2017 – Hydrogen Storage
Summary of Annual Merit Review of the Hydrogen Storage Sub-Program

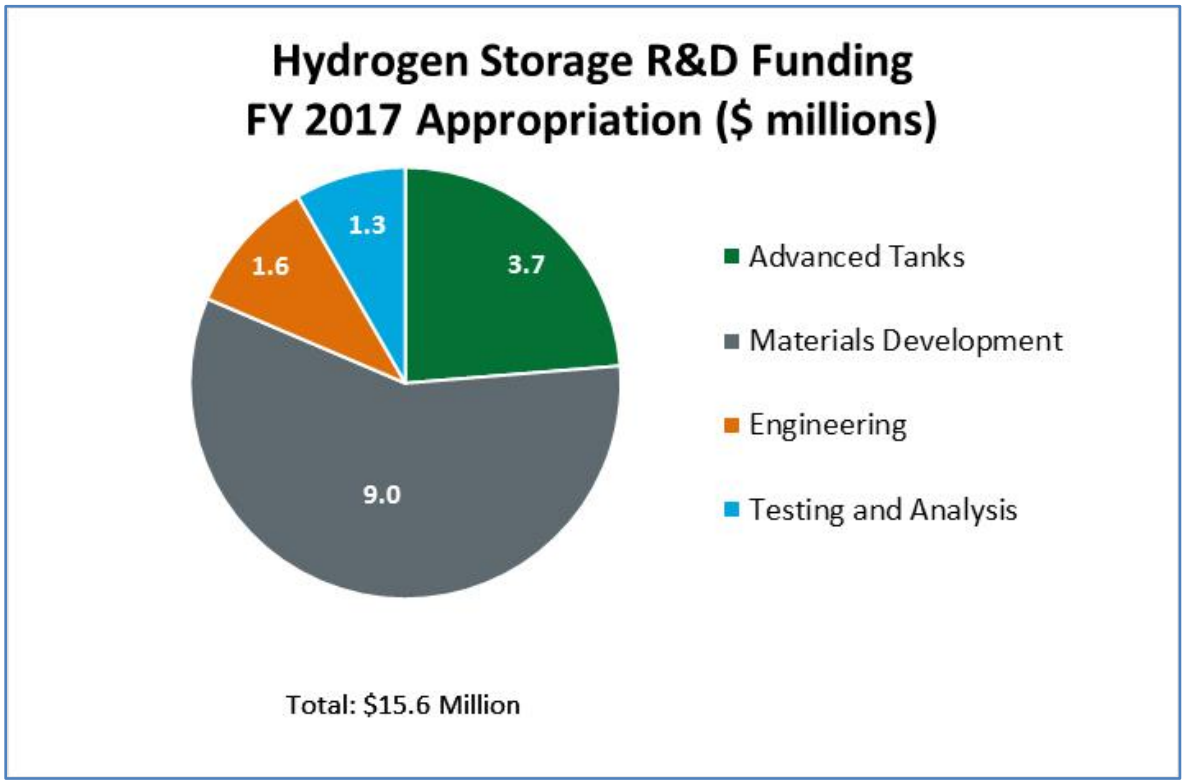
Summary of Reviewer Comments on the Hydrogen Storage Sub-Program:

In fiscal year (FY) 2017, the Hydrogen Storage sub-program portfolio continued to focus on onboard automotive applications through its two-pronged strategy, pursuing strategic near-term and long-term pathways with the potential to meet the cost and performance targets.

In general, reviewers noted there is an adequate balance within the sub-program's research and development (R&D) portfolio, resource allocation, priorities, and technical goals. They commended the sub-program's management and openness to engagement, communication, and collaboration with key partners in academia, national laboratories, industry, and other agencies in the federal government. The Hydrogen Materials–Advanced Research Consortium (HyMARC) was cited as an innovative approach to leveraging foundational scientific understanding and world-class resources and facilities across multiple stakeholders, and as a catalyzer for groundbreaking advances in hydrogen storage materials with the potential to meet the sub-program's ultimate goals. Reviewers encouraged continued and careful coordination across HyMARC's core and support teams as well as with individual materials development efforts to prevent overlap in activities and maximize results. In general, they recommended that greater attention be given to aligning progress made under the sub-program's R&D portfolio with the needs of and interface with hydrogen infrastructure.

Hydrogen Storage Funding:

The chart on the following page illustrates the appropriated funding for FY 2017. The sub-program received $15.6 million in funding in FY 2017. Under FY 2017 activities, HyMARC core and support teams continued work on the discovery, development, and validation of novel materials with the potential to store hydrogen and meet the targets. Multiple HyMARC seedling projects focused on materials development for metal hydrides and sorbents, and the sub-program also initiated an effort on advanced cryocompressed hydrogen storage systems.



Majority of Reviewer Comments and Recommendations:

The Hydrogen Storage portfolio was represented by 28 oral presentations in FY 2017. A total of 25 projects were reviewed. In general, the reviewers' scores for the storage projects were good, with scores of 3.4, 2.7, and 3.1 for the highest, lowest, and average scores, respectively.

Advanced Tanks: Three projects on advanced tanks were reviewed, with a high score of 3.0, a low score of 2.7, and an average score of 2.9.

Reviewers considered these projects to be relevant in addressing challenges unique to the development and manufacturing of promising high-pressure hydrogen storage systems. They commented favorably on the modeling and computational activities used across the advanced tanks portfolio to better understand phenomena affecting feasibility and market readiness of the concepts pursued, including balance of plant (BOP), materials compatibility, and required strength for alternative, conformable, high-pressure hydrogen storage systems. Overall, the reviewers thought the efforts under the advanced tanks portfolio incorporated strong experimental activities but recommended further leveraging collaborations with industry experts, including original equipment manufacturers, to maximize the potential for these approaches to be successfully demonstrated at greater scale and lower cost.

Materials Development: Eighteen materials-based hydrogen storage projects were reviewed, with a high score of 3.4, a low score of 2.7, and an average score of 3.1.

In general, reviewers commended the unique set of capabilities that has been expanded through the overall HyMARC effort, as well as the technical progress made through the wide range of projects in the sub-program's materials development portfolio. Reviewers praised the progress made by the HyMARC core and support teams in the past year as they address the foundational scientific gaps in the thermodynamics, kinetics, and capacity of hydrogen storage materials. They complimented the coherence of the effort and strong collaboration between the first round of HyMARC seedling projects and the national laboratory capabilities. They reiterated that the focus of the sub-program should continue to be on materials with a realistic chance to meet DOE's onboard storage targets that cannot be theoretically met by high-pressure hydrogen storage tanks. Reviewers are satisfied with the HyMARC core group's approach to utilizing model systems to understand material concepts and direct computational multiscale model development efforts, but suggested that the pathway from these model systems to more complex, relevant systems be more clearly described. Through close collaboration between the HyMARC core, support, and seedling projects, the materials-based projects will continue to have an increased level of coordination between experimental and theoretical efforts and to place more emphasis on meeting projected material-level property requirements to meet the system-level targets.

Engineering: Two projects related to hydrogen storage engineering were reviewed, with a high score of 3.3, a low score of 2.9, and an average score of 3.1.

In general, reviewers commended the improvement in accessibility, accuracy, and user interface of the system-level models developed by the Hydrogen Storage Engineering Center of Excellence (HSECoE) in prior years. Reviewers also commented favorably on the hydrogen storage system designs for unmanned underwater vehicle systems developed under the engineering portfolio and praised the teams for their ability to work closely with the U.S. Department of Defense (DOD) and DOE groups to demonstrate an important extension of fuel cell technology to a new type of mobile application. Overall, reviewers recommended that projects prioritize approaches that reduce cost, enable scale-up, and maximize potential to achieve goals beyond gravimetric and volumetric capacity.

Testing and Analysis: Two projects related to testing and analysis were reviewed, with a high score of 3.4, a low score of 3.1, and an average score of 3.2.

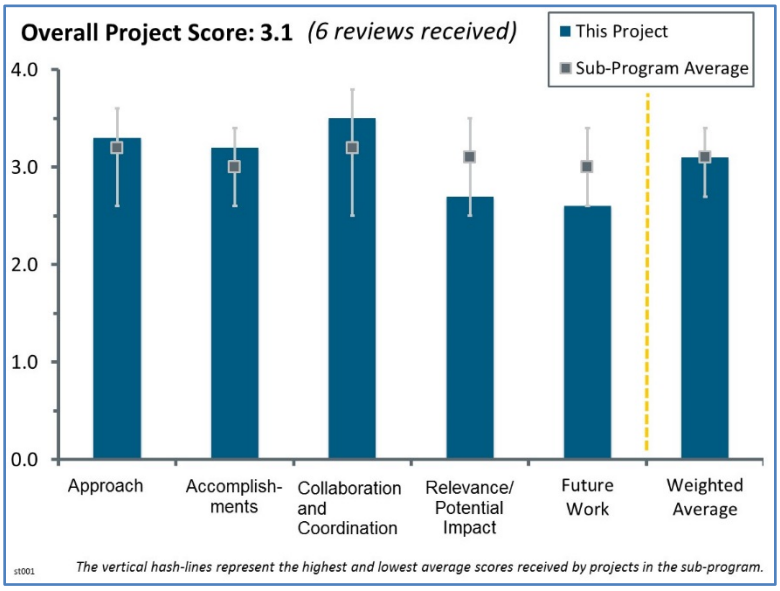
In general, reviewers commended the projects for effectively applying strong physical and chemical modeling and analysis while providing sensitivity studies to understand tradeoffs for hydrogen storage system materials and performance. The reviewers commented on the projects' ability to foster strong collaborations with external researchers to provide increased technical background for more accurate cost analyses and commended the transparency of assumptions and technical rigor. The reviewers recommended more interaction with industry to validate some of the cost projections, such as those for compressed natural gas. Overall, the reviewers recommended

that more experimental validation be considered in the analyses and that efforts focus more on breakthrough hydrogen storage system technologies. In general, reviewers agreed that the analyses should consider new hydrogen storage materials that are being commercialized for other applications, such as alane, and identify key cost drivers for new hydrogen storage materials where R&D could lead to cost reductions.

Project #ST-001: System-Level Analysis of Hydrogen Storage Options

Rajesh Ahluwalia; Argonne National Laboratory

Brief Summary of Project:



The main objective of this project is to develop and use models to analyze the onboard and off-board performance of physical and materials-based automotive hydrogen storage systems. Specific goals include conducting independent systems analysis for the U.S. Department of Energy to gauge the performance of hydrogen storage systems, providing results to materials developers for assessment against system performance targets and goals and for guidance in focusing on areas requiring improvements, providing inputs for independent analysis of onboard system costs, identifying interface issues and opportunities and data needs for technology development, and performing reverse engineering to define material properties needed to meet the system-level targets.

Question 1: Approach to performing the work

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

- The Argonne National Laboratory (ANL) systems analysis project has served a very useful role by independently assessing design variations and engineering features for diverse hydrogen storage systems and materials. The project has identified areas that show potential for improvement and those that are already limited to current values. Most major factors have been considered and also reevaluated over the past eight years.
- The approach effectively utilizes thermodynamic and kinetic models to guide the hydrogen storage system designs and operating conditions. Overall, the project does excellent work to consider barriers and provide sensitivity analysis. The discussion of the results could be improved by including correlation data to increase confidence in modeling results whenever possible. The impact testing analysis is interesting but should be shown to align with a drop test in the industry standards. This impact test seems to be different from the industry standard testing.
- The approach to the work is soundly based in chemical engineering principles; however, some of the system models use reduced-order algorithms to approximate the results, which can add significant variability and skew the performance characteristics of the overall system. The project needs to ensure these factors are noted when reporting results.
- The project uses a good approach toward analysis, but more validation needs to be included, and the analysis needs to be refined.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- The project has made notable progress in several technology areas. First, the analysis of cryo-compressed autofrettage, performance, and operating pressure versus dormancy was useful. Second, the updated

700 bar system based on the correct density at 15°C was necessary from the previous DOE record. Finally, the reverse engineering analysis for the improved thermal conductivity was a significant improvement.

- During fiscal year (FY) 2017, the ANL team focused mostly on cryo-compressed hydrogen storage systems with primary results for buses and other types of fleet vehicles. The team assessed issues such as the impact of liquid hydrogen (LH_2) pumping rates on filling efficiency, contributions on the factors influencing tank dormancy, and a comparison of stainless steel versus aluminum liners on these Type III vessels. The project team concluded that a 500 bar storage pressure and a 2 mm stainless steel liner gave the largest gravimetric and volumetric capacities. Nevertheless, there is little current interest in the United States in cryo-compressed storage for any vehicle class. ANL also reported work on a couple of issues with 700 bar gas storage vessels and found negative impacts from compact sorbent carbons on storage parameters. Apparently, the project team will look at completing its analyses of high-pressure (i.e., ~350 bar) metal hydride storage tanks, but no specific results were presented.
- Adequate progress was achieved on the compressed gas tanks, adsorption systems, and cryo-compressed systems that were analyzed.
- Assessment of life-cycle costs and durability of the more complex systems being studied—using compressed storage as the baseline—is suggested.
- Savings of 1.1% carbon fiber seems too small. It would be beneficial to see some more revolutionary approaches to reducing the thickness of the container, with more optimal design and better failure theories.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.5** for its collaboration and coordination.

- The project has a high level of collaboration with the key institutions involved in the technology being analyzed within the project. The coordination of the performance modeling within the project and the cost modeling performed by Strategic Analysis, Inc. (SA) is an excellent example of collaboration between projects.
- This ANL team continues to interact very well with the other organizations via both effective interchanges of technical inputs and communicating its outputs.
- It appears that the ANL group collaborates well with SA; however, it was somewhat unclear how much collaboration occurs with other technologists.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **2.7** for its relevance/potential impact.

- The project continues to provide important modeling results for assessing the Hydrogen Storage sub-program goals and strategies. The outcome of this project has the potential to direct hydrogen storage designs and operating parameters toward the DOE research and development goals and objectives. The effort from this year seemed to include other applications (e.g., buses) rather than just light-duty vehicles (LDVs). The project includes several tasks, and it would be useful during the presentation of results for the project slides to indicate the reason for conducting certain analyses. For example, the principal investigator (PI) did not explain the reason for considering cryo-compressed tanks for a bus application when this application has additional volume on the roof compared to an LDV.
- The potential of this effort for generating novel improvements is likely to be limited because additional variations for hydrogen storage systems have been considered during FY 2016 and FY 2017. While the cryo-compressed storage systems were shown by ANL to do very well with the onboard targets, severe issues remain with the necessary LH_2 infrastructure that is required. From current and past analyses by the ANL project and others, there are virtually no known solid storage media candidates that can simultaneously satisfy the updated 2020 DOE targets, let alone the ultimate targets. Over the past decade, ANL and others have found that the variety of design features is always a compromise of contradictory requirements and behavior for either physical or chemical storage systems. The probability of finding a breakthrough system that simultaneously meets all the 2020 vehicle targets is low.

- While this analysis project has provided insight and validation of other system performance characteristics in the past, the value of the projects or the focus of the analysis on those projects seems to provide neither significant impact nor insight into valid pathways for improvements in the performance of the technologies. The group should focus on forward-thinking ideas to quickly assess the potential improvements of various approaches.
- There is very incremental progress—savings of 1.1% on carbon fibers (carbon fibers are getting cheaper). The project needs to focus more on reducing the factor of safety used by improving the design and developing better capabilities to predict burst pressure.

Question 5: Proposed future work

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

- A review of the technology from the ST-126 (Center for Transportation and the Environment) project is suggested. This project should also conduct a review of life-cycle costs and reliability pertaining to the more complex systems.
- The proposed future work is unclear at the moment with the substantial budget cuts under the current administration. This lack of clarity is not the PI's fault, but it has to be noted in an assessment of the project's future work.
- The proposed future work seems to be only an incremental progression of the current work. The project's role and effort in supporting ongoing tank projects is unclear. Additional sensitivity analysis regarding the reverse engineering or system designs would be helpful to increase the future impact of this project. It was good for the future work to include validation tasks for the various modeling.
- Future work seems incremental and more of the same. Better failure theories and conformable designs of pressure vessels are needed to make game-changing progress.
- Because the ANL team has now completed rather in-depth assessments of 700 bar compressed hydrogen gas and cryo-compressed storage vessels, further analyses on these approaches are not recommended at the present time; little payback can be expected. Because ANL has already published the comprehensive requirements that absorption and adsorption materials must achieve to meet the DOE targets within the past couple of years, there is little need for additional work on this topic at the moment. Furthermore, neither recent materials discovery projects nor the international research literature have identified viable new candidates for independent evaluation by ANL.

Project strengths:

- The project strength is that the effective modeling provides excellent guidance regarding key parameters for physical-based (e.g., tank designs) and material-based (e.g., reverse engineering) storage. Another project strength is the researchers involved in this project because they have the needed technical depth and attempt to integrate the latest information from other researchers.
- The ANL team has developed and implemented a variety of models for assessing and predicting the attributes and limitations of nearly all types of hydrogen storage systems. The team has provided the valuable constraints required for various storage media if they are to meet DOE targets.
- Project strengths include the many analysis tools and good integration.
- The project creates value for the Hydrogen Storage sub-program by validating approaches and evaluating forward-thinking ideas.
- The project has a good analytical assessment of various technologies.

Project weaknesses:

- The lack of experimental validation of results minimizes the impact of this effort.
- The project could be improved by highlighting the data or examples that validate the modeling results in the presentation. The PI received several questions regarding correlation with test results, which should be addressed in the slides to increase the confidence in the results.
- Because there have been limited design and materials advancements on hydrogen storage technology within the past couple of years, the ANL team has very few "new" storage systems presently available for it

to evaluate at this time. It appears that its efforts are now addressing secondary aspects rather than those critical issues with the potential for a technological breakthrough.
- The project needs to focus more on evaluating forward-thinking ideas and continuing to assess ideas for improvement in balance of plant in systems because it is not likely that any new materials will be created under the current budget situation.
- Project weaknesses include the incremental approach and the need for more effective failure criteria.

Recommendations for additions/deletions to project scope:

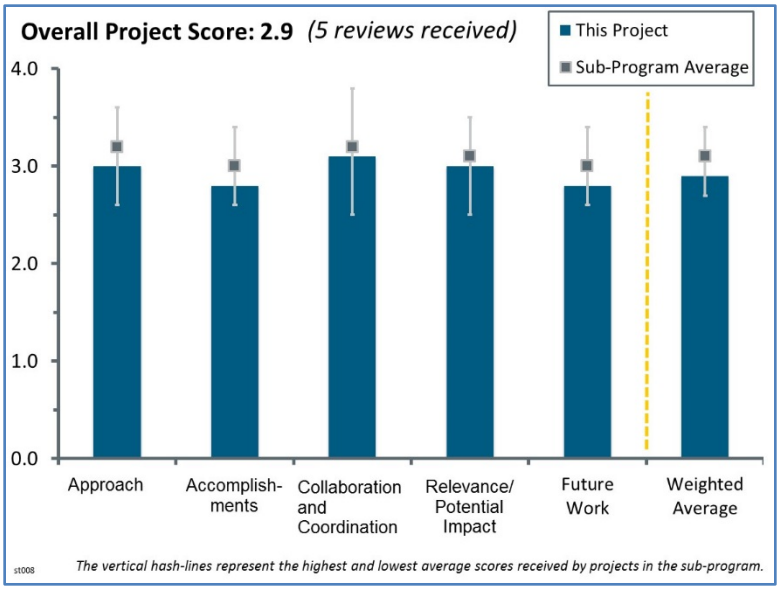
- The project should pursue developing DOE records for the other hydrogen storage system, similar to the 700 bar compressed hydrogen system. Additional sensitivity analysis regarding the reverse engineering or system designs would be helpful in increasing the future impact of this project. This project should focus on developing strategies and proactive guidance for research and development to achieve the targets. The impact analysis should ensure the test approach aligns with the industry standard tests.
- It is recommended that the FY 2018 support for this project be reduced, with released funds allocated to projects that search experimentally for more promising hydrogen storage materials.
- The project should focus more on validation of the ANSYS analysis.

Project #ST-008: Hydrogen Storage System Modeling: Public Access, Maintenance, and Enhancements

Matt Thornton; National Renewable Energy Laboratory

Brief Summary of Project:

The ultimate goal of this project is to provide and enhance publicly available material-based hydrogen storage system models that will accept direct material property inputs from material developers to accurately predict material-based hydrogen storage system performance. In support of that goal, this project maintains, enhances, and updates the Hydrogen Storage Engineering Center of Excellence (HSECoE) hydrogen storage system modeling framework and model dissemination web page.



Question 1: Approach to performing the work

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

- The goal of this project is to provide hydrogen storage system models developed under the HSECoE to researchers to evaluate the performance of new materials in engineered systems relative to the U.S. Department of Energy (DOE) technical targets. Another task is to manage the HSECoE model dissemination webpage. The intent is that material researchers can input property values for their materials into the HSECoE models and assess whether the final storage system will meet DOE targets. The project is currently at its midway point. A number of models have been developed to date, including the tank cost model, the finite element model for metal hydrides (MHs), and the framework models for physical storage, chemical hydrogen (CH), MHs, and adsorbents (ADs). In the past year, the team has focused on the AD/CH system estimator and the AD isotherm fitting tool. The team has also improved the website access and support. All of these activities are important because automotive hydrogen storage is a challenge that needs to be overcome to ensure commercialization of fuel cell electric vehicles.
- This project has continued the development and refinements of predictive modeling techniques for alternative hydrogen storage media (e.g., MHs, CH, and ADs) started in fiscal year (FY) 2016. This task is currently focused on the media and storage configurations assessed during the completed HSECoE project. The intent of these online models is to allow outside users in the international hydrogen research and development community, who possess the appropriate software, to make comparisons over a range of parameters and operating scenarios against reference materials. The objective is to assist materials researchers in identifying viable candidates with the potential to meet the DOE vehicle performance targets. The project provides a level of technical support (at least for the near term) to the model website to assist outside users.
- The approach is appropriate and well defined. The user-friendly modeling framework is very useful to system analysts evaluating a candidate storage system. The tools allow users to do a scoping estimate of the system parameters and identify barriers to meeting the DOE technical targets.
- The web development and maintenance team is maintaining the website with the addition of minor tweaks and tools that eliminate the need for ancillary software.
- The approach is to enhance and disseminate hydrogen storage system models and provide guidance on material properties.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.8** for its accomplishments and progress.

- This task has made significant progress in updating, refining, and maintaining the HSECoE model dissemination website. Continual international interest and activity with the website were indicated by the tracking statistics given during the DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR) presentation. While such simulations are helpful tools in understanding behavior, they do not necessarily hasten discovery or development of the specified targets. The team spent considerable effort improving support documentation and making other changes to the formatting and approach to enhance the usefulness of the website. These activities should make this website a better resource.
- The team completed the isotherm fitting routine that converts raw data of excess hydrogen adsorption into Dubinin-Astakhov parameters. The agreement between the fitted model and data was good for compacted 0.4 g/cc MOF-5. There were notable improvements made in the system sizing functions for both AD and CH storage systems. There was significant decline in the website analytics. The number of users and sessions decreased 70% compared to the previous year.
- The main accomplishments seem to be in improving the models and making them more accessible to the wider hydrogen storage community.
- There is not much to comment on regarding the website and model maintenance. It appears to be on track.
- Most of the metrics presented pertained to gravimetric and volumetric efficiencies. One major bottleneck with these materials can be charging time. There appeared to be no mention at all of charging rates in the entire presentation. A material can have acceptable gravimetric and volumetric efficiencies, but if the charging time is too high, it will not be useful to the community.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.1** for its collaboration and coordination.

- A very close interaction reflecting technical interchanges among the team members from the different national laboratories as well as outside members has occurred throughout this project. The progress made on both the adsorption and CH storage models indicate excellent cooperation.
- There are strong collaborations among partners in the HSECoE. The project is well coordinated. Work is integrated seamlessly into the model framework.
- There is no real collaboration with other members of the HSECoE. The collaborations page lists a number of collaborations but provides no real documentation on their roles.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.0** for its relevance/potential impact.

- This project is essential in keeping all the developed models in one place and making them available to end users. The potential impact can be enhanced if the test data used for model validation are also included on the website so that users can validate their own models if needed.
- This project has made very good progress in making the numerical models developed during the HSECoE accessible to the general hydrogen storage community. It still remains unclear just how much other research groups are willing or able to fully utilize the tools being developed.
- The models and website are relevant, as demonstrated by the Internet analytics.
- Automotive hydrogen storage continues to be a major challenge, so this project is important and relevant.

Question 5: Proposed future work

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

- The specific tasks and goals presented for this project should lead to better experiences for the outside users. The level of effort and plans are well balanced.
- The future work is appropriate. The team should devise a plan to encourage outside users to provide user experience data.
- The proposed future work appears to be reasonable, although the development and incorporation of new models that have not been validated pose grave concerns. The new models have not been vetted or discussed with other members of the HSECoE, many of whom have had significant contributions to the inception of the original models.
- The team really needs to address metrics beyond just gravimetric and volumetric capacities.

Project strengths:

- The great strength of this project is the same as it was during the FY 2016 AMR review. Namely, the core team members have extensive knowledge and expertise on all of the hydrogen storage media as well as the appropriate software analytical packages to develop and execute the modeling codes for the website. This is an ideal collection of experienced individuals to continue and extend the HSECoE objectives.
- The team is made up of experienced researchers who are knowledgeable of the various hydrogen storage systems and are directly involved in the model development.
- The investigators appear to be maintaining a website of HSECoE models that is well received by the research community.
- The proposed hydrogen storage system models are useful for estimating the material properties required to satisfy the DOE system targets.

Project weaknesses:

- There are currently no significant weaknesses found with either the current approach or planned activities over the next year. The team is well focused to complete the project goals.
- The investigators should (as a sign of courtesy) at least recognize other team members of the HSECoE that have contributed significantly to the development of these models. Any new model should be vetted with the HSECoE team members to ensure accuracy and consistency.
- It was not clear how the proposed models will provide a full accounting of all important metrics pertaining to automotive hydrogen storage. For example, heat removal is a critical rate-determining step during hydriding with certain hydrogen storage materials, but it was not clear where and how different heat removal strategies could be explored within their models.
- The lack of feedback from outside users is a project weakness.

Recommendations for additions/deletions to project scope:

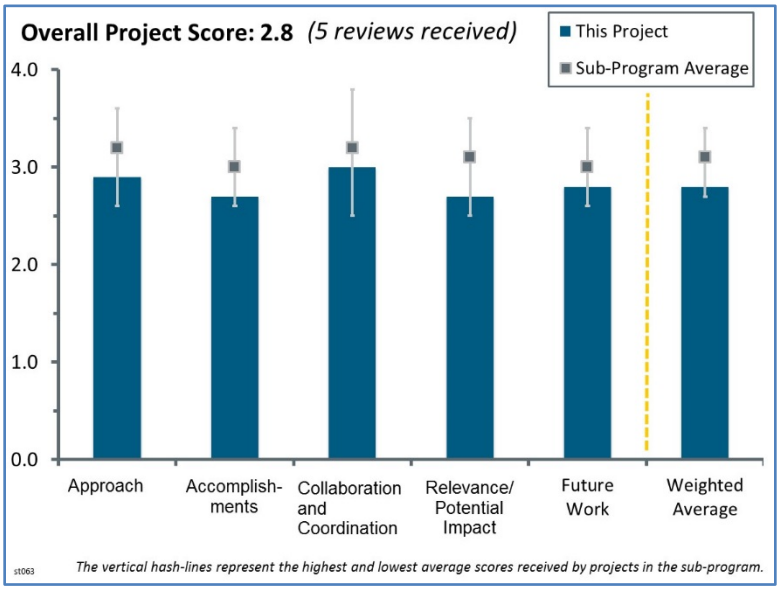
- This project has been making very good progress toward its objectives and has provided improved documentation for users on the website. It is recommended that the scope of the project be supported at its current level during FY 2018 in order to perform all of the tasks described in the future plans.
- The models seem to be optimized, and the data are accessible to the wider hydrogen storage community, so this effort seems to be close to completion.
- The team should consider including raw test data that have been collected by the HSECoE partners.

Project #ST-063: Formation and Regeneration of Alane

Ragaiy Zidan; Savannah River National Laboratory

Brief Summary of Project:

The overall goal of this project is to develop a low-cost rechargeable hydrogen storage material with favorable thermodynamics and kinetics, and high volumetric and gravimetric hydrogen density. Specific objectives include (1) development of cheaper techniques to synthesize alane (AlH_3), which avoids the chemical reaction route that leads to the formation of alkali halide salts such as LiCl or NaCl; (2) utilization of efficient electrolytic methods to form AlH_3; and (3) development of crystallization methods to produce α-AlH_3 of the appropriate phase, crystal size, and stability.



Question 1: Approach to performing the work

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

- High hydrogen density and low desorption temperature make AlH_3 one of the few materials with a chance to meet targets. The focus on cost reduction makes sense. However, the electrochemical method seems unlikely to ever come close to meeting cost targets. Replacing $LiAlH_4$ with $NaAlH_4$ seems like it would have a small decrease in cost, but there is a significant increase in cost/complexity associated with forming the tetrahydrofuran (THF) adduct.
- The project addresses barriers for production of a material that has potential to meet U.S. Department of Energy targets. The title suggests that the project looks at production and regeneration of AlH_3, but most of the work presented is relevant to production. Although first fill is a cost to be considered, the majority of a storage material needs to be produced from spent fuel if it is not simply rehydrogenated onboard.
- Previous work described the great benefits of electrochemical methods for AlH_3 production from $LiAlH_4$ and Al electrodes (made by compressing spent AlH_3). This year the focus appeared to be more on methods to make $NaAlH_4$ and using ball milling to make AlH_3. This was confusing, and it is not completely clear whether ball milling is now the preferred approach. If so, it seems to be consistent with the end of the project electrochemical work by Ardica.
- The barriers presented and those addressed were disjointed. The first barrier, reducing dendrite formation, was not discussed at all. The new "dry" mechanochemical method appears to bypass the electrochemical work completely. The focus was indeed on cost reduction, which was done well experimentally, but because of the nature of the material, it was not well integrated with the previous efforts.
- The approach taken to regenerate AlH_3 appears to be duplicative work performed by the Dow Chemical Company (Dow) and others many decades earlier. AlH_3 is not a hydrogen storage material that is expected to be used for automotive applications. However, AlH_3 does appear to be very promising for portable power because of the high-quality hydrogen produced and the relatively low dehydrogenation temperature.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.7** for its accomplishments and progress.

- There is nice progress with scaling up the conventional process. It is nice to see large quantities (200 g) of high-quality AlH_3 being produced. The electrochemical method seems to be stuck on separation of the AlH_3-THF adduct. There is limited progress toward recovering high yields of α-AlH_3. The electrochemical approach seems unlikely to bring down costs in any significant way.
- The accomplishments on the electrochemical portion appear to be the use of $NaAlH_4$/THF to increase conductivity. It is unclear how effectively this addresses the DOE goals because the main benefit is cost, and this has not been quantified, especially with respect to the cost of the subsequent ligand exchange before crystallization. The mechanochemical method shown is really only applicable to first fill. Crystallization appears successful with long-lived powders, but no details of what work has been carried out are given.
- Progress on some of the objectives is questionable in some aspects of this project. It seems like a waste of resources to use density functional theory (DFT) calculations to determine bond strength of various materials, state that it does not completely aid in crystallization prediction, and then use a known transamination process after the fact. There appears to be no progress regarding changes to the electrolyte and improvements in conductivity; there was no increase in conductivity shown over the previous year's results. The mechanochemical method developed to produce AlH_3 from $NaAlH_4$ is impressive and may reduce costs, but scaled cost projections were not detailed or discussed. The most impressive progress is the increase in crystallization scale and purity. A greater than 13 times increase in scale is encouraging and shows good strides toward optimizing the process.
- The presenter noted that the project team has been working on the regeneration of AlH_3 for over 10 years. The project title is "Formation and Regeneration of Alane." It seems this past year that the focus was on formation using a ball milling approach, and very little focus was on regeneration—at least, regeneration was not covered in the presentation.
- This is a difficult problem—regenerating spent AlH_3 back to high-purity α-AlH_3 that will meet the DOE cost and efficiency targets—as evidenced by the decades of research on perfecting the production of α-AlH_3. Given the fact that α-AlH_3 is not expected to be used for automotive use, the associated costs and efficiency may not apply. There is no graph or timeline detailing the progress of lowering the cost or increasing the efficiency of the process (e.g., waterfall plot), so the progress and accomplishments cannot be adequately assessed.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.0** for its collaboration and coordination.

- Collaboration with several institutions was presented, and it appears that the engagement between groups is beneficial to all those involved.
- Some collaboration with Ardica and the California Institute of Technology (Caltech) is evident, with the latter providing nuclear magnetic resonance (NMR) analysis to strengthen characterization of shelf life. However, overall the project appears mostly self-contained within the parent institution.
- This is a relatively small project with its own focus. The team was sharing some calculation results with Ardica for separation and recover steps.
- There are few collaborations. The team is essentially just working with itself (project partners are SRI International and Ardica). With the exception of the NMR work at Caltech, there are no collaborations within the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) or the Hydrogen Materials–Advanced Research Consortium (HyMARC).
- The collaboration was rated at 2.5 solely based on the fact that there were very few details given on what was collaborated on or with whom. Collaboration efforts with Ardica seem to be minimal at best.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **2.7** for its relevance/potential impact.

- This project may not meet current goals or objectives directly, but it is closer and more feasible than most other options currently being investigated. Other industries are interested in this technology beyond transportation, so possibly transitioning funding from the DOE Fuel Cell Technologies Office (FCTO) to a more relevant organization may be beneficial and more appropriate.
- In regard to relevance, the overview slide did not specifically address any barriers in the FCTO Multi-Year Research, Development, and Demonstration Plan. Listed barriers were more in line with project milestones likely negotiated with FCTO managers, so it is unfair to dock the project too much. For potential impact, it looks like the expertise developed in the project is being leveraged in support of new emerging applications in small power applications. It would have been helpful to see more quantitative connection to the FCTO goals on non-vehicular applications.
- The project has made some progress by improving the synthesis of AlH_3, which has potential to contribute to FCTO goals. Further progress could have been made if the project investigated a full refueling cycle or several cycles.
- From an automotive standpoint, the relevant impacts on regenerating AlH_3 appear to be minimal, because AlH_3 is not expected to be used as an automotive fuel (which is what the FCTO is focused on). However, the relevant impacts for portable power may be moderate.
- The project is primarily focused on development of an electrochemical method to form AlH_3. This method has been pursued for many years, and despite considerable effort, the team is not much closer to an economical method for the production of α-AlH_3. The Dow method with $NaAlH_4$ is unlikely to lower cost because formation of a THF adduct (as opposed to a diethyl ether adduct) requires exchanging with triethyl amine, which probably adds more cost than it reduces. This effort is unusual and therefore unlikely to have any significant impact on other projects.

Question 5: Proposed future work

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

- The future work proposed is logical to a point. Effective crystallization of AlH_3 from the adduct is the key to manufacturing the material at large scales at low cost. This is an appropriate focus and is critical to success. Developing guidelines for production and shipping is important and will indeed need to be addressed; however, effort should be directed toward identifying an optimized and automated process before standards and guidelines are produced.
- Although the presentation does not make this clear, it appears that the project is finishing shortly. There may be insufficient time to complete all the work proposed, and the researchers may need to prioritize. Optimization of crystallization parameters for other adducts seems open-ended and could be complex. Efforts directed at certification of AlH_3 quality and developing standards for shipping and storage could be more achievable and be of some value to the community.
- The future work is quite limited, so it is assumed that the project is coming to an end.
- No future work was proposed because the project is wrapping up.
- There does not seem to be any planned future work. It is not clear whether a cost estimate has ever been performed using the conventional Dow recipe. If so, it should be compared to the electrochemical route. The group has shown nice progress scaling up the Dow recipe to 200 g batches. A detailed understanding of the true costs associated with this method may help target future work on the most costly steps. Any future work on alternative methods should focus on AlH_3 recovery from adducts. This seems to be the critical step.

Project strengths:

- This project shows strength in its creative development of solutions to mitigate encountered problems. The reduction of feedstock cost and development of a new process are strong additions to the project and may help reduce the manufacturing cost. The increased batch size for crystallization is incredibly encouraging and may lead to an optimized process with larger yield. The stability of the material produced is also great to see.
- AlH_3 is a promising compound with useful capacity and hydrogen purity, so efforts to overcome cost and stability issues with this compound are valuable.
- There is nice progress with the scale-up to 200 g.
- The project strength is the application of AlH_3 for portable power.
- The 10 years of experience is a project strength.

Project weaknesses:

- The project appears defocused and lacking coordination. Modifying a method developed four years ago in the final year of the project comes unexpectedly and helps give the impression that the work is a series of experiments that are not part of a larger, well-considered strategy. There does not appear to be opportunity for any detailed, and perhaps more general, understanding to be communicated with the rest of the Program so that other projects can benefit. A publication describing the understanding learned would be desirable; the last paper (not patent) appears to be from 2012, before the current phase began.
- The project is disjointed in some regards. One of the main focus points, reducing dendrites during the electrochemical process, is not mentioned at all. The mechanochemical process seems to usurp the electrochemical method, and the path forward is unclear regarding which process will be used in the future. The use of DFT calculations on different adducts does not appear to have added any value to the project, as previously known methods were used.
- The project lacks focus. There is no clear plan for reducing costs. The electrochemical route has been pursued for a number of years with little success. Modifications to the Dow recipe do not seem to be targeting the most costly steps.
- From looking at the historical perspectives (patents and publications) of AlH_3 from the late 1940s to the present, it appears that no novel approaches have been explored. Most of the attempted ideas were looked at by Dow and others.

Recommendations for additions/deletions to project scope:

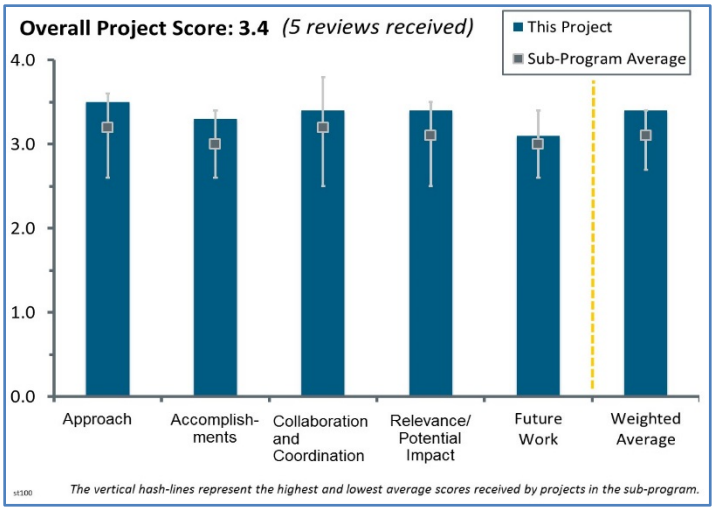
- The project should develop a detailed cost model of the Dow process that includes a realistic assessment of costs associated with each step. For example, solvent handling, materials storage issues, and safety aspects need to be considered along with the cost of precursors and energy requirements.
- The project should be focused on reducing feedstock costs and crystallizing larger batches of high-quality AlH_3. A single process should be selected and focused on to reign in the scope.
- This is not applicable because the project is ending.

Project #ST-100: Hydrogen Storage Cost Analysis

Brian James; Strategic Analysis, Inc.

Brief Summary of Project:

The goals of this project are to (1) conduct independent Design for Manufacture and Assembly (DFMA) cost analysis for multiple onboard hydrogen storage systems, and (2) assess/evaluate cost-reduction strategies to meet DOE cost targets for onboard hydrogen storage for light-duty fuel cell electric vehicles (FCEVs).



Question 1: Approach to performing the work

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

- The approach is to use DFMA to assess the cost of developing technologies, understand the manufacturing costs of the technologies, and project the ability to meet DOE's cost targets. The methodology is also used to identify some interesting areas for future cost avoidance.
- The project has an excellent team with clear goals.
- The approach of this project was focused on the key barrier of hydrogen storage, which is the cost. The project provides transparent assumptions and effective analysis for the various cost studies. An improvement in the approach could be to include additional verification of the results based on supplier cost estimates or confirmation.
- The analysis to address the cost comparison between four systems was completed in the first year in this five-year project. The weakness is that there is no way to validate how closely it will represent the real cost.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- The accomplishments surrounding cryo-compressed tanks for buses—understanding the impact of multilayer vacuum insulation, understanding the balance of plant on tanks, and costing out the pathway for new ligands in the manufacturing of MOF-74—will contribute to the success of the Hydrogen Storage sub-program. It is recommended that the project focus on some of the materials that are closer to being commercialized in the DOE Hydrogen and Fuel Cells Program (the Program), such as AlH_3 manufacturing, and also cost out the metal hydride-based storage system for fuel cell electric forklifts, which could actually facilitate the commercialization of hydrogen storage technologies into the marketplace.
- The project was able to make progress with several key hydrogen storage systems, such as cryo-compressed system cost estimates, metal–organic framework (MOF) material cost, and compressed natural gas (CNG) tank cost assessment. The main presentation should have included the last reviewer slide with the cost comparison for cryo-compressed and cold-compressed for the light-duty vehicles (LDVs). The cold-compressed slide with the tool development would eventually be interesting, although it seemed incomplete.
- The goal was to compare the four ways, and the team has done this. Many simplifications have been made in the process, but overall it can be used to provide guidance.
- The team is making good progress, but there seems to be an overdependence on data from other models, some of which are becoming dated. A sanity check to go back to more current manufacturing and design data, rather than have this analysis rely upon another analysis, would make the project better.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- The principal investigator clearly demonstrated collaboration with experts in the areas of compressed tanks (the Institute for Advanced Composites Manufacturing Innovation, Pacific Northwest National Laboratory, and Argonne National Laboratory [ANL]), cryo-compressed tanks (Lawrence Livermore National Laboratory), and MOFs (Lawrence Berkeley National Laboratory).
- The project appears to have a high level of collaboration with several experts in the field. In the past, ANL provided the performance analysis, and this project provided the cost analysis. It was interesting that this project was attempting to integrate the performance with the cost analysis in its development. It was unclear whether ANL was involved in this tool development. This project appears to have heavy collaboration with national laboratories, and it should expand to collaborate with industry to confirm its cost results.
- The team has done a great job. In addition to the current developers, some outside vantage points might be beneficial.
- The team has been collaborating with other laboratories to get a sense of the costs that are in circulations. However, more collaboration with different industries that are actually manufacturing different components would be beneficial. Also, some sort of validation, which can be obtained through collaboration with industry, is crucial.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.4** for its relevance/potential impact.

- The project is highly relevant for guiding hydrogen storage system designs and strategies toward commercialization. Without this project, it would be difficult for the Hydrogen Storage sub-program to discuss and assess cost projections.
- The project should continue to contribute practical costing guidance to the Hydrogen Storage sub-program and the hydrogen storage community for future decision making in these areas.
- The impact can be huge if the predictions take into account the actual drivers and have a way to validate them.
- This project is accomplishing the goals that it is tasked with, but the Program as a whole seems to be devoting a good deal of effort to analysis on a yearly basis, to the point that it is analyzing analysis.

Question 5: Proposed future work

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

- Good work is proposed.
- The future work appears to be the appropriate next steps. Additional discussions should occur with industry regarding confirming the CNG tank estimates and other cost estimates, if possible. The reverse engineering of material cost should be emphasized as a key item in the future work plan.
- It is recommended that the team steer the project to assess those technologies within the Hydrogen Storage sub-program that are nearing commercial success. Compressed tanks are on a solid pathway in the market, while adsorbent technology has a long way to go prior to being adopted in the commercial space for LDVs. However, metal hydrides for material handling equipment and AlH_3 for portable power are technologies that are being transitioned into the commercial space and could benefit tremendously from a thorough cost assessment.
- Coordinating a review with the ST-126 project (which is innovative but high-risk) is suggested. The project should also conduct a study of life-cycle costs and system reliability for the more complex systems being evaluated.

- The project is not a five-year project, as future work focused only on-fine tuning project methods, which will have only a secondary effect. It is suggested that the team focus more on validating cost predictions, as many component costs are very difficult to predict; anyone can have models, but it is important to apply error bars based on uncertainty, which will allow the team to compare different methods more effectively.

Project strengths:

- The strength of this project is the transparency of assumptions and disciplined approach to the cost analysis.
- The strong team that is familiar with the issues in hydrogen storage and good collaborations are project strengths.
- The project uses a good methodology to combine different costs of different materials and processes. It has a good approach for cost predictions.
- The quality of the people working on it is a project strength.

Project weaknesses:

- There are no glaring weaknesses.
- The overreliance on the analysis of others, as opposed to manufacturing data, is a project weakness.
- The project weakness is the lack of comparison of cost estimates with supplier values to provide confidence in the projections. The tool development for cold-compressed seems incomplete, and the team should consider other functional reasons for selection of Type III versus Type IV vessels, such as the permeation into the vacuum space and liner stability.
- There is no validation. The project needs to address cost with error bars because of the uncertainty of costs of composites due to the low fidelity of manufacturing processes, which leads to lower yield.

Recommendations for additions/deletions to project scope:

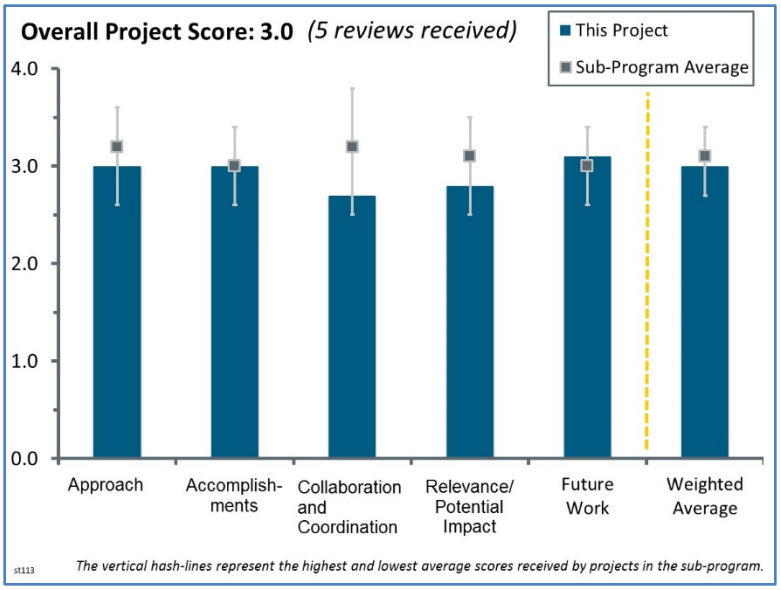
- Additional effort should be included to help guide research to achieve the DOE cost targets. For example, the reverse engineering of the material cost or determining the correct balance between performance and cost for carbon fiber for compressed tanks would be helpful.
- For the Hydrogen Storage sub-program, there should be larger but less frequent analyses.
- The project can be easily completed in three years based on the objectives. It should not be funded for five years unless other metrics are added to the project. There may be more deserving projects.

Project #ST-113: Innovative Development, Selection, and Testing to Reduce Cost and Weight of Materials for Balance-of-Plant Components

Jon Zimmerman; Sandia National Laboratories

Brief Summary of Project:

The overall objective of this project is to identify an alternative to high-cost metals for high-pressure balance-of-plant (BOP) components. The project goals are to (1) reduce weight by 50%, (2) reduce cost by 35%, and (3) expand the scope of construction materials for BOP.



Question 1: Approach to performing the work

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

- The use of stacking fault energy (SFE) to determine whether a material may be acceptable in a hydrogen environment may be a good screening tool, assuming the relative reduction in area is a good indicator for hydrogen compatibility. There are concerns that the methods of calculating the SFE may overpredict the measured SFE, especially in the case of Mn-containing materials. As a result, the calculated SFE may provide general guidance, but it may throw out acceptable materials and include unacceptable materials. The use of the face-centered cubic (FCC) lattice parameter is just one step further removed from providing a correct assessment of the acceptability of a particular alloy for use in hydrogen service.
- The premise of this project was that first-principles computations using density functional theory (DFT) and other simulation methods to assess chemical compositions and crystal structures of SFE values of alloys would identify suitable candidates for hydrogen storage BOP components. Experimental materials testing of test specimens either after hydrogen exposure or in a hydrogen gas environment would selectively verify predictions. The goal was to find higher-strength and lower-cost alloys compared to the industrial standard of 316L austenitic stainless steel. While the screening approach based upon SFE properties was extensive, this would address only a portion of the parameters necessary to design and manufacture cheaper and lighter BOP components. Important issues such as the impact of welding and fabrication methods were not addressed.
- The approach has some shortcomings. The materials discovery and experiments are being done without any reference to manufacturing. Even if the team discovers a new material that may be cheaper and may weigh less, the cost of manufacturing components with that material may make it prohibitive. This is an important issue that should have been taken into account. Also, the amount of weight and cost the team was trying to reduce was not made clear or stated. The type of BOP components being considered, their shape, their current weight, and current cost should have been the benchmarks.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

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

- The identification of specific commercially available alloys that meet the cost and strength targets is a significant accomplishment for this project.
- This project is scheduled to end in September 2017 after nearly three years of effort. The Sandia National Laboratories (SNL) researchers conducted an extensive series of simulations based upon DFT modeling of

SFE variation with alloy composition ratios. The impact of hydrogen on fatigue life was measured and related to model predictions. Two tentative candidates (i.e., XM-11 and Nitronic 60) that had ~40% the cost of 316L stainless steel were found favorable for hydrogen use. On the other hand, the figures on slides 14–17 showed substantial spreads on performance parameters with respect to lattice dimensions, Mn versus Ni ratios, and calculated SFE values. Hence, selection of specific "best" candidates seem problematical even without consideration of important characteristics that were presumably outside the scope of the project.

- After three years, the team has used materials discovery to identify other materials that may work, but there has been no testing or manufacturing of these materials for any BOP components. The team should have involved manufacturers of these components to see how the new materials will perform under manufacturing and how their properties hold up under pressure.
- It is unclear whether the modeling component of the project led to any specific alloys that are worth researching in more detail.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.7** for its collaboration and coordination.

- The project has a variety of collaborators involved with the supply chain and to assist in testing: a metal manufacturer (Carpenter Technology), a metal user (Swagelok Company), and a company with high-pressure testing experience. It may be beneficial to involve original equipment manufacturers in the selection process to expose them to the project research and possible new materials.
- Most of the effort seems dominated at SNL, with very little direct communication or involvement with its project partners, Swagelok Company and Carpenter Technology. If these companies did provide some detailed technical support, it did not seem to be included during the DOE Hydrogen and Fuel Cells Program Annual Merit Review presentation. The Hy-Performance Materials Testing organization apparently performed fatigue evaluation in gaseous hydrogen as a subcontractor.
- It was expected that the team would collaborate with manufacturers and other parts of SNL that were dealing with the entire system.
- Collaboration is relatively limited in scope and number.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **2.8** for its relevance/potential impact.

- Reduction of system cost and mass are critical to successful acceptance and implementation of fuel cell electric vehicles. This research to identify new materials that can achieve these objectives is important to the research, development, and deployment portfolio for hydrogen storage.
- This project does examine one of the Achilles' heels in widespread utilization of hydrogen as a fuel for vehicle transportation and other applications (i.e., the high cost of hydrogen-compatible materials needed for the BOP components for both onboard storage systems and the infrastructure). The team has identified at least potential lower-cost candidates that maybe viable; however, this project did not evaluate a number of other critical factors that must be considered before BOP components become commercially acceptable.
- It is not clear how much weight and cost savings the team is talking about. It seems unlikely that the project will make a significant impact, as this may be a very small cost compared to the entire cost of the system. Also, materials discovery is just the beginning of the study, so it may be worthwhile to see in absolute what the cost of the BOP is compared to the pressurized tank cost before moving forward in this direction.
- It is unlikely that this project will have much relevance to future hydrogen transportation. The authors list a 35% reduction in cost and 50% reduction in weight for the material. However, the authors should list the likely reduction in weight and cost for the overall vehicle storage system resulting from the better materials. It is assumed that much of the cost of valves and regulators is manufacturing costs and not material costs, so the system gain may be much less than for the material. It seems that basing project relevance on today's high costs for BOP is inappropriate, because the high cost is most likely due to small-scale production, and costs are expected to drop as valves and regulators are manufactured in mass.

Question 5: Proposed future work

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

- The tasks planned for the remainder of fiscal year 2017 are reasonable to finish this stage of the project. It would be good to provide a web-based tool for SFE estimations based on composition to let other researchers test its performance.
- The proposed future work is more testing of different materials at high pressure, which is only a small part of the puzzle.
- There are concerns about having a web-based tool for general use. Others may use this data without understanding its limitations. A high-SFE, low-cost material may not be acceptable for use in hydrogen. A disclaimer should be included. Based on the unexpected results of Nitronic 60, it would be very beneficial to be able to evaluate fatigue characteristics of materials at high pressure and low temperature. The crack growth mechanisms of the new materials should be evaluated as compared to typical stainless steels in a variety of conditions to understand the similarities and differences of these materials in a hydrogen environment.

Project strengths:

- SNL has decades of hydrogen embrittlement and compatibility experience that provides a sound basis for this study. The SNL researchers have considerable expertise in DFT and other simulation methods, as well as extensive in-house capabilities for in situ high-pressure experimentation.
- The project was able to identify materials that met the strength and cost targets and develop methods that might be able to identify new materials that may have similar strength and cost characteristics.
- The project has a great approach to materials discovery and uses good testing methods to characterize strength.

Project weaknesses:

- The correlations between SFE and the FCC lattice parameter and a material's hydrogen compatibility are not strong. Further research is required to identify parameters that are better indicators of the material's acceptability.
- The project did not pay attention to actual costs and components of BOP to be manufactured, and it did not couple the calculation with manufacturability.
- The basis of this project rests primarily on making a correlation of SFE parameters with the ultimate discovery of low-cost and high-strength alloys for BOP components. It has neglected many of the other processing and manufacturing issues necessary to achieve this objective. Extrapolation of these current specific properties being evaluated by SNL to high-performance components still seems to be a very large stretch.

Recommendations for additions/deletions to project scope:

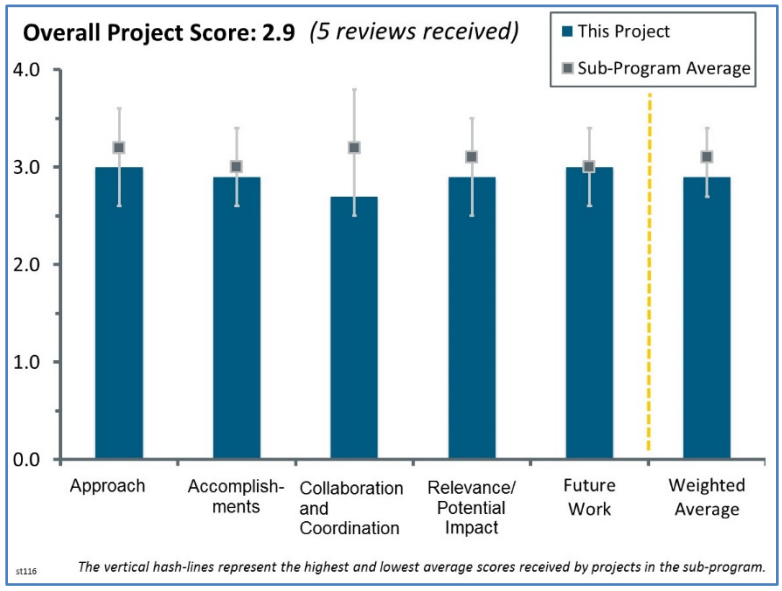
- Prior to initiating any of the future activities presented on the bottom portion of slide 21, an intense evaluation via relevant interested outside parties (e.g., materials researchers, alloy producers, and BOP component manufacturers) should be conducted by organizing a workshop or working group to assess whether any future project does provide sufficient insights to justify selections of any specific alloy for development of hydrogen components via the commercial entities. The ability of a national laboratory such as SNL to perform these activities has numerous benefits of objectivity and specialized expertise.
- An effort should be made to address issues in implementing the alloys identified. The machinability and formability of these materials and the ability to produce these materials in bulk should be evaluated.
- Collaboration with a systems group to address materials with manufacturing process feasibility that will reduce cost and weight is recommended.
- The project should eliminate the modeling work, which seems quite unproductive, and instead use the remaining resources to test whether one of the materials selected from the property tables (e.g., Nitronic 60) can be used for making BOP components (valves, regulators, etc.).

Project #ST-116: Low-Cost α-Alane for Hydrogen Storage

Tibor Fabian; Ardica

Brief Summary of Project:

Overall objectives of this project are to reduce production cost of α-alane (aluminum hydride, or AlH_3) to meet the U.S. Department of Energy 2015 and 2020 hydrogen storage system cost targets for portable low- and medium-power applications. Results will enable broader applications in consumer electronics (e.g., smart phones, tablets, and laptops), back-up power, unmanned aerial vehicles, forklifts, and vehicles.



Question 1: Approach to performing the work

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

- The work addresses lowering the cost of AlH_3 production through experiments and cost analysis of an electrochemical method. The approach is designed to provide much of the information needed to establish the economics of this process.
- It is a reasonable approach; looking at various strategies to lower costs makes sense. The cost model looks useful for understanding what it will take to meet cost targets. There is no clear path/strategy for getting from 0 to 300 MT/year. This is probably not going to happen in a single step, so it may be useful to develop a long-term plan that incorporates realistic intermediate steps and applications. The 92% $NaAlH_4$ yield at 2,200 psi is an exciting result and a nice development, but yields for conversion to AlH_3 are still very low (~20%). It is not clear what the plan to improve this is.
- The approach presented addresses most of the barriers well but falls short in a few areas. The process itself is in need of further investigation, because there are several important factors toward feasibility that have yet to be addressed. Capturing AlH_3 adduct at high yields from a continuous process before decomposition is a hurdle that needs to be overcome in order to prove that a continuous process is possible. The crystallization process is the main driving force behind cost, and it appears to have a relatively small amount of consideration put toward it. Recovering the cathode product will allow for cost to be reduced further, but optimization of the crystallization process should take precedent, as the amount of cathode material recovered from the reaction becomes trivial if the amount of AlH_3 produced remains low.
- The project does an economic evaluation of AlH_3 production from "spent AlH_3" using the electrochemical approach with experiments to benchmark and quantify assumptions about key steps in the process.
- Ardica's approach is based on the process proposed by Savannah River National Laboratory (SRNL). There does not appear to be a clear and obvious collaboration with SRNL or the other collaborators, resulting in the appearance of uncoordinated research efforts.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- There is good progress toward establishing a baseline for the cost of making 320 MT of AlH_3 with semi-quantitative insight into some of the challenges reducing efficiency. This effort covers (1) $NaAlH_4$ utilization, (2) adduct formation, (3) adduct conversion, and (4) $NaAlH_4$ regeneration. The adduct formation and conversion have been investigated in detail previously. Some of the work on amine choice

appeared repetitive, and it would have been helpful to put the current effort into perspective with this previous work that established a quantitative baseline. However, it would be recommended to have the electrochemists at Ardica focus remaining efforts on approaches to reach the target of 80% recovery of the $NaAlH_4$ in the limited time remaining.

- There is lots of nice work, but the 300 MT/year required to meet the cost target of $1/g seems impractical. Perhaps this could be improved with regeneration. It seems like the electrochemical process will be difficult to make this work. The switch from $LiAlH_4$ to $NaAlH_4$ seems like it provides a small cost reduction, but the additional hassle of using tetrahydrofuran (THF) and exchanging with triethyl amine seems like it outweighs any savings. Overall, it is good work, but the research does not seem to be much closer to significantly lowering costs.
- The most encouraging progress made has been the reduction in feedstock cost by changing the feedstock entirely, which is no easy feat late in a project. However, this cost reduction means nothing if process conversions and production rates remain low. A major assumption involved in the cost estimates (which still remain much higher than the goal) is that 90% of adduct is recovered in the crystallization process. Progress is slow in this area, with only roughly 30% recovered as of the time of presentation. The process is a difficult one; however, the low material yield is an indicator of poor progress. The use of a new membrane in the process is an accomplishment leading to a relatively high yield of adduct, bringing this aspect of the process closest to the assumed values in the cost model. Recovery of the cathode material and regeneration using spent AlH_3 needs optimization and further investigation, as yield is still too low.
- The project has made progress toward meeting goals by investigating individual steps in the production and identifying critical areas for improvement. The overall progress of preparing AlH_3 that meets the cost target is lagging.
- Ardica has verified that AlH_3 regeneration is a very difficult problem that is likely to be proven cost-ineffective. Historically, the critical step to the production scale-up of α-AlH_3 has been the solvent removal and crystallization processes.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.7** for its collaboration and coordination.

- Collaboration with the groups involved in this research is clear and appears to be beneficial to all the other projects related to this work.
- The project might have been a little more successful through stronger collaboration. It had the appearance of not reaching out to experts in the AlH_3 field.
- Collaboration with SRNL is claimed to have improved since the last review, although the only outcome seems to have been the use of the density functional theory calculation as one factor in ligand selection for preparing an adduct suitable for crystallization trials. It is unclear so far how effective these calculations are in identifying new ligands.
- There are essentially no collaborations listed. The collaborations table lists Ardica (itself), its subcontractor (SRI International), and SRNL. James Evans at University of California, Berkeley, seems to be the only real collaborator here.
- There does not appear to be a clear and obvious collaboration with SRNL or the other collaborators, resulting in the appearance of uncoordinated research efforts.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **2.9** for its relevance/potential impact.

- Hydrogen density and low desorption temperature make AlH_3 one of the few materials that could meet targets. However, it is still not clear how a primary (non-rechargeable) system such as this could be used on a vehicle. Portable power, unmanned aerial vehicles, and unmanned underwater vehicles make more sense in the near term.

- Project aspects align with some of the DOE Hydrogen and Fuel Cells Program (the Program) and DOE research, development, and demonstration objectives, but relevance to vehicle targets is a stretch and may not be completely fair. It would have been informative to learn what markets benefit from a 320 MT quantity of AlH_3. It may be too small for vehicles and too big for small power applications. There seems to be a large cost increase to build infrastructure for smaller production facilities. Reducing the cost of AlH_3 production is important.
- This project is relevant toward the goals and objectives outlined in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan in that it has the possibility to produce one of the best-fitting hydrogen storage materials currently available. Increasing scale and yield and reducing cost for AlH_3 will allow for further research into its use as a hydrogen storage material. However, the high cost and low yield currently demonstrated do not support progress toward those goals. The material still remains too costly, and the overall process yield is still much lower than it needs to be to be viable.
- The work does advance toward the Program goals by investigating a method for AlH_3 production with potential low cost. However, it is marginal whether the conversions and efficiencies achieved will meet the cost targets for low-power applications.
- Given the likelihood that AlH_3 will not be used as a hydrogen storage medium for automotive use, the production and regeneration of spent AlH_3 may not be as relevant or impactful. However, the use of AlH_3 for portable power does show a higher degree of relevancy for other program offices.

Question 5: Proposed future work

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

- The project is nearing completion, so there is little opportunity to do much more. Overall, recovery of α-AlH_3 from adducts should be a focus for improving total yield. This is the hardest step. The final report should include everything: other AlH_3 phases, impurities, and stability. The null results are important for the general community. A good example is the intermediate adducts that have been identified. This is very useful information.
- The project is wrapping up with some proposed near-term future work.
- The project is near completion, and there is little time for future work. The work proposed is unlikely to be achieved in the remaining time and is not particularly well structured. "Further develop strategies…" is not clear or planned in a logical manner. The investigators should identify the most critical problem and direct efforts toward a solution.

Project strengths:

- The project is strong in its development of the initial step of the process. The cell design and optimized process yield a decent amount of adduct, which is a good starting point. The change of feedstock material is important and allows the material cost to drop slightly, which is a step in the right direction. The possibility to reuse spent AlH_3 to regenerate the feedstock with a non-catalytic process is encouraging, but the rate needs to be investigated in order to optimize recovery.
- There are some nice developments over the years. The team clearly has considerable experience with this system and a strong understanding of the various challenges involved in the synthesis. The cost model is a nice, realistic look at what it will take to make this a viable material. It is certainly challenging, but it is nice to see these business challenges/barriers becoming clearer.
- The project has developed a cost model that takes account of most of the factors relevant to AlH_3 production and has tested some of the important parameters underlying the model.
- Ardica took on the very challenging task of regenerating spent AlH_3, and it is commended on an honest effort. This project dovetailed nicely with its portable power applications.
- The team's expertise in portable power applications is a strength.

Project weaknesses:

- There are no obvious weaknesses. Ardica attempted to solve a very difficult problem.

- The overall yield of the process is still too low to be viable. The focus was split between the three aspects of the process when most of the effort should have been placed on optimizing adduct recovery. Recycling the feedstock with spent product is not appealing if the process cannot produce product at a high enough yield to drastically reduce cost. The transition between the three areas of focus is also not clearly demonstrated. Removing large amounts of adduct from the electrochemical cell and transporting it to the crystallization process is a large challenge that will need to be demonstrated in order to develop a continuous process.
- The project relies on large-scale production, which does not appear to be consistent with the low-power applications central to the project. Cost targets for all efficiencies are short, and the approach to bridge gaps appears to be mostly Edisonian.
- Slide 24 ("Critical assumptions and issues") states THF-based adducts cannot be adequately converted to AlH_3. This was identified as a concern and one (of many) potential issues with the electrochemical method years ago. It is not clear why work has continued on AlH_3-THF. Issues with adduct separation have been known since previous work under the Metal Hydride Center of Excellence. Improvements in AlH_3 separation (recovery) are needed to get the cost closer to targets.

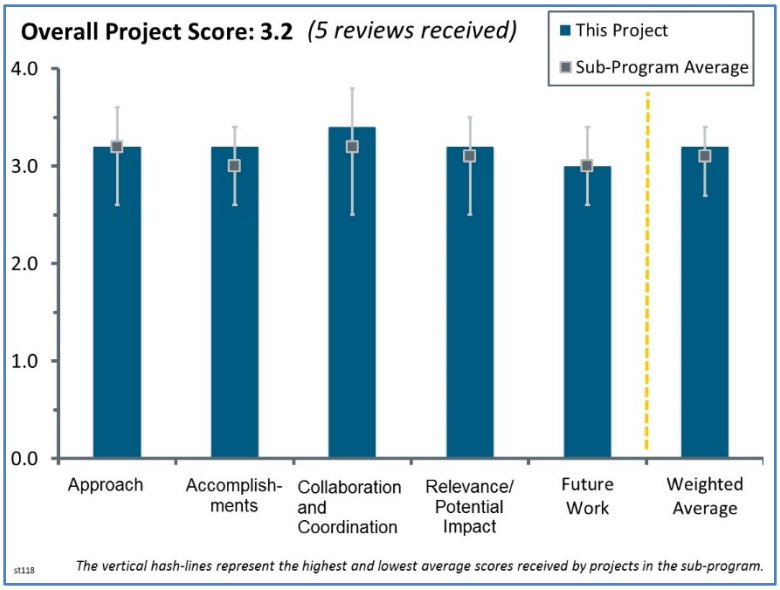
Recommendations for additions/deletions to project scope:

- The team should spend more effort on optimizing the crystallization process, and the recycling of spent material should not be investigated until the yield has increased dramatically enough to reduce cost.
- The key barrier is α-AlH_3 recovery. Future work in this area should focus on recovering α-AlH_3, either from adducts or from a more direct route.

Project #ST-118: Improving the Kinetics and Thermodynamics of $Mg(BH_4)_2$ for Hydrogen Storage

Brandon Wood; Lawrence Livermore National Laboratory

Brief Summary of Project:



The objectives of this project are (1) to combine theory, synthesis, and characterization techniques at multiple length/time scales to understand kinetic limitations and possible improvement strategies in $Mg(BH_4)_2$ with relevance to other light-metal hydrides, and (2) to deliver a flexible, validated, multiscale theoretical model of (de)hydrogenation kinetics in "real" Mg-B-H materials and use predictions to develop a practical material that satisfies 2020 onboard hydrogen storage targets. Current project year objectives are to synthesize MgB_2 nanoparticles with <10 nm diameter, measure x-ray absorption and emission spectra for bulk $MgB_2/Mg(BH_4)_2$ during stages of (de)hydrogenation, and compare measured and simulated spectra on informed models to determine local chemical pathways.

Question 1: Approach to performing the work

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

- The combination of validated theoretical models that incorporate anharmonicity and temperature to predict material properties and phase mixing in these complex hydrides and the parallel validation with experiments is the perfect approach. It will lead to a greater understanding of how the reaction pathways can be manipulated and has a reasonable chance of addressing some of the U.S. Department of Energy barriers.
- This is a nice combined computational/experimental approach. The focus on understanding mechanisms and pathways in $Mg(BH_4)_2$ addresses the key challenge(s) with this high-capacity material. Tailoring intermediates between dehydrogenated and hydrogenated makes sense. A confinement-free approach to nanosizing seems like a good one.
- Barriers are reasonably addressed, and the project is integrated with other efforts; however, removal of surfactants from the nanoparticle surface may be more difficult than it appears.
- Although the project is developing new models of $Mg(BH_4)_2$-related processes, it is not immediately clear what new insight is being gained.
- The study should balance thermodynamic and kinetic aspects of the hydrogen release process. It should build a testable model experimentally.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- The insights gained into the Mg-borohydride system from bulk to nanoscale have been impressive. The thermodynamic and kinetic insights have been somewhat surprising and insightful. There are many results presented here, and the depth and improvements of the suite of tools should place the team in a position to

leverage this to other systems as needed in future programs in the DOE Office of Energy Efficiency and Renewable Energy.
- The progress validating the $Mg(BH_4)_2$ phase diagram and shedding new light on how nanosizing affects thermodynamics and reaction pathways is nice. Synthesis and characterization of high-purity nanoscale MgB_2 is an accomplishment. The kinetic analysis of hydrogen uptake confirms a lower initial hydrogenation barrier in nanoscale material, as predicted. The in-depth investigation into initial hydrogenation of MgB_2 may be useful for identifying ways of tailoring the reaction pathway.
- The team has made steady progress toward the overall project objectives.
- The work is technically good, and results are interesting. However, it is difficult to see how it may enable the development of a practical high-capacity hydrogen storage material in the foreseeable future.
- It appears little progress has been made regarding Phase III goals, yet the project is scheduled to end in two to three months.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- The team works very well with the Hydrogen Materials–Advanced Research Consortium (HyMARC) and external collaborators.
- Collaborations are with the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) and HyMARC partners. Collaborations beyond Lawrence Livermore National Laboratory (LLNL) and Sandia National Laboratories (SNL) with other consortium members or seedling projects are encouraged.
- The collaborations are great.
- There are strong collaborations with partner SNL. It is unclear how the University of Michigan is contributing to the project.
- The team is in a unique position to collaborate with other institutions.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- The tools and methodologies are valuable in and of themselves, but the project has gained deeper insights in determining that the nanosizing of Mg-borohydride would probably not be a unique solution to the hydrogen storage problem (but perhaps in a hybrid situation or with catalysts, this could change). It is a shame that this project is ending, as the methodologies and insights have been the most impressive the reviewer has seen in this field.
- The project supports understanding reaction pathways in $Mg(BH_4)_2$ and how they are affected by nanosizing. The project is well aligned with the Hydrogen and Fuel Cells Program (the Program) objectives and goals. Considerable progress has been made in understanding these materials and explaining observed behavior, but the real value/impact comes with predicting and testing new materials systems. This should be the focus.
- This project is clearly relevant. However, the complexity of the $Mg(BH_4)_2$ system (and the unclear nature of the project's accomplishments to date) suggest that the impact on the Program will not be immense.
- The project tries to support and advance progress toward the Program goals and objectives. However, at the current stage, it is difficult to see how it may lead to the development of a practical material for on-board hydrogen storage.

Question 5: Proposed future work

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

- Overall, the plans for future work look good. The project will likely continue to provide new insights into reaction mechanisms. The project team needs to translate these new insights into new materials systems,

not just validate models with existing experimental data. Researchers should consider expanding collaborations to broaden the impact.
- Continued funding and effort in this project are beneficial for the overall DOE objective.
- The future work is logical, but there is only so much time left.
- The proposed catalyst work will add another layer of complexity to an already challenging system.
- Future work could be better defined. It is not quite clear why Ti catalysts are a specific focus. Also, other bullet points are quite generic.

Project strengths:

- The project is focused and well integrated with other efforts. It provides important new insights into these complex systems. Overall, it is excellent work.
- Project strengths include the good collaboration between LLNL and SNL. $Mg(BH_4)_2$ is an important hydrogen storage material, and an effort aimed toward making it function more efficiently is badly needed.
- The scope of the problem is well defined, and the approach has been excellent. The project team works strongly with other partners and is results-driven, publishing several good papers.
- A project strength is the unique position of the principal investigator and team in collaborating with other institutions.
- The collaborations are great.

Project weaknesses:

- It is unclear how the project has improved understanding of $Mg(BH_4)_2$.
- It is not clear that the project at the present stage shows the path to novel real-world materials.
- Understanding the catalysts moving forward might be too difficult to achieve without knowing the chemical specifications. Plans to deal with this are not obvious to the reviewer.
- Research has provided new insight into specific mechanisms, improving understanding. However, the goal is to ultimately guide development and optimization of new material systems. So far, it has fallen a little short in this area. Slide 7 indicates that confined systems are thermodynamically beneficial, while smaller particle sizes will tend to increase $B_{12}H_{12}$ formation. Given these results, it is not clear why was the focus was on synthesizing MgB_2 nanoparticles as opposed to confining MgB_2. Computational work should guide the synthesis efforts, not the other way around.
- The possibility of losing future funding is a project weakness.

Recommendations for additions/deletions to project scope:

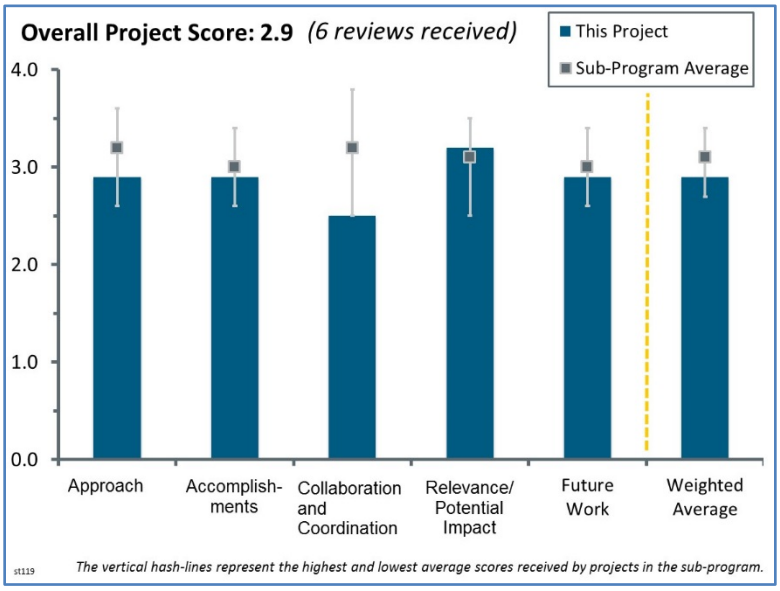
- This project should be extended, if at all possible. The catalyst part is going to need more time.
- The project should focus on converting mechanistic insight into new materials or strategies for meeting targets. It is not clear whether there is any hope of forming $Mg(BH_4)_2$ without going through $B_{12}H_{12}$.

Project #ST-119: High-Capacity Hydrogen Storage Systems via Mechanochemistry

Vitalij Pecharsky; Ames Laboratory

Brief Summary of Project:

This project is developing novel high-hydrogen-capacity silicon-based borohydrides (Si-BH) and composites with the aim of achieving low-cost, high-performance hydrogen storage materials. Si-BH materials are predicted to have borderline thermodynamic stability. Researchers will use stabilization strategies based on hypersalt formation using alkali and alkaline-earth cation additions to bring the enthalpy of desorption into the targeted range. The project will also investigate borohydride/graphene nanocomposites that utilize graphene's advantageous properties.



Question 1: Approach to performing the work

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

- This project is investigating hydrides based upon B and Si to determine whether any combinations of these elements can be "discovered" to serve as viable hydrogen storage media with the potential to satisfy the U.S. Department of Energy vehicle requirements. This is a reasonable approach that examines systems not previously characterized to any significant extent. The researchers recognize the issues of limited reversibility, the risk of reaction temperatures that are too high for hydrogen absorption/desorption, and risk for extensive impurity contents. The preparation methods are acceptable, as are the characterization techniques (i.e., volumetric measurements with mass spectroscopy, nuclear magnetic resonance [NMR], x-ray diffraction [XRD], differential scanning calorimetry, thermogravimetric analysis, and Fourier transform infrared spectroscopy [FTIR]) being used to identify reaction and decomposition products along with the subcontracted computational modeling at University of Missouri, St. Louis (UMSL).
- The project is focused on developing Si-BH materials, which on paper have high gravimetric and volumetric hydrogen capacities. The theoretical approach seems to be very sound. As far as the experiments are concerned, the emphasis is on solid-state reactions, specifically mechanochemistry. One concern with mechanochemistry is that the energy formed during the ball milling decomposes the relatively unstable Si-BH species, even if they form during the process. It would be desirable to attempt to perform this under gentle conditions, for example through low-temperature solution approaches.
- The investigators utilize a standard "grind and find" approach, ball milling Group I borohydrides with reactive precursors to produce novel borohydrides. This work is novel in that reactive Si-based compounds are utilized in hopes of preparing Si-BH compounds. The hydrogen storage properties of the materials produced have been screened using standard analysis, and their characterization is attempted using standard methods.
- The overall approach is good, as the partners use theory and the literature to guide the most feasible candidates for mechanochemistry methods.
- The project has a very interesting approach. The search for Si-BH compounds could lead to a low-cost material.
- Ball milling as a means for materials synthesis offers a unique alternative method for materials synthesis. However, its scalability for large-scale application might be limited.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- During the past year, the team has produced, via mechanochemistry methods, several MBH_4-SiS_2 and Li-B-Si-H systems and investigated their relevant properties for hydrogen storage applications. While these materials do not currently meet the required DOE performance targets necessary to pass the defined go/no-go decision, they do exhibit behavior that appears rather promising. The results obtained via NMR, XRD, and FTIR do help identify the formation of these Si-based complex borohydride phases. This study complements and extends prior results on other B-based hydrides.
- The product characterization effort of this project is much improved from last year. In addition to the "quick and dirty" temperature programmed desorption screening of the materials, NMR and infrared spectra have been obtained for the products. Most notably, one compound (sadly not a Si-containing product) has been structurally characterized through Rietveld analysis of powder X-ray data. Unfortunately, no isothermal desorption studies have been carried out, and only over-optimistic "onset desorption temperatures" are still reported. While the efforts to date have generated some very interesting new phases, the Si-containing phases remain poorly characterized. Moreover, none of the Si phases have been found to have an adequate hydrogen cycling capacity, and all of these phases are plagued by some level of B_2H_6 elimination during discharge.
- Reasonable progress has been made to find possible Si-BH materials since the last DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR), and the project has adapted its focus toward more promising combinations of materials.
- There is good progress toward overall DOE and go/no-go milestones, but the project would definitely benefit from collaboration with the Hydrogen Materials–Advanced Research Consortium (HyMARC).
- The most promising and high-capacity Si-BH species seem to be decomposing under ball-milling conditions. It is surprising that no other synthetic approaches have been attempted to isolate these species.
- The project has made adequate progress as defined.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.5** for its collaboration and coordination.

- The collaboration is very good to good.
- During the first approximately 18 months of this project, essentially all tasks have been performed at Ames Laboratory (Ames) or, for the subcontracted computational work, at UMSL. However, the principal investigator (PI) indicated that plans are underway to utilize capabilities from Hydrogen Storage Characterization Optimization Research Efforts (HySCORE) and HyMARC. High-pressure synthesis of M-Si-B solids at the Sandia National Laboratories facility was explicitly mentioned. It is also recommended that the neutron capabilities at the National Institute of Standards and Technology and in situ NMR at Pacific Northwest National Laboratory are added for characterization of the reaction and decomposition products, as well as utilizing modeling and simulation capacities at Lawrence Livermore National Laboratory and Lawrence Berkeley National Laboratory.
- Interactions among partners concerning theory-driven experiments are good. Plans were presented for more needed collaboration with other partners, such as HyMARC, in the future.
- Collaboration would be much improved if the project were included with HyMARC.
- The authors should explore more avenues for collaboration with HyMARC and HySCORE.
- There is little collaboration outside of Ames.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- The project definitely supports and advances progress toward the DOE Hydrogen and Fuel Cell Program goals by looking at alternative, new, and unexplored Si-based systems for reversible hydrogen storage.
- Demonstrating a fully reversible Si-BH material has the potential to significantly advance the state of the art in the area of hydrogen storage materials.
- The project has good alignment to DOE goals, and this project brings Ames' unique mechanical synthesis capacity to bear on the issues.
- Despite its great potential and the progress that has been made toward developing borohydride-based materials as hydrogen carriers, no compounds have yet been identified that can be utilized in practical applications. This project explores a previously uncharted section of borohydride compositional space in hopes of finally locating the "holy grail" material.
- If new Si-containing borohydride-based phases can be discovered and demonstrated to meet approximately the derived materials properties with respect to storage capacities and reversibility, possess absorption–desorption properties capable of withstanding polymer electrolyte membrane fuel cell operating temperatures, and have negligible contamination of the hydrogen supply gas to satisfy the DOE storage system targets, this project would be very useful to the DOE Fuel Cell Technologies Office goals. However, the challenge of simultaneously satisfying all of these requirements is very great, as clearly demonstrated by failures from essentially all boron-based hydrