentation that relates this work to efforts within the metal hydride CoE.
- Good collaborations. It is not quite clear what each of the collaborators have specifically contributed during the last year.
- International collaboration in modeling can be extended with leading laboratories of IPHE countries.

Question 5: Approach to and relevance of proposed future research

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

- Armed with the capability to rapidly screen a bevy of compositions, the team is widening the search to include a broader range of metals and higher order systems.
- The plans for FY06 and FY07 are laid out in a general sense. Two go/no-go decisions are coming up. It is not clear which materials pathways will be selected for expanding the materials space of interest. There is a desire to find materials with heats of adsorption in the 20-50 kJ/mol H_2 but little indication of what materials will be considered.
- The future work seems generally good, but light on specifics. I have my doubts on whether the ternary $LiNH_2$-MgH_2-$LiBH_4$ work should continue (because of temperature, compositional instability, kinetics and NH_3 problems).

- Project has effectively planned its future.
- Not well defined. Li-NH_2 base systems have inherent limitations associated with cycling stability and hydrogen purity. In addition, it is not clear which systems using 20-50 kJ/mol and >7 wt.% capacity are proposed.

Strengths and weaknesses

Strengths
- The computational and measurement capabilities built up for this project are impressive. They represent a resource that could be broadly useful to the hydrogen storage community.
- Approach: willingness to move on when no good indications are found. Model guided experiment.
- The high throughput tools being developed in this project appear to bring improved ability to rapidly screen materials.
- A nice combination of first principle calculation and experimental (combinatorial) efforts. In some ways this work is similar to ST10 [UTRC materials discovery project], but somewhat different techniques are used and independent comparison of the two will be useful to DOE.
- Combinational experimentation and molecular modeling.
- The knowledge generated in this program will greatly contribute to the future research in terms of "what not to do". Clear conclusion was timely made in terms of what not to do in future research for on-board hydrogen storage.

Weaknesses
- Metal hydrides in any form most probably won't meet the current 2015 DOE targets for wt.% H and g H/L.
- High throughput synthesis seems to be taking a long time to bring on line. This is not a trivial item to create, but if it does not come on line and stay on line, the program loses its most powerful method to evaluate the new systems' actual ability.
- Progress appears to be a bit slow. DOE funding is relatively modest, but UOP is contributing more than DOE so one could reasonably expect faster progress.
- The past work on the alanates and ternary system was useful, but the latter should probably not be continued. (PI has already abandoned any future work on the alanates). Potential progress in an amide-containing system seems doubtful, given high desorption temperatures, low kinetics and probably ubiquitous NH_3 contamination. Increased activity on the borohydrides, although difficult and high-risk, should be encouraged.
- Analysis of results on the basis of cycle 1 and cycle 2 can not be representative for selection of final systems.
- Unfortunately, due to original selection of the scope of the project, based on current results the project has relatively low probability of success of meeting the DOE targets.
- Difficult to analyze the likelihood of future success since we are not privy to materials to be used in high throughput synthesis. Hopefully the power of the process will permit a breakthrough.

Specific recommendations and additions or deletions to the work scope

- With the combinatorial capability now in place, why not open the door to more than just metal hydrides. It seems that this project should have a substantive connection to the metal hydride CoE to avoid duplication of effort (or is that connection already in place).
- Improve interaction with the MHCoE to utilize these high throughput tools.
- The past work on the alanates and ternary system was useful, but the latter should probably not be continued. (PI has already abandoned any future work on the alanates). Potential profit in an amide-containing system seems doubtful, given high desorption temperatures, low kinetics and probably ubiquitous NH_3 contamination. Increased activity on the borohydrides, although difficult and high-risk, should be encouraged.
- Additions to project scope are not necessary.
- Add "useable" capacities for down selecting the candidates, which is measured capacity minus hydrogen equivalent of energy requirement to maintain the system at operating temperature on board. Identify new areas of search for new materials (other than alanates).

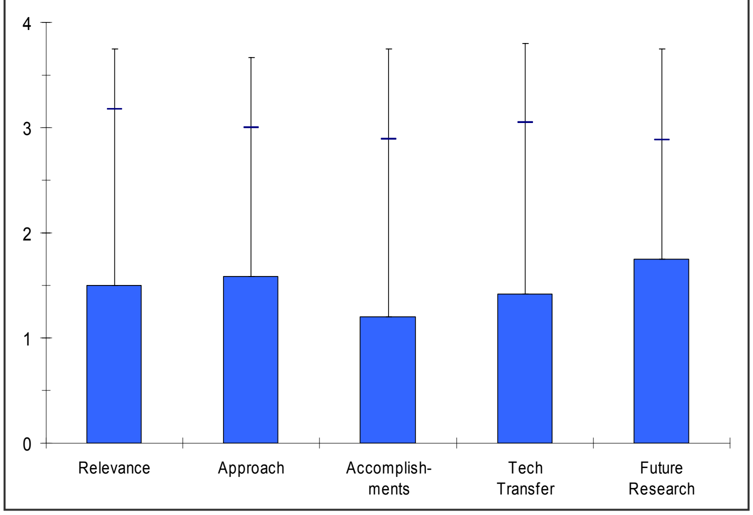
Project # ST-12: Hydrogen Fuel Cells and Storage Technology Project at UNLV

Clemens Heske (co-PI) Presenting; Balakrishnan Naduvalath (co-PI) University of Nevada-Las Vegas (UNLV)

Brief Summary of Project

The purpose of the project is to develop a fundamental understanding of interaction of atomic and molecular hydrogen with materials pertinent to the storage and use of hydrogen, thus enabling improved conceptual development, design and testing of storage options, fuel cells, and hydrogen combustion applications. The project emphasizes fundamental research at the atomic and molecular levels to understand the mechanisms of hydrogen adsorption/desorption from potential storage materials, catalysis of hydrogen adsorption and dissociation on platinum surfaces (fuel cell applications) and rate coefficients for atomic and molecular hydrogen interactions in both thermal and non-thermal populations (hydrogen combustion applications).

Overall Project Score: 1.4 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **1.5** for its relevance to DOE objectives.

- This project encompasses an immensely broad range of technical research; however, much of the work being done to date appears to be in developing the technical competence of UNLV. While this in itself is not troubling, the need to develop competence in so many diverse areas seems to be a poor use of federal funds. I would recommend that the PI concentrate on a very few (1-3) specific technical areas for concentrated effort which might provide a greater benefit.
- This work is not very well aligned. Much of it is not on hydrogen storage. Some of the storage work is in doubtful areas such as 300K storage in nanotubes. It may be helpful for UNLV but is not likely to advance H_2 storage. Metals on conducting polymers may or may not be productive depending on the actual work done.
- Partially addresses President's Initiative, but appears to be duplicative of other work already completed. Stated purpose during the review is to "increase the infrastructure of UNLV". It's unclear how this supports the President's Initiative.
- This project is very broad and fundamental. From a practical reference plane of the President's Initiative and DOE RD&D plan, it is very hard to see how the quantitative storage targets are addressed or how anything in that vein will come out of this in the 2006-2010 critical time frame (not to mention fuel-cell needs). Weight, volume, cost and refueling time considered secondary to vague fundamental understandings.
- This project is comprised of a family of fundamental research tasks proposed by individual investigators that touches on selected aspects of the science involved in hydrogen storage and fuel cell function. The relevance of this collection of tasks is hard to gauge because it seems to replicate much of the research already under way in the HFCIT Program. The project is very generously funded and with these funds they are building "infrastructures" for physical and chemical studies that are orchestrated to supposedly address issues of relevance to hydrogen storage and fuel cells, while also educating students.
- The project objectives are to improve UNLV capabilities in hydrogen storage and fuel cell technologies. At present, the project has little relevance to the DOE objectives to arrive at storage solutions that meet the DOE targets.

Question 2: Approach to performing the research and development

This project was rated **1.6** on its approach.

- Despite extensive research already being conducted in carbon nanotubes [SWNT] and $NaBH_4$ and growing evidence that neither SWNT nor $NaBH_4$ is likely to be able to approach the DOE storage targets, this project appears to be directing a substantial portion of their funding toward the pursuit of work that is unlikely to add to the scientific knowledge base nor to produce a storage material that can support the need for viable storage systems for hydrogen fueled vehicles. The PI should be encouraged to focus efforts in more fruitful areas.
- Many of the approaches are unlikely to yield practical results. As the speaker said, they are sharpening their tools; as such the work benefits them but is not likely to advance the storage of hydrogen. The $NaBH_4$ system is not suitable as a storage source for thermal decomposition. As noted the nanotube work has been largely abandoned elsewhere. Work at multiple GPa is of little interest, if that pressure were an option, modified AlH_3 would be the system of choice. The theory work may be of some value. Conducting polymer work seems a few years behind the work in the literature, hopefully they are replicating work done already to learn technique.
- Research within UNLV appears to be integrated. Project takes on too many tasks, therefore making project level progress difficult to assess in the future.
- The effort is presented as a bewildering array of poorly connected fundamental studies and people doing those studies. The relatively large number of materials to be incorporated are the subject of studies being done elsewhere and are nowhere supported as to their potential for achieving DOE gravimetric and volumetric targets. Stated objective is an interdisciplinary exercise. This seems to be a very fundamental effort with limited practical relationship to HFCIT needs.
- There is nothing novel or compelling about the research thrusts, the methods, the objectives, or the systems to be investigated. The presenter spent too much time on a few word charts. Summarizing the nature of at least some of the tasks through examples of results would have been more effective. The research is at such a fundamental level that it is not likely to reveal any near term insights of value to the HFCIT Program in meeting 2010 storage or fuel cell performance goals or overcoming major barriers.
- The approach appears to be to work in areas of interest to the individual investigators rather than a comprehensive, focused approach to develop hydrogen storage materials. The focus on fuel cells detracts from the storage effort and vice versa.

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

This project was rated **1.2** based on accomplishments.

- From information presented it is almost impossible to determine what has been accomplished. It appears that technical progress has been slow, despite high levels of spending. The presentation states that 66% of the project is complete which implies that some $2.5 million has been spent. One can always hope that once all the facilities are in place, progress to be reported next year will be substantial and more appropriately in line with the extremely high levels of spending committed.
- One wonders why they started a year after they received the grant, but for the moment they can not be evaluated on results as they have not had time to generate much information. However as much of this has already been done it is unlikely to be of any value.
- Only progress made is procuring equipment and selecting personnel, due to project starting in Jan. '06.
- Project just started apparently. Not much yet in the way of results.
- Given the level of funding allocated to this project, they should be expected to start producing seminal research results in a very short period of time. Based on what was presented, it looks like they are just getting started, so it is probably not fair to express concern about the absence of informative results at this time.
- The project is just starting so no progress as evident has been made.

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

This project was rated **1.4** for technology transfer and collaboration.

- There appear to be no collaborations outside UNLV. The PI mentioned a desire to work with an auto OEM and to more closely collaborate with the centers of excellence, but there were no reports of concrete plans in those areas.
- Interaction inside the group seems possible (remains to be seen if it materializes) but clearly not very well attached to outside groups. The work chosen shows a lack of interaction with the cutting edge of practically meaningful hydrogen storage.
- No collaboration outside of UNLV currently, though it was mentioned that UNLV would like to work with others in the future.
- There are a number of UNLV collaborators, but no apparent connection to outside collaborators.
- The presenter mentioned several times that the project at UNLV would have appreciable outreach but that the outreach was yet to come. Because most (if not all) of the tasks in this project align with other ongoing HFCIT supported projects, it is essential that appropriate coordination/collaborations develop to avoid unnecessary overlap. The project management at UNLV should take the lead in fostering these interactions.
- At this point, the university investigators are just getting organized. No outside collaborations can be established until UNLV has capabilities and can reach out to collaborators. The management structure is not apparent. There does not appear to be one project manager who will try to keep the team focused on the end product.

Question 5: Approach to and relevance of proposed future research

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

- The presentation provided few details about future work planned, whether there are any specific targets or metrics, or whether or not there is a technical timeline with goals.
- Plans were not clearly laid in many cases.
- There is a large basket of fundamental studies proposed with little apparent connection.
- The future work plan as discussed by the presenter may lead to some interesting insights that guide other researchers to solutions for barrier/road block issues, however, the large funding base provided for this project would be better spent if it focused on finding near term solutions rather than on building infrastructures and starting a collection of loosely connected basic research tasks.
- The presentation indicated areas of interest to the individual investigators. Research pathways were not discussed.

Strengths and weaknesses

Strengths
- The biggest strength UNLV has is the quality of its researchers and the potential they have to make substantial contributions to the hydrogen program if only their work can be focused on relatively few areas that align with UNLV's strengths and are directed toward technical areas critical to the success of the DOE program.
- Number of people involved could lead to progress.
- Plenty of funding for the project. Many resources to deploy to the project.
- A variety of subtasks and scientific disciplines.
- It is not possible to discern any strengths attributable to this project at the present time. Next year's Peer Review should be a critical go no-go decision point. Major pay backs in terms of demonstrably useful research results should be forthcoming or at least in evidence at that time.

Weaknesses
- There are too many different projects in too many different technical areas. Too much work appears to be directed toward carbon nanotube research and to $NaBH_4$. Unfortunately these areas seem to have little value as viable storage media. Very little has actually been accomplished technically.
- Choice of target systems, too much of the work seems meant to bring the labs new equipment and to teach and to allow the PIs to enter the hydrogen storage field, and thus a substantial part of the budget is to bring the groups up to speed, not to advance hydrogen storage.
- Lack of collaboration with industry and/or national labs. Scope of project is too broad. Capability of UNLV in the various subjects covered by this project not clear.

- No logical connections among the subtasks or near-term connections to practical needs.
- The project tasks give the impression of being 12 wish list items for a selected group of chemists and physicists. There is no engineering component and that is without question a serious omission if the goal of the UNLV project is to have a beneficial impact on hydrogen storage and fuel cell development. There seems to be a preponderance of emphasis on electronic structure. This aspect of the project could be consolidated and reduced to allow some engineering studies. Federally funded programs should not be about giving scientists what they want; it should be about getting useful science done.
- This project lacks focus. Tasks appear to have been selected on the basis of the individual PIs' area of interest and expertise and not coordinated with each other in a focused approach to address a particular barrier or issue.

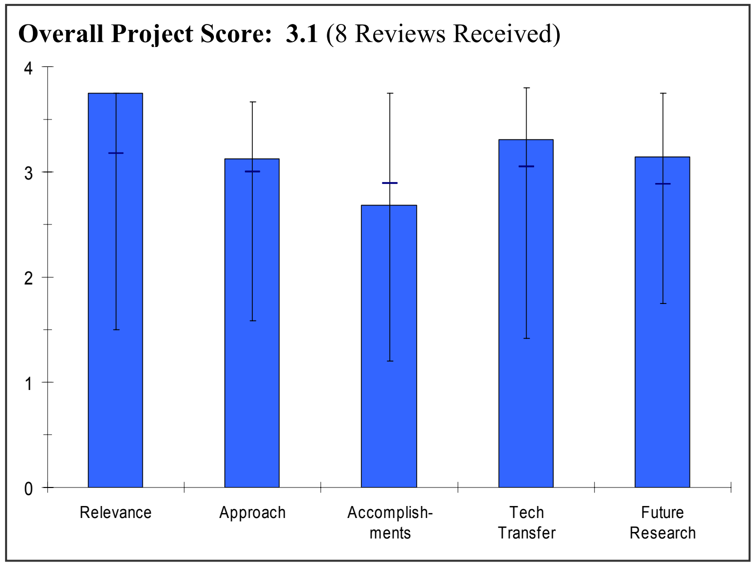
Specific recommendations and additions or deletions to the work scope

- Find partners with practical interests.
- Recommend stopping work on $NaBH_4$ and nanotubes. Consider increasing work on fuel cells, e.g., thin wall membranes.
- Redirect research to something more aligned with the goals. The work with potential to advance its actual field is more basic in nature, for example the modeling work on collisions, and so this should be funded by NSF or BES, not EERE. The primary aim is to buy UNLV equipment as best can be seen.
- Narrow scope of project.
- Link more closely with DOE to align project with DOE needs.
- Focus work on areas not previously addressed.
- Define some real connections to DOE targets and the RD&D multiyear plan. Find partners with practical experience.
- As presented at the review, this project has all the features and attributes of a centralized research activity that should be sponsored by the DOE Office of Science rather than by EERE. At next year's HFCIT Peer Review, this project should be given a one hour slot in which the presenter(s) demonstrate(s) that they are (1) making or on the verge of making contributions that are relevant to HFCIT goals, (2) developing a strong outreach to the HFCIT centers of excellence and other contributing institutions/organizations as appropriate, and (3) diversifying their task structure beyond fundamental physics and chemistry studies to embrace some engineering studies.
- Propose a management plan that identifies a leader who has the authority to direct UNLV's efforts and maintain focus on the hydrogen storage targets. Short of that, perhaps some of the CoEs could reach out to UNLV to bring up to speed those investigators whose interests most closely mirror those of that CoE.

Project # ST-13: Research at Sandia National Laboratory as part of the DOE Metal Hydride Center of Excellence

Lennie Klebanoff; Sandia National Laboratory-Livermore

Brief Summary of Project



[NOTE: This review is on Sandia's contributions, not on the entire DOE Metal Hydride Center of Excellence. Each of the partners is evaluated separately.]

Sandia National Laboratories has been selected to lead the DOE metal hydride CoE, which is composed of 8 universities, 3 industrial partners and 5 other national/federal laboratories. The CoE is focused on developing new complex 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 advanced complex hydrides, destabilized binary hydrides, novel intermetallic hydrides, and other reversible hydride-based materials. In addition to new materials discovery, Sandia will work with all CoE 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: Relevance to overall DOE objectives

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

- The work is firmly pointed at the key needs of the program across all its efforts.
- The metal hydride CoE presentation was well orchestrated, clearly and concisely presented, and left a good impression of the functionality of the CoE. This is a major HFCIT program that is designed to be well aligned with the hydrogen vision. The multi-presenter format worked well because each major topic was covered by a PI working in that topical area.
- The effort completely supports the Hydrogen Fuel Initiative and Multi-Year RD&D Plan for Storage.
- Hydrogen storage is the key enabling technology critical for the success of hydrogen as a transportation fuel. Any work which can further understanding of the basic science of hydrogen storage is vitally relevant to DOE objectives, the President's Hydrogen Initiative and the objectives of the Multi-Year RD&D Plan. The metal hydride CoE is a key research activity which supports all these objectives.
- Obviously, the CoE provides strong value towards DOE targets.

Question 2: Approach to performing the research and development

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

- Management approach is good and well thought out. The individual projects are generally well oriented as well.
- The full set of capabilities established or in the process of being established by the MHCoE (at SNL and partnering institutions) represents an impressive array of tools for the study of hydrogen in metal [hydrides]. Emphasis in the program as a whole is on demonstrating DOE targets for wt.% H and g H/L. The work plan is in accord with community wide understanding of what needs to be done to develop a suitable metal hydride

storage material that meets the DOE targets. The lead presenter made it clear that the work plan is a living plan and that the plan is revisited and revised as appropriate to make changes in emphasis stemming from discoveries, from modeling guidance, and from results that show selected material candidates have no hope of meeting target values for hydrogen storage.
- This is due [the score?] to ambiguous decision points and a lack of clarity surrounding the details of go/no-go decisions. Need to make these decision processes more transparent.
- This is a large effort with many different useful facets. The work described largely covered SNL parts of the CoE. Only a brief introduction to the CoE was given. Other CoE components were presented elsewhere. The overall SNL approach is a combination of theoretical and, more so, experimental techniques. This approach is comprehensive and cannot be faulted. There is some overlap with other efforts within the CoE and world in general, but that is OK.
- The CoE is taking a logical, methodical, and thorough approach to addressing the barriers to a viable hydrogen storage system.
- Destabilizing the thermodynamics is key towards achieving any kind of realistic system. Fast throughput and modeling of materials is crucial to identifying new materials. Either method on its own will be unreliable.
- CoE structure well organized.
- Good management of CoE.

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

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

- Amide work on durability is an important contribution, even though it would have been nice if the durability could have been improved. Hopefully this will guide the type or amount of work in this area. LiAlN compound is interesting development though does not seem practical in current form. New complex hydrides are also interesting but almost everything seems "in study" with no hydrogen results. Theory used to pick systems is a good development. Theory approach used seems good. Monte Carlo was a significant step forward in this area.
- In summary, several of the reported FY 2006 accomplishments included (1) ruling out alanates, (2) getting ca. 5 wt.% reversible with Li-Mg-amide, (3) predicting ca. 10 wt.% (theoretical) for Li-Al-N phases, (4) initiating study of nine new materials, including Li-Al-K phases and $Ca(BH_4)2$, and (5) developing a mini hot plate array for combinatorial thermal treatments. Progress in FY 2006 was good but not outstanding in terms of moving closer to DOE hydrogen storage targets.
- Good progress in some areas. However, in areas such as alanes, the regeneration should take a higher priority.
- There has been good progress and understanding, as it should be for a project of this magnitude. The work on the amides was excellent; unfortunately the fine results are not very promising from a DOE target point of view: NH_3 problem, low temperature kinetics, cyclic life, etc. Similarly, project scientists are to be commended in recognizing the limits to the alanates. The new synthesis techniques being developed are welcome. Theoretical methodology has been refined and improved.
- Noteworthy SNL accomplishments include the Monte Carlo approach which is innovative and can help predict possible new storage materials. SNL uses good technique by developing a theory, using experimentation to evaluate the theory and then revisiting theory based on the experimental results. On the other hand, some work is likely to have little value; e.g., the solid state synthesis of Ca-B-H has very low kinetics and reversibility.
- Minimal improvements were demonstrated this year. Good decision to reduce work on amides. Hopefully this CoE hasn't hit the ceiling of what can be accomplished. Has thermodynamics destabilization reached the limit? Slide 17 demonstrates cycling issues and revealed that NH_3 is released in the $LiNH_2/MgH_2$ mix. This was one of the few presentations that demonstrated extensive cycling tests.
- Limited scope of work and small subset of hydride materials were studied relative to funding level.
- Current materials do not appear promising.
- New theoretical tool developed, but not clear if it has the capability to identify promising materials with reasonable certainty.

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

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

- Well coordinated inside the program, but also well attached to the greater scientific community in this area.
- Tightly organized, multi-institutional program that is performing a broad based study of hydrogen storage in metal [hydrides]. The integration of contributions appears to be well managed, as reflected in the one hour CoE presentation and supporting presentations from partnering institutions. The MHCoE has established a Coordinating Council.
- The CoE has wealth of experienced partners. It is not clear how the these interactions are nurtured.
- Many good CoE collaborations, at least on paper, via the CoE. But it is not quite clear from the presentation how they provide synergism and specific contribution to the SNL activities described here. It is hard to see how the collaborations are working from organization, communication and group kinetics.
- The CoE has assembled a world class group of partners to work toward the goals of hydrogen storage.
- Obviously the best researchers in the country are integrated into this CoE.
- Modeling and experimental work do not appear to interact or connect with CoE partners or to other researchers.
- CoE structured well for interactions, collaborations.
- Collaborations appear to be limited to characterization of materials.

Question 5: Approach to and relevance of proposed future research

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

- Appropriate plans, addressing the key short comings of the materials they study.
- The future plans do build in a logical way from what is being learned program wide. The flexibility to redirect and refocus has been demonstrated even in the first full year. Removing/eliminating barriers might take a while for this program. Knowing when enough effort has been expended to justify abandoning specific materials approaches is going to be important for the managers of this CoE.
- I agree on the plans for the future: eliminate alanate work, minimize amide work and focus on the search for new materials, including borohydrides. Off ramps have been effectively used in their last year and seem to be adequately factored into future plans.
- There is so much to learn about metal hydrides and so many possible storage materials to evaluate that future plans are reasonable, build on past research and may very well have some chance of success meeting the program goals.
- Interesting that work on amides is being reduced and borates are increasing. Work on alanes continues. Will there be an overlap with the chemical CoE in the future? The CoE has made some important no-go decisions on alanates and amides which helps them to move on to other more promising materials. Rapid thermal processing technique should prove valuable.
- New materials effort seems limited.
- Good decisions on mid-course directional changes.
- New rapid screening method proposed.
- Where does Intematix fit in to CoE work?

Strengths and weaknesses

Strengths
- Quality of team, management approach, potential storage levels, willingness to leave non-productive systems, interaction between theory and experiment and experiment and engineering.
- The MHCoE is off to a good start. It appears to be well managed and well integrated in terms of partner connection.
- The CoE has some of the most experienced and knowledgeable partners in the field. The barriers are understood. Good progress in some areas.
- A diverse spectrum of scientists and engineers…and excellent laboratory facilities. Long experience in H-storage materials.
- Strong partners doing valuable research. Monte Carlo work innovative and important to be able to predict possible new materials.
- Strong researchers and powerful fast throughput systems will be very helpful in stepping up the pace of new materials discovery.

- Great collaboration with various academic, governmental and industrial institutions. Shifting effort away from alanates and amides towards other systems.

Weaknesses

- Some team members are not as cooperative as would be desirable it seems. Seems like teams are not talking to each other. Kinetics and temperature are still major questions with little progress from last year. Obviously progress can not be made every year in the key challenges, but sooner or later progress is required.
- The storage of hydrogen in metals has been studied for years. In spite of the very large number of new mixed metal compositions for which hydrogen storage data are now available (from the MHCoE and other HFCIT contractors), there is little encouraging evidence that any metal hydride can achieve the 2015 DOE system goal of 9 wt.% H.
- The presentation did not clearly address the interactions of the partners and how the collaborations among the partners results in a more synergistic approach.
- It seems SNL is leading the CoE in ways DOE wants, but it is not quite clear it is making the fullest use of CoE collaborations for its own optimization of time and resources. I sense there is some tendency toward working in a vacuum.
- There appear to be some communications challenges to ensure that work being done among the partners is well coordinated and that possible overlap is minimized.
- Fighting thermodynamics- have they hit the limit? Still little discussion or presentation of other important aspects of storage such as material heat capacity, thermal conductivity and diffusivity which all greatly affect system design.
- Lack of truly innovative concepts for on-board hydrogen storage in the area of metal hydrides. Delaying no-go decision on amides and alanates. Useable capacities of materials are not considered.
- Need more emphasis on experimental materials efforts.
- Need more interactions and partnerships with CoE partners and external partners.

Specific recommendations and additions or deletions to the work scope

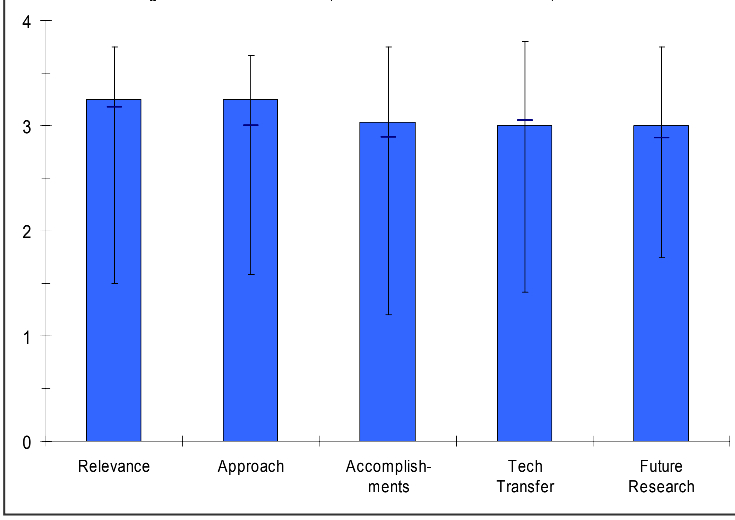
- Should focus on why materials predicted to be good did not live up to expectation $Ca(BH_4)_2$ for example, and try to improve model prediction, or improve experimental speed to working system. Highly unlikely this will recycle at 350°C based on thermodynamic or practical considerations; they should know better than thinking at 100°C and 100 bar above the desorption they could get good reversal. Go to theory and find the right conditions see slide 39 for correct conditions. I would recommend management reinstall a sense of urgency in the CoE partners, while hard to pin down it seems like the partners' focus and speed has become more diffuse in the last half year, and if so, that will hurt the overall program.
- The above stated perception about the value of studying metals for hydrogen storage is shared by many veterans of metal hydride science and it is incumbent on the MHCoE to provide in the not too distant future some definitive evidence that metal mixtures of any composition are worthy of study from the standpoint of DOE's goals for hydrogen storage. One option for dealing with this issue is to make a well considered case that the present DOE target values (particularly for 2015) are unnecessarily high.
- Perhaps go more than "rescue" amide work; maybe probably zero it out. It is suggested SNL start considering the economics of the new systems and synthesis methods being studied.
- Projects should clearly move past alanate research.
- Generate more "outside-of-box" concepts as opposed to focusing on further development of already known systems. Consider "useable" capacities of materials as opposed to considering measured wt.% capacities. Would be good to present 3 parameters for each material, that is measured/predicted wt. capacity, delta H of desorption and operating temperature. Develop strategies (systematic approaches) for materials discovery as opposed to rather empirical process based on "prior art."

Project # ST-14: Lightweight Intermetallics for Hydrogen Storage

J.C. Zhao; General Electric, Inc.

[Partner of the DOE Metal Hydride Center of Excellence]

Overall Project Score: 3.1 (6 Reviews Received)



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 FY 2006 include identifying the crystal structures of $Mg(BH_4)_2$ using XRD, neutron diffraction and computer modeling, and performing combinatorial and computational screening of catalysts and dopants for $Mg(BH_4)_2$ to try to make it reversible on-board a vehicle.

Question 1: Relevance to overall DOE objectives

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

- This project is part of the MHCoE. The focus is on combinatorial testing of candidate metal hydride storage materials and on coordinated studies to identify new candidates and elucidate reaction pathways.
- Project is properly focused on national needs to solve on-board storage problem vis-à-vis the President's Hydrogen Fuel Initiative and DOE RD&D plan. Volumetric targets not addressed much.
- Aimed at key problem of the material and material has potential to approach 2010 goal.
- Material research aligns well to the President's Initiative.

Question 2: Approach to performing the research and development

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

- Approach is efficient and precise, aimed well at important goals.
- Focusing on one material, magnesium borohydride, could be beneficial in not having the distraction of pursuing multiple materials at the same time.
- The high throughput approach seems like a good one, although novel promising materials were not really found. In going forward, with the focus on $Mg(BH_4)_2$, it is not clear whether this is going to utilize the high-throughput approach, or a more directed focus on one specific material.
- Although combinatorial techniques are central to other DOE projects, this project provides some clearly different synthesis techniques that are likely more amenable to commercial scale-up. PI's organization is a very well-known facility based in practical materials science.
- Reported successful development and application of a robust, combinatorial measurement system. Strongly focused on $Mg(BH_4)_2$ and related metal hydride systems; could in principle be more broadly applied within the MHCoE program. In situ XRD and neutron diffraction are providing meaningful structural and mechanistic information.

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

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

- Combinatorial work on LiAlSi blends useful, if not advancing the storage limits known. $Li_6Mg(NH)_4$ system a good development. $Mg(BH_4)_2$is an interesting development too.

- Combinatorial/high throughput screening methodology appears to be valuable for material selection.
- Though nothing promising was found in the light-metal systems, or the amide/imide systems, there still was good technical progress, and it's good to see that this group is willing to move on to new areas if they don't see promise. The synthesis and decomposition of $Mg(BH_4)_2$ is a promising avenue for this group to explore further.
- A good start has been demonstrated, perhaps slightly below expectations for the relatively high funding for this project. Many preliminary results are negative, but those are important results anyway. It is good to see contractor knows when to quit. "Amide" results, like others, again show the NH_3 problem and strongly suggest such work be generally deemphasized.
- Screened more than 10 ternary systems. Found that vacancy ordering influences structure. Working on $Mg(BH_4)_2$ with 16 wt.% H theoretical capacity. Several new compositions identified for further study. But, still no demonstrated breakthrough composition that can meet the FY 2006 goals for storage capacity and delivery.

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

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

- Part of the MHCoE.
- Collaborations dubious with SNL or other places.
- Doesn't seem that the communication between GE and Sandia is terribly good. For instance, the Sandia presentation proposed future work on the Na-Si-H system, but immediately after, GE showed a slide saying that the Li-Na-Si system had been thoroughly screened, and they had given up on it. How does the GE work on $Mg(BH_4)_2$ fit in with the Sandia work on borohydrides? Is there redundancy here?
- Good collaborations, at least on paper, within the CoE. No CoE or outside industrial collaborations.
- Solidly integrated into the MHCoE. It seems this project is getting samples from most synthesis sub tasks of the overall CoE.

Question 5: Approach to and relevance of proposed future research

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

- Appropriate plans.
- Focusing on magnesium borohydride dopant predictions can be valuable to the entire MHCoE.
- Strong focus on $Mg(BH_4)_2$ seems like a good idea; need to ensure that Sandia (also focusing on borohydrides) is not going to duplicate this effort!
- I must question the strong emphasis on $Mg(BH_4)_2$ for the future effort, given the high desorption temperatures seen thus far and the doubts on reversibility. Very good to try catalyzing the reaction, but don't wait too long on the go, no-go decision.
- Future plans build sensibly on findings to date within the project and within the CoE as a whole. Removing/diminishing barriers will be a challenge for the entire CoE.
- Scope of proposed research for 2006/2007 is too limited to Mg boron hydride. Need more innovative ideas for future plans.

Strengths and weaknesses

Strengths

- Willing to end work that will not meet goals.
- Project appears focused. Very good collaboration.
- A good materials science lab with long experience on combinatorial experience.
- The main strengths are an experienced staff, thoughtfully developed equipment, and intelligent application of computational tools.
- Good experimental design including in situ structural characterization of hydride material (XRD) and detailed gas phase analysis. Prompt assessments of results and timely go/no-go decisions on aluminides, silicides and amides.

Weaknesses

- Duplicative to Sandia work.
- High temperature for reversibility may be problematic for this material.
- Possible overemphasis on $Mg(BH_4)_2$ as a solution. A "one card" gamble.
- No mentionable weaknesses were noted.
- Again, useable capacity issue. For majority of known metal hydrides (including destabilized) the useable capacities range from 2.5-2.9%. Not clear whether the proposed systems are/will be outside of this box. Thermodynamic aspects (endothermic heat effects of hydrogen desorption) are not considered. Also, the project is heavily focused on magnesium boron hydride that reduces probability of success.

Specific recommendations and additions or deletions to the work scope

- Need to split up work between SNL and GE and work together.
- Continue searching for "new and different" materials as much as possible.
- I must question the strong emphasis on $Mg(BH_4)_2$ for the future effort, given the high desorption temperatures seen thus far and the doubts on reversibility. Very good to try catalyzing the reaction, but don't wait too long on the go, no-go decision.
- The plot on slide 6 of the presentation (also presented in other places in the talk) tells a story about metal hydrides and the DOE storage targets; this information needs to be reconciled. All the materials represented in the slide fall on a line that lies considerably below the pathway to meeting DOE targets. That's happening for a reason and it's telling us something that needs to sink in, i.e., metal hydrides may be classically limited in what can be expected from a hydrogen storage perspective.
- Estimate storage energy efficiencies of the materials by considering enthalpies of desorption (useable capacities). Generate more approaches beyond Mg boron hydrides.

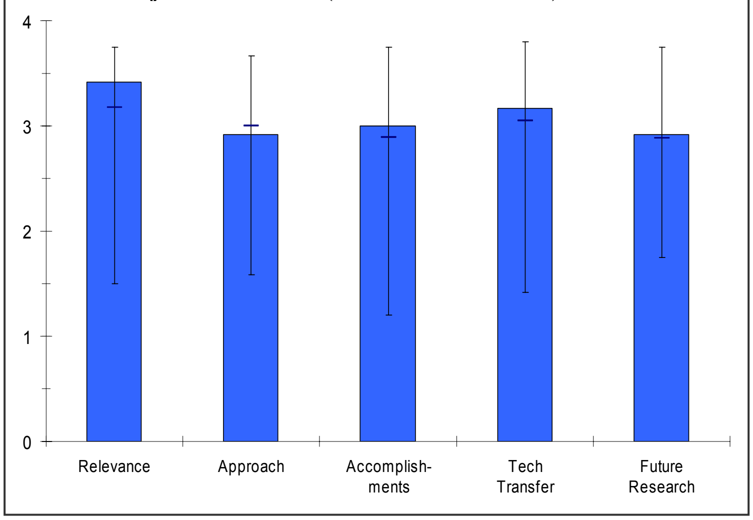
Project # ST-15: Synthesis & Characterization of Alanes for Automotive Applications

Jason Graetz (co-PI) presenting; Jim Wegrzyn (co-PI); Brookhaven National Laboratory (BNL)
[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

The objective of this project is to understand the strengths/weaknesses of using 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 ≥ 8 wt.% (gravimetric) and ≥ 0.10 kg-H_2/L (volumetric). AlH_3 polymorphs with suitable H_2 pressures at temperatures near the operating temperature of a PEM fuel cell (~85°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 (Go/No-Go decision in FY06).

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Important and novel work aligned well with targets.
- In line with program objectives. Work is of relevance to attainment of R&D goals.
- On-board storage in solid structures is perhaps the single most important need for the development of the hydrogen economy. The focus on alane is one of the more promising pathways.
- Fully supports the multi-year RD&D plan.

Question 2: Approach to performing the research and development

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

- Focused on key technical barriers.
- Reasonable, systematic approach to the objectives of the project. The link to and integration with the MHCoE is instrumental for covering scientific and technical barriers. Project profits from access to unique materials characterization facilities. The system engineering part could be more ambitious.
- Sound approach from theory and synthesis to experiments to tanks.
- The study of polymorphs leads to understanding the decomposition characteristics of AlH_3, and seems to show how the material must be synthesized and how it must be treated. The presenter, however, was not clear in his presentation as to how the accumulated data would be used. The polymorphic nature of the material, with no clarity on what parameters will determine which polymorph of alane will form, leads me to be concerned about the control that one might have over this material if on-board a vehicle, especially how the temperature would be controlled.
- Very disappointing to see this work focused so strongly on decomposition. Regeneration is really the key obstacle, but is a much harder problem to solve. Should have been focused on this from the beginning.

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

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

- Good progress with respect to objectives. The volumetric H capacity for the aluminum hydride really stands out - three times the DOE system target! The direct hydrogenation of spent Al powder requires extremely high hydrogen pressures placing a doubt to the applicability of the material; the 'No-Go' decision was correctly taken. System target/value and not just materials should always be kept in mind - may affect the project's progress and deliverable.
- The presenter showed very definitive properties for the polymorphs of alane. This work seemed to be very well thought out and performed. It is not clear, from the presentation, however as to how these data will be used.
- The team made interesting progress on understanding polymorphs and decomposition. However, I think this is the wrong problem to focus on. They need to concentrate on regeneration. The consideration of rehydriding with pressure seemed really like a waste of time. This team should have known at the outset that a 9 kJ reaction is simply not going to be rehydrided with modest pressure. Why was this even part of the project?
- Quoting formation energetics rather than the more conventional decomposition reactions made it appear as though all the signs of delta-H and delta-G were incorrect. This was a bit distracting. Decomposition of AlH_3 is weakly endothermic.
- Direct decomposition is a valuable finding, showing the need for phase purity.
- In the case of solving the regeneration problems the systems can be the most efficiency.

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

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

- Good coordination inside CoE, appropriate outside connections.
- Incorporation into MHCoE is beneficial so is the foreseen collaboration through IPHE, however link to industry was not clear.
- The presence of the CoE provides a natural collaborative mechanism. Another reviewer (or listener) remarked on the fact that due to the regeneration issues, the alane projects should be housed in the chemical hydride CoE rather than in the metal hydride CoE. I do not agree; there is a large alane body of researchers in the [Metal hydride] CoE. The regeneration is one issue - albeit an important one.
- Would be good to expend the collaboration with IPHE countries research centers.

Question 5: Approach to and relevance of proposed future research

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

- The future work needs to focus on regeneration. More work on kinetics and decomposition is scientifically interesting, and will certainly need to be done if this material is even to make a viable storage technology. However, if there is no pathway to regenerate it efficiently, the work on kinetics will be wasted effort. Regeneration strategies don't look very promising - Yes, delta-G appears in an exponential, but it needs to be reduced by quite a bit (e.g. two orders of magnitude away from where it needs to be?). Is there really a possibility to change delta-G by this much via the approaches mentioned to rehydride with pressure?
- Plan includes subscale tank development and theory work, regeneration work, which is commendable in a subproject. Regeneration is especially important.
- Future research plans appear reasonable however the plans for the full system approach could be more ambitious.
- While the work being proposed on regeneration of the alane is very important, there was no indication as to how the work on the polymorphs will be used in any future work.
- The most important problem - regeneration is proposed for future work.

Strengths and weaknesses

Strengths
- Amount of hydrogen stored.
- The incorporation in the MHCoE strengthens their research and expands their vision of materials and possible systems. Access to unique characterization facilities, expertise, technical resources and instrumentation. The IPHE collaboration scheme is beneficial.
- A major strength is the need for this type of research. Another is the presence of the CoE.
- High scientific level of experimental and technological approach.
- Good and quick no-go decision regarding synthesis of AlH_3 from elements. Considerations of the thermodynamic aspects of hydrogen desorption. Strong experimental basis at BNL. Planned regenerability studies for AlH_3.

Weaknesses
- Material must be removed and put back in tank.
- Engineering aspects are an issue. The progress towards the system, as opposed to material, targets should be addressed, to avoid confusion.
- The work seems somehow disjointed. It was difficult in the presentation to determine what the results meant in the real world. How will an alane system be designed, for instance, that will avoid the temperature instabilities of some of the alane polymorphs. Another issue is, of course, regeneration. An off-board regeneration system is going to be much more expensive.
- Planned scale-up study (1 kg tank) appears irrelevant on this stage of the project. Addition of NaH or LiH would bring the system to well-known alanates. Decomposition of AlH_3 at > 40ºC is of great safety concern since equilibrium pressure for AlH_3 is 10^5 bar at ambient temperature.
- AlH_3 has already been studied in quite some detail from DFT approaches (structure, thermodynamics, etc.). Are the proposed modeling efforts really going to add value beyond what has been done already?
- Not substantial.

Specific recommendations and additions or deletions to the work scope

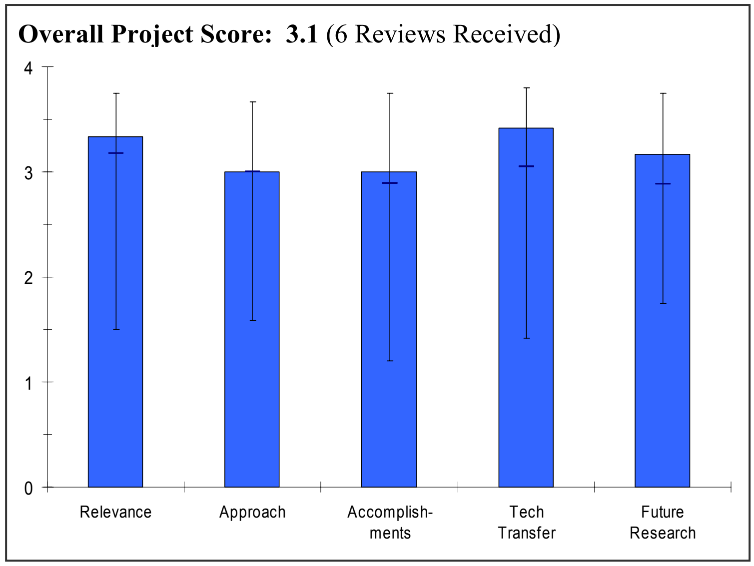
- Probably need a focus on the tank refill for offboard system. Need to work on regeneration process and push down the cost. This is critical!
- This is a promising material with the potential to reach the targets, however regeneration and associated costs are still problematic and should be intensively addressed. Increasing effort and speeding up progress on first principle analyses, using input coming from crystal structures collaborative work, could benefit the project. Also interaction with the chemical hydrogen storage CoE - link with the ionic liquids work - could be considered, for the regeneration off-board.
- Need to look at the ramifications of the developed data as stated above.
- Expand collaboration with IPHE country research centers and universities.
- Eliminate scale-up studies for alane-based tank. Address potential pressure build-up issue for AlH_3. Develop alternative approaches in case a no-go decision regarding AlH_3 would have to be made.

Project # ST-16: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage

Greg Olson; HRL Laboratories LLC

[Partner of the DOE 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 include:

1. Identify and test new high capacity Li- and Mg-based destabilized hydrides
    a. Screen candidate $LiBH_4$ + MgX destabilized systems and evaluate energetics and kinetics
    b. Down-select systems for additional work
2. Apply nano-engineering methods to address kinetics limitations
    a. Develop solid state approaches for efficient synthesis of nanoscale reactants
    b. Assess hydrogen exchange rates in nanoscale MgH_2/Si and destabilized complex hydrides
    c. Evaluate sorption kinetics of reversible metal hydrides in nanoporous scaffold hosts

Question 1: Relevance to overall DOE objectives

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

- This project is part of the MHCoE. A nano engineering approach is being taken to the study of hydrogen release through destabilization. Also looking at ways to minimize microstructural dimensions to enhance diffusion.
- The focus on the thermodynamic destabilization of the high capacity material $LiBH_4$-MgH_2 is very good because it may have the potential to meet the DOE 2010 capacity goals.
- Addresses key problems (capacity, thermodynamics, and kinetics) in a planned way, and allows high capacity.
- Contractor focuses completely on storage problem with full attention to DOE targets necessary to realize RD&D objectives and HFI.

Question 2: Approach to performing the research and development

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

- Studying destabilization through addition of alloying elements. Basically, they are manipulating the activity of the strong hydride former to lower binding energies (an old, well known approach). Also, applying dilution milling methods, porous scaffold structures, and aerogel matrixing to shorten diffusion paths or more correctly increase surface area to volume ratios.
- The two-fold approach of thermodynamic destabilization and nano-size kinetic effects to lower hydrogenation and dehydrogenation temperatures is excellent, particularly for the materials approaches based on $LiBH_4$. The intended study of scaffold effects on the $LiBH_4$-MgH_2 system performance is excellent.
- Approach is quite good. More efficient way to address delta H and look for more suitable high capacity materials. Then attack remaining barrier of kinetics.

- The approach has been pioneering and has offered a way out of the thermodynamic dilemma that restricts the light metal hydride thermodynamics. The approach is catching on and has been emulated both within and outside of the DOE program (a true measure of its conceptual success).

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

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

- Working mainly on Li- and Mg-based hydrides. They report having characterized 12 reactions. Getting 5 to 10 wt.% H capacity. New light shed on loss of reversibility in $LiBH_4$. Dilution milling helps but doesn't extrapolate. Some results coming in for the porous scaffolds and the aerogels.
- The results obtained with the MgH_2-Si system, although not very encouraging, are comprehensive and should be sufficient to make a reasonable go/no-go decision in September 2006. The results of the scaffold approach lowering the reaction temperature of $LiBH_4$ are interesting, albeit there are hydrogen capacity penalties due to the presence of the scaffold. They have set the stage for further scaffold work on the $LiBH_4$-MgH_2 system.
- Studied a significant number of new materials predicted to be good. Looked at morphology effect. Scaffold - aerogel work is a nice alternate to the homogenous catalyst route.
- Progress has been very good and the effort pursued with unusual logic and well-contemplated direction. Good, frank discussion of remaining problems, e.g., MgH_2-Si system. The problems remain with kinetics, but the nanoparticle and scaffold approach has made good progress. It certainly remains to be seen if desorption temperatures low enough for fuel cell or ICE vehicles can be practically achieved.

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

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

- Well integrated into MHCoE. Part of "destabilization sub team."
- Technology transfer/collaborations appear excellent. This project is a part of the metal hydride CoE.
- Good inside collaboration in the CoE. Also good attachment to industry and outside academia.
- Good collaborations within the CoE, with partners' roles clearly defined.
- Good collaboration across the entire MHCoE.

Question 5: Approach to and relevance of proposed future research

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

- Future plans build sensibly on findings to date within the project and within the CoE as a whole. Removing/diminishing barriers will be a challenge for the entire CoE.
- The proposed study of Li-Si-N systems is good. The proposed study of scaffold effects on the kinetics of the $LiBH_4$-MgH_2 system is good.
- Suitable based on problems identified and goals.
- The work plan is clear and logical and cannot be improved much. The search for new systems is especially important. Coordinator of the destabilized hydride group of the MHCoE.

Strengths and weaknesses

Strengths

- The presenter (presumably the PI for this task) seems to be keenly aware of the issues he is addressing and the limitations of the approaches used in his project. The presentation was delivered in a very clear concise manner. Some conceptually interesting thinking is going into this project.
- Very sound approach of combining thermodynamic destabilization and nano-size kinetics to lower the reaction temperature of high capacity hydrogen storage materials.
- Concept power, capacity possible.
- A powerful new thermodynamic approach, combined with highly capable technical people. Excellent track record so far.

- Excellent focus on scaffolding of $LiBH_4$ to improve on kinetics.
- Excellent job of leading sub-team on destabilized hydrides.

Weaknesses

- There are no serious weaknesses to this project. The chances of a successful outcome will rest on getting lucky with some alloyed composition and/or microstructural embodiment that happens to exhibit an uncharacteristically rapid release of hydrogen at a temperature below say 200°C, yet still stores a large enough quantity of hydrogen to meet DOE targets for 2010 and eventually 2015. "A tall order."
- Kinetics.
- Group has a tough problem with kinetics. "Nano" is an overworked term and will be a difficult solution to economically and permanently apply.
- Destabilization is a trade-off. Introducing destabilizing elements will reduce gravimetric capacity as well as reduce delta H. Can useable capacity be higher than 2.5-2.9%, i.e., outside of the common "box", e.g. MgH_2 as reference. (Useable capacity is defined as a difference between measured capacity and hydrogen equivalent of energy requirement to compensate for endothermic heat effect upon hydrogen release from the material.)
- None.

Specific recommendations and additions or deletions to the work scope

- The "destabilization" plot in slide 7 of the presentation might lead some people to believe that compositions with lines headed towards the DOE target boxes will actually get there at low enough temperatures. This is a clever but also deceptive way to indicate we might be headed in the right direction.
- None.
- Scaffold types may help. If it would be possible, the $LiBH_4/MgH_2$ system should be tried in the aerogels.
- Even before moving on to a prototype system, some preliminary cost estimates of this approach should be made. Should also add some preliminary safety studies.
- Introduce useable capacity as a parameter for materials selection.

Project # ST-17: Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

Bob Bowman (PI); Jet Propulsion Laboratory

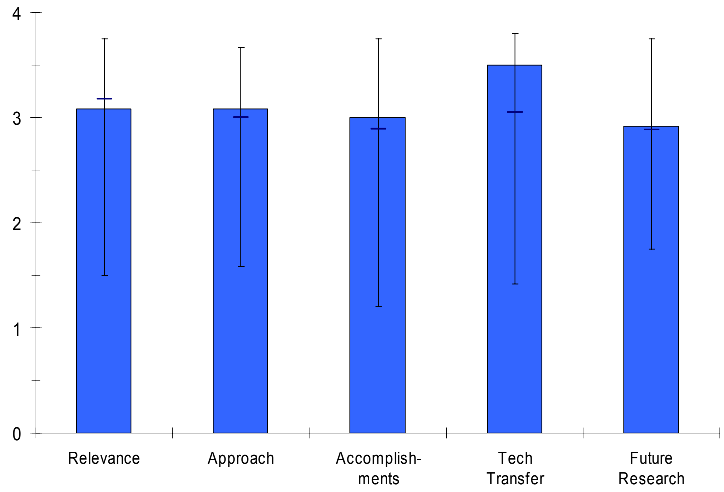
[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

The overall objectives of this project are:

1. Validation of initial storage properties and reversibility in light element metal hydrides and assess their aging durability during extended cycling
    a. Nanophase, destabilized hydrides based upon LiH, MgH_2, & $LiBH_4$ produced at HRL, Caltech, & other MHCoE partners.
    b. Complex hydrides (e.g., amides/imides, borohydrides, & AlH_3-hydrides) provided by SNL, NIST, BNL & other MHCoE partners.
2. Support developing lighter weight and thermally efficient hydride storage vessels and experimentally demonstrate their compatibility with appropriate complex and destabilized nanophase hydrides.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- The project gives an independent validation of the MHCoE materials. The focus on life testing is an important development aspect.
- Good systems to study to help the goals of the program.
- PI fully addresses H-initiative and RD&D plan in terms of real targets.

Question 2: Approach to performing the research and development

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

- A wide collection of topics with other researchers (HRL destabilized hydrides, BNL AlH_3, amide work, etc.). Mostly looks like they're doing NMR studies of materials for researchers. Is this "service facility" really the model for this project? NMR studies are certainly important in this area, but they seem like a bit of a waste considering the PI's talents. From the approach slides, they seem to really be focused on durability, hydride bed designs and lifetime testing. But, the results slides don't show this focus.
- The project is well structured and reasonably integrated with the activities of the MHCoE. The PI has clearly described the role and the contribution of JPL. The timing of the contribution in the decision phase requires better description.
- Both basic, applied and engineering studies are a good approach. Systems have right capacities.
- Project is well designed but task 5 (engineering analysis should be extended).
- This project provides very valuable support services to all project groups of the MHCoE. They are important contributions: (a) validation of PCT properties, (b) cyclic testing, (c) NMR, and (d) hydride tank design. The PI is especially capable in all areas and is serving a valuable role to the entire CoE.

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

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

- Lots of interesting NMR work, but it still looks like bits and pieces, and isn't really clear what the overall goal is. Focus doesn't seem to be really on the most promising materials (LiH/Ge, $NaAlH_4$, etc.).
- The project shows a very good progress according to the objectives.
- Generated information on phases and changes in bonding for other CoE partners. Germanium work seems of no point.
- Would be good to include in the task 5 the investigation of heat and mass transfer and impurities role in reactors.
- Given the recent start and relatively low funding (to date) for this project, admirable progress has been made in a short time. Key inputs of new data have been added to all project areas of the CoE. NMR results impressive in such a short time.
- Progress towards Sept. 2006 on defining top-level parameters for a storage vessel has not been demonstrated.

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

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

- The project has a good integration in the MHCoE with important collaborations.
- High quality partners inside and outside the CoE.
- Very comfortable and thorough collaborations with most of the CoE members. PI is well known to the outside world and long-experienced in scientific collaboration.

Question 5: Approach to and relevance of proposed future research

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

- Plan forward in the future is unclear. What is the direction and mission for this project? How does it fit into the CoE? Didn't see much mention of durability, hydride bed design, etc., in the future plans.
- The future work is well presented and technically feasible, because the presentation of achieved results demonstrates competence and adequate resources. Life testing and system studies require a better description of technical resources and test facilities.
- The most important problems: alanes and engineering analysis and design would be good to expand the investigation in that directions.
- Good. Continue as planned.

Strengths and weaknesses

Strengths
- The described results and the work plan show adequate resources and technical personnel to carry out the characterization work.
- Well designed project, well developed cooperation.
- PI's long experience, capability and reputation. Provides critical NMR contributions to the entire CoE.
- To provide analytical and testing support to all CoE groups. Future development of storage vessels conceptual designs based on JPL's experience.

Weaknesses
- JPL should be doing something other than just supporting others with NMR work.
- Not substantial.
- None obvious.
- Presentation was overloaded with spectroscopic data for various systems studied without successful delivery of messages on what the conclusions were. Project only provides support to other MHCoE members on characterization and stability testing. Selection of materials for testing and characterization is questionable (e.g., Mg-Li-N-H).

Specific recommendations and additions or deletions to the work scope

- Would be good to extend the task 5 (engineering analysis + design).
- The presentation contains an evident mismatching between the Task and the planning: Task 5 is not included in future steps. The life testing work must be presented, because there is a preliminary milestone in August 2006. Details on the life testing methodology must be indicated and discussed.
- Most of what was shown was data, but there was not a great deal of interpretation as to what this meant for advancing hydrogen storage. It would be highly desirable to tie this a route to progress.
- To add in task 5 the research of thermal problem, impurity problem and storage vessel scale effects.
- Continue to provide exactly this sort of support to all CoE project groups.

Project # ST-18: Metal Hydride-Based Hydrogen Storage

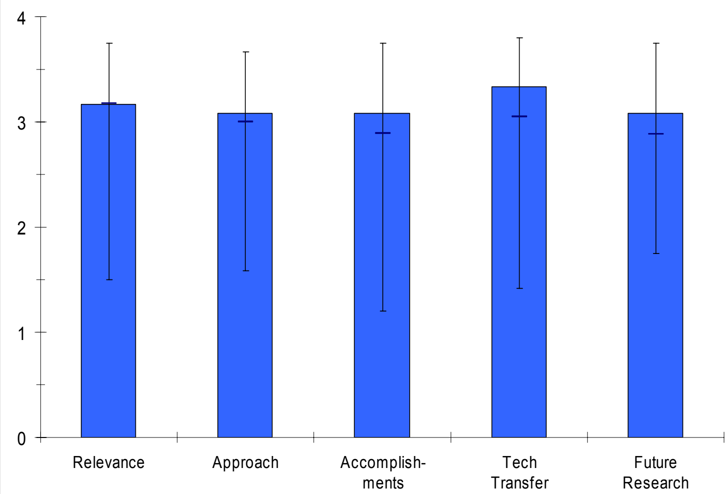
Ian Robertson; University of Illinois Urbana-Champaign

[Partner of the DOE 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 CoE partners with structural and chemical insight of candidate systems and providing experimentally based and validated theoretical modeling. Specific objectives in FY 2006 are to determine degradation during transfer to analytical instruments and conduct structural and chemical analysis of systems of interest to partners, and to develop a structural database for information sharing with partners. The approach combines use of advanced characterization capabilities with first principles electronic and thermodynamic calculations.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Relevance is good in experiment and theory, working on problems of importance.
- The Hydrogen Fuel Initiative and RD&D plan are not directly addressed. By service association with the CoE, it can be reasonably assumed that these objectives are reasonably incorporated in this work.
- This project is part of the MHCoE. Electron microscopy methods are being used to examine the micro- and nano-scale structure of hydrogen storage materials. Also, exploring how defects and contaminants affect hydrogen uptake and release kinetics. Companion theoretical studies are examining the energetics of hydrogen uptake and released. A much needed capability within the MHCoE.
- Project only provides support on materials fundamental understanding and modeling to the key CoE participants.

Question 2: Approach to performing the research and development

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

- Theory approach is potentially complemented by experiment. But [there is] not a clear plan to improve hydrogen cycling at moderate temperature. This work may help plan better materials or improve current ones, but it is not clearly planned to happen.
- As best I can tell, this project seems to be a service to the CoE for experimental and theoretical skills that are not otherwise available. But it not clear how some of the work differs from others in the CoE and other DOE projects, e.g., VASP thermo calculations at UT [United Technologies], Ti catalyst studies. But I accept that there must be unexplained differences. How does the modus operandi function? Does the contractor get requests from the other CoE members each meeting? Or did the contractor pick general areas of support early in the CoE to continue for the duration.
- Well-designed and planned project. Possible segregation of components in charge - discharge operation should be investigated.

- Transmission electron microscopy (TEM) coupled with energy dispersive spectroscopy and electron energy loss spectroscopy (EELS) is being used to interrogate the fate of hydrogen storage materials. Paralleling electronic structure calculations provide information that can be correlated with the EELS results and with storage material performance (e.g., kinetics).

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

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

- Made catalog of signs [signals?] of materials sullied by air or e beams. Matching known TP data in a meaningful system with calculation is a good accomplishment
- The project has barely started (15%), but there seems to be some progress already made. Good start on structural database, services to UH [University of Hawaii], HRL, etc.
- The effects of sample contamination by ambient impurities have been evaluated. The kinds of reactive metals that catalyze hydrogen release (e.g., Ti and Nb) tend to oxidize in ambient environments. These results offer important insights about metallic storage material processing and handling limitations/requirements. Beginning to study how contaminants affect kinetics. DFT and Monte Carlo calculations are progressing. Excellent agreement obtained between measurement and calculation. Issues involving how repeated hydridation and surface contamination influence storage material restructuring are being explored.

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

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

- Many partners listed, but not clear how they bring new theoretical power to the CoE.
- There are stated collaborations with several CoE partners. Are there any citable examples of iterative interaction [effective feedback] yet?
- This project is effectively melding into the activities of the MHCoE. Coordination/collaborations were spelled out in the presentation. Results are passed on to other MHCoE member institutions through an on-line data access website.
- Excellent deal of collaboration with MHCoE partners.

Question 5: Approach to and relevance of proposed future research

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

- Plan seems to be help on what ever they are asked to do.
- Rather straightforward. Is that what the CoE partners want at this point in time? What is the mechanism to change the work plan to suit changes in technology and CoE emphasis?
- The plans for the future follow naturally from both the recognizable needs of the entire MHCoE for advanced, high resolution electron microscopy and the results of FY 2006 activities. The DFT/MC calculations and associated modeling can be expected to provide seminal insights into how electronic structure and impurity elements affect structure and performance of metal hydride storage materials.

Strengths and weaknesses

Strengths

- Potentially powerful methods.
- UI seems to have some important specific skills useful to the CoE.
- High Theoretical level, good coordination in MHCoE.
- The electron microscopy PI is a recognized expert in the field of micro- and nano-structure science. This level of electron microscopy should be an integral part of all three hydrogen storage centers of excellence.
- Good spectroscopic evidences provided with respect to validating models and predictions.

Weaknesses

- Seems to have no well defined direction. Theory and experiments should go together, not act separately.
- It is not clear if the CoE has a mechanism to maximize its benefit from UI and how it keeps UI from duplicating other DOE efforts in the same area.
- None.
- This project has no perceptible weaknesses.
- Issues of adequacy of the results on samples obtained in situ in the chamber of spectrometer with those of actual systems operating under reaction conditions.

Specific recommendations and additions or deletions to the work scope

- Develop their own plan to create or predict a higher capacity, good delta H material.
- Not substantial.
- The DOE nanoscience centers will have many tools for exploring materials at the nanometer scale. As these centers come on line and begin accepting users, the CoE managers should explore the available capabilities of the nano centers to take full advantage of what they can offer the HFCIT program.

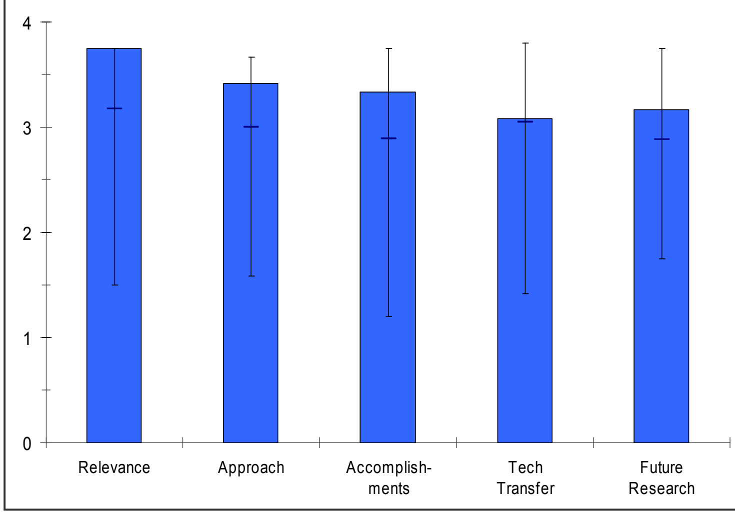
Project # ST-19: System Level Analysis of Hydrogen Storage Options

Rajesh Ahluwalia; Argonne National Laboratory

Brief Summary of Project

The overall objectives of this project are to: 1) Perform independent systems analyses for DOE; 2) Model and analyze various developmental hydrogen storage systems; 3) Analyze hybrid systems that combine features of more than one concept; 4) Develop models that can be used to "reverse-engineer" particular technologies; and 5) Identify interface issues and opportunities, as well as specific needs for technology development. This is being done through the development of thermodynamic and kinetic models of processes in advanced metal hydride, carbon/sorbent, and chemical hydrogen storage systems.

Overall Project Score: 3.4 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- This project provides very relevant support, in terms of analysis and assessment, for all of the primary hydrogen storage system candidates.
- Provides an important independent tool for analysis and assessment to the DOE program managers.
- Can provide important insights to system improvements and optimization that involve trade-off of multiple system parameters.
- This is a very valuable tool that can be used by both DOE and the researchers to help determine the pathways for hydrogen storage that are worth pursuing.
- This is particularly important since hydrogen storage is the most critical need for achieving the hydrogen economy.
- High quality analysis vital to guide experimentalists in meeting targets.
- The project provides valuable enabling tools and analyses that support the storage program.
- This kind of modeling is required to determine if adsorbents particularly at 77K could ever be practical for system design. It identifies clearly (within error of some assumptions) what kind of storage capacitates are required to offer a clear advantage over just compressed technologies. It helps to place all the different claims at different operating conditions into some kind of relative order.

Question 2: Approach to performing the research and development

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

- The researcher has identified the key areas of storage which can be analyzed by this method and has developed detailed processes for building the models. It all appears to fit together well. The approach that would be used for the metal hydride storage systems is particularly well developed.
- Good decision on making tool Excel-based. This probably made things harder for developers, but it will make the model useable by almost anyone. Good Job!
- Model shows high degree of rigor and sophistication. Combines ease of use and rigor.
- The approach is very good and intended to provide tools and analyses that DOE will use to evaluate the progress of storage projects.

- The approach includes providing an analytical tool to researchers within the DOE Hydrogen Storage Program.
- Making the tool available to the PIs will be a valuable asset in assisting to make them think of their materials and their affects on system performance. It will certainly put the push on improving volumetric capacity.

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

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

- The results appear to be accurate. However, it is difficult to tell. The presentation did not offer the methodology for obtaining and/or developing input for the models. Low results for the reversible alanate and for activated carbon are expected to be low, so there is no surprise.
- Model for experimentalists is a great contribution. Storage Team needs to see that all materials researchers have access and training.
- Analysis Working Group formation should be a great benefit to program.
- So far, ANL has succeeded in providing the analytical tools and models required. The MH storage system analytical tool is particularly interesting as it considers volumetric efficiency which is not being done elsewhere.
- Analytical capability has been extended to compressed gas/liquid storage, metal hydride and carbon-based storage systems.
- Useful extension of capability to examine regeneration efficiencies/and energy requirements for chemical hydrogen storage systems.
- This year, the tool was made a bit more user friendly and modeling on chemical hydrides was added. The tool still needs to include more information about system fill performance, heat balances, etc and system dormancy rates under various operating conditions.

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

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

- Good contacts with various groups to get data needed for model.
- Storage Analysis Working Group should really help storage analysis efforts.
- Considering the scope and goals of the project ANL is doing a good job of coordinating with others in the field, with DOE and with the centers of excellence.
- Need to develop a closer working relationship with the TIAX work.
- Extensive collaborations have been established with the storage centers of excellence and independent researchers.
- There does not seem to be a single mechanism for coordinating with the projects. Project leaders need to have access to models quickly so they don't waste their time working with materials that won't work. Perhaps the CoEs can act as coordinator.
- More collaboration, to avoid duplication, with TIAX would be useful.
- Need to link with H_2A especially in the area of chemical hydride regeneration.
- Should also work more closely with TIAX to define the system design and UTRC/Ovonics, etc. to better understand system design limitations.
- This tool is especially valuable for the carbon CoE as it stresses the importance of the volumetric capacity of a material and what is required if it is to provide any significant advantage over cryo-compressed gas alone.

Question 5: Approach to and relevance of proposed future research

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

- It appears that the "real" work for utilizing the models will now begin.
- This year's work has set a high standard, but development of the chemical hydride tool will be another great contribution.
- Future work to continue what they are currently doing is a good plan and consistent with the project's goals and with the needs of the hydrogen storage program.

- Future plans to extend and expand the analytical capability appear to be reasonable and appropriate.
- More information is required on the system fill, heat balance and well to wheel efficiencies as this will help determine if adsorption based technologies' potential offers any advantages over metal hydride based technologies.

Strengths and weaknesses

Strengths

- Good approach.
- Delivered quality tool for program and experimentalists.
- Strong analytical modeling skills and experience support the storage program at DOE and the CoEs.
- ANL is doing some innovative work not being done elsewhere.
- Seems to provide good value for the budget being spent.
- Good progress and technical accomplishment.
- An independent, unbiased analytical tool for storage system performance analysis and assessment.
- Simple tool that provides good insight for decision making about which technology has advantages over another and where the optimal or crossover points may lie.
- Appears to be very useful tool(s).
- Addresses a wide gamut of storage methods.

Weaknesses

- None--assuming model is proven.
- System design includes many assumptions and not enough specification based upon real world specs or system performance. Admittedly, there is not much public information available to include in the model.
- Although the model developing methodologies appear to be logical, we don't know enough about the inputs to determine if the analysis tools are really accurate.
- The interfacing mechanism is unclear.
- The results of the analyses is only as good as the assumptions that are input into analysis thus it is important to continue to solicit information on the input parameters from various researchers in the storage program and then take a conservative approach to developing the specific inputs for the analysis tool.

Specific recommendations and additions or deletions to the work scope

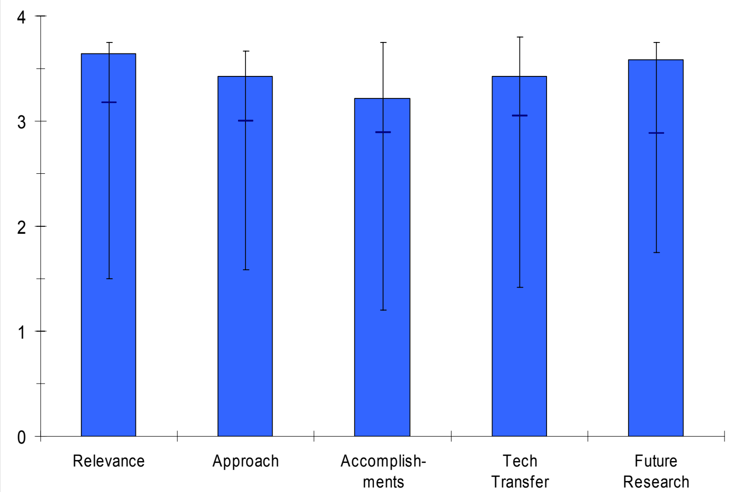
- Consider adding sensitivity analysis tabs to tool to give researchers a quick feel for what improvements might have most impact.
- Use feedback from users to improve model--both function and ease-of-use.
- Looking forward to seeing CHtool.
- Is model transparent, i.e., can users see Visual Basic subroutines?
- The MHtool for analyzing hydrogen storage systems needs to be validated against hardware.
- ANL & TIAX should be encouraged to continue close communications regarding analytical models to ensure consistency.
- ANL needs to develop an organic collaborative working relationship with TIAX. These activities are necessary and can be further enhanced by further coordination and collaborative work between ANL and TIAX.
- Please add detailed heat balance and energy balance for fill procedures on sorbent based systems. Please include a thorough dormancy analysis under various driving conditions similar to what Lawrence Livermore National lab presented with Dr. Aceves.
- Develop formal interfacing processes that will streamline analyses on particular candidates.
- Expand collaborations with TIAX.

Project # ST-20: Analyses of Hydrogen Storage Materials and On-Board Systems

Steve Lasher; TIAX LLC

Brief Summary of Project

Overall Project Score: 3.4 (7 Reviews Received)



TIAX is evaluating the projected manufactured cost and performance of four broad categories of on-board hydrogen storage options: baseline (compressed hydrogen), reversible on-board (e.g., metal hydrides), high surface area sorbents (e.g., carbon-based materials), and regenerable off-board (e.g., chemical hydrides) systems. 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 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 **3.6** for its relevance to DOE objectives.

- Early estimates of the potential cost of hydrogen storage systems are very important and provide valuable insights to both the researchers and DOE program managers.
- This project is focused on system level evaluations of on-board hydrogen storage units. At the present stage, the validity of the assumptions that have to be made to complete the analysis tends to limit the accuracy and therefore affect the influence of the results on the hydrogen vision.
- The project provides valuable enabling tools and analyses that support the storage program.
- These independent analyses are key, especially if the program is to rationally assess storage claims and relative benefits.
- Sensitivity analyses (tornado plots) are good to identify key areas where R&D can make a difference.
- This project provides a "reality" check on the status of key hydrogen storage systems in relation to the DOE targets. It is important to the assessment of the overall progress towards the storage goals.
- Excellent project.

Question 2: Approach to performing the research and development

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

- The model development process has been established and includes inputs from researchers, developers and stakeholders.
- Sensivity analyses for input variables are very important since many of the parametric inputs are still being experimentally determined and are subject to large variability.
- The systems analysis studies use the best information available on system component performance and knowledge based assumptions vetted by appropriate HFCIT program participants, developers, and stakeholders.
- The work is comprised of technical assessment, cost modeling, and persistent refinement. Single and multi-variable sensitivity analyses methods are employed.
- As results come in from the storage centers of excellence and other relevant projects in the HFCIT Program, the level of detail in the systems analysis studies will increase and the confidence level will go up.

- The approach is very good and intended to provide analyses that DOE will use to evaluate the progress of storage projects.
- Analyses deliver critical parameters to describe storage performance within the larger vehicle system.
- The approach being pursued is excellent and very thorough.

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

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

- Cost and performance systems analysis results were presented in detail for four system types. It was concluded that sodium alanate and sodium borohydride based systems will not meet 2010 performance targets.
- Continued refinement and extension of model to all primary hydrogen storage candidates.
- Interestingly, the systems analysis results and the results reported by developers for the same systems were in good agreement; most probably because the assumptions were the same. Question is--were the assumptions generally correct?
- TIAX has provided the analysis needed to support the storage program.
- Good results.
- The results obtained on the sodium borohydride system are very good.
- Would be good to intensify engineering part of project.

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

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

- Good collaborations to gather information on system inputs and model structure.
- Apparently some collaboration on model development, but the contributions of the collaborators are not apparent.
- The people performing these systems analyses appear to be as thorough as possible in doing their homework. This gives confidence that the results are credible. Mainly, this credibility comes from recognizing that the systems analyzers took great pains to obtain the very best information and insights available for each system they treated. This occurred most probably because of networking and coordination with a broad spectrum of knowledgeable people during the input gathering stage.
- Considering that the main goal of the project is to analyze work being done by others for use by DOE in evaluating the progress of storage projects, the interfaces reported seem to be appropriate.
- Need to develop an organic collaboration with the ANL activities.
- Work with H_2A and other contractors keeps this group knowledgeable about latest work in area.
- This project appears to have excellent interactions with the system developers in obtaining information related to the TIAX analyses. Such interactions are critical to the accuracy of the TIAX analyses.

Question 5: Approach to and relevance of proposed future research

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

- Future plans seem reasonable- continual updating of input parameters based latest experimental data is essential.
- The future plans involve wrapping up the reported studies and moving on to yet another set of systems.
- Future plans are being developed in conjunction with DOE and focus on key analyses needed by DOE.
- The next area of focus will be on the liquid hydrocarbon (HC) system being developed by Air Products. This is definitely the next system that should be evaluated.

Strengths and weaknesses

Strengths

- Strong analytical skills and long experience working with DOE and in the field of hydrogen, fuel cells and storage.
- Provides good value for the budget.
- TIAX is providing valuable results to the DOE and tech team on system analysis and especially cost model development.
- Good analysis to guide programs.
- The approach and execution of this project are both excellent.
- High scientific level of research and good CoE organization.
- The model provides an important cost estimate and comparison among the various hydrogen storage technologies from a total system perspective including life cycle analysis.
- Doing these kinds of analyses can be a "depressing and thankless chore". It's a good thing we can find folks who are willing to do them because they are important to the program.

Weaknesses

- Some redundancy with the ANL analysis and assessment modeling effort.
- The focus on sodium alanate and sodium borohydride is outdated since developmental work on these systems is being substantially reduced or eliminated because these technologies do not show the potential to meet DOE performance targets.
- Systems studies always have a soft spot in them that others tend to "poke at". The problem comes from having to define important answers when you don't have all the important details nailed down.
- None.
- Non-substantial.

Specific recommendations and additions or deletions to the work scope

- Focus of this work should continue to be on cost analysis to minimize over lap with ANL work.
- HFCIT systems analyzers have to lay their wish list on the table. The information they most definitely need to make credible analyses should be known to the entire community of developers, data gathers, and stakeholders.
- TIAX should be encouraged to carefully check for reasonableness of any data being received from suppliers with other information sources available, such as other suppliers or OEMs which have worked with the supplier. TIAX should do its best to evaluate information for feasibility and validity before accepting it at face value.
- TIAX should be encouraged to closely communicate with ANL regarding analytical models to ensure consistency.
- It is not clear how the TIAX and ANL work interact together and how the project can leverage their expertise to increase their output. TIAX has many valuable expertise that should be better integrated and coordinated with the ANL system analysis work.
- To intensify engineering investigations according to project.
- None.
- Consider Monte Carlo methods for better estimates of uncertainties.

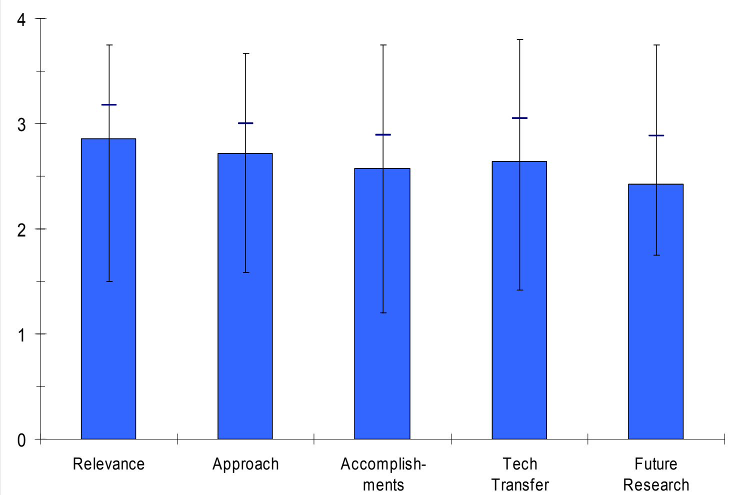
Project # ST-21: Carbide-Derived Carbons with Turnable Porosity Optimized for Hydrogen Storage

Jack Fischer PI; University of Pennsylvania; Yury Gogotsi (Co-PI), Drexel University

Brief Summary of Project

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

Overall Project Score: 2.6 (7 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Generally aligned to program objectives & relevant to President's Initiative.
- Material potential for the DOE system target is not clear and material itself is identical to activated carbon.
- Certainly aimed at key goal of gravimetric, probably challenged on volumetric goal.
- This project is one of the independent, novel material awards that started in the beginning of FY04. Penn is trying to develop high surface area carbons that are made by removing the metal atoms from materials such as Ti, Si, Zr, or B carbides. The project goal is to produce materials that can meet the 2010 DOE target of 6 wt.%. The relevance is lessened somewhat because it appears that even with additional development, as discussed in the presentation, the material capacity would be about 6 wt.%, and thus the system level capacity would be much lower.
- This project is targeted towards the gravimetric, volumetric and cost goals of the hydrogen storage effort.
- This project aims the development of new improved solid state hydrogen storage materials. Storage is a critical component of DOE's RD&D plan.

Question 2: Approach to performing the research and development

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

- The approach is well thought out and has the potential to produce porous carbon structures at relatively low cost. The effort is focused on understanding precursor characteristics, processing conditions, and post treatments that are necessary to produce subnanometer pores and pore size distributions for binding hydrogen. The presentation indicates that the 2007 target of 4.5 wt.% can be met at LN_2 temperature and 50 atm pressure. It's hard to see how this approach can yield materials that, when placed in an appropriate system, would meet the DOE targets.
- The project approach is an interesting one towards introducing large volume fractions of very small porosity into a carbon matrix.

- Well-thought, reasonable approach capitalizing on the design rationalization of carbon materials. Good emphasis on methods and reproducibility giving confidence to the data and to the sample screening results. Nice coupling of theory with experiment.
- CDCs unlike activated carbon but like MOFs offer the advantage of having a narrow/uniform and tunable pore size distribution. However they have a much lower surface area and pore volume. They would have a clear advantage if they could be functionalized in a way others cannot. This is yet to be shown.

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

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

- Creat[ing] small pores can be an interesting technology.
- 4.5 wt.% excess is not extraordinary today; but not bad for activated carbon. Not bad for 7 months work however. [The project started in the beginning of FY05].
- There appears to be solid progress in developing the understanding of the fundamentals involved in tailoring these carbide-derived carbons for maximum hydrogen uptake.
- There is no comparison plot of the pore size distributions of the TiC, ZrC, SiC, and B_4C materials that are being studied. How do they compare?
- Interesting analysis showing that the gravimetric hydrogen storage capacity normalized to total pore volume is optimized in materials with primarily micropores rather than mesopores. Promising results reported here assist in getting a better insight into the hydrogen adsorption mechanism in porous carbon. Still this [CDCs] needs to be demonstrated that this is a 'workable' solution.

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

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

- Strong points. Selection of evaluation for the mechanism investigation.
- Partly connected.
- Collaborations between Penn and its partners are in place and it is apparent that each has a significant role in the project.
- The best performing materials should be sent to SwRI for independent verification of the hydrogen storage results.
- Nice mix of expertise and testing facilities/methodologies. Industrial link is missing and should be sought after much earlier than intended in the project plans.

Question 5: Approach to and relevance of proposed future research

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

- Scope to [be] superior [to] activated carbon is not clear.
- Plan is more like goals, only the use of catalysts is at all specified. One clear item is round robin test, and that is good.
- Near-term and future plans are presented in some detail to inspire confidence that maximizing the hydrogen uptake in these materials can be accomplished.
- The program objectives and work needs to be re-aligned with DOE's short-term deliverables based on system capacity requirement. The use of 77K temperature is not a practical solution and a room temperature sorbent should be given higher priority. The proposed work does not address these.
- The future work to increase the volume fraction of very fine pores and to increase the heat of adsorption in these pores is good. Introducing catalyst particles into such fine pore structures may be difficult.
- Well planned future activities for a better understanding of the fundamentals of hydrogen adsorption in porous [materials]. Nevertheless, a breakthrough may not be so easy to achieve. Good use of resources and mix of techniques.
- Priorities should be set on increasing the strength of the hydrogen bond substantially above that of normal physisorption. If successful, then the push for higher surface area is justifiable.

Strengths and weaknesses

Strengths

- The presentation was very good. Sufficient detail was presented to judge that progress has been good. Some novel carbon materials have been produced with controlled pore size and distribution. These materials have higher hydrogen bonding energy than more conventional high surface area carbons and have the potential to have greater hydrogen uptake. Plans are well formulated.
- PI's experience and competency in the field.
- Excellent science. The materials studied are potentially low cost ones.
- Very good approach followed: looking at the rational design of adsorbents.
- Cost.

Weaknesses

- There is no clear advantage upon activated carbons in term of hydrogen uptake due to the surface area.
- Volumetric storage not likely to be obtained. “Hazy” plan for progress. Delivered hydrogen pretty low because so much is held at pressure below engine/fuel cell operating pressure.
- The presentation indicated that the material itself barely meets the 2010 target (6 wt.%). The system would be considerably lower.
- The program objectives and work needs to be re-aligned with DOE's short-term deliverables based on system capacity requirement. The use of 77K temperature is not a practical solution and a room temperature sorbent should be given higher priority. The proposed work does not address these.
- Given the current results, this project does not look like it has a high probability of meeting the 2010 DOE gravimetric target, even at a temperature of 77K.
- Still a risk area that may not deliver by the “end of the day.”

Specific recommendations and additions or deletions to the work scope

- Materials for independent confirmation important to achieve. Be sure to include some “gold standard” labs. Need to work on improving deliverable hydrogen.
- Investigate any means to increase hydrogen uptake such as doping with light metals to determine if these materials have the possibility to achieve the 2010 targets on a system basis.
- The program needs to be reviewed and re-aligned with the overall DOE goal.
- Recommend to clarify the difference and benefit over the activated carbon. At this moment it is not clear the superiority of this material
- It may be useful to do some hydrogen permeation measurements through free-standing membranes of these microporous materials. This could give information on hydrogen diffusion through these structures.
- Need to tie in the material development work with the final storage system targets. Theoretical modeling for these types of materials could assist progress, however it must be challenging since these are amorphous materials. Kinetics and hydrogen diffusion issues may also be addressed on CDC prepared membranes. Consider emphasizing the added value of the uniform pore size in the CDCs giving them an advantage over the high surface areas activated carbons.
- Recommend to clarify the difference and benefit over the activated carbon.
- At this moment, the superiority of this material is not clear.
- Determine how to make good pores in high quantity and increase binding energy.
- Industrial link is missing and should be sought after much earlier than intended in the project plans.

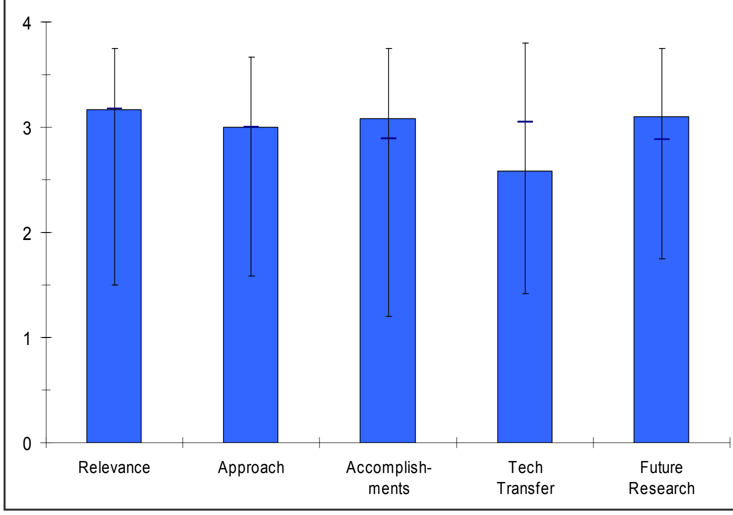
Project # ST-22: Hydrogen storage in Metal-Organic Frameworks

Omar Yaghi; UCLA/University of Michigan

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. Scale-up of favorable MOFs will be done and samples will be delivered to DOE for independent verification of storage capacity.

Overall Project Score: 3.0 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- This project involves exploratory studies of metal organic framework (MOF) structures that have large internal surface area and have shown modest ability to store hydrogen at low temperature (77K) and high pressure (50 to 100 bars).
- Project is planned to address multiple challenges to support the Initiative.
- This project has the potential to develop low-cost hydrogen storage materials that can be added to high pressure hydrogen gas tanks, to significantly increase the tank hydrogen storage capacity, albeit at lower tank temperatures such as 77K.

Question 2: Approach to performing the research and development

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

- MOFs are synthesized by methods developed over several years by the PI and his co-workers. They are then characterized by XRD to confirm their structures and tested for hydrogen storage capacity.
- MOFs may have potential to address storage uptake and volumetric barriers.
- The metal-organic framework approach being pursued in this project is outstanding, truly world-class.

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

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

- From the presentation, it is hard to tell what was done specifically for this HFCIT project and what was part of the history of accomplishments by the PI and his group. In round numbers, the project achieved [ca. 7 wt.% H] at 75K and 50 bar. These conditions are not likely to be viewed as being attractive for vehicle applications. But, there has been some nice science done by the Yaghi group over the past five or so years to elucidate the key features of MOF materials as sorbents.
- A lot of good work has been done in this project, but clear progress to DOE targets is not apparent.
- The project reports the development of a MOF-177 material that exhibits 7.5 wt.% hydrogen storage at 77K. This is the highest adsorption-based hydrogen storage value ever obtained to date.
- This is the first time an adsorbent reaches an excess capacity of 7 wt.%.

- Presenter has not provided comparison of volumetric storage characteristics of MOFs with those of compressed hydrogen (700 bar, 298K as well as 50 bar, 77K). Surface area characteristics of MOFs should be also expressed in volumetric terms as more critical for MOFs.

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

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

- It is not obvious that this project is very well connected to any aspect of the HFCIT program.
- Collaborative relationships not clear though a couple of different organizations were mentioned.
- Significant technology transfer appears to be taking place through interactions with BASF. However, collaborations with other DOE hydrogen storage researchers appear to be somewhat more limited.

Question 5: Approach to and relevance of proposed future research

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

- Striving to get higher and higher effective internal surface areas is certainly the way to go, but they could "hit the wall" pretty soon (if they haven't already).
- Future research plan is laid out though not many details shown.
- Generally, increasing surface area would diminish the bulk density and thus have a negative effect on the volumetric energy density. One should optimize both the gravimetric and volumetric densities.
- The future research approaches may lead to MOF materials with significantly high hydrogen capacities at 77K, and perhaps at higher temperatures as well.

Strengths and weaknesses

Strengths
- The PI and his group are world leaders in the discovery/development of MOF materials. Lots of nice science has been done by that group. An impressive body of knowledge has been developed.
- MOFs present an interesting and new approach to solve some hydrogen storage challenges. Researcher appears to be very capable.
- Remarkable capability of synthesizing new improved materials.
- Highly innovative, world class research project that is rapidly yielding important results.

Weaknesses
- It just doesn't look like MOFs will meet DOE hydrogen storage targets at all or at least under conditions that are attractive for vehicles. Incremental advances beyond the present achievements won't be enough.
- Future plans not very detailed. Performance to DOE targets not clear.
- The group deserves better adsorption characterization capacities.
- More interactions of this project with DOE researchers would be beneficial to the carbon-based community at large.

Specific recommendations and additions or deletions to the work scope

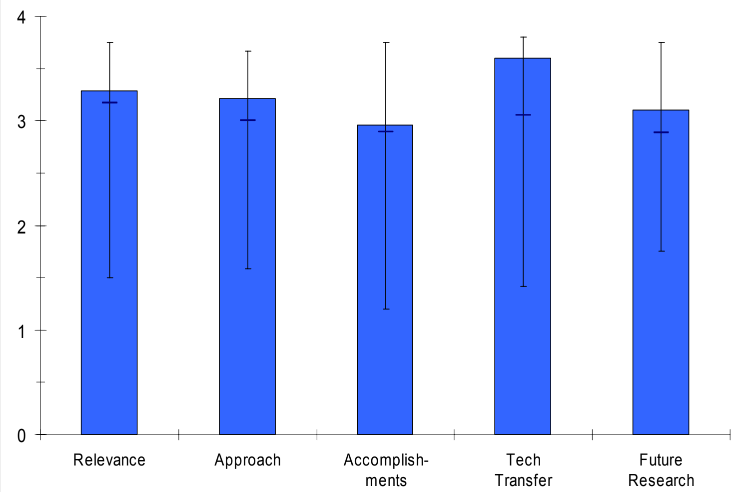
- Show performance to DOE targets more clearly. Solidify details of future work. More clearly identify the roles of other collaborators in project.
- Conduct calculations on total surface area requirement for the adsorbents per storage vessel to store required amount of hydrogen, based on experimental data. Compare specific surface areas of MOFs (volumetric) with that required per storage vessel to see if those can be attained.
- None.

Project # ST-23: NREL's research as part of the DOE Carbon Center of Excellence

Mike Heben; National Renewable Energy Laboratory (NREL)

Brief Summary of Project

Overall Project Score: 3.2 (8 Reviews Received)



[NOTE: This review is on NREL's contributions, not on the entire DOE Carbon Center of Excellence. Each of the partners is evaluated separately.]

The focus of the National Renewable Energy Laboratory's work is on hydrogen storage in carbon-based materials in conjunction with the DOE CoE on carbon-based hydrogen storage materials. The objectives are to determine the extent to which metal-carbon hybrid materials can reversibly store hydrogen, to tailor the mechanism of hydrogen storage through nanostructural control, and to develop low cost, reproducible, and potentially scalable processes for production. NREL performs activities in five task areas in support of the DOE mission and ensures that CoE activities are aligned with DOE goals, promotes communication and collaboration to expedite progress towards targets, and creates a nimble research and technology development environment to pursue new opportunities as they arise, in support of DOE goals.

Question 1: Relevance to overall DOE objectives

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

- Goal is good, moderate delta H is certainly a need. That said, several of the several projects are unlikely to meet the goals even if fully successful, most of the actual results are still all theoretical, despite 2 years of these theories existing, little or no testing of the ideas experimentally exists.
- This project is obviously aligned with the President's hydrogen vision and the RD&D objectives. Storage is key to the Hydrogen Initiative and the carbon-based option is a part of the overall effort. However, it seems obvious that this option is further behind in its science base than the other two options being pursued and it is not clear that it can get much beyond the 2006 target of 6%.
- The CoE initiative and its work program is completely in line with the overall DOE objectives.
- Carbon based sorbents are a critical group of novel materials for hydrogen storage. The diversity and depth of the program makes it an important component of the storage subprogram.
- From the basic research of H_2 physisorption in nanomaterials we have obtained 2 major key aspects that enhance this weak interaction: the existence of Pi-systems and metal sites. Two approaches of the hydrogen storage problem are based in a combination of these two: MOFs and metal decorated carbon based materials (C_{60}, CNTs, etc). My personal opinion is that both are equally important, and even though they are built with a different philosophy, they actually belong in the same family of materials that combine Pi-systems and metal sites.
- Adsorbent based materials have the potential to offer alternatives to metal hydride approaches however the CoE really needs to move away from reporting storage values at subambient conditions. Subambient conditions will greatly complicate a tank based system and reduce further the challenging volumetric issues that most adsorbents face. A plausible explanation as to how milder enthalpies (8-12 kJ/mol) can be achieved at 100-200 bar pressures - Are there exceptions to the Van't Hoff plots??

Question 2: Approach to performing the research and development

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

- Approach is largely sound, theory to experiment to development, but the process seems stalled in theory in many areas. Spillover work is however a nuts and bolts program possibly making progress. Program should get credit for expanding its focus since last year to include more programs that are not carbon-nanotube-focused. On the management side, the CoE has put in place leaders in the area and seems to meet often and try to get people working. I may not fully agree with all aims, but they are managing the people to try to accomplish them.
- The progress suggests the approaches are appropriate, but it is difficult to assess them given the limited information available on so many projects. Certainly the fostering of collaboration is a good approach.
- Targets appear not feasible within the tight timeframes proposed at least judging from the current status and progress made.
- Broad R&D portfolio, new ideas; offers potential for higher density materials and goes beyond the SWNTs increasing the chance of success. Well organized and focused. Coupling of theory/modeling with experiment is beneficial to the project execution, timing and overall progress.
- This program has a strong focus on theoretical/modeling approach. It is not clear if the current structure and management scheme can narrow down the choices in a timely fashion. The synthesis, scaling and storage prototype testing are not clearly defined.
- Again, numbers reported must move in the direction of ambient temperatures and a plausible explanation for how 100-200 bar pressures can be achieved with 10-12 kJ/mol enthalpies. MOF and nano engineered molecules seem interesting and easily modified/synthesized but work on carbon nanotubes needs to be seriously considered. Particularly NREL as a project needs to move away from buckyballs etc. These molecules seem difficult and expensive to synthesize. The CoE is young but it needs to increase the pace in which modeled molecules are actually synthesized and proven to be stable.

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

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

- Spillover work is an accomplishment, nearly doubled capacity available. Many theories have produced ideas to pursue (small D [diameter] nanotubes, methods for propping tubes at critical distance). Made B [boron] doped nanotubes but storage currently low. Potential Fe addition to bucky ball, not clear yet, but believe cross linked to another ball. If there was not conflict over the validity of the predictions this might be higher, the key in the end is real, independently verified hydrogen storage.
- I would rate the progress as excellent in the given time, but because of the limited science base as mentioned in [question] 1 relevance above, I doubt the effort will overcome all the barriers in the storage area.
- Meeting the deadlines of go/no-go for SWNT. Standardized reference points for reporting correct amount of physisorption hydrogen need to be applied to all CoE members. Same applies for BET surface area, i.e. standard reference points, procedures etc.
- A fair amount of work, good progress, substantial accomplishments. Significant degree of innovation and novelty for discovering new promising materials - still though, need to accelerate shift from models to materials synthesis and demonstration. Careful steps were taken for understanding potential sources of errors, for validating measurement techniques and looking into data repeatability and accuracy.
- Very good progress is made on molecular modeling aspect. Good progress is made in some areas of synthesis, identification and storage testing. The issue of SWNT go/no-go should be resolved soon and free up more resources to the other molecular candidates. The synthesis and testing and characterization should be given higher priority in the coming years.
- The theoretically promised materials have not been synthesized yet.
- Much more progress was made than in the previous years, MOF is the highlight along with James Tour work on nano engineering carbon nanotubes. It seems as though the work is converging to structured molecules of combined metals and organics. MOF start with metal and add organics; nanotubes start with organics and functionalize in metal. Both methods seem to converge to the same idea of achieving these Goddard rules. Some evidence was presented regarding that the metal would not agglomerate.

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

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

- Connectivity good.
- NREL seems to be doing a superb job on this aspect.
- CoE is well covering many different kind of material and technologies.
- Well structured network; good blend of modelers and experimentalists; strong collaborative effort. Leading role in the organization of many conferences and extensive list of publications and presentations.
- There is a good mix of expertise in this CoE. It's not clear how often there are internal reviews and how closely the various group communicates with each other.
- CoE has strong partners and is well organized, however NREL really needs to explain and push to partners and reviewers the volumetric and enthalpy/pressure challenges that are key to the existence of CoEs.

Question 5: Approach to and relevance of proposed future research

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

- Though it will be important to increase resources devoted to verifying predictions in reality, this can not be the theory CoE.
- The plan is logical, but I do question the rush to systems work given the lack of strength in the science base.
- Fundamental understanding on issues related to hydrogen physisorption needs to be focused on. Targets for [FY]07 appear to be very unlikely based on current status.
- The proposed work is appropriate for further progressing towards reaching the objectives. If the SWNT work is not finally retained (there is a 'Go'/'No-Go' decision point still this year), experience accumulated so far in the field is valuable. SWNTs could be the molecular building blocks for advanced adsorbers. Passage from materials' scientific exploration to engineering design could be accelerated.
- Surface areas need to increase significantly in order to improve volumetric capacity. Need to increase impetus on MOFs. Work on the “bucky bells” etc. seems academically or scientifically interesting but should seriously be evaluated for practicality to H_2 storage.

Strengths and weaknesses

Strengths

- Very good team that seems to be actively collaborating.
- Strong leadership to achieve targets with carbon-based materials, even [once] it was quite difficult. Use of basic science and calculations to show the enhanced physisorption is very good.
- Many members working on different synthesis routes.
- Strong collaborations, diversity in expertise, innovation, novelty, and an overall systematic approach that increase the probability of success.
- Excellent progress on molecular modeling. A good mix of candidates for synthesis and testing. Strong technical background in the area. The spillover work is promising.
- Outstanding theoretical work.
- Many novel ideas and easily synthesized and modifiable molecules are evident. Partners show great control over their materials.

Weaknesses

- Realization of this material to on vehicle tank is not clear.
- Integration of efforts between members not obvious. Progress towards goals.
- Still a risk area that may not deliver. Indeed, a breakthrough in this research area may be difficult; in any case, if it is to happen, the CoE is the best mechanism for achieving it through the optimal use of resources and integration of efforts. Management of such a big group/CoE is challenging – nevertheless NREL is on track with the coordination/communication scheme already in place.

- The program needs more focus on empirical development such as synthesis, identification, and testing. The program needs more internally defined criteria on go/no-go decisions.
- The theoretically promised materials have not been synthesized yet.
- Volumetric capacities remain low. NREL needs to give plausible argument as to how this can be addressed. A technically plausible plan also should be presented on how to produce good storage capacity at 1100-500 bar range with lower enthalpies (6-12 kJ/mol). How can the thermodynamics be bent?
- Yaghi has left, so the only real progress in physical storage is Yang's work. Need to emphasize the things that are working more. Dillon is talented but asking her to realize these materials almost alone is not wise, more resources must be devoted to this effort.
- BC nanotubes probably aim at too low a target storage.
- As mentioned above, the science base is weak.

Specific recommendations and additions or deletions to the work scope

- Be sure to evaluate leadership as well as tech work.
- Regarding the spillover results, mechanism of hydrogen atoms interactions need to be checked by measuring reversibility, kinetics, etc as a 1st step.
- Equal attention should be paid to the gravimetric and volumetric storage capacity of the materials investigated. Down selections and go/no go decisions on materials/approaches should be fully respected and the project should be flexible enough to move on when required to other materials. Use effectively the mechanism currently in place for the management of this sizeable, expertise-diverse CoE; this is critical to the success of the project. Associated challenge: re-direction of resources, within the CoE, when and where it is required.
- Advantages of the carbon based physisorption is pressure balance. If the bonding energy became too large whether this advantage is still remaining or not is questionable. Physisorption is quite difficult to measure accurately with a small amount of material, common protocol for the measurement is very important. Repeatable, reliable measurement being established in the project is very precious and work is appreciated.
- Need to verify theory predictions, Manpower distribution needs to change to many people trying to verify high storage predicitons and few on theory. Key is to make material progress in concert with the predictions. This is only likely with several more people working on making these materials, give Dr. Dillon some serious help. This goal of 12 kJ for room temperture storage is almost certainly not going to work except at high pressure, they really need to check this calculation.
- I would recommend emphases on the science base for at least two more years, then go to systems work after an assessment.
- Need to show the milestones and roadmap for the entire program. Need to show approximately when the decision points are and methodology to reach consensus. It is recommended to pull the go/no-go decisions slightly forward. The program need to start some priliminary work on storage system development or coordinate with the system analysis work. The CoE mangement needs to make the decision making process more transparent. The CoE needs to re-aligned some of its goals versus results obtained by ANL and TIAX analyses.
- Extra effort must be put in the synthesis of the proposed materials.
- Seriously consider reducing SWNT work and increasing significantly work on MOF type materials, conductive polymers and clathrates.

Project # ST-24: Enabling Discovery of Materials With A Higher Heat of H_2 Adsorption

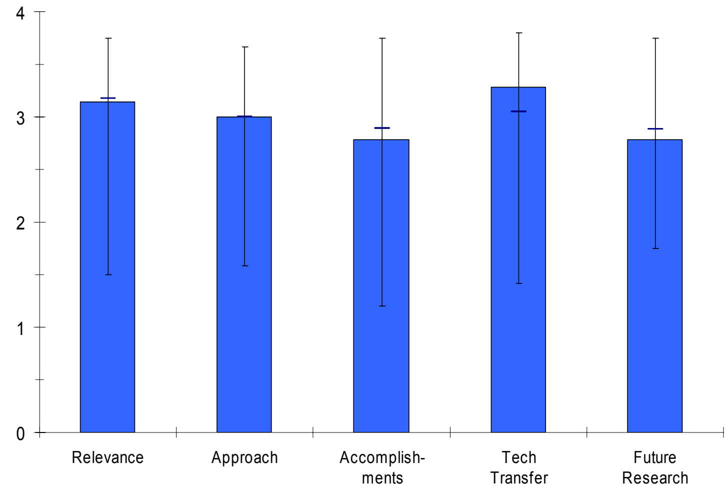
Alan Cooper; Air Products & Chemicals, Inc.

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

In this project, Air Products is developing a hydrogen storage measurement technique that could accelerate new materials development, providing critical guidance to DOE and their contractors enabling new materials development. General quantitative computational models are being developed for new materials resulting in efficient materials discovery/optimization towards meeting DOE system targets for hydrogen storage.

Overall Project Score: 3.0 (7 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Well aligned and of relevance to the DOE objectives.
- As part of the Carbon CoE, this program has high relevancy.
- This project is part of the carbon CoE. They measure H_2 adsorption and heat of adsorption, and they calculate the Gibbs excess adsorption energy. These are all fundamentally important parameters for assessing hydrogen storage materials.
- Supports progress by partners, not key to program but useful to those outside the program.

Question 2: Approach to performing the research and development

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

- Should achieve their goal with this approach.
- The project approach is excellent, particularly as it combines theoretical and experimental aspects in the proper proportions. The aspect of rapid, inexpensive measurement techniques can be expected to be central to success.
- Good, systematic, clear approach engaging theory and experiment.
- The approach does not address the storage goals adequately. The decision making process is not clear.
- The measurements being made provide important technical data and guiding insights for the development of carbon-based hydrogen storage media. The results of modeling heats of adsorption provide insights about the limitations of carbon based materials and about what can be done to improve the storage capacities.
- Provide "guidance" to others? Can this be regarded as a task?

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

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

- Established capsule method.
- Developed a physisorption calculation method.
- Would have liked to see more of the funding used.
- The theoretically promised materials have not been synthesized yet. The progress of the project is not satisfactory.

- The sorption capsule technique for simple, inexpensive hydrogen storage measurements via a weighing approach is excellent. The SWNT data at 25°C is particularly revealing in terms of the potential for pure SWNTs to be able to store any significant levels of hydrogen at room temperature. The bundling morphology of SWNTs is shown to have relatively little influence on hydrogen storage behavior. Fundamental modeling indicates that boron incorporated into graphite (but not nitrogen) can enhance hydrogen bonding.
- Satisfactory degree of accomplishments and sound progress. Innovation, under both modeling and experiment, to support the materials development work and speed up the overall progress.
- The high throughput screening (HTS) measurement tools in place at Air Products are of great value to the HFCIT program. The presenters showed that the HTS equipment provides accurate results and demonstrated that carbon nanotubes adsorb hydrogen on a scale similar to but slightly greater than graphite. Specific results of interest are (1) that only a fraction of the H_2 is strongly adsorbed because the heat of adsorption drops with increasing H_2 loading and (2) the nature of similarities and differences in how homogeneous and heterogeneous carbon nanotubes adsorb/desorb H_2.
- Wasn't the capsule technique developed previously?
- How does the cutting and measurements on SWNTs relate to NREL work? Why are we still doing this?
- I'm not convinced of the validity of the ab-initio calculations on the B-C structure.
- The proposed materials and the first results do not seem to be very promising.
- The heat of adsorption is the key parameter associated with the gravimetric and volumetric hydrogen storage capacities and temperature/pressure conditions of materials that store hydrogen by adsorptive mechanisms.

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

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

- Well connected.
- Through the carbon-based CoE, this project is making significant overtures for others to disseminate and employ the rapid measurement techniques and fundamental modeling approaches that are being developed.
- Increased collaboration with members of the CoE.
- Air Products appears to be well coordinated with the CoE, including NREL and other partners.

Question 5: Approach to and relevance of proposed future research

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

- Path to objective is not clear, no likely systems were defined and method of finding them is not clear.
- The future study of hydrogen spillover effects is good.
- Reasonable plans for the future.
- Well paid attention to the accuracy of hydrogen adsorption measurements and effort on increased collaboration with partners in this field.
- It is not clear how the go/no-go decision affects this project. What contingencies are planned?
- The future work builds on FY 2006 progress and focuses directly on key barrier issues for carbon based hydrogen storage materials.

Strengths and weaknesses

Strengths
- Very solid work, both experimentally and theoretically.
- Systematic approach to the problem; innovation. Fair attention paid to accuracy of hydrogen adsorption measurements and of predictive modeling.
- The PIs have higher degree of competency in the field.
- This project is an important part of the CoE. Air Products is well equipped and well staffed to make seminal contributions to the progress of the CoE.

Weaknesses

- No clear route to goal of adsorption at significant density on carbon based materials at room temperature and moderate pressure.
- There appears to be a certain reluctance to pursue new materials unless further funding is forthcoming.
- Speed of transition from SWNTs to other materials.
- Redundant work on SWNTs. Ambiguous approach on future direction. Some contingencies are not addressed.
- Not clear what the value-added component of this project is relative to the CoE. Much of the capability seems redundant to other partners.
- There are no obvious weaknesses in the organization and conduct of this project.

Specific recommendations and additions or deletions to the work scope

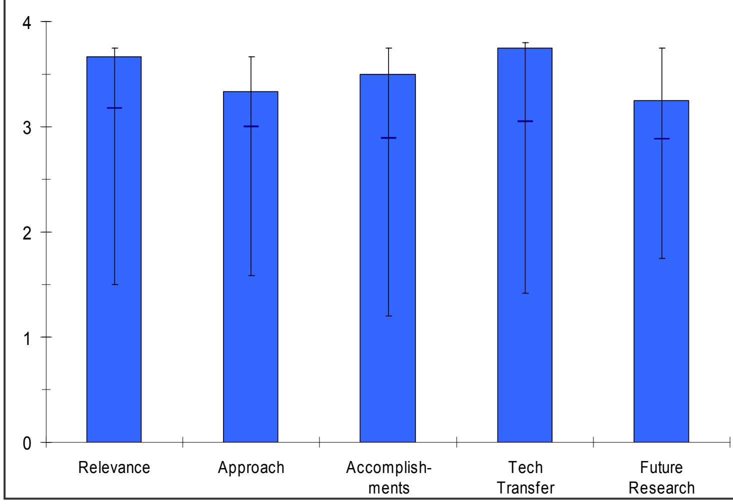
- Need to make concerted effort to calculate or otherwise define systems with high capacity in physisorption, make them, and test them.
- Accelerate move to new boron and nitrogen-containing materials building up on recent work. Consider possible benefits of intensifying partnerships and further exploring collaborations for new hydrogen materials testing program.
- None.
- Keep up the good work. These seemingly basic measurements and calculations are essential to developing the understanding required to make progress towards removing the remaining barriers in the hydrogen storage and delivery area.

Project # ST-25: Neutron Characterization in support of the Carbon and Metal Hydride Centers of Excellence

Dan Neumann, Presenting; Terry Udovic (co-PI); NIST

[Partner of the DOE Carbon and Metal Hydride Centers of Excellence]

Overall Project Score: 3.5 (6 Reviews Received)



Brief Summary of Project

The overall objective of this project is to support the development of hydrogen storage materials by providing timely, comprehensive characterization of CoE-developed materials and storage systems using neutron methods. This information will then be used to speed the rational development and optimization of hydrogen storage materials that can be used to meet the 2010 DOE system goal of 6 wt.% and 45 g/L capacities. In FY 2006, structures are being characterized, and compositions and adsorption/absorption site interaction potentials for hydrogen in/on several candidate materials are being identified. CALPHAD calculations of potentially promising alloy-hydride phase relationships are being done. These interactions will be refined and studied to obtain a greater understanding of them. This information will be extended to characterization/calculations of new materials.

Question 1: Relevance to overall DOE objectives

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

- Neutron characterization is an important experimental support activity for the objectives of both the metal hydride and the carbon-based materials centers of excellence.
- Important tool to help expedite storage material selection process.
- Fully and directly addresses the President's HFI and multi-year plan in support of the C & MH CoEs.
- NIST efforts are highly relevant to the Hydrogen Initiative. NIST plays a critical role in the characterization of materials that are developed by the MH and carbon CoEs.
- Provides critical support to MH and carbon CoEs

Question 2: Approach to performing the research and development

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

- The focus of the neutron activities is good. Neutrons are being employed for chemical composition studies, crystal structure determinations, the location of hydrogen sites in crystal structures, and hydrogen binding sites. The CALPHAD activity appears to be somewhat non-interactive with the neutron activities and not well-integrated with them.
- Ability to characterize materials under real world conditions instead of lab conditions is/will be a valuable tool for material selection.
- This heavily cost shared project provides neutron services and thermodynamic calculations to both the carbon and MH centers of excellence. Although some neutron work is done via other collaborations, it is none the less invaluable to have the principal national neutron analysis facility involved in the DOE program. Response to request from CoE partners seems to be very quick.
- The approach at NIST is to utilize their neutron source to characterize materials by determining structures, compositions, and adsorption/desorption interaction potential of hydrogen in newly developed metal hydrides

and carbon-based materials. In some instances, NIST utilizes their computational expertise to determine phase relationships in promising alloy hydrides. The approach aligns closely with the objectives of both the metal hydride and the carbon-based centers of excellence.
- Neutron methods are critical to understanding hydrogen in or on materials.

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

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

- Neutron studies have been conducted in a number of areas of importance to the metal hydride and carbon-based materials CoEs. The establishment of the hydrogen adsorption sites in the MOF material is particularly notable.
- The project has just started but has generated many useful sets of data already. Cost to DOE is very low.
- NIST has achieved all of the objectives set out by the CoE partners. They provided accurate compositions of materials synthesized by the CoE partners. NIST determined the hydrogen adsorption sites in MOFs. They also observed what appeared to be evidence of hydrogen spillover in carbon nanohorns.
- Provided good support to both MH and carbon CoEs.
- Difference Fourier technique appears to be a powerful tool to determine H binding sites.
- in-situ measurement technique very valuable in understanding reaction pathways.

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

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

- Neutron studies are part of two of the three centers of excellence. The integration of the neutron characterization work with the xenters' activities and needs appears excellent.
- This project closely supports both the carbon CoE and MHCoE. Project appears to have good collaborative relationships with other team members.
- Good collaborations with many of the carbon and MH CoE members.
- Collaborations are excellent. NIST work is for the most part directed by the CoEs, so data is immediately transferred to the CoE partners and is used to structure follow on work.

Question 5: Approach to and relevance of proposed future research

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

- There is no discussion of future neutron in-situ and higher pressure activities, which would seem to be quite useful.
- Near term - support nanotube go/no-go decision.
- Continue providing neutron services as needed.
- Proposed work focused on continuation of the neutron scattering of various metal hydride systems and on thermodynamics computations. The proposed work is clearly laid out and should help speed the discovery of new promising materials.

Strengths and weaknesses

Strengths
- Basically, neutrons are being employed as an important analytical tool by both the metal hydride and the carbon CoEs.
- NIST has high capability in neutron methodology. Strong relationships with carbon CoE and MHCoE.
- High competency in the field. Good utilization/synergy of the resources within the national laboratories. Powerful analytical techniques and independent analysis.
- World class neutron facility with rapid interaction/collaboration ability.
- NIST utilizes their neutron source and expertise to support materials development efforts in the metal hydride and carbon-based centers of excellence.

Weaknesses

- This work does not appear to be as valuable in coming up with new materials. If volume of materials to be characterized increases, is there capacity to handle it?
- The CALPHAD thermodynamic H-Li-Mg-B-Si database does not include nitrogen.

Specific recommendations and additions or deletions to the work scope

- Continue to support and speed the material selection process.
- The project provides technical/analytic service to the CoEs. The work could have been shown as part of the poster presentation. The proper evaluation of this project is done by their primary customers such as metal and carbon CoEs.
- This reviewer is not convinced CALPHAD calculations are that useful to the overall effort. There are many other first principle modeling and thermodynamic calculation projects within the DOE program. But it is OK to keep that in the project.
- Why is the CALPHAD work being done? What project or PI is it being done to support?
- Expand the CALPHAD thermodynamic database to include nitrogen.
- NIST may be able to aid the CoE partners in determining the pathways to improved materials. Within the constraints of available resources, the CoEs should be encouraged to utilize NIST expertise in materials development as well as characterization.

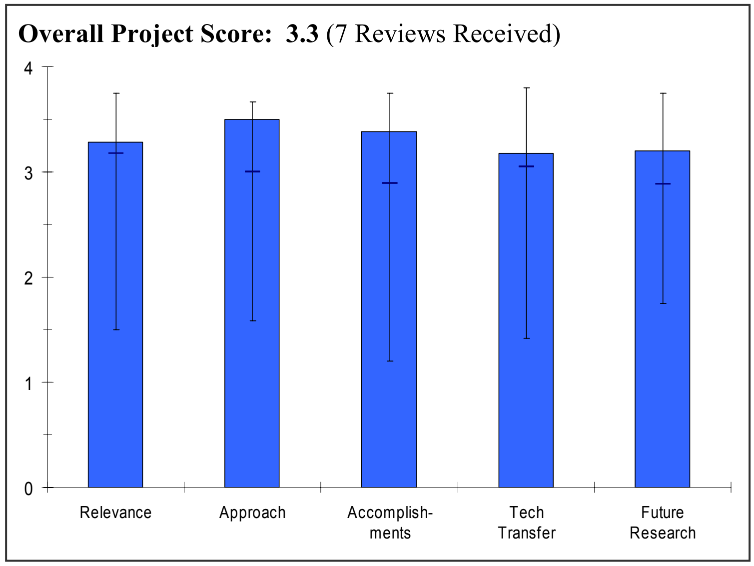
Project # ST-26: Cloning Single Wall Carbon Nanotubes for Hydrogen Storage

James Tour; Rice University

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

The overall objective of this project is to develop nanostructures and nanoengineering processes that enable synthesis of hydrogen storage materials that can be used to meet the 2010 DOE gravimetric (6 wt.%), volumetric (45 g/L) hydrogen storage 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.



Question 1: Relevance to overall DOE objectives

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

- This project is obviously aligned with the President's hydrogen vision and the RD&D objectives. Storage is key to the Hydrogen Initiative and the carbon-based option is a part of the overall effort. However, it seems obvious that this option is further behind in its science base than the other two options being pursued and it is not clear that it can get much beyond the 2006 target of 6%.
- Aligned if 60 g/L volume goal is feasible. Ability to make pure confomers of nanotubes of one diameter will assist in finally defining the potential.
- Meeting DOE 2006 targets for carbon nanotube seems difficult based at least on current hydrogen wt.% status.
- This is a leading research group developing their synthesis methods [for] large scale production of aligned single wall carbon nanotubes. Emphasis on cloning is less important for this nanotube application than for others done by this group. The program as constituted is designed for relevance to advancing carbon nanotube synthesis in general rather heavily focusing on the hydrogen storage application.
- The project is focused on hydrogen program goals and addresses key targets of RD&D objectives.
- Cloning nanotubes is a very interesting idea. Cloned nanotubes decorated with metals look promising materials for hydrogen storage [due to] pi-systems, large surface areas and metal binding sites.

Question 2: Approach to performing the research and development

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

- Cloning is a suitable approach, as is the goal of close spacing with control.
- Looks good.
- Concept and technique are novel but concerns about data reproducibility.
- The approach to making tubes with controlled intertube separation seems promising. Here collaboration with Yakobson is important. Also the approach to large scale synthesis is promising. The approach to making tubes with room temperature 6 wt.% capacity is high risk.
- Good approach exploring nanoengineering and moving systematically into the prediction of optimum structures and hydrogen storage capacities.
- Nanoengineering seems to be the only solution to hydrogen storage problem.
- Reproducible nanotube production process with optimized parameters is critical to their use as storage medium.

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

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

- Made 75 to 80% density nanotube bundles. Cloned nanotubes. Storage at 3 wt.% or so. Accomplished a swelled fiber and then cross linked to hold value at 9 angstroms.
- Doing extremely well.
- Hydrogen absorption barriers should be carefully considered when designing the CNTs [carbon nanotubes]. Project needs to consider several issues, i.e. densification won't be useful if it impacts hydrogen diffusion.
- Progress with cloning is good, but not of high relevance to hydrogen storage program. Progress with vertical tube alignment is very good and will help with thermal management. Use of oleum [fuming sulfuric acid?] to control the interlayer separation is going well. The progress with adding Li and cross linking agents is good. Interaction with Yakobson work is progressing well for the interlayer spacing control project.
- Significant accomplishments – robust approach.
- A lot of milestones and decision points in very near feature.

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

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

- Probably could be better linked to others, NREL seems their main partner.
- Good. But seems to be mostly relying on own work.
- More collaboration is needed with other groups within the carbon CoE.
- This group interacts well with industry and the research field overall. The Interaction within Rice University is strong.
- Collaborations through the CoE.
- A good balance of theory and experiment.

Question 5: Approach to and relevance of proposed future research

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

- Cross linking of individual nanotubes at various spacings. Lithium intercalation. Downselect to best sizes.
- Logical progression.
- Dopants for enhancement of interactions need to be selected carefully and several dopants might need to be considered. Data reproducibility might be a concern.
- With a focus on the milestone of at least 4 wt.% hydrogen mass-uptake at room temperature in 2006, the challenge seems large from where they are now. Advancing the science and technology to meet other goals seems more promising.
- Rather ambitious program but a systematic approach has been adopted for the near future work.
- The RT [room temperature] adsorption measurement of the C/Li systems should be carried out sooner than planned to show their real potential. There is no point of perfecting the SWNTs bundle geometry if the potential of achieving high RT adsorption is not there.

Strengths and weaknesses

Strengths
- Ability to design precisely defined systems.
- Knowledge and hard work.
- The Tour group is very strong in the synthesis of nanotubes. They are doing well with mass production methods, nanotube alignment and control of intertube spacing.
- Novelty and robustness of approach.
- Techniques and success in densification of CNTs.

Weaknesses

- None obvious from the presentation.
- Engineering aspects are not yet addressed — Heat of filling for a 5-kg hydrogen system, able to be filled in a reasonable time, is not a trivial problem; 'showstopper'.
- The prognosis of meeting hydrogen uptake goals is very challenging for both the short term and the time line of the program. Has the team considered whether the amount of lithium uptake needed to meet 2010 DOE goals for room temperature hydrogen storage is reasonable from an experimental viewpoint. Focus is very strong on increasing capacity. Little work is in progress to evaluate other needs for a hydrogen storage system.
- CNT properties impact on hydrogen physiosorption not thoroughly considered. Densification of CNTs is a good approach, however over densification should be avoided, how to control? reproducibility?, etc. Intercalation should be carefully considered and optimized specially in these reported dense systems
- Reasonable chance this will never work. But it is important to find out.

Specific recommendations and additions or deletions to the work scope

- Continue as planned. The results speak for themselves.
- Consider whether scale-up needs to be addressed earlier on in the project. Also, should the work on the Li-doped system with the room temperature uptake be given higher priority in the program?
- Recommend less emphasis be given to nanotube chirality, and recommend that the team focus primarily on tube diameter control. Recommend that difficult challenges in developing a good hydrogen storage material other than storage capacity be identified and the probability for successfully addressing these challenges be assessed.
- Recommendation to consider shifting to basic research.
- As soon as possible validate that the 9 angstrom materials are making major headway in storage.

Project # ST-27: Advanced Boron and Metal loaded High Porosity Carbons

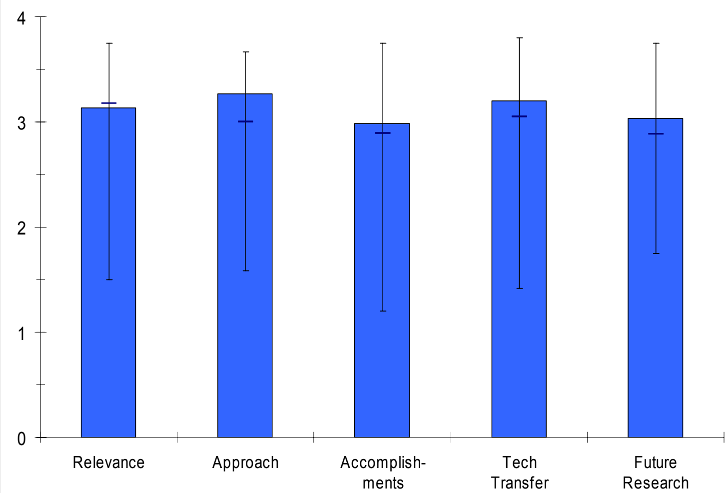
Peter Eklund; Pennsylvania State University

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

The overall objective of this project is to develop advanced hydrogen physi/chemisorption materials that have reversible, low mass density, low volume, good 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 H_2 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 sp^2 framework without serious structural distortions.

Overall Project Score: 3.1 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- The project serves the overall DOE objectives and supports the hydrogen program; it addresses a number of key barriers.
- Onboard hydrogen storage is critical to the success of the Hydrogen Fuel Initiative.
- This project is part of the carbon CoE. The effects of loading boron and certain metal atoms into the framework of high porosity carbons on hydrogen storage capacity is being investigated.
- The program goals address pertinent barriers for the DOE program on hydrogen storage. Science advances and technology advances are both addressed.
- Boron in C based materials enhance the H_2 binding and the B-C materials look promising for hydrogen storage applications.

Question 2: Approach to performing the research and development

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

- Well founded approach involving and coupling a number of techniques and exploring a number of possibilities.
- Good fundamental science approach towards incorporating boron into carbon materials.
- Boron incorporation into carbon is accomplished by electric arc vaporization. Electron microscopy, hydrogen adsorption measurements, neutron diffraction, Raman spectroscopy, and DFT calculations are performed to characterize the products.
- Approach of boron doping to enhance binding energy seems promising. The BC_3 approach may have high pay-off but may be hard to achieve, but this is a good idea for a research program. Combining calculations with experiment in a strongly coupled way is highly encouraging.
- A good combination of techniques and approaches for a spherical investigation of the problem.

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

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

- A satisfactory list of accomplishments following the use of complementary methods and taking advantage of access to different techniques, both experimental and theoretical. Substantiated claims of boron substitutes into the carbon framework (doped SWNTs).
- Good progress in incorporating boron into carbon lattices. Progress towards meeting the hydrogen storage capacity target has been limited.
- It was shown that boron additions increase the overall binding energy for hydrogen. Unfortunately, not all of the boron in the target gets into the carbon lattice. There seems to be some limits to how much boron one can introduce. DFT calculations provide some insight about H binding energy. Progress is modest at best.
- The team effort has made a lot of progress in the past year in synthesis by three different approaches, in understanding the role of boron through very successful neutron work at NIST, and through developing a high throughput synthesis method. The discovery of a surface roughening technique is another significant advance. The research quality is high.

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

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

- A good collaboration scheme under the CoE.
- Greater coordination and independent testing of storage materials is expected as the project progresses.
- Collaborations exist with several partners in the CoE.
- Interactions among Penn State collaborators seems good. Good interactions with industrial groups at Air Products and Carbolex. Productive collaborations with NIST in doing important scientific advance in boron-carbon materials synthesis are noteworthy.

Question 5: Approach to and relevance of proposed future research

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

- Well planned future activities concentrating on the main issues to be resolved using a continual developmental feedback loop of synthesis, hydrogen storage and design/modeling. Appropriate actions have been decided to verify and extend the observed enhancements in storage capacity and binding energy bearing in mind the actual system targets.
- The research plans build on the results of the FY 2006 effort. This will include volumetric studies of hydrogen storage in B-substituted carbons and continued development of high-impact boron-carbon structures.
- Proposed research on boron-carbon systems is impressive. This should be strongly pursued. Proposed work matches emphasis to increase hydrogen uptake. Some effort to check other factors on their barriers to achieving the 2010 DOE target for hydrogen storage (viewgraph 2) should also be contemplated.

Strengths and weaknesses

Strengths

- Kg level of CNT is producible and controlled production of enhanced physisorption material.
- Complementarity of methods used and collaboration with key research groups in this field.
- Good fundamental science approach towards incorporating boron into carbon materials.
- Both from a scientific and a programmatic standpoint, this is the strongest program I was asked to evaluate. The group uses two approaches that are backed up by a strong experimental program at both Penn State and NIST and a strong, tightly coupled theory/experimental program. Although the hydrogen storage problem is very hard, the approach taken shows promise and progress has been outstanding.

Weaknesses

- Energy to create the CNT is enormous.
- Tight timetable; need to timely move from theoretical calculations to material synthesis, demonstration of hydrogen storage performance and actual design of a viable storage system.
- Although the group is cognizant of the many factors needed to be successful in the hydrogen storage problem in general, the group could say more about the future plans about addressing some of the factors in hydrogen storage, other than increased storage capacity. In defense of this research group, increased storage capacity is the most important consideration right now because it is viewed as a show-stopper.
- No perceptible weaknesses.

Specific recommendations and additions or deletions to the work scope

- It is not clear that the modification of CNT has potential [or not]. Especially energy to create such a material seems quite inefficient.
- Because of the high capability of this team, they may be a team that can see if physisorption may have other attributes for hydrogen storage that chemisorption does not have, and to make some quantitative comparisons between the big picture outlook between chemisorption and physisorption. Additional funds would be needed to investigate this enhanced scope, but in the long term this may be an important investment for the overall program.
- The thermodynamic 'penalty' for cryogenic hydrogen storage may be too high; intensify your efforts following your current approach accounting also for operability.
- Issues raised about roughness effects should be explored to assure that there are no misconceptions.

Project # ST-28: Hydrogen Storage by Spillover

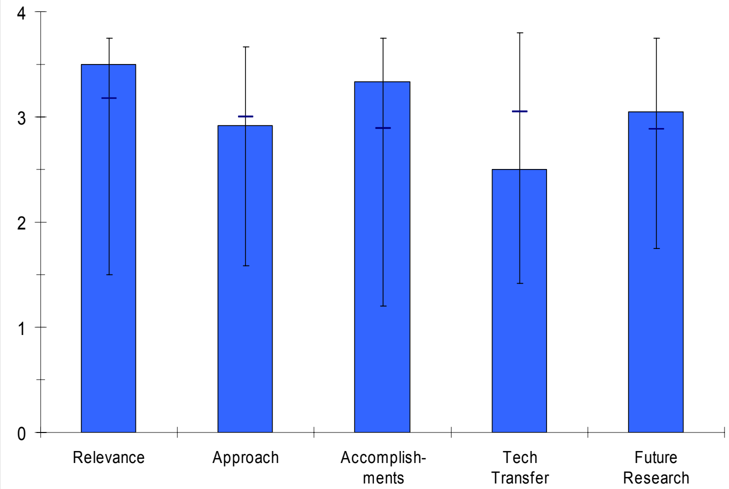
Ralph Yang; University of Michigan

[Partner of the DOE Carbon 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 6 wt.% (and 45 g/L) at room temperature. This will be done by developing and optimizing our 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.

Overall Project Score: 3.2 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- This project is investigating the implications of a previously known surface science phenomenon called spillover in the context of hydrogen storage.
- This project is focusing on room temperature hydrogen storage in inexpensive carbon-based materials.
- Possibly the most well aligned program in the CoE.
- Project seems to fully address President's HFI and DOE RD&D plan.
- Interesting concept on catalyst performance that may produce useful results for many other materials, not just limited to carbon structures?
- Energetics of hydrogen spillover of 3-4 kcal/mol is optimal for hydrogen storage application at ambient temperature. The concept of spillover effect for hydrogen storage is novel.

Question 2: Approach to performing the research and development

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

- A bridge building approach is used to emulate conditions for spillover that occur in certain catalysis embodiments. There was much discussion about the applicability of the concept after the presentation. The presenter needs to address the concerns expressed.
- The project focuses on optimizing the hydrogen spillover effect from catalyst particles into hydrogen-storing substrates, such as carbon and MOFs. It may potentially have wide applicability to a number of different materials systems.
- Approach seems to be productive. Need to work harder on improving rates.
- There are a number of world-wide efforts on carbon that are exploring a spillover (metal addition) approach. It is not quite clear what is different about this "bridging" method. In any event, this is a rather low-cost effort that deserves to continue.
- Bridge building technique seems to be the key difference to traditional metal doped carbon molecule approaches. This seems to be making the difference.
- Volumetric storage density of ~40 g H_2/L was measured based on pelletized powdered obtained after adsorption. Need to consider compacted bulk density of pelletized material to consider meeting DOE system targets.

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

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

- The reported results showed a bridge enhancement effect. Unfortunately, the storage capacity levels were well below ones of interest for meeting DOE [wt.%] H system targets. More experiments are needed to confirm the spillover notion.
- Excellent progress is reported for hydrogen storage at room temperature, with 4 wt.% reported (but not described in detail). This is the highest room temperature value reported for a carbon-based material to date.
- Doubled hydrogen uptake and roughly 4 wt.% at low pressure (100 atm).
- Progress has been made, at least as stated on paper, for carbon and MOFs. A patent has apparently emerged that involves making and attaching the metal/carbon bridge to the storage substrate. Contractor has developed a carbon that has multiple weight percent reversible H-capacity at room temperature (as well as reasonable volumetric capacity). However, given the dismal history of reproducibility in carbon, it is imperative that the results be independently checked.
- Has achieved one of the best room temperature carbon based materials to date. Still has work to do on volumetric and kinetics and try out other materials other than activated carbon.
- Although the project is in relatively early stages, the approach of "bridging spillover" may lead to materials meeting 2010 weight targets.

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

This project was rated **2.5** for technology transfer and collaboration.

- Supposedly, some verification work was done by NREL and NIST.
- This project is a part of the carbon-based materials CoE. However, somewhat expanded interactions with the CoE members would be highly beneficial.
- Seems a bit isolated, but certainly connected to outside programs.
- There is relatively little collaboration (only NREL and NIST). Connections should be made to confirm the preliminary results and to think toward the building of a demonstration tank.
- Dr. Yang should now be working more closely with other material producers to see if his bridges can be applied to and enhance their materials.
- In this stage the project is "localized" at the University of Michigan. Planned collaboration is only with respect to verification and characterization. There was no scientific collaboration on the material development discussed.

Question 5: Approach to and relevance of proposed future research

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

- The future plans are certainly appropriate because they should resolve many of the issues about the importance of spillover. Let's see what the project produces for next year's review.
- The project displays a focused, clear plan for the future work.
- Plans are appropriate with the exception of the most important thing, getting independent confirmation.
- Reasonable, albeit rather lacking in specifics.
- Important to try concept on different receptors such as MOFs which may yield better results, still needs to propose plan on how to improve the volumetric density, Does this phenomenon only work on a single layer adsorption of the catalyst? Is this why kinetics are slow? Did not propose a plan to improve kinetics.

Strengths and weaknesses

Strengths
- The spillover concept is sufficiently intriguing that it deserves more study.
- The reported value of 4 wt.% hydrogen storage at room temperature via the spillover approach is the highest room temperature value reported thus far for a carbon-based material.

- Potential for getting actual high density hydrogen storage on light materials.
- Seems to be achieving reasonable room temperature storage levels in carbon for the first time. Should be easy to reproduce.
- Novel approach for hydrogen storage that can be applied to a series of materials.
- Not working at 77K, actually attempting storage at room temperature.

Weaknesses
- Based on what was presented in the talk, several issues need to be resolved before there will be any community wide acceptance of the concept's significance or utility. Additional confirmatory experiments must be done.
- Speed of the hydrogenation/dehydrogenation process.
- Uses an expensive catalyst (Pt).
- Volumetric storage densities were evaluated based on volume of pressed pellets. Since this parameter is critical for carbon-based materials, there is a need to provide more thorough measurements of volumetric densities that can be attained in the storage vessels.
- The reported 4 wt.% room temperature hydrogen storage value needs to be independently reproduced by other research organizations. Specimens should be sent to SwRI for independent analysis.
- Slow kinetics. Still precious metals are required but hopefully that could be significantly reduced with the introduction for the bridges to aid spillover.

Specific recommendations and additions or deletions to the work scope

- The bridge may add to the volume and mass of the storage material embodiment in a detrimental way. The PI should give attention to this matter.
- Focus on economics (base metal catalyst?), improved volumetric capacity, thermodynamic measurements and practical container considerations (heat rejection during rapid recharge). More partners would help. Highest priority should be to confirm preliminary results.
- Focus on improving kinetics, and lowering pressure required. MUST get the material tested at SwRI to confirm result.
- Dr. Yang should now be working more closely with other material producers to see if his bridges can be applied to and enhance their materials.
- None.

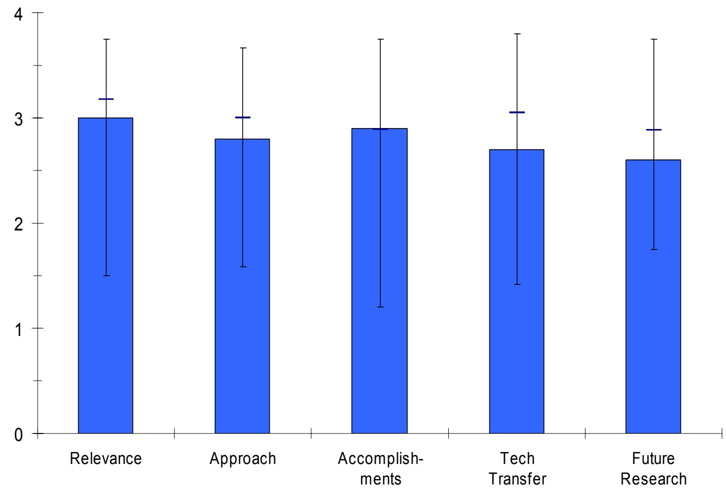
Project # STP-02: Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

Leon Shaw; University of Connecticut

Brief Summary of Project

The University of Connecticut is investigating, modeling, and developing a novel, mechanically activated, nanoscale Li_3N-based material that is able to store and release ~10 wt.% hydrogen at temperatures below 100°C with a plateau hydrogen pressure of less than 10 bar. Research in FY 2006 is focused on the effects of mechanical activation on hydrogen sorption/desorption kinetics of the $LiNH_2$ and LiH mixture, stability of LiH in different environments, and dehydrogenation behavior of the MgH_2 and $LiNH_2$ mixture.

Overall Project Score: 2.8 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- The project seeks to lower hydrogen reaction temperatures in the lithium amide system through the approach of mechanical activation.
- The project gives good support to meet DOE objectives on relatively new storage materials. The PI did not directly refer to the DOE objectives.
- Investigating the fundamental mechanisms involved in mechanically activating metal hydrides to increase the kinetics of reversible hydrogen storage is very relevant to the Hydrogen Fuel Initiative.
- The effort adequately addresses the need for solving the storage problem by optimizing the amide systems. Storage is a key problem for the Hydrogen Fuel Initiative and RD&D plan.

Question 2: Approach to performing the research and development

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

- The project approach appears to be over-extending itself. It should just focus on understanding and optimizing mechanical activation effects.
- The project is well organized and technically structured to overcome the main problems of the studied hydrides. The approach examines all the technical possibilities in a complete manner to reduce the sorption/desorption temperatures.
- The approach is to mechanically activate metal hydrides by ball milling, chemically modify amides to destabilize them, and to employ catalysts to enhance adsorption and desorption.
- Contractor is focusing on mechanical milling to solve the temperature and kinetics problem with $LiNH_2$, $LiNH_2$+LiH, and $LiNH_2$+MgH_2 along with several associated other details (e.g., the stability of LiOH in O_2-containing environments). This is a relatively overworked area not likely to get very far toward DOE 2010 system targets and beyond.

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

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

- Mechanical activation studies to date have been thorough, and do suggest some lowering of hydriding/dehydriding temperatures. Results suggest that mechanical activation at room temperature appears to enhance a complicating and potentially deleterious effect of decomposition of $LiNH_2$ to Li_2NH plus NH_3.
- The progress is very good with clear comprehension and appraisal of the possible modification mechanisms. The use of separated approaches gives convincing answer on the possible improvements and limitations. The problem of ammonia production is well considered and will deserve continuous attention. The stability results must be better explained even in relation to the used methodology, not completely clear.
- Connecticut has demonstrated that mechanically activating lithium amide-lithium hydrides and lithium amide-magnesium hydrides decreases the activation energies of hydrogen adsorption/desorption in these systems. Dehydrogenation starts at room temperature, but temperatures over 200°C are required for complete release of hydrogen. Two catalysts investigated so far have not improved kinetics.
- Extensive nice work has been done. Progress has been made in accelerating low temperature kinetics, but ubiquitous NH_3 has been again confirmed, an “Achilles' heel” of these particular systems when it comes to supplying a fuel cell with H_2. The PI is optimistic about defining ball mill conditions where NH_3 does not occur, but similar marginal results from around the world cause this reviewer to have some skepticism.
- Conclusion appears to be wrong: loss of H_2 during mechanical activation does not indicate reversibility at room temperature

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

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

- This project may benefit from expanding its collaborations with other research activities, particularly in the area of catalysts for the lithium amide system.
- The network of collaboration may be improved with some exchange with the MHCoE.
- There is evidence of collaboration between Connecticut and PNNL. However, their relationship to the rest of the MHCoE is not too clear.
- Collaborations rather limited.

Question 5: Approach to and relevance of proposed future research

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

- The catalyst and theoretical/modeling aspects of the future work should be eliminated and the focus remain on understanding and optimizing the mechanical activation effects. Mechanical activation processes should be performed at lower temperatures, such as liquid nitrogen temperature.
- The future steps are well justified by the experimental results and analysis of the work already done.
- Future plans are presented but their relation to other work in the CoE is not clear.
- Li-amide and all its mixtures are highly overworked areas which have not lived up to promise during the last year particularly. I am not in opposition to a little more work, but I think there is substantial risk is spending much more time and money on this system that is unlikely to produce NH_3-free H_2. I do not criticize the diligence and skill of the participants; they have perhaps just chosen a questionable system.

Strengths and weaknesses

Strengths

- Mechanical activation lowers the hydrogen generation temperature by approximately 100°C, at least on the first dehydrogenation cycle.
- The project is well organized with clear targets and technically justified approaches.
- Good, careful experimentation.

Weaknesses

- The project has limited collaborations.
- An overworked family of materials that have potentially insurmountable problems (e.g., NH_3 generation and N mass transport). I must also question the very widespread modern tendency to use ball milling as the solution to all storage materials problems. Ball milling is not cheap under such long time conditions.
- It appears that ball milling of the $LiNH_2$ promotes its decomposition to $Li_2NH + NH_3$ at temperatures of approximately 50°C. This would appear to have a deleterious effect on the reaction $LiNH_2 + LiH = Li_2NH + H_2$, since it reduces the amount of $LiNH_2$ available for this reaction. Furthermore, the potentially mitigating reaction $½ NH_3 + ½ LiH = ½ LiNH_2 + ½ LiH$ does not occur completely, and so much of the NH_3 escapes, with the loss of its associated hydrogen. This is why the milled material shows only 5.5 wt.% hydrogen, as compared to 6.5 wt.% for the unmilled material.

Specific recommendations and additions or deletions to the work scope

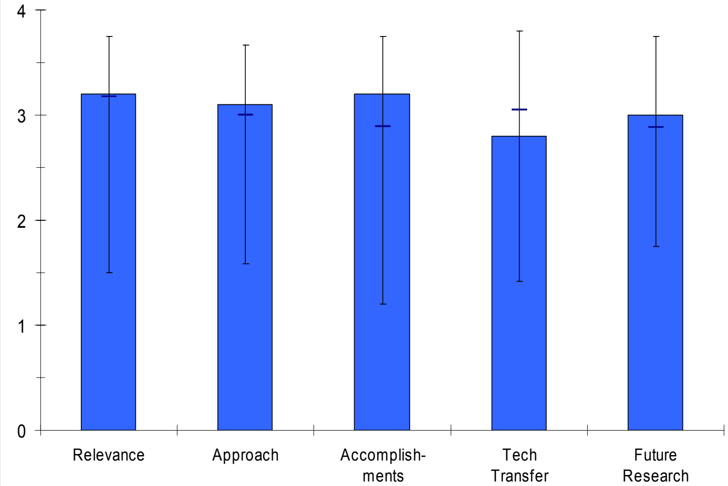
- The project approach appears to be over-extending itself. It should just focus on understanding and optimizing mechanical activation effects.
- The project must include, more clearly, methodologies for stability tests and for addressing the problem of NH_3 production with different hydrides.
- Be prepared to move on to newer materials with more potential and less problems. Also, I think we need to see some practical processing cost numbers associated with such long-time ball milling.
- The project needs to include effects of cycling on hydrogenation/dehydrogenation capacities and temperatures. Ball milling at lower temperatures such as liquid nitrogen temperature should be examined. Study of catalyst effects should be eliminated, since the project is not large enough to investigate this well, and this is already being examined by other researchers.

Project # STP-03: First-Principles Modeling of Hydrogen Storage in Metal Hydride Systems
Karl Johnson(PI); University of Pittsburgh; David Sholl, Carnegie Mellon University
[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

The University of Pittsburgh and Carnegie Mellon University are computing thermodynamic properties of metal hydride alloys, including ΔH for known reactions to test the accuracy of the approach and ΔH for new reactions to identify promising destabilized compounds. Interfacial properties of hydrides are also computed in this project. Hydrogenation in destabilized hydrides and other systems is studied to assess reversibility, identify common hydrogenation pathways that might be applicable to other materials, and assess the role of interfacial transport. The goal is to design a practical destabilized hydride system.

Overall Project Score: 3.1 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Good effort, largely aimed at discovery of suitable novel materials/reactions. Well aimed at the relevant problems to support the HFI.
- This first principles modeling of metal hydride systems is very valuable to the MHCoE in identifying promising hydrogen storage materials that have sufficient capacity and low activation energies. The work is very relevant.
- Important contributions to the MHCoE.
- The project gives good support to meet DOE objectives.
- Materials do not meet targets. Destabilized materials still promising and need to be understood.

Question 2: Approach to performing the research and development

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

- The project offers a useful tool for selecting hydrides with potentially interesting characteristics.
- Good computational methods. Mapped new hydrides including some with reasonable capacities.
- Modeling/DFT approach is a good candidate for discovery of novel reactions, and can screen reactions much faster than experiment. Proved utility of this approach in present year by prediction of a handful of reactions with high densities and suitable thermodynamics.
- The approach appears sound.
- Modeling approach focused on materials and processes (e.g., destabilized hydrides) studied in the CoE.
- Looking at critical thermodynamic properties of materials.

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

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

- The project has well progressed in relation to the fixed objectives. The lack of experimental data limits the validation of the results of the various models' application.
- Good results for new hydrides. Interesting results for oxide surfaces.

- Computational screen has produced several candidate reactions! This is exactly the kind of thing that DFT is useful for in a materials discovery effort. Nice to see a good demonstration of this utility. Not clear whether phonon (zero-point) contributions have been included in these energetics or not. Last statement on summary slide needs a bit of explanation, since experimentalists at this meeting (HRL, Stanford) claim that Mg_2Si is not reversible under any conditions investigated thus far.
- University of Pittsburgh has investigated over one hundred reaction schemes that had not previously been studied for hydrogen storage. Pittsburgh believes that the accuracy of the computational methods is within about 15% after comparing the results with experimentally determined values of heats of reaction. Five new destabilization schemes were identified that have high capacity and favorable thermodynamics. Presumably the CoE partners will try to synthesize these materials and determine their characteristics.
- Screened large number of reactions and identified a few promising ones.
- Supported Mg_2Si experimental work.

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

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

- The coordination with some MHCoE must be improved, because of the common interest in identifying suitable hydrides.
- Need to work more closely with experimentalists to confirm results. Oxide formation hypothesis could be confirmed.
- Dissociation studies: based on premise the dissociation of H_2 might be a strong kinetic barrier. This project should communicate with the effort at Stanford; these authors seem to have shown quite convincingly that H_2 dissociation is not a limiting factor.
- The collaboration among the CoE partners with Pittsburgh appears strong. If the other CoE partners follow through with these promising leads, it will reinforce the value of the CoE concept to the DOE program. This could well be an illustration of the total effort and accomplishment of the CoE is greater than the sum of the efforts of individual partners on their own.

Question 5: Approach to and relevance of proposed future research

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

- The future steps are well justified by the experimental results and analysis of the work already done.
- Computation approach sound and should continue, need to initiate more collaboration with experimentalists.
- Need to see a pathway (either within this project, or generally within the CoE) that these novel predictions are going to be experimentally tested! This was not apparent from the CoE's presentation [Sandia presentation, there was not a formal center presentation.] (not really a criticism for this project). Why not? Is there a lack of coordination between this effort and Sandia? Make sure to coordinate future efforts with Sandia and Stanford to avoid computationally investigating kinetic mechanisms that have already been experimentally proven to be not rate-limiting.
- Future work plans are a little vague.

Strengths and weaknesses

Strengths
- The project has adequate resources and expertise in applying a set of models.
- Sound computational approach. Examination of destabilized materials.

Weaknesses
- The project has limited collaborations.
- Need more collaboration with experimentalists.

Specific recommendations and additions or deletions to the work scope

- The project requires more collaborations to fruitfully integrate theoretical activities with the experimental ones.
- Ensure that these results are incorporated into the University of Illinois data base for use by the CoE members.

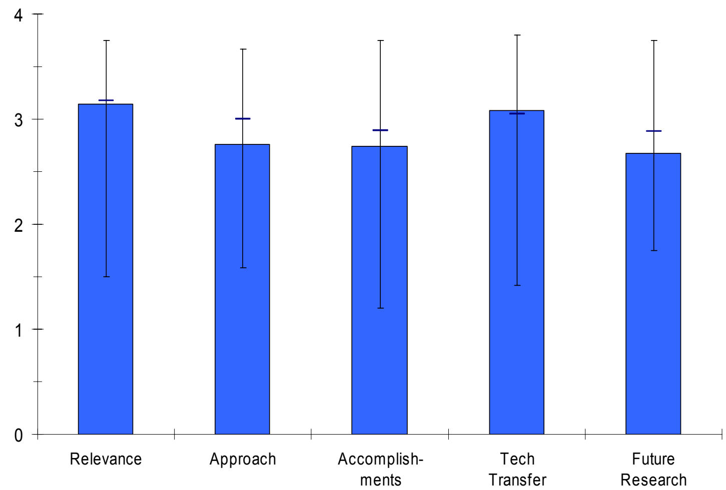
Project # STP-04: Hydrogen Storage Research in support of the DOE National Hydrogen Storage Project

Don Anton; Ted Motyka (PI), Ragaiy Zidan, Savannah River National Laboratory (SRNL)

[Partner of the DOE Metal Hydride Center of Excellence]

[SRNL has several projects supporting the DOE Hydrogen Storage Program. All storage work was covered under this single review. SRNL is a member of the MHCoE; partner to Alfred University (microspheres), and partner to the UTRC materials project.]

Overall Project Score: 2.8 (5 Reviews Received)



Brief Summary of Project

This project at SRNL is conducting research to identify rechargeable hydrogen storage media with a gravimetric capacity of 7.5 wt.% or greater. In addition, this project is developing and modeling the performance of gravimetrically and volumetrically efficient solid state hydrogen storage systems.

Question 1: Relevance to overall DOE objectives

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

- SRNL has provided support to the development of new materials with the potential to store hydrogen.
- SRNL contributes to the metal hydride CoE efforts by developing hydride synthesis/regeneration processes and engineering on-board systems that affect the release of hydrogen in a controlled fashion. This later activity is critical to understanding how these storage systems can be implemented in fuel cell vehicles. Not sure how relevant the hollow glass microspheres work is to the mission of the MHCoE.

Question 2: Approach to performing the research and development

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

- Molten state processing work, and alanate-based materials discovery efforts seem to have a strong overlap with UTRC project (and SRNL is listed as a collaborator on the UTRC project). Since both of these efforts have a considerably high amount of funding, it is not clear that both projects are actually adding value. No indication is given as to why the microspheres work should be pursued. What are the advantages of this approach? What sorts of densities, rates, cost could one estimate to be achievable for these microspheres?
- Multiple approaches in materials discovery are being pursued by SRNL. In addition SRNL is providing support to several organizations that are involved in the DOE hydrogen storage program.
- The approach is ad hoc. The work is a mixture of significantly different projects.
- SRNL is investigating alane rehydrogenation and is planning to make preliminary system designs. They continue to look at various alanates synthesized by means of a molten salt process to produce the alloy. In addition, SRNL is leading the engineering design effort for the CoE. The next generation system designs are building upon their current prototype system development efforts. This latter effort addresses the storage technical barriers of system-based rather than materials-based metrics.
- Technical barriers not addressed.

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

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

- For the amount of money in this program (and the possible duplication in some aspects with UTRC), very little seems to have been accomplished in the current year.
- The significant accomplishments that SRNL reported are the development of baseline system models, mass flow models in packed beds, and the fabrication of new system prototypes. In addition, SRNL has developed mechanical-chemical synthesis techniques for producing kilogram quantities of catalyzed complex metal hydrides. In addition, SRNL is assisting Alfred University by evaluating hollow glass microspheres that the university has prepared for their hydrogen storage characteristics.
- Significant progress in several areas during the past year. It is time for SRNL to focus its activities on selected areas that have the greatest potential for meet the gravimetric and volumetric targets for hydrogen.
- Projects appears in early stages to judge.

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

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

- Extensive interactions with a number of hydrogen storage research organizations.
- High degree of interaction with the specific project. Need a closer interaction with the alanes activity in the MHCoE.
- Collaborations appear to be in place through the CoE partners.

Question 5: Approach to and relevance of proposed future research

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

- Alane work: should show some simple theoretical estimate of the efficiency of the proposed electrochemical process. It is critical to know something about the efficiency to evaluate whether or not this idea could possibly work. System-level work and modeling is still the most unique portion of this project. This aspect should be a focus going forward, and the PI should ensure that there is no duplication of effort in this regard with the other analysis activities at Argonne and TIAX.
- The future plans appear to be "more of the same"; activities - need to focus on specific materials that show the potential for meeting DOE performance target. Work on materials that clearly won't hit the target shown must be minimized to complete in a reasonable time frame.
- Future plans were presented. They indicate that work on systems with higher capacity than the alanates will be emphasized in response to comments from last year's AMR [annual merit review]. However, continued work on alanates is also in the plan. It's not clear how much work on the higher capacity materials is planned relative to the work on alanates. The engineering design task will be emphasizing safety related aspects of on-board hydride systems.
- Timeline ends on 9/30/2006. [National laboratories are funded through annual operating plans.]

Strengths and weaknesses

Strengths
- SRNL shows strong experience and capability in a range of materials discovery.
- Strong competency in the area. Innovative ideas on the alane regeneration. Good progress. This program has the only system design work.
- The engineering task is providing important insights into the issues facing the design of on-board hydride systems. That task is also addressing thermal management issues as they relate to integration into refueling stations.
- Multidisciplinary research focusing on several materials and engineering related issues. Collaboration with other CoE members.

Weaknesses

- Given the funding available, the range of activities seem to be too broad- effort should be focused to ensure a critical mass of activities in areas where the materials under development (e.g. alanes) show a real potential for being able to meet the DOE wt.% requirements.
- The project composed of various and substantially different subtasks.
- One of the review comments from last year was to undertake cycling tests with alanates; no cycling results were shown.
- Progress and data validation of concepts.

Specific recommendations and additions or deletions to the work scope

- Focus the activities in order to increase the probability of developing material, using the unique capabilities of SRNL, to meet performance requirements for hydrogen storage.
- Continue supporting activities.
- Need to ask the BNL work on alanes to better coordinate with the SRNL activities. There are a lot of beneficial synergies between the two for the MHCoE activties.
- Show the total project budget. Only the budgets for 2005 and 2006 were shown. The SRNL budget may not be adequate for the amount of work they present.

Project # STP-05: Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure & Kinetics of Nanoparticle and Model System Materials

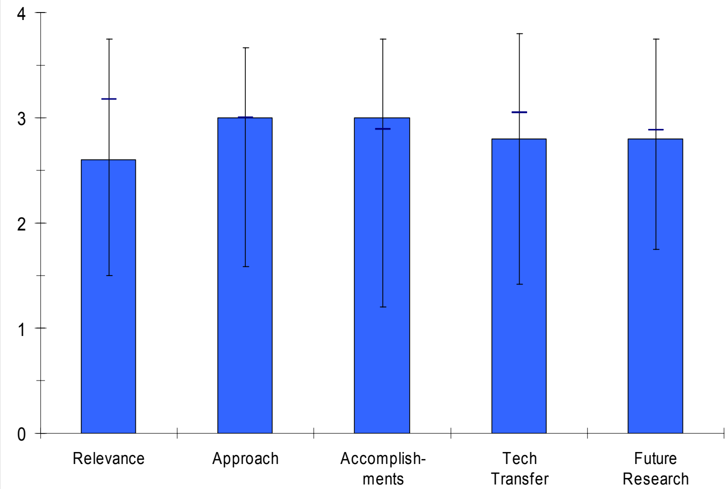
Bruce Clemens; Stanford University

[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

In support of the DOE Hydrogen Program, Stanford University is conducting research in the following three areas: in-situ structural studies of hydrogen storage materials using high brightness x-ray source at Stanford Synchrotron Radiation Laboratory, light metal hydride model material systems to investigate phase change and catalytic processes associated with hydrogen cycling, and kinetic modeling of nanoparticle phase transformations to illuminate mechanisms of hydride formation in nanoscale materials.

Overall Project Score: 2.9 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

This project earned a score of **2.6** for its relevance to DOE objectives.

- President's HFI and RD&D plan indirectly addressed in work, but effort is rather fundamental and supportive without much reference to practical system goals.
- The project addresses some key objectives of the DOE plan.
- The project up to now was aimed at answering the fundamental question whether Mg_2Si can be re-hydrided. The scope, however, is too narrow to have a chance of success in meeting the DOE targets.

Question 2: Approach to performing the research and development

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

- Synchrotron light source is a good addition to DOE's portfolio and makes this project unique. Thin film work provides interesting (and unexpected) insight into the hydriding mechanisms for several reactions.
- The synchrotron XRD work is useful and should help support other DOE-supported activities. The thin film work may have some merit, but this approach is being used elsewhere (not much in DOE program). Maybe a little different approach. How are the nano-thermodynamic calculations different from others. Are they believable?
- The project offers an interesting method to solve main problems of Mg-based hydrides.
- Thermodynamic model is too simple. Is it possible to use macroscopic surface energy?
- The in-situ spectroscopic approach is good in the development of fundamental understanding of the problem of hydriding magnesium silicide.

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

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

- Thin-film Mg_2Si studies provided interesting results, though all attempts to hydride were still unsuccessful. This thin-film geometry could be useful in studying mechanisms for other reversible reactions as well. Could similar experiments be performed with MgB_2 rather than Mg_2Si? Thermodynamic modeling of effect of nanoparticle size on hydriding is interesting, however, the results seem to suggest (contrary to the text on the slide) that a very small ~1-2 nm particles are necessary to move MgH_2 into a reasonable temperature/pressure

regime. Is it feasible to imagine making such particles and having them survive cyclic hydriding/rehydriding? (The DFT studies could directly consider the change in bonding for H in MgH_2 as a function of proximity to the surface; how many atomic layers down does one have to go before becoming "bulk-like"?
- The project is rather new, but some useful results have been recorded. This film work has been successfully put into place and will hopefully provide good fundamental results in the future. So far, not much profound in the way of guiding our path to the practical future. The nano-MgH_2 calculations are not very convincing from a practical perspective. PI suggests profound positive changes in MgH_2 thermodynamic stability with drastically reduced particle size, but in fact such results have never been experimentally seen over some decades' work on Mg. The nano-Mg does not tend to stay nano.
- The project shows interesting results with the preparation of nanoscale samples. The thermodynamic modeling for nano size systems offers new research opportunities.
- Experimental results are very useful and interesting.

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

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

- Rather limited. For the synchrotron XRD work alone, the DOE can benefit more if a more thorough set of collaborations could be developed within the CoE and other parties.
- The coordination is well justified and appropriate to the planned activities.

Question 5: Approach to and relevance of proposed future research

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

- Will be very interesting to see what can be learned from synchrotron studies in the future. Future work should focus on this important aspect. Not clear what is planned in this area? Not clear what is going to be done in the area of nanoparticles. Does the thermodynamic modeling predict particle sizes that can be realistically synthesized? Can some of the modeling predictions be directly tested experimentally?
- Generally reasonable.
- The future steps are well justified by the experimental results and analysis of the work already done. The combination of practical and theoretical activities increases the possibility of success.
- Should be better focused on key barriers.

Strengths and weaknesses

Strengths
- Potential to support other DOE-supported activities, synchrotron source service, only thin film studies within DOE program(?).
- The project has adequate expertise and instrumental resources.
- Very good experimental equipment and cooperation in MHCoE.

Weaknesses
- Not very close to those who need to meet DOE targets in the required time frame.

Specific recommendations and additions or deletions to the work scope

- Need to confirm (for the first time) that Mg thermodynamics can actually be significantly changed. Contractor should try to demonstrate distinctly improved nano-MgH_2 thermodynamics (more than one cycle) within 6 months.
- Size effects in thermodynamic equilibrium are well-known but not investigated for nanoparticles. Would be good to extend investigations in this direction.
- Suggest to apply more reactive probe molecules (e.g., chlorine) to understand whether magnesium silicide will react at all under the experimental conditions. After quick go/no-go decisions, consider other more promising materials for fundamental in situ studies (project scope needs to be expanded).

Project # STP-06: Fundamental Studies of Advanced High-Capacity Reversible Metal Hydrides

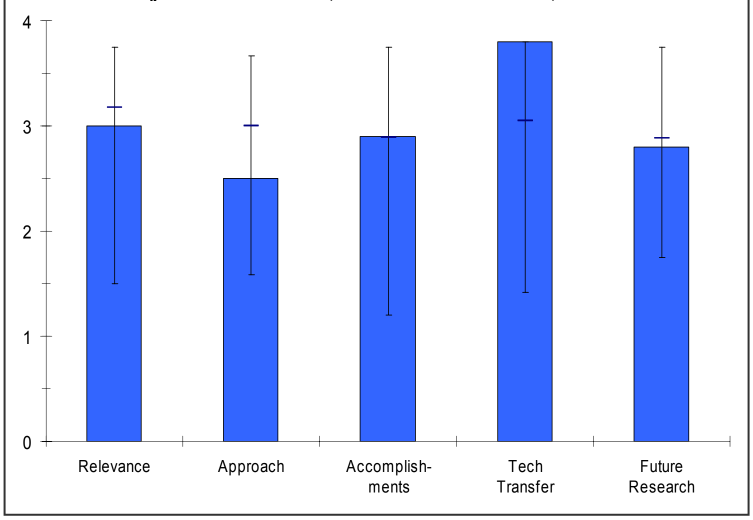
Craig Jensen; University of Hawaii

[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

The University of Hawaii is developing advanced high-capacity, reversible metal hydrides for hydrogen storage. The objectives of the research are to characterize the active titanium species in Ti-doped $NaAlH_4$, develop a model of the mechanism of action of dopants in the dehydrogenation and re-hydrogenation of $NaAlH_4$ and related capacity hydrogen storage materials, determine the enthalpy of dehydrogenation of high capacity hydrogen storage materials, and develop catalysts to improve the hydrogen cycling kinetics of "thermodynamically tuned" binary hydrides with potential to meet the DOE 2010 system gravimetric storage capacity target.

Overall Project Score: 2.9 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Contractor does address President's HFI and multiyear RD&D plan, at least indirectly. The effort thus far is mostly fundamental in nature, at least as presented in specific detail here.
- The project contains activities able to better drive decision on some key objectives of the DOE plan.

Question 2: Approach to performing the research and development

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

- Trying to elucidate the role of Ti in $NaAlH_4$ has been a long-standing puzzle. The current PI has worked on this problem for several years now, but there is still no mechanism forthcoming. At what point does one cut their losses and work on something else? This was the main criticism of this project last year too.
- The approach is based on using a wide variety of experimental tools (often via collaborations) to understand the mechanism of Ti enhancement of $NaAlH_4$ and Na_3AlH_6 H/D kinetics. The approach seems to be derived from Hawaii activities prior to this contract and is sometimes confusing in both time frame and applicability. PI should be reminded to focus on the end objective - to extend the Na-alanate findings to more promising systems. Is that possible, or is Na alanate unique?
- The project considers all the necessary steps to optimize alanates. The project is effective in anticipating no-go decision on alanates by starting the study of alternative hydrides, well selected and motivated.
- Task 3 and task 4 should be coordinated with ST-15 and STP-5 [Brookhaven and Stanford University] projects.
- Prior data obtained by the author as well as by other institutions (e.g., UOP) have clearly shown that Ti-doped alanate will not meet DOE targets.

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

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

- How is it known that Al_3Ti is catalytically inactive? Other results (i.e., from Sandia and BNL) have suggested possible mechanism for Ti at the surface of Al to act as a hydrogen dissociation catalyst. Small point: Al_3Ti is tetragonal, so it's not clear what is meant by "orthorhombic Al_3Ti"?
- An impressive list of findings have been published. It seems to this reviewer that results should have been collected into a useful, unified model of kinetics enhancement by now. All the world seems to be realizing the alanates are not solution and we look forward to the PI carrying this work to the next stage, apparently borohydrides. When will we learn more about the new 11 wt.% borohydride?
- The project has well analyzed the effect of Ti species on alanate behavior. The kinetics of the dehydrogenation process is well characterized and improved by Ti dopants. The work on novel hydrides just started has already given interesting results with a claimed 11 wt.%.
- Spectroscopic results obtained for $NaAlH_4$-Ti systems are useful, however, no mechanisms for potential improvement of kinetics have been revealed.

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

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

- One of the best spectra of collaborations within the DOE program - CoE, national and international. Most praiseworthy! The relationships among University of Hawaii, Hawaii Hydrogen [Carriers LLC] and UOP are not clear relative to the DOE CoE effort described here.
- The project has well organized and justified collaborations.

Question 5: Approach to and relevance of proposed future research

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

- Work on $LiBH_4/MgH_2$ catalysts is interesting; should consider expanding this effort in favor of the proposed $NaAlH_4$ work. Also, HRL has tested a whole host of catalysts for this reaction; need to ensure that this work is not being duplicated.
- Reasonable. Get to the bottom of the Ti catalyst story ASAP and get on to the future. Get beyond alanates quickly, as planned.
- The future steps are consistent with the eventuality of a discontinuation of activities on alanate. The alternative hydrides already chosen all deserve potentialities.
- Would be good to coordinate with ST-15 and STP-5 [Brookhaven and Stanford University] projects.

Strengths and weaknesses

Strengths
- Excellent command of analytic tools. A hard-working PI, group and other collaborators. An impressive example of the power of external collaboration.
- The project has adequate expertise and a consolidated network of collaboration of high level.
- High scientific level of PI and collaborators, close coordination and collaboration.

Weaknesses
- Probably trying to do too much at once. This reviewer is a bit confused by the apparent loose and incomplete ends.
- Non-substantial for project in general.

Specific recommendations and additions or deletions to the work scope

- The cancellation of alanates must be the result of an overall evaluation involving all the results achieved in the Program and the joint evaluation in the MHCoE.
- Would be good to extend collaboration with IPHE-country laboratories.
- Suggest moving away from alanate systems much faster.
- Get to the bottom of the Ti catalyst story asap and get on to the future. Get beyond alanates quickly, as planned.

Project # STP-07: High Throughput Combinatorial Chemistry Development of Complex Hydrides

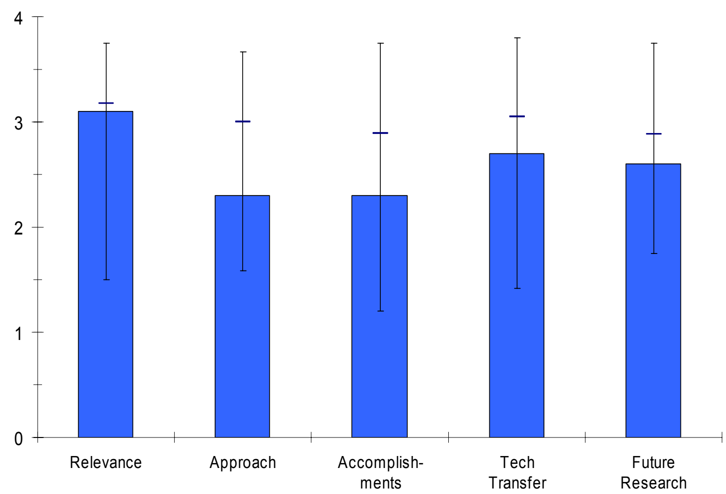
Guanghui Zhu; Intematix Corporation

[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

The objective of this Intematix Corporation project is to discover catalysts for metal hydride systems that achieve fast kinetics and high selectivity, thus meeting DOE's 2010 targets for start time (4 s), flow rate (0.02 (g H_2/s)/kW) and refill time (3 min). The approach consists of metal hydrides preparation, combinatorial catalysts preparation, and high throughput screening of catalysts. Work in 2006 is focused on screening catalysts for MgH_2+Si, Li-Mg-N-H, and $LiBH_4$+MgH_2 system dehydrogenation and rehydrogenation. Catalyst screening for $Mg(BH_4)_2$ and $Ca(BH_4)_2$ dehydrogenation may also be studied depending on the synthesis progress at Sandia National Labs.

Overall Project Score: 2.5 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- The project appears to have relevance to the metal hydride CoE. It's a little hard to tell though because so little information was contained in the poster.
- Work is in support of Sandia and HRL projects within CoE, and thus indirectly is connected and attentive to the President's HFI and DOE RD&D plan.
- The identification of catalysts and new hydrogen storage systems is a critical aspect for reaching the DOE targets.
- Scope of the catalyst search is only applied to well known chemical hydride systems with well known limitations that limits overall probability of success of the project. Combinatorial approach is good.
- Rapid screening important to identifying promising material candidates for further study.
- Supports both MHCoE and CHCoE. [There are 2 separate cooperative agreements between Intematix and DOE; one covering the work with the MHCoE and one covering the work with the chemical hydrogen CoE.]

Question 2: Approach to performing the research and development

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

- The title of the poster is "High Throughput Combinatorial Chemistry Development of Complex Hydrides." From the information contained on the poster, it is difficult to determine if in fact the approach is high throughput or combinatorial. The techniques used in this study are considered proprietary to the members of the CoE.
- The project is very focused toward mostly one area, discovering new catalysts for specific H-storage reactions using combinatorial screening. The second limited area involves some computational efforts to prejudge systems. It is not clear to me how the latter differs from other a priori computational efforts scattered throughout the DOE program.
- The combinatorial approach is a good one.

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

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

- Intematix performed a database search and calculations to identify 15 systems that have capacity of > 6 wt.% and P-T windows that are close to the operating conditions of interest. In addition they showed some screening data for Mg_2Si hydrogenation. No catalysts were found for the conditions of interest. This is not a lot of progress in over a year since the start of the project. There are several milestones between now and September with little indication of where they are in relation to the milestones.
- The results have been limited so far, given the fact the project started in Jan. 2005. To be fair, much time and trouble was spent in setting up the high-throughput equipment and procedures and so progress should be more observable in the next reporting period.
- Despite significant searching, no catalysts have yet been identified for the hydrogenation of Mg_2Si.
- Some success on catalyst search for chemical hydride CoE, but not much support to MHCoE.

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

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

- Collaborations are between the CoE members and appear to be good.
- There are only two collaborations at the moment. SNL and HRL. The CoE concept should make the way for more.
- The project appears to be very well interfaced with the needs and issues of the other projects in the metal hydride CoE.
- Need to have more interactions with CoE members.

Question 5: Approach to and relevance of proposed future research

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

- Most of the work listed as future in fact has very near-term milestones. The collaboration with HRL which may represent the best hope for a significant Intematix contribution to the CoE has a September milestone for catalyst selection.
- Reasonably good, and entirely centered on activities and reactions pioneered by HRL and SNL. That is good and proper, but I have my doubts on the future of the Li-amide system.

Strengths and weaknesses

Strengths
- A needed catalyst screening support for the other CoE partners.
- This is a key activity for the success of a number of approaches in the metal hydrides CoE. The rapid combinatorial screening approach appears to be working well.

Weaknesses
- It appears to be somewhat difficult to perform the in-situ catalyst screening process at the elevated temperature and pressure conditions required of some hydrogen storage approaches.

Specific recommendations and additions or deletions to the work scope

- Intematix needs to be more forthcoming in its presentations.
- Expand support to other CoE partners and other storage systems (e.g., AlH_3, other borohydrides,…).
- The milestone for the identification of Mg_2Si hydrogenation catalysts is June 2006. What happens if no suitable catalysts are identified by that time?
- Why continue with Mg_2Si system?
- None.

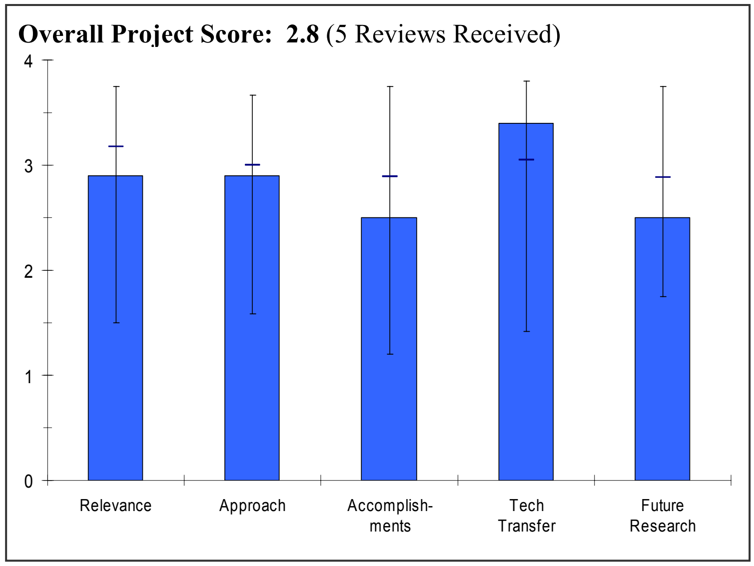
Project # STP-08: Synthesis of Nanophase Materials for Thermodynamically Tuned Reversible Hydrogen Storage

Channing Ahn; California Institute of Technology (CalTech)

[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

Nanoscale hydrides and hydride precursors are necessary to understand kinetic limitations, which are ultimately tied to refueling rates. This CalTech project is using a variation of a gas condensation technique to synthesize hydrides with smaller particle sizes and higher purity than those achievable with mechanical attrition.



Question 1: Relevance to overall DOE objectives

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

- This nano-size approach, if successful, will require that techniques be developed to synthesize larger quantities of materials.
- Very largely addresses the storage needs to achieve the President's HFI and DOE's RD&D plan.
- Clearly focused on what is emerging as the key problem in the sub area of complex hydrides.

Question 2: Approach to performing the research and development

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

- The gas condensation approach is considered to be a good one from the viewpoint of the quality of the nanosized material obtained.
- The project uses a vapor condensation method to produce nanosized particles for increasing the reversibility and kinetics of H-storage reactions, in particular the HRL destabilization reaction $Mg_2Si + 2H_2 \leftrightarrow 2MgH_2 + Si$. The use of vapor condensation is a much-needed tool within the DOE program. I am a little nervous about the very strong focus on the Mg_2Si reaction alone, so far. It may have inherent limits.
- An intelligent approach to the kinetics problem, only real question is if particles will retain their size.
- Stabilization of nano-particles during cycling is not considered.

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

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

- The quality of synthesized nano-size Si particles was very good. No results were presented on the synthesis of nano-size Mg particles.
- Respectable so far, given the rather small funding level for this project. Interesting Si results. The PI is to be complimented for the frank admissions of problems and negative results. Negative results are indeed needed results for the whole picture.
- Made particles and showed they had thin layers of oxide relative to typical materials. Reduced particle size further.

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

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

- The project appears well coordinated with other activities associated with Mg_2Si.
- Excellent collaborations.
- Very well connected. With many participating partners making meaningful contributions.

Question 5: Approach to and relevance of proposed future research

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

- The project should be starting some work on another hydrogen storage material, since it is possible that the hydrogenation of Mg_2Si may not be possible under reasonable conditions, even with the nano-size approach.
- Fine, but should soon move on to other systems than Mg_2Si. That system may turn out to be fundamentally irreversible. It is perhaps not too early to think about the economics of making nanoparticles by vapor condensation into inert gas. Too expensive for large scale vehicle application?
- Plan is good if a bit slow.
- Not clear which systems are proposed to be investigated besides magnesium silicide.
- Why continue on Mg_2Si since it does not appear to be reversible?

Strengths and weaknesses

Strengths
- The gas condensation approach looks like a good way to synthesize high quality nano-size materials.
- Use of a technique other than ball milling to make nanosized materials.
- Well focused on key problem.

Weaknesses
- The quantities of materials that can be synthesized by the gas condensation approach appear to be on the low side.
- A bit too focused on one storage reaction, $Mg_2Si + 2H_2 <-> 2MgH_2 + Si$.
- Program seems to be progressing slowly.
- Limitation to the Mg_2Si systems. Stability of nano-particles under operating conditions is not addressed.

Specific recommendations and additions or deletions to the work scope

- Add another key material for nano-size synthesis and study to this project.
- Expand to other systems where nanosized reactants may have benefit. Start to assess economics and cyclic stability (size retention) of nanosized particles, especially in Mg-based systems.
- Speed-up a go/no-go decision on magnesium silicide approach. Address stability issues for nanoparticles under operating conditions.

Project # STP-09: Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

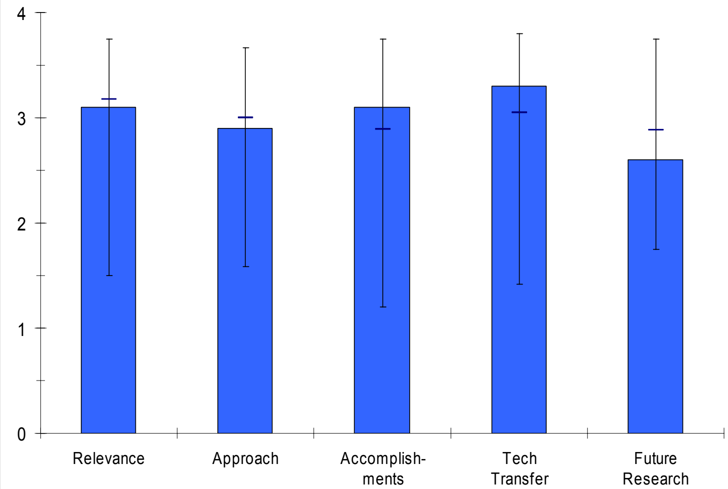
Dhanesh Chandra; University of Nevada-Reno

[Partner of the DOE Metal Hydride Center of Excellence]

Brief Summary of Project

The primary objective of this University of Nevada-Reno (UNR) project is to determine the effects of gaseous impurities (ppm levels of O_2, CO, H_2O etc.) in the H_2 on long-term hydriding/dehydriding of complex hydrides, and a related secondary objective is to determine the mechanisms of degradation. Research in 2006 is focused on thermodynamic studies, including hydrogen charging/discharging effects, vaporization thermodynamics of precursor materials, and differential scanning calorimetry, as well as crystal structure studies.

Overall Project Score: 3.0 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- The project indirectly supports the President's HFI and the DOE's RD&D plan. It is not completely clear how some of the diverse activities fit in.
- This program is focused on what will be an area of concern when the kinetics problems are beaten. It is not the most important problem, but it is good that someone is working on problems that will emerge so that the DOE Hydrogen program moves swiftly.
- The objective of the work is to study the effects of gaseous impurities on the capacity and performance of complex metal hydrides. The work at UNR is highly relevant to the MHCoE. Understanding these effects on storage materials is important in the specification of hydrogen quality as a fuel for fuel cell vehicles. Equally important is understand the generation and release of gaseous species upon repeated cycling that may be harmful to a fuel cell.
- There is misalignment with the alloy selected for testing versus the future direction of the MHCoE. The decision on alloy selection should be a consensus among all the principals.

Question 2: Approach to performing the research and development

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

- The project needs to be re-aligned with the ongoing progress in the metal hydride CoE and other related work. There is not enough integration among the relevant projects.
- The project was apparently created to develop a database of experimental knowledge on gaseous impurity effects in various candidate hydrides. This objective is extremely important to solving the on-board storage problem. However, several other activities have seemingly crept into the project. Because this project is rather lightly funded, this will almost certainly dilute the main objective, impurity studies.
- Sound approach to aging, could benefit by sampling gas released form hydride bed to see to what extent impurities were removed, and what purity is going to the fuel cell. This would allow a mass balance on impurities to confirm results, and would give the added benefit of showing how pure the gas going to the fuel cell will be. However, much of the other work is interesting for its own sake, but not very helpful to advance

storage. The various phase transformations and suggestive rate work do not much add to our knowledge of how to store hydrogen. That work would be better done for NSF or BES.
- UNR is studying the effects of pressure cycling on the capacity and performance of metal hydrides, in 2005, Li_3N as a precursor/model compound. In addition to determining the loss of capacity, UNR is also attempting to determine the nature of structural and compositional changes in the material on cycling in order to determine degradation mechanisms. UNR also looks for volatile species released from the system that could be harmful to the storage system or fuel cell system components.

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

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

- The technical progress based on the selected alloy is good. The characterization work is very good. The main issue is the pre-mature choice of the alloy. This alloy (and corresponding family of alloys) is subject to potential no-go.
- Good, given the very small funding this new project has received. The impurity cycling on the amide system has been useful. The experiments should be redesigned with selected individual impurities and levels. Is the loss seen with the Li_3N studied due to non-H_2 impurities or NH_3 loss?
- Should check for ammonia levels in exit gas, not only to see if NH_3 loss is exacerbated or diminished by impurities, but also to ensure capacity loss is not due to reaction with N group. Alternately could check N still in sample.
- Excellent progress in understanding a lot of phenomena which are caused by impurities.
- Progress has been quite good for the funding received. Over 1000 cycles have been completed on Li_3N that showed about a 2% decrease in capacity.

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

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

- The alloy selection is out of step with the MHCoE findings.
- Good collaborations in place and to be developed, apparently.
- Adequate and improving.
- UNR has active collaborations with a number of organizations some of which provide a service to UNR to characterize these materials

Question 5: Approach to and relevance of proposed future research

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

- This is a very valuable project. The effectiveness of this project would greatly enhance if there is better coordination on alloys to be studied. Need to address the uncertainties and contingencies.
- The plan has seriously deviated from the main practical objective, impurity/cyclic life quantification, to a confusing variety of other fundamental studies: Li_3N evaporation, crystal structures, DSC studies, lattice dynamics, etc. Why? Aren't many of these other studies going on elsewhere within the DOE/CoE program?
- Future work seems less well formulated. Amides have been largely discounted for hydrogen storage due to ammonia formation. Boron based materials are growing in importance, BH_4 based hydride testing seems more valuable than the explicitly planned work.
- Should be focused on the impurity effects in systems with [on] more big scale.
- A comprehensive research plan is in place for 2007. The plan includes impurity studies, high-pressure cycling studies, in-situ hydriding/dehydriding x-ray diffraction and neutron diffraction studies, and vapor pressure studies. The plan almost seems too ambitious for the budget.

Strengths and weaknesses

Strengths
- Good technical capabilities. Good characterization techniques.
- Impurity/cyclic life studies very important to storage success.
- Important work and many strong tools available.
- Project is well designed and integrated with other research in frame work MHCoE.
- Very good suite of analytical equipment that is augmented by collaboration with NIST and ANL neutron sources.

Weaknesses
- There is a significant disconnect between the substantial work done versus the future direction of the MHCoE candidate alloys. Need stronger coordination with the MHCoE.
- Too many other diversions.
- Diffuse focus, should focus strongly on more work in the key area - degradation of storage material.
- It is not clear how close the collaboration between UNR and the MHCoE. As the CoE shifts focus, so should UNR.

Specific recommendations and additions or deletions to the work scope

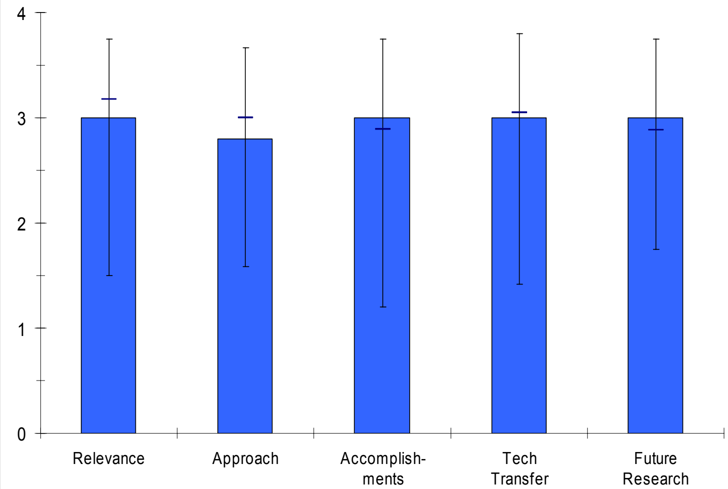
- The project performed substantial work on an alloy that is being discontinued for further work. This project should be considered for re-alignment. The future work scope does not match the future direction of the MHCoE. The proposed could be substantially rationalized. Some of the work could be allocated to SwRI. This project should be closely monitored for its effectiveness.
- Consider virtual elimination of all activities other than impurity/cyclic life studies. There is a widespread dearth of impurity cycling data on most modern storage materials, including alanates, amides, destabilized hydrides, etc. Such data is important to practical engineering considerations, as well as developing trends that may be applicable to other future materials. Suggest more funding for the principal (impurity) effort.
- Focus on hydrides more likely to see use (boron based), and modify apparatus to look for degradation gases in effluent stream, or at least look for loss or conversion of all elements in the material.
- All is good. I recommend expanding the investigation of impurities effects on properties of scales "systems with additional financial support.
- UNR should be strongly encouraged to look for evolution of fuel cell-harmful species upon cycling complex metal hydrides, particularly those that contain N. The experiments on impurity tolerance should be conducted one impurity at a time at various concentrations to enable a fuel quality specification for fuel cell vehicles. This information should be available for consideration by SDOs [Standard development organizations] such as SAE who are attempting to define an international standard for hydrogen fuel quality for fuel cell vehicles.

Project # STP-10: Chemical Vapor Synthesis of Nanocrystalline binary and complex Metal Hydrides for Reversible Hydrogen Storage

Zak Fang; University of Utah

[Partner of the DOE Metal Hydride Center of Excellence]

Overall Project Score: 3.0 (5 Reviews Received)



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 nanosized solid metal hydrides, and to demonstrate the effectiveness and unique properties of nanosized solid hydride materials for hydrogen storage. This year, the University of Utah has demonstrated the feasibility of synthesis of nanosized metal and metal hydride powders using CVS reactors and discovered that a combination of lithium hexaaluminum hydride (Li_3AlH_6) with lithium amide can produce a system that has 7% reversible hydrogen storage capacity at temperatures below 300°C. An on-going effort is directed toward PCT analysis of this material system. The University of Utah team has also improved and developed a unique high energy, high pressure reactive milling process for synthesis and processing of complex metal hydride material systems.

Question 1: Relevance to overall DOE objectives

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

- This project is targeted at discovering and producing new nanocrystalline reversible hydride materials.
- The project addresses some key objectives of the DOE plan.
- Relevance of ideas is good, but would be higher if the decomposition temperatures could be lowered.
- Materials selection is only limited to alanates and amides that is questionable based on prior work.

Question 2: Approach to performing the research and development

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

- The project approach is considered to be good. The CVD synthesis approach looks promising and is potentially scaleable to larger material quantities.
- The project addresses a new class of hydrides including a proprietary storage material and different technical preparations.
- Not clear exactly how the materials discovery was made: Was it simply a guess? Intuition? Nevertheless, the discovery is interesting.
- Lack of thermodynamic heat balance considerations ("useable" storage capacity). Stability of nano-sized hydrides upon cycling is not addressed. Gas phase analysis (presence of ammonia, etc) has not been presented.

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

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

- A significant amount of results have been obtained. Hydrogenation and dehydrogenation temperatures are relatively high.
- The project has already analyzed and developed novel systems with over H_2 7 wt.%.
- Very impressive amount of work in the first year of a project with little funding! Demonstrated a reversible >7 wt.% storage reaction. Novel idea demonstrated (w/ combination of Li_3AlH_6 and $LiNH_2$), and next year will refine some of these ideas. The processing and thin film growth ideas and results look interesting as well. Temperatures of decomposition still too high (~200-350°C). Why are the temperatures of decomposition for the second desorption so much higher (all the way to 350°C) than the first time (where the reaction seems to be largely complete by 250°C)?
- For the amide work at high temperatures, it's quite likely that there is some decomposition to NH_3.

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

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

- Technical collaborations are taking place in a number of areas.
- The project has some collaborations under development in the coming year.

Question 5: Approach to and relevance of proposed future research

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

- The future work looks reasonable.
- The future steps are consistent with the already achieved results.
- Main approach should be to (a) understand the mechanisms for this reaction, and (b) to try and overcome the obstacle of high temperatures of desorption, and understand the thermodynamics of this two-step reaction (are both steps high-temperature steps, or are one or more simply kinetically limited?). Also, need to obtain and present data on the kinetics of rehydriding. Also, MS should be performed to verify the levels of NH_3 and other species being evolved during this reaction.

Strengths and weaknesses

Strengths
- A good, solid project. A lot of progress is reported, despite the relatively small funding on the project. The CVD approach to materials synthesis looks promising. The high pressure hydrogen atmosphere milling is interesting.
- The novel materials already developed are a good scientific and technological basis.

Weaknesses
- The thermodynamics of the new lithium-based material needs to be determined.

Specific recommendations and additions or deletions to the work scope

- None.
- Materials selection for future research is questionable based on prior art. Suggest reconsidering project scope to move away from alanate/amide systems. Incorporate a quick go/no-go decision on Mg_2Si systems.

Project # STP-12: ORNL's Hydrogen Storage Research in support of the DOE National Hydrogen Storage Project

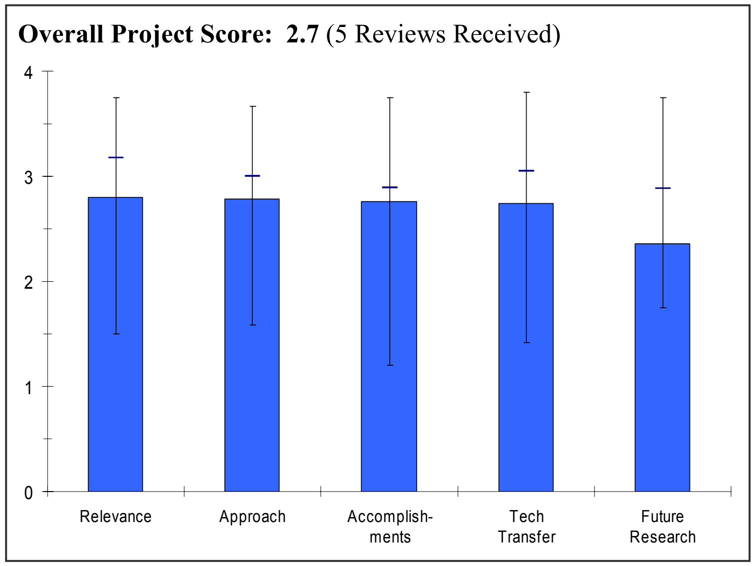
Gilbert Brown, Metal Hydride Center and Dave Geohegan, Carbon Center; Oak Ridge National Laboratory

[Partner of the DOE Metal Hydride and Carbon Materials Centers of Excellence]

[Oak Ridge is a partner in both the Metal Hydride and Carbon Centers of Excellence. Both projects were covered under this single review.]

Brief Summary of Project

Oak Ridge National Laboratory (ORNL) has two major areas of research on hydrogen storage. As part of the carbon-based hydrogen storage CoE, ORNL is attempting to control the synthesis and processing of a novel form of carbon – single-walled carbon nanohorns – as a medium with tunable porosity for optimizing hydrogen storage. For the metal hydride CoE, ORNL is developing solution-based synthetic methods for the preparation of complex anionic materials and amides of light elements for reversible storage of hydrogen.



Question 1: Relevance to overall DOE objectives

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

- Low capacity materials. High cost carbon fibers produced by laser desorption or (maybe) arc synthesis. Alanates still low capacity compared to targets.
- Reversibility is key.
- This project covers ORNL activity in two centers of excellence - carbon and metal hydride. The two areas of research folded into a single presentation makes it difficult to review each separately when composite scoring is necessary.
- Project focused on working towards DOE targets and well aligned with the overall RD&D objectives.
- These are complicated and bulky molecules that are unlikely to achieve any storage density targets.

Question 2: Approach to performing the research and development

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

- Good control over tube & horn properties; good characterization capabilities. Volatile hydride concept interesting, but capacity suffers. Synthesis not so important. Reversibility needs to be addressed more directly.
- A novel carbon-based material - nanohorns- is being developed for potential hydrogen storage and is based on existing experience and expertise at ORNL. In addition, the synthesis of metal hydrides is being studied. The approach taken for each of these very different areas is generally will thought out and effective. Unfortunately the ability of the subject materials to meet minimum requirements for gravimetric hydrogen storage density appears to be very low.
- Well thought approach taking advantage of long expertise in synthesis and of access to a range of characterization techniques. Working interactively with other members of the CoE to understand and optimize these materials.

- [Carbon Project:] The project needs to be integrated with other carbon nanotube research and modeling work ongoing within the carbon CoE. [Metal Hydride Project:] More integration with complex hydrides solid synthesis efforts within the CoE needed.
- [Carbon project:] PI is trying to synthesize a complicated molecule or cluster of molecules and then decorate (without control on location) with precious metals. This process sounds incredibly expensive and the nano horn clusters can't possibly be robust enough to maintain form and cluster shape.

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

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

- Good synthesis and characterization results; poor capacities of fibers. Good alanate synthesis; little progress on reversibility.
- Good progress has been made supporting the project's stated goals and objectives. Unfortunately the materials being studied alanates and nanohorns appear to have storage capacities that fail to meet even the minimum system requirements.
- [Carbon project:] Need collaboration with modeling efforts within the carbon CoE to estimate properties/ evaluate the feasibility of enhancing hydrogen physisorption. Good progress demonstrated in relatively short time. Effective synthesis-processing-characterization loop for growth of tunable porosity, surface area and graphitic structure SWNT and metal decorated SWNT with optimized hydrogen storage capacity.
- Materials have been synthesized and tested but results are poor.

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

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

- Little evidence of external collaboration.
- Strong interaction in both CoEs.
- Established collaboration with other members of the CoE in the form of sample performance characterization.
- [Both projects:] Need to strongly interact with experimentalists and theoreticians within the respective CoEs.
- Didn't list any key partners who are experts in the field.

Question 5: Approach to and relevance of proposed future research

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

- [Project A, Carbon Center] Need to address low temperature tube synthesis. Assume work will stop in the area of carbon nanotubes; go/no-go decision stops nanotube work. Need alternate paths for Project B [Metal hydride center], i.e., if new material isn't reversible, what new approaches will be pursued to attain reversibility.
- Future work should carefully filter out work on materials that have little or no potential to meet storage system requirements (such as alanates and/or nanohorns?) Then focus remaining resources on new materials discovery and/or materials that show promise of meeting targets (amides/imides?).
- Sufficiently planned future activities, building upon recent progress and existing expertise.
- [Carbon Project:] Focus on basic research for effects of optimized properties of the nanohorns. [Metal Hydride Project:] Strong collaboration within the solid state development group of complex hydrides needed.
- Why make more when the samples provided have low storage capacity.

Strengths and weaknesses

Strengths
- Good synthesis, characterization, and modification capabilities.
- Strong materials synthesis and testing capability at ORNL.
- Strong synthesis and processing background; good foundation for sound R&D.
- [Carbon project:] Synthesis capabilities of nanohorn with no apparent graphitic impurities and some tunable properties. [Metal Hydride Project:] Synthesis trials of the low stability complex hydrides with new routes.

Weaknesses

- High dollar, low capacity materials. Alanate work has limited scope. Characterization and synthesis are good, but needs to be more focused on solving reversibility issues with some Edisonian component to try a number of approaches. Some value to understanding why an approach doesn't work, but need ability to try multiple approaches.
- Materials selected for initial study appear to have limited potential to meet DOE system targets.
- Quite challenging field which may not deliver within the tight timescale set for reaching the storage system targets.
- [Carbon project:] Need to integrate theoretical calculations to help optimize properties.
- Materials use expensive catalysts haphazardly placed on the molecules - no control compared to the MOF approach. The materials are bulky and contain many dead spots for storing hydrogen. It is unlikely that these materials will ever achieve reasonable storage densities.

Specific recommendations and additions or deletions to the work scope

- Alanates—attack reversibility more aggressively.
- Refocus future work on new materials discovery.
- Keep close track of progress towards targets and set milestones. Project (A) [Carbon Center] In view of the tight schedule, intensify efforts for understanding the supercritical hydrogen adsorption mechanism for the development of optimized SWNTs and composites with tunable pore sizes, and for getting better insight in their metal decoration with very fine metal clusters in high loadings. Consider added value/feasibility of addressing synthesis scale-up and operability issues, much earlier in the program than foreseen. Comment: Under Project (B) [Metal Hydride Center] it is mentioned: "Percentage of effort in remainder of FY06 and FY07: 10-15% catalyzed alanates, 40-45% metal borohydride, 40-45% metal amide/imide (M-N-H)" contrary to what it was announced during the MHCoE presentation where the effort for a/imides was said to be reduced down to 5% and the work on alanates to be suspended. This may point to the need for better communication within the MHCoE.
- [Carbon project:] More focus on optimization of properties through using modeling efforts within the CoE. [Metal hydride project:] Integration of efforts with solid state synthesis ongoing work within the CoE and also with basic research.
- This project should be terminated. The results demonstrated are extremely low and the synthesis methods are complicated. This project is academic at best and should strongly be considered for termination with the SWNT go/no-go decision. Expensive catalysts are being used and still delivering low results. This work has been done previously and is unlikely to provide valuable knowledge or insight for breakthroughs in future materials.

Project # STP-15: Conducting Polymer as New Materials for Hydrogen Storage

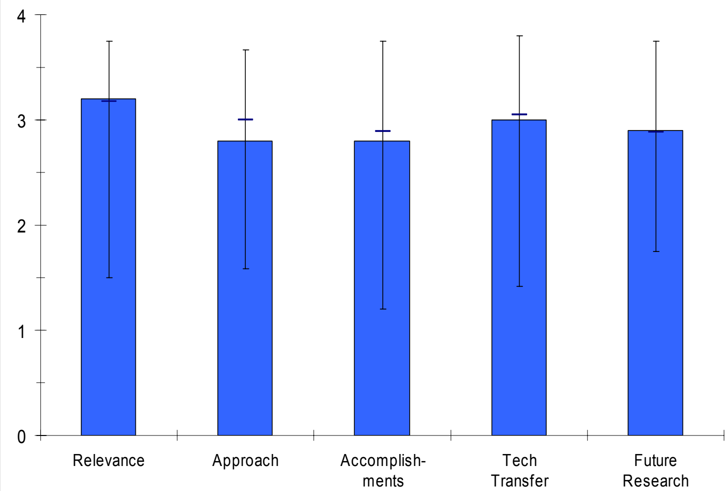
Alan MacDiarmid; University of Pennsylvania

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

The goal of this University of Pennsylvania project is to identify and demonstrate the conducting polymer species previously reported in the literature to give ~8 wt.% hydrogen storage. 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.

Overall Project Score: 2.9 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Potential game changer material with uncertainty in results.
- If conducting polymers, or any low-cost polymers, were discovered that could reversibly store and release significant quantities of hydrogen, then this would constitute a major breakthrough in hydrogen storage materials.
- The project addresses most key objectives of the DOE plan.

Question 2: Approach to performing the research and development

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

- Need to address the material handling and purification and its effect on the storage capacity.
- Good approach except use of TPD for H_2 quantification. Use of PCT or TGA seems indicated for materials that can be made in gram quantities.
- This project is providing a thorough investigation to determine the potential of conducting polymers as hydrogen storage materials.
- The project presents an interesting development and application of polymers. The project is well concentrated in solving and verifying chief performances.

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

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

- The current results are affected by the materials' quality. However, the most recent literature results are very promising.
- Good progress in material characterization and initial results obtained. Seems to confirm that materials do not take in much hydrogen.

- Despite thorough analysis, the results of the Korean work that reported 8 wt.% hydrogen in conducting polymers have not yet been reproduced.
- The PI did not present all the results. Only part of the experimental activity is presented, showing interesting progress.
- Although a negative result was obtained, this work is important in attempting to verify a previous result. Null result not exciting, but still important.

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

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

- Well connected.
- There appears to be good collaboration with NREL on this project.
- The project has close collaboration with key partners.

Question 5: Approach to and relevance of proposed future research

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

- Plan seems appropriate, but again TPD seems to be a suboptimal method to determine H_2 uptake.
- There is a go/no-go decision point at the end of FY2006 based on establishing greater than 1 wt.% hydrogen storage in polyaniline.
- The future steps are consistent with the already achieved results.
- Suggest that the impressive capabilities of this laboratory be applied to other new, innovative materials

Strengths and weaknesses

Strengths
- A novel and innovative idea. Strong competency in the field. The most recent literature results suggest 3 wt.% capacity at room temperature.
- Team is well poised to address question.
- The PI is a world-renowned researcher on conducting polymers and received the Nobel Prize for his work in this area.
- The basic expertise and the established collaborations can guarantee successful results.

Weaknesses
- The current results are marginal.
- TPD is not the best way to measure H_2 uptake. Go/No-Go point seems awfully low for a hydrogen storage medium, consider raising to at least 2% in unmodified, room temperature, polymer.
- It may be that the reported Korean work that indicated significant hydrogen storage in conducting polymers was in error, and that conducting polymers are not capable of storing any significant quantities of hydrogen at room temperature.

Specific recommendations and additions or deletions to the work scope

- Need to leverage the activities with the most recent literature results.
- Change to PCT measurements of hydrogen. At the very least confirm with volumetric or TGA in a large sample. If hydrogen is taken up, obtain delta H using PCT curves at various temperatures.
- Should it be determined that conducting polymers are not suitable vehicles for hydrogen storage, this project should be continued, but redirected into a more promising area of research that builds on the research interests of the PI. Based on the slides that were provided during this review, the PI appears to be interested in investigating the production of hydrogen from ethanol via an electrical discharge route.

Project # STP-16: Enhanced Hydrogen Dipole Physisorption

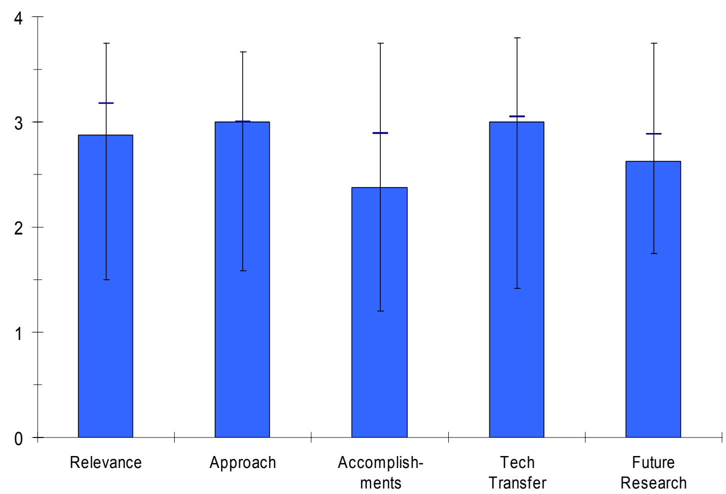
Channing Ahn; California Institute of Technology

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

The goal of this California Institute of Technology 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).

Overall Project Score: 2.7 (4 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Aligned well, though gravimetric goal not clearly dealt with. Still very valuable work.
- Aerogels and activated carbon are materials that have to be studied. Nevertheless the first results do not look promising at all.
- There is a possibility of getting close to the DOE 2010 targets with this approach, albeit at a temperature of 77K.
- Potentially physisorbents can provide higher storage densities than compressed hydrogen.

Question 2: Approach to performing the research and development

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

- Approach is appropriate and probable to lead to progress.
- The basic approach of increasing the surface area per unit volume, and increasing the adsorption enthalpy by additions such as boron to carbon aerogels is sound.

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

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

- Showed that one can to some extent overcome area limitations with catalysts; 38 g/L in activated carbon.
- A value of 5.4 wt.% hydrogen at 77K with an activated carbon is reported.
- Project did not demonstrate a significant progress towards meeting DOE targets versus prior art.

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

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

- Nicely connected.
- There appear to be good collaborations with other members of the carbon CoE.

Question 5: Approach to and relevance of proposed future research

This project was rated **2.6** for proposed future work.
- Appropriate plans, though unclear how the 1.1 nm pore size will be achieved.
- The future plans look very general and specific targets must be fixed.
- The proposed research on boron additions to carbon aerogels is good.

Strengths and weaknesses

Strengths
- Sound understanding of physisorption processes in materials. Interesting analyses of volumetric effects in high porosity, adsorbing materials.

Weaknesses
- It may be quite difficult to achieve the optimum pore size of 1.1 nm in the carbon-based materials. There does not seem to be a clear route to get to this objective.

Specific recommendations and additions or deletions to the work scope

- Establish a route with backup plans to achieve 1.1 nm pores with maximal surface area to mass ratio.
- None.
- Explore higher pressure operation (500-700 bar).

Project # STP-17: Optimization of SWNT Production and Theoretical Models of H_2-SWNT Systems for Hydrogen Storage

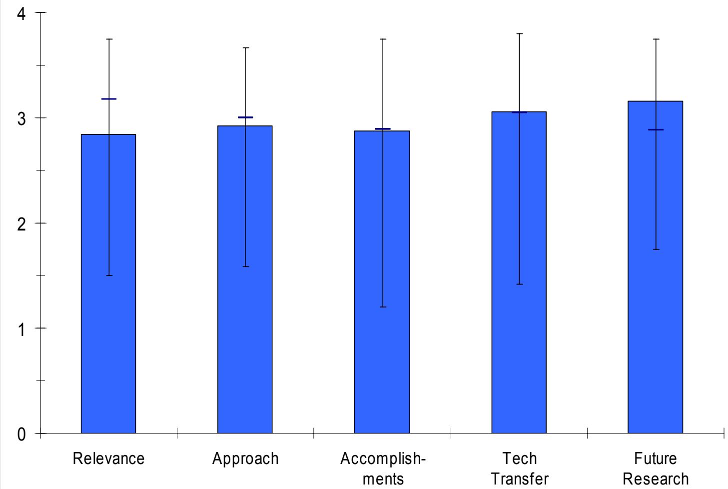
Boris Yakobson; Rice University

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

Rice University is developing predictive models of materials structures 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 SWNT). In 2006, Rice is exploring full utilization of physisorption by van der Waals dispersion forces, using HIPCO method to produce nanotubes of preferred diameter (and length) for better hydrogen adsorption, and performing quantum mechanical computation for precise description of van der Waals attraction.

Overall Project Score: 2.9 (7 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- Nanotubes still low capacity materials.
- The methodology is interesting but the materials are not very promising for hydrogen storage.
- This project has two major thrusts - modeling of the hydrogen storage capability of single-walled nanotubes (SWNT) and enhanced production of SWNTs.
- The program has a strong experimental group and a strong theory group. More interaction between experiment and theory should be encouraged regarding focusing the program along more relevant directions in the cloning project.
- The project assists in realizing and quantifying the interactions of hydrogen with materials. This could play an important role in directing research resources in a later stage.

Question 2: Approach to performing the research and development

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

- Good mix of QM and classical approaches to get results for large systems.
- The milestone plans and roadmap for this project is ambiguous. Good level of integration within the Rice program and a few other projects. The threshold for go/no-go decision should be transparent.
- The strategy of this theoretical investigation is novel and useful for the storage problem in C-based materials.
- The approach proposed to address both of the technical objectives of this project is sound and is based on utilizing the experience and capabilities at Rice.
- Approach is very good. Theory group is addressing important issues for enhancing uptake and for increasing the temperature for efficient uptake. Consideration of spillover effect should be encouraged.
- The project needs to be integrated with other storage work done within the carbon CoE.
- Same approach as all the other projects. No good explanation is given on how these modeled nanostructures will be formed. Isn't this work being done by Jim Tour and Ralph Yang already?

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

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

- Interesting results for metal decorated tubes. Classical force field for H_2 adsorption onto SWNTs.
- It is difficult to distinguish the accomplishment of this specific project. The work is to address theoretical concepts on H_2-SWNT.
- Interesting results for carbon nano-foam.
- Significant progress has been made in each area this year. SWNT production of >1 g/hr has been demonstrated of extended operational period. Model for predicting hydrogen storage potential for carbon nanostructures has been developed and model output is being assessed for accuracy. Initial storage capacities for these structures appear to be well below the system targets. Additional model improvement and refinement is planned.
- Since goals of the program are for increased hydrogen storage, more progress and emphasis on above 77K storage capability needs more consideration.
- Focus on modeling is needed as a start instead of the HIPCO CNTs generation process. Theory results should be directing the experimental efforts which should come in a later stage. Validation of the model was not addressed.
- Results match reports from 10 years ago. No novel method or results reported. Only thing possibly novel is the carbon foam? What are results and how is it made?

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

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

- Good within university. May want to work more with CoE and others.
- The collaboration with the H_2 spillover work is very good.
- Collaborations are in place with NREL and Air Products and should be expanded to other partners in the carbon-based CoE. Benefits would flow in both directions - to Rice for additional assessment of the modeling effort and to the other partners to explore performance parameters for nanostructures.
- Collaboration with group at Michigan is noted as a plus and collaboration between this experimental group and industry is strong. Collaboration between Yakobson and Tour on the control of intertube spacing is good. Collaboration between Yakobson and Tour on cloning could be better.
- Need to strongly interact with many experimentalists and theoreticians within the CoE.
- Collaboration seems weak at best. What has been delivered to Air Products or NREL?

Question 5: Approach to and relevance of proposed future research

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

- Calculations for spaced tubes look interesting. Will this work be discontinued if go/no-go decision decides SWNTs are not an option.
- Need to address the approach to 7-8 wt.% capacity at cryo conditions. Need to address the route to room temperature materials sorbent development.
- The targets are clearly set and the accomplishment of those will be important.
- Planned research appears reasonable and proper to build on past results. Emphasis should be on model refinement and use to identify structures with the highest potential for hydrogen storage. Then small scale productions of these specific structures should be pursued to validate model findings.
- A good part of future work is with Yang at Michigan. Collaboration between Tour/Hauge and Yakobson to determine intertube distance is a good project. Consideration of other factors in hydrogen storage besides uptake capacity should be considered.
- Need to focus on model optimization instead of the HIPCO reactor.
- The metal dopant and spillover mechanisms are already being worked on. What new knowledge are they contributing? Why are they not partnered with Ralph Yang of U of Michigan to work on spillover concepts.

Strengths and weaknesses

Strengths

- Solid computational work. Good approach to large scale simulations. Nanotube expertise--synthesis and characterization.
- High competency in the field. Good utilization/synergy of the resources within the national laboratories. Powerful analytical techniques and independent analysis.
- Strong SWNT capabilities at Rice coupled with extensive experience and expertise in the field.
- Tour/Hauge is a strong synthesis group and they keep a good, reliable experimental program going. Yakobson is a strong theorist on mechanical properties and is doing a good job with the nanotube separation problem.
- Theory is crucial and needed to direct materials design and results validation. Approach captures main key properties affecting H_2 physisorption.

Weaknesses

- May need more collaboration with others doing similar work. SWNTs still low capacity materials.
- Need to address the approach to 7-8 wt.% capacity at cryo conditions. Need to address the route to room temperature materials sorbent development.
- More emphasis should be given to increasing the temperature where hydrogen can be bound to carbon. Metal particle addition may not be enough. Too much emphasis is given in experimental program to controlling nanotube chirality during growth for hydrogen storage.
- HIPCO process should come in a later stage or be part of other projects. No clear link exists between the theory work and the HIPCO process.

Specific recommendations and additions or deletions to the work scope

- Focus on search for new structures/geometries that maximize storage potential – Continue production improvements at a low effort level until scale-up is justified - production of SWNT structures with low storage capacity serves little purpose.
- The budget increase from $75K to $175K should provide money for a postdoc and a graduate student to address the design of a functionalization strategy for increasing hydrogen storage and for studying the spillover effect.
- More focus on model modification and deletions of current HIPCO process.
- Furthering the model to include other materials and dynamic modeling consideration.
- The results are very poor and PI doesn't present any convincing arguments as to how this will be overcome. These materials have been poor performers and heavily researched in the past. It is unclear what value if any this project is delivering.
- Concentrate on carbon foam, drop everything else. [According to one reviewer].

Project # STP-18: Development of Carbon-Based Materials and Characterization of Hydrogen Adsorption by NMR

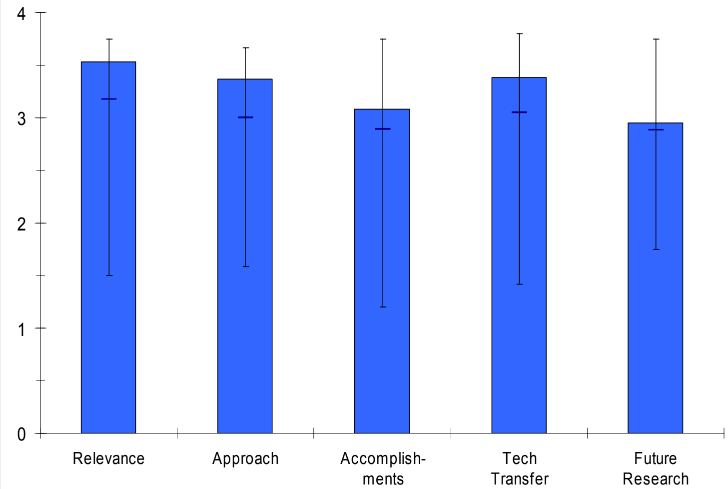
Yue Wu; University of North Carolina

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

The University of North Carolina is using NMR techniques to support team members of the DOE carbon CoE in developing reversible carbon-based hydrogen storage materials with 7 wt.% materials-based gravimetric capacity, with potential to meet DOE 2010 system-level targets. In 2006, this project is conducting NMR measurements of hydrogen adsorption in boron-doped carbon nanotubes and boron-doped graphite, investigating if boron atoms are incorporated in the framework of nanotubes and graphite, and investigating effects of doping treatment on hydrogen adsorption in polyaniline.

Overall Project Score: 3.2 (6 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- This project, under the umbrella of the carbon CoE, is well aligned with the DOE R&D plan.
- This project is intended to develop an NMR characterization tool for in-situ measurement of hydrogen storage in nanostructures.
- The reliable evaluation of hydrogen has been a contentious problem for the past ten years, and the work done by this group is impressive as a reliable measurement tool. However, more emphasis should be given to comparison of hydrogen capacity measurements between the NMR and other measurement techniques.
- Any analytical technique for measuring hydrogen storage in determining where, how many bonds are etc is always a valuable tool to the community.

Question 2: Approach to performing the research and development

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

- Good approach, involving a technique complementary to existing adsorption capacity measuring methods, giving also information on microscopic structures and dynamics. It supports the CoE members in developing reversible carbon-based hydrogen storage materials.
- Straightforward modification and improvements to existing NMR facility is planned to allow observation of hydrogen in nanostructures at pressures up to 100 atm.
- Approach is very promising from a scientific standpoint because it gives not only a measure of hydrogen uptake, but a determination of the importance of various binding sites as a function of temperature and pressure, once these aspects of the NMR capabilities of this group are implemented.
- Use of NMR technique to support CoE in developing carbon-based hydrogen storage materials.
- Is this setup only suitable for boron doped carbon structures?

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

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

- Project appears on schedule—the technique seems to be selective enough to identify promising adsorption sites and measure site-specific H_2 adsorption isotherms in B-doped carbon materials considered by the CoE.
- The NMR facility improvements have been completed and initial measurements on provided samples have been conducted successfully.
- Needs more collaboration with other projects in the program to utilize/enhance these capabilities. This fundamental research type of work can be used to validate and understand results generated within the CoE.
- The progress of this group has been impressive with the boron doped nanotubes. The calibration standard has been developed and tested. Different binding sites have been identified and progress made in establishing some relative importance in binding. Preliminary work has been done on doped polyaniline with controversial results that could be important. More progress is needed in comparing the hydrogen uptake measurements by this group using NMR and other groups using other techniques.
- Not enough was presented on the success of the technique to identify where H_2 is. Is this a project to test NMR under various conditions and materials or to determine if boron doping is effective?

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

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

- Good interaction with members of the CoE involving mainly sample characterization work and comparison of in-situ high pressure NMR adsorption data with other techniques.
- Collaborations are in place with partners in the carbon CoE. This project will provide valuable support to the CoE partners who are developing new storage materials.
- More interaction is advised with other members within the CoE.
- A strong point of this program is not only the promise of the method for characterizing many types of samples, but also the possibility of working with many collaborators who study a diverse ensemble of different materials.
- Seems to be involved with good partners. Collaborations should increase if tool is seen as valuable by other PIs.

Question 5: Approach to and relevance of proposed future research

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

- Proposed work is sufficiently planned, builds upon present experience and expands current studies - very much dependent though on the plans and progress of the material suppliers who are the co-workers from the CoE. May need to also incorporate a more systematic study of errors associated with the technique.
- Plans for future work are a reasonable mix of improvements to the characterization tool and continued support for CoE partners.
- Start working on nanohorns and other carbon materials as soon as possible (sooner than proposed in the plan).
- Proposed research overall is very interesting and will advance the program. Since many of the groups focus significant effort on hydrogen adsorptions at 77K, it would be beneficial for this group to develop capability to make NMR measurements at 77K soon, consistent with their future plans.
- H_2 adsorption measurements of the boron doped systems should be carried out soon to show their real potential. There is no point of perfecting the doping techniques if the potential of achieving high RT adsorption is not there.
- Again the focus should be on NMR, not boron doping.

Strengths and weaknesses

Strengths

- Selectivity of the characterization tool.
- Extensive experience and expertise in NMR characterization.
- NMR in-situ measurements capabilities.
- The group has been developing a complementary method for hydrogen adsorption studies with the ability to obtain binding energies for specific sites. The technique can be applied to many kinds of samples across several programs. The group is aggressive in seeking out groups to provide samples for them to measure and interpret.
- Good techniques and lab facilities.

Weaknesses

- Limitations of the technique. Work program strongly dependent upon developments in the work of the material suppliers/partners in the CoE.
- Needs more collaboration and integration within the CoE.
- Many groups working on hydrogen adsorption on carbon based systems and other physisorbed systems are focusing their efforts on hydrogen uptake at 77K. This NMR group should put effort in gaining measurement capability at 77K, as outlined in their planned future work.
- Program is not focused in where it is going or what it intends to accomplish.

Specific recommendations and additions or deletions to the work scope

- Consider including in the work program a more systematic study of the sources of errors in the measurement technique, and validating measurements, before proceeding further to more challenging materials.
- Consider offering characterization support to other organizations in the DOE Hydrogen Storage Program.
- Applying the NMR measurements to other carbon based materials.
- The group should put emphasis on developing the low temperature capability and should put emphasis on comparing their hydrogen uptake measurements with those made at 77K by other techniques. This would give more confidence all around in the reliability of the various techniques.
- Needs to explain for which hydrogen storage materials this technique would not be suitable to make measurements.

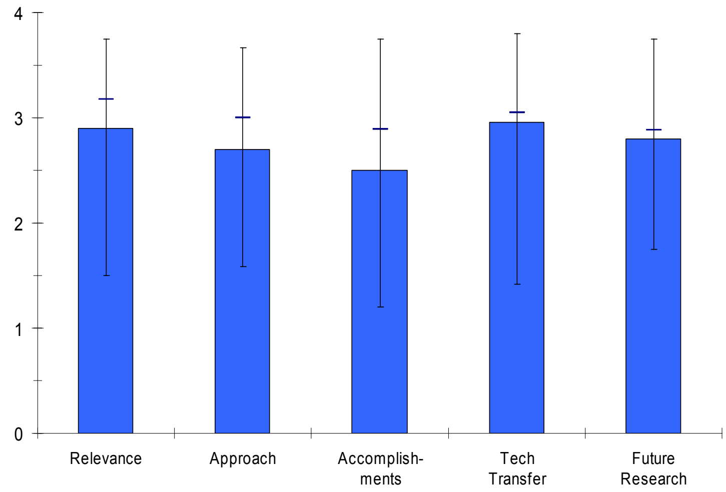
Project # STP-19: Synthesis of Small Diameter Carbon Nanotubes and Mesoporous Carbon Materials for Hydrogen Storage

Jie Liu; Duke University

[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

Overall Project Score: 2.7 (5 Reviews Received)



Goals of this Duke University project include demonstrating small diameter single walled carbon nanotubes with potential to meet the DOE 2010 goal in hydrogen storage properties, as well as demonstrating the storage potential for 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 nanotube 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 **2.9** for its relevance to DOE objectives.

- Good alignment to the overall DOE objectives working under the umbrella of the CoE.
- Effect of CNT diameter on storage capacity is already known. It is irrelevant since all nanotubes have poor storage capacity regardless of diameter.
- This project is obviously aligned with the President's hydrogen vision and the RD&D objectives. Storage is key to the hydrogen initiative and the carbon-based option is a part of the overall effort. However, it seems obvious that this option is further behind in its science base than the other two options being pursued and it is not clear that it can get much beyond the 2006 target of 6 wt.%.

Question 2: Approach to performing the research and development

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

- Systematic approach assisting in answering fundamental questions related to hydrogen storage in carbon materials; developing novel synthesis techniques that are able to yield tailored SWNTs for high hydrogen uptake.
- Nothing novel is being proposed?
- Looks good.

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

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

- Significant progress was demonstrated. Highlights of this work include the understanding of the relation between the carbon feeding rate and the diameter of prepared nanotubes and the development of a simple method for metal nanoparticles decorating of these materials.
- Nothing novel has been accomplished.
- It is difficult to understand what is accomplished during the period. 33% completion is noted in the summary slide. The tasks and specific objectives appear amorphous.
- Given the limited resources, this project could be better served if narrowed to one subject instead of 3.
- Doing extremely well.

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

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

- Extended on-going collaboration with a number of partners from the CoE concerning the material characterization.
- Are they really collaborating?

Question 5: Approach to and relevance of proposed future research

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

- Sound future plans that include the expansion of work to bulk synthesis, upscaling and systematic study of the impact of metal decoration on carbon materials hydrogen storage capacity.
- Based on other people's assumptions. This work has been done several times before without success.
- Logical progression.

Strengths and weaknesses

Strengths
- Novelty of the technique and fundamental understanding of the control mechanism of CNT diameter through carbon feeding rate variation.
- Knowledge and hard work.

Weaknesses
- Feasibility and cost considerations related to upscaling.
- The accomplishments/results are difficult to understand. Need to improve the presentation clarity by defining terms and baseline. Need to clearly state the baseline and benchmarks. The dispensing heat transfer requirement for cryo-compressed system at 100K is not defined or addressed (e.g., how much energy is required to cool room temperature hydrogen to store at 100K?).
- None obvious from the poster presentation.

Specific recommendations and additions or deletions to the work scope

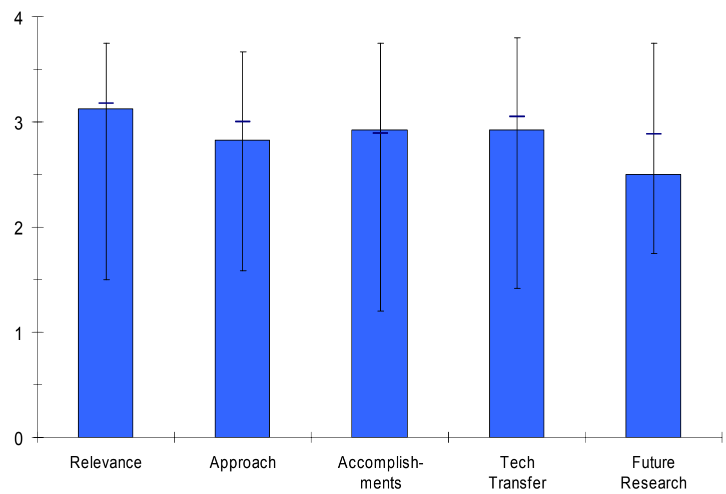
- Concentrate efforts on the demonstration of large scale production capability for small diameter SWNTs and high surface area mesoporous carbon materials with right amount of metal loading.
- Terminate this project.
- Continue this science-based project as-is, but begin to think of ways to make larger quantities for tests by others.

Project # STP-21: Carbon-Based Hydrogen Storage
Ted Baumann; Lawrence Livermore National Laboratory
[Partner of the DOE Carbon Center of Excellence]

Brief Summary of Project

Designing new nanostructured carbon-based materials that meet the DOE 2010 targets for on-board vehicle hydrogen storage of 6 wt.% H_2 is the objective of this Lawrence Livermore National Laboratory (LLNL) project. Metal-doped carbon aerogels 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.

Overall Project Score: 2.9 (4 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- The proposal to increase the hydrogen uptake by doping carbon aerogels with various metal particles is aimed at addressing the goals of the hydrogen storage problem. This is a high risk project that should be explored in the context of a high risk project. The light weight and high porosity is an attractive feature of the carbon aerogel materials. Carbon aerogels without metal additives have not been able to demonstrate sufficient hydrogen storage capacity, and the question is whether metal doping can lead to a large enhancement in storage capacity at room temperature.
- Project is limited by many of the drawbacks that CNT technology has but so far the material looks easier to synthesize and tune than CNTs.

Question 2: Approach to performing the research and development

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

- The required target capacity for the proposed system should be closer to 7-8 wt.% on system basis.
- The approach of controlling the nanopores and macropores to understand the interplay of these parameters with hydrogen uptake is encouraging. The use of different dopants to vary binding energies is desirable. The approach should emphasize that initial work will be done at 77K where quantitative studies can be done, rather than at room temperature where DOE has programmatic interest.
- Better approach than using carbon nanotubes since preparation of the materials is simpler and more scalable. Metal deposition also seems simpler and more controllable than on carbon nanotubes. However, overall the project is limited by many of the same drawbacks that CNTs have.

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

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

- Carbon aerogel samples have been prepared and characterized by a variety of techniques. Hydrogen adsorption measurements done by Ahn at Caltech shows that the hydrogen uptake of their materials depends on specific surface area so that optimization can be carried out. The addition of metal particles showed changes in the hydrogen uptake with specific surface area, but so far the effect has been to decrease the hydrogen uptake.

Measurements thus far have been at 77K, which is appropriate for exploring the pertinent effects, since uptake at room temperature is too low. Eventually, measurements at room temperature will be needed to compare the characteristic hydrogen storage behavior of these materials to others in the program.
- PI demonstrated good process in synthesizing and characterizing the aerogels. More work needs to be done to reduce precious metal loading and fully understand pore size effect on storage capacity.

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

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

- Collaborations with Ahn at Caltech are very good. In the future there are plans to interact and collaborate with Wu in North Carolina on NMR measurements. More collaborating may be possible and desirable.
- Working well with C. Ahn.

Question 5: Approach to and relevance of proposed future research

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

- It is not clear if the current activities address the minimum storage capacity of 7-8 wt.% requirements.
- Plans for FY06 are to control pore size distribution and to study different dopants, both metal and boron, which are consistent with the present program of this group. Plans to work with Wu on NMR characterization represent a step forward.
- Proved that one can obtain high surface area aerogels. However it seems that the doped materials did not show any improvement over other materials with the same surface area probably due the inaccessibility of the metal sites. Accordingly one should solve this problem before going to higher surface area.
- Good to include go/no-go points on volumetric density and metal doping reduction.

Strengths and weaknesses

Strengths
- This group has great expertise in the preparation and characterization of carbon aerogels. They are also experts in doping carbon aerogels with metals and for characterizing the resulting changes in properties. They are adventurous in trying to explore new applications for their materials.
- Aerogels should be much easier prepared than nano tubes.

Weaknesses
- It is not clear if the current activities address the minimum storage capacity of 7-8 wt.% requirements.
- The group does not have much prior experience with hydrogen storage applications. They need to focus more on what the metal doping does for hydrogen storage and why.
- Aerogel seem to have the limitation of surface area similar to that of activated [carbon]. Heat transfer and volumetric density looks like it will remain a challenge as well.

Specific recommendations and additions or deletions to the work scope

- The team should measure relative benefit of a specific dopant in a carbon aerogel host as compared to other carbon hosts. A comparison should be made of room temperature vs. 77K uptake for carbon aerogels vs. other carbons both in their pristine and doped forms.
- Could these materials make good insulators for cryo vessels?

Project # STP-25: Electrochemical Hydrogen Storage Systems

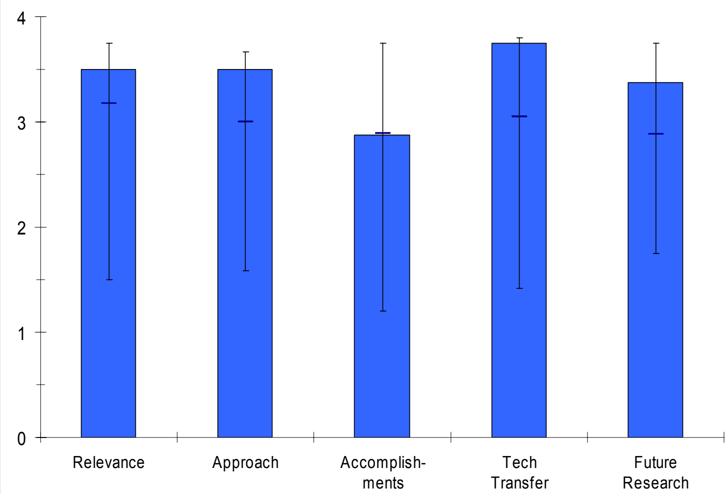
Digby Macdonald; Pennsylvania State University

[Partner of the DOE 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.

Overall Project Score: 3.3 (4 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- This project aligns fairly well with the President's initiative, working on efficient regeneration.
- This work is directed at investigating electrochemical approaches to convert borates back to borohydrides, as well as possible new electrochemical routes to hydrogen storage.
- Regeneration of sodium borohydride can be done either chemically or electrochemically. PSU is looking at electrochemical routes to regenerate sodium borohydrate (borate to borohydride). Cost effective and energy efficient regeneration is required to prove the feasibility of using sodium borohydride as a on-board storage material. The project is highly relevant to the mission of the chemical hydride CoE.
- This program addresses a critical issue in developing a new method to regenerate B-O to B-H.

Question 2: Approach to performing the research and development

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

- Approach appears to be well organized and structured.
- Project appears to coordinate with the chemical hydrogen storage CoE.
- The electrochemical approach is excellent.
- The approach down to two alternative paths appears sound. One path is direct electrochemical reduction while the other path is through polyhedral boranes.
- The program is well-designed. Very good interaction with other CoE partners.

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

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

- Project appears to have made good progress in its borate and polyborane work.
- The voltammetry technique for the detection of $BH4^-$ in electrochemical reactions appears to be quite useful. The results suggest that the electrochemical conversion of borate to borohydride is quite difficult. The polyborane work appears to be making progress.

- Progress in the direct reduction route appears to be the determination that numerous attempts at direct reduction have not been successful so far. Alternative pathways through intermediates are being pursued. The other path has identified suitable solvents and reference electrode. Electrochemical transformations have been shown to occur in the B_{12} and B_{10} systems, but their exact nature is unknown.
- The initial electrolysis results are promising. The barriers are identified.
- Not clear how project is performing to DOE targets.

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

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

- This project shows very good collaboration, including national labs and industry.
- This project is well interfaced with the chemical hydrogen storage CoE activities.
- Collaboration appears strong between PSU and other CoE members.

Question 5: Approach to and relevance of proposed future research

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

- This project appears to have a strong plan for future work.
- The project has excellent plans for future work.
- Future plans are to further research promising leads in both paths. However, the go/no-go decision on borohydride regeneration is approaching without assurance that the electrochemical approach will be successful in that time frame.

Strengths and weaknesses

Strengths
- Project appears to have a solid plan.
- The PI and his team have excellent electrochemical expertise.
- Strong collaboration. Innovative approach. The initial results are promising.

Weaknesses
- It is not clear how this project is performing to DOE targets.
- Difficult thermodynamic barrier.

Specific recommendations and additions or deletions to the work scope

- In the future add this project's performance to the table showing DOE technical targets.
- The CoE 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.

Project # STP-26: Chemical Hydrogen Storage Using Ultra-High Surface Area Main Group Materials

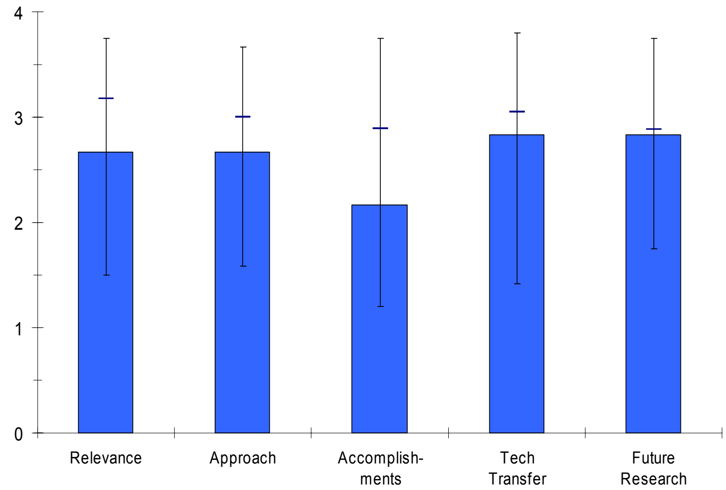
Philip Power; University of California-Davis

[Partner of the DOE Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The goal of this University of California project is to identify hydrogen storage materials enabling DOE targets and increase the understanding of synthetic approaches and physical properties of main group element clusters, such as Si, B, Al, and alloys thereof, as well as BP and BN compounds. Over the past year, efforts have been directed towards designing simple routes to such compounds using mild conditions and studying weight and volume of the synthesized materials as well as the reversibility of hydrogen uptake.

Overall Project Score: 2.5 (3 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- The emphasis on this project is to develop new, relatively simple routes to hydrogen storage materials, based on nanosized particles of light elements.
- This project intends to discover new, viable chemical hydrogen storage materials.

Question 2: Approach to performing the research and development

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

- The approach of attaching hydrogen or hydrogen-containing species to the surfaces of nanosized particles of light elements such as B, Si, and Al is an interesting one.
- Approach is directed toward the synthesis of new candidate storage materials using main group elements and "mild" synthesis conditions.
- Fully characterize the new materials including hydrogen take-up, release and regeneration.

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

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

- Nanosized Si and B particles have been successfully synthesized.
- Several nanoparticulate/nanocrystalline compounds have been synthesized and characterization is underway for these new materials.
- No definitive data on hydrogen take-up, release or regeneration was reported - apparently these measurements are currently underway. Composition and reactivity characterization has begun and some compounds appear to be promising.

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

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

- This project is a part of the chemical hydrogen storage CoE.
- UC-Davis is a member of the chemical hydrogen CoE.
- Specific collaborations with LANL, PNNL, U of Penn and U of Alabama were listed.

Question 5: Approach to and relevance of proposed future research

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

- Having successfully synthesized nanosized Si and B particles, the future thrust of the project is to attach as much hydrogen as possible to the surfaces of these particles.
- Planned future activities appear to be reasonable.

Strengths and weaknesses

Strengths
- This is a potentially simple approach for developing a new type of hydrogen storage material based on nanosized elemental particles.
- Builds on synthesis capabilities at UC-Davis.

Weaknesses
- It may be difficult to attach substantial amounts of hydrogen to the surfaces of the nanoparticles. The nanoparticles may not remain nanosized after hydrogen uptake and release cycling. The surfaces of the Si and B nanoparticles may be highly susceptible to poisoning, particularly with oxygen.

Specific recommendations and additions or deletions to the work scope

- Obtain preliminary assessment of hydrogen up-take and release as quickly as possible after compounds are synthesized in order to determine which materials should receive more extensive characterization. Narrow the number of potential candidate materials in order to focus on the more promising candidates.
- Project is heavily focused on synthesis and characterization of new materials. Suggestion is to conduct performance evaluations for hydrogen storage at earlier stages.

Project # STP-27: Main Group Element Chemistry in Service of Hydrogen Storage and Activation

Anthony Arduengo; University of Alabama

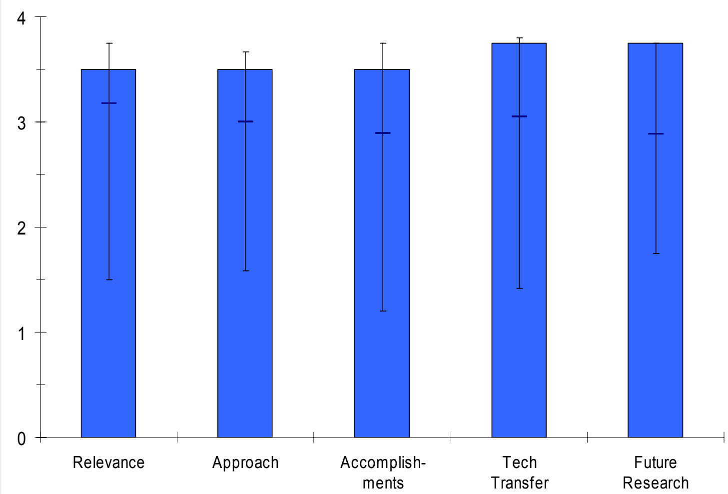
[Partner of the DOE Chemical Hydrogen Center of Excellence]

Brief Summary of Project

The objectives of this project are:

- Develop new chemistries to enable DOE to meet the 2010 hydrogen storage targets.
- Develop and implement imidazolium-based H_2 activation chemistry
- Develop and implement systems based on polyhydrides of main group elements: phosphorus, boron, nitrogen
- Develop and implement cyanocarbon systems for H_2 storage
- Provide computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE CoE for chemical hydrogen storage to reduce the time to design new materials and develop materials to meet DOE's 2010 hydrogen storage targets.

Overall Project Score: 3.6 (4 Reviews Received)



The University of Alabama has developed new cyanocarbon, carbene and carbenium ion chemistries to meet DOE 2010 hydrogen storage goals. New conceptual models have been developed for improving weight percent beyond 1:1 stoichiometry to meet DOE 2015 goals. Electronic structure methods were used to successfully predict reliable values of the thermodynamic, kinetic, and spectroscopic properties of compounds for chemical hydrogen storage. Experimental and computational work is ongoing.

Question 1: Relevance to overall DOE objectives

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

- This project is directed at the synthesis of new, unique materials for chemical hydrogen storage.
- The objective of this project is to develop new chemistries for hydrogen storage.
- Work is very well focused on developing new chemistries to meet storage targets

Question 2: Approach to performing the research and development

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

- High degree of integration with the other activities in the CoE. The conceptual approach is outstanding. The approach is well-balanced mix of theoretical work and experimental approach.
- The project has a very sound fundamental chemistry approach, with both computational and experimental elements.
- Chemistry based experimental/theoretical approach provides another tool for identifying potential new materials and in understanding behavior of current materials
- Synthesize new, novel organo-nitrogen compounds.
- Determine electronic structure to obtain thermodynamic and kinetic parameters.
- Develop models for hydrogen storage, release and regeneration.
- Characterize promising materials.

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

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

- Good progress narrowing down the choices. Comprehensive thermodynamic work. They had a fairly good strategy on some of the experimental and synthesis work.
- Good list of accomplishments in both theoretical and experimental studies
- Computational approach to study regeneration and other storage parameters of ammonia borane.
- Initial carbene (2 wt.% material capacity measured) and cyanocarbon (1 wt.% material capacity measured) compounds synthesized and preliminary characterization underway. Phosphocarbon compound has exhibited uncatalyzed hydrogen uptake at room temperature.
- Interesting initial results with the carbenes and cyanocarbons. Very interesting initial results on a new material, where hydriding and dehydriding can be activated by radiant energy.

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

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

- Active collaboration with a number of chemical hydrogen CoE members.
- This project is a part of the chemical hydrogen storage CoE.

Question 5: Approach to and relevance of proposed future research

This project was rated **3.8** for proposed future work.

- Planned experimental and computational activities appear to be reasonable.
- The proposed future work looks excellent.

Strengths and weaknesses

Strengths
- Builds on strong chemical synthesis and characterization capabilities and extensive related work on similar compounds.
- This project is very strong in its chemistry.
- Innovative approach for chemical hydride storage. This presents the possibility of onboard chemical hydride regeneration.

Weaknesses
- None.

Specific recommendations and additions or deletions to the work scope

- This project is already 40% spent at this point in time. Perhaps the project scope needs to be reduced somewhat, to focus on the most promising hydrogen storage avenues identified to date.

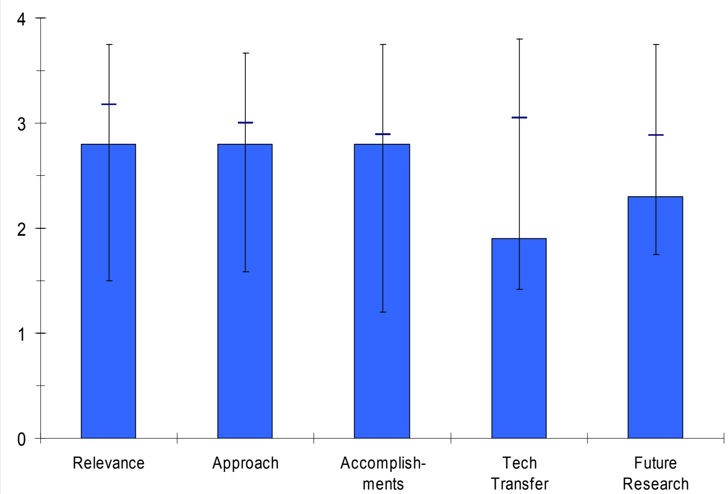
Project # STP-37: Clean Energy Research Project: Advanced Metal Hydrides

Jim Ritter, presenting; Ralph White (PI) University of South Carolina

Brief Summary of Project

The University of South Carolina Clean Energy Project addresses research for hydrogen production, storage, and use. Currently, 5 tasks make up the Clean Energy Research Program initiated in FY04 and then continued in FY05. Hydrogen Production: Low Temperature Electrolytic Production – This task will focus on production by electrolysis of anhydrous gaseous HCl and by the electrolysis of gaseous SO_2. Hydrogen Storage: Development of Complex Metal Hydrides. This task will focus on the storage and retrieval of hydrogen in metal doped complex metal hydrides (alanates). Chemical Hydrides. The possibility of using sodium borohydride to store and release hydrogen will be investigated. Fuel Cell MEAs: Diagnostic Tools for Understanding Chemical Stresses and MEA Durability Resulting from Hydrogen Impurities. Fuel Cell MEAs: Durability Study of the Cathode of a Polymer Electrolyte Membrane Fuel Cell. This is a cross-cutting project.

Overall Project Score: 2.6 (5 Reviews Received)



Question 1: Relevance to overall DOE objectives

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

- This project partially supports the hydrogen program vision in working on some of the technical barriers.
- Hydrogen storage is the key enabling technology critical for the success of hydrogen as a transportation fuel. Any work which can further understanding of the basic science of hydrogen storage is vitally relevant to DOE objectives, the President's Hydrogen Initiative and the objectives of the Multi Year R&D Plan. It is important, however, to ensure that the most capable researchers are identified to receive federal funds so that the most effective use can be made of taxpayer's dollars.
- The project is targeted at meeting the DOE 2010 hydrogen capacity targets.
- The development of high-hydrogen loading solid materials for storage is one of the most important components of the hydrogen program. This project appears to be addressing the right issue.
- Not clear how physiochemical pathway applies to DOE program
- Why still looking at Na alanate?

Question 2: Approach to performing the research and development

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

- Work has focused on metal hydrides, as previously recommended, may be duplicating work previously done by others.
- PI is looking at materials that have not been fully considered for hydrogen storage. This may be because historic evaluations have been thought to be limited by thermodynamics.
- The off-board regeneration of the $LiAlH_4$ with THF is interesting, if the hydrogen storage capacity can be increased.
- Working with more-or-less standard doped-alanates using solubility properties in THF presents a quite reasonable method to both study the systems and maximize the reversible hydrogen storage capacity. The incorporation of new materials that may result in higher hydrogen loadings is also good. However, the fact that high temperature is needed for this particular conversion should not be forgotten.

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

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

- Project has done a good amount of work, but it is unclear if the work is leading to overcoming DOE technical barriers.
- Thermodynamics of $LiAlH_4$ would not normally be expected to achieve levels of H storage at reasonable temperature and pressure that meet the program goals. The PI has investigated reactions with solvents that may be able to alter thermodynamics to make the material more suitable. However it is unclear how this can be translated into a practical system solution for vehicular transportation. There would have to be some way to accomplish the rehydrogenation and the addition/removal of the solvent without adding significant complexity/cost/etc.
- The results indicate a reversible hydrogen capacity of 4 wt.% at 160°C, via the route of regenerating the $LiAlH_4$ offboard using THF. Some interesting very new results with a new, undisclosed material were indicated.
- A lot of the data is discouraging from the loading temperature standpoint, but it is definitive in determining the limits of the system. The new (proprietary) material is presenting some very impressive reversible hydrogen capacity data. Use this material to gain some valuable information that can be used on other materials, but don't get bogged down with something that won't work for this program.

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

This project was rated **1.9** for technology transfer and collaboration.

- Project has some collaboration with others, but no industry relationship.
- Collaboration & partnering seem limited; there is no real discussion of how the collaborators interacted with the PI in this project.
- Although collaborations are presently somewhat limited, the PI indicates a strong interest to interact with or to join the metal hydride CoE.
- Does not appear to be any.
- Essentially no interaction with researchers in DOE hydrogen storage program

Question 5: Approach to and relevance of proposed future research

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

- Fair plan for future research is identified, but it should be more closely aligned with DOE goals and targets.
- The practicality of a vehicular system using these materials needs to be assessed as part of any future research plans.
- The future work appears to be focused on the new material system that has just recently been discovered which has a higher hydrogen capacity.
- Aside from continuing to explore these materials, none was presented.
- Future work not identified

Strengths and weaknesses

Strengths
- Researchers are better focusing on project than in past.
- PI is taking a new look at materials that traditional thermodynamics might have excluded.
- This project introduces the approach of regenerating complex hydrides off-board and provides some interesting results in this regard.
- Good technical knowledge. The approach seems to be working in maximizing reversibility.

Weaknesses

- Work in project appears to be somewhat misdirected as work may be duplicative of other work.
- There is skepticism that a viable hydrogen transportation, storage, and regeneration systems approach to vehicle needs can come from this work.
- This project would benefit from interactions with the metal hydride CoE.
- Are they (or anyone) ever going to get there? They did not adequately address partnering or future direction.

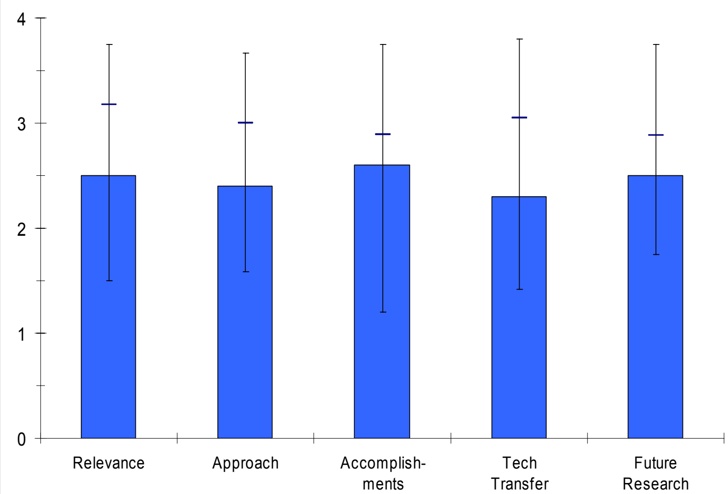
Specific recommendations and additions or deletions to the work scope

- Work with DOE to get project more closely aligned with DOE targets.
- None.
- They need to find the material that will meet the goals. Don't spend a lot of time on materials that won't. It's alright to develop technique on some of the low performers (even $LiAlH_4$ fits this category), but know when to stop.

Project # STP-43: Hydrogen Research at University of South Florida

Lee Stefanakos; University of South Florida

Overall Project Score: 2.5 (5 Reviews Received)



Brief Summary of Project

This multi-faceted University of South Florida project is investigating several hydrogen production techniques; hydrogen storage primarily in the area of advanced metal hydride compounds, and electrode improvements. This is a cross-cutting project started in 2004, with additional funds in 2005.

Question 1: Relevance to overall DOE objectives

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

- A lot of what USF is doing is relevant to the program. They started with a large menu of projects that address various aspects of DOE hydrogen and fuel cell needs and have whittled the non-performers out of the mix.
- Project appears to partially address some of the goals of the MYPP.
- Hydrogen storage is the key enabling technology critical for the success of hydrogen as a transportation fuel. Any work which can further understanding of the basic science of hydrogen storage is vitally relevant to DOE objectives, the President's Hydrogen Initiative and the objectives of the Multi Year R&D Plan.
- Project appears to partially address some of the goals of the MYPP.
- The majority of the work presented here deals with some potentially interesting metal and mixed hydrides (Task 2.1). This area remains one of critical importance.
- The hydrogen storage activities of this project are targeted at identifying and investigating new materials consistent with the DOE hydrogen storage targets.
- It is important to ensure that the most capable researchers are identified to receive federal funds so that the most effective use can be made of taxpayer's dollars. It is important that this research be focused for maximum benefit rather than a broad survey of various technologies that are related to the needs of the hydrogen initiative.
- Most of work appears to be outside of current DOE storage program - lots of work on production, fuel cells, delivery. Likely those efforts are also not connected to DOE

Question 2: Approach to performing the research and development

This project was rated **2.4** on its approach.

- There was no discussion on how the materials that were chosen for synthesis and study came to be chosen. However, the materials that were chosen appear interesting enough to be considered. The remaining approach including synthesis and characterization via electronic structure calculations seems reasonable.
- The initial approach had elements that may not have been that well thought out. Fortunately, a number of these elements have now been discontinued and the current approach appears reasonably good.
- It is unclear what aspects of the research being reported are to be evaluated. The PI seems to be investigating a range of technologies in many areas. I am submitting evaluation for the two storage "tasks."
- Go/no-go criteria are not clear.

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

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

- The PI is to be commended for looking at $Zn(BH)_4$, a material that has not been thoroughly studied. While this compound could theoretically carry and release a high weight percent of hydrogen, and gravimetric results tend to indicate a significant reduction in weight, there is some question whether that is due to hydrogen release or the decomposition of B2H6. If the latter, this appears to be a dead end.
- 8.4 wt.% gravimetric capacity of $Zn(BH)_4$ may show some potential, but other materials looked at in this project don't appear to show promise.
- The fact that $Zn(BH_4)_2$ shows TGA data with 8.4% by hydrogen coming off at 100ºC is good. The fact that the reaction is reversible is good, but there is nothing showing that it is entirely reversible. 8.4% is just the upper limit - and that doesn't even include system weight. It may not meet goals even at best. It may still be a good test material, however.
- The project reports that synthesis of a $Zn(BH_4)_2$ material with a gravimetric capacity of 8.4 wt.% that shows reversibility at 100ºC (the amount of this reversibility is not indicated).
- Work on $LiNH_2$: Question claims of 7.5 wt.% given thermodynamics of the reactions. Further work is needed to confirm the results.
- Nanocomposite: little of value seen in the work or results.
- The new results for $LiBH_4$ complexes look to be worth following up.
- Very recent new results indicate a $LiBH_4$-based material system with an 11 wt.% gravimetric dehydration capacity at approximately 150°C.
- There doesn't seem to be much in the way of progress other than some initial characterization measurements validating the successful synthesis of some of these materials.

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

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

- Collaboration & partnering seem limited; there is no real discussion of how the collaborators interacted with the PI in this project.
- Collaboration appears to be primarily with universities in Florida.
- Should consider developing stronger collaborative relationships with industry.
- It's good to have a large number of academic collaborators, but some industrial participation would really help.
- There appears to be relatively little research interaction of this project with the larger hydrogen storage community. Such interaction would be greatly promoted if other researchers can reproduce some of the results that have been reported.

Question 5: Approach to and relevance of proposed future research

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

- Future work for Task 2.1 seems to be reasonable and might be beneficial if the PI focuses on a select few materials and can expand the scientific knowledge base about these materials. Work in other task areas reviewed should be deemphasized (and PI acknowledges that some such work will cease in the future).
- Encouraging that comments from last review have resulted in focusing this project on advanced and nanomaterials, but any future work must align more closely to DOE targets.
- Watch out for following up with materials that won't reach the longer term goals regardless of what you do with them. Use them only for technique improvement.
- The future work on this project should focus on verifying, understanding, and optimizing the interesting results that they have reported.

Strengths and weaknesses

Strengths

- Project appears to be responding to previous review comments.
- The project personnel are very aware of DOE goals and are quick to discontinue projects that do not appear to have a chance to meet the goals.
- Some interesting results, if they can be verified by other researchers.

Weaknesses

- It is unclear what aspects of the research being reported are to be evaluated. The PI seems to be investigating a range of technologies in so many areas to the extent that one questions if any one research topic is getting sufficient attention and funding. 12 technical "tasks" are reported in this poster and it is unclear how much funding is allocated to any one technical area.
- Some of the materials being looked at in this project don't appear to have much potential.
- Too many projects to start with diluted the effort.
- Presumably, the purpose of the new effort on electronic structure calculations of complex borohydrides is to serve as a theoretical guide for the selection of potential new complex borohydrides for experimental study. This effort would benefit from interactions with similar activities in the chemical hydrogen storage CoE.

Specific recommendations and additions or deletions to the work scope

- PI ought to focus on one or two key areas of storage research and concentrate there, rather than a scatter shot approach to many aspects of hydrogen transportation.
- Testing is needed to determine if there is truly reversibility of the znbh4 at reasonable temperatures.
- Work with DOE and the Storage Team to get better alignment with DOE targets and goals.
- Watch out for diborane production, and make sure you know how to handle it and trap it if you get it.
- Need project focus.
- This project should send some of its $Zn(BH_4)_2$ and $LiBH_4$-based materials to SwRI for independent evaluation of the results reported.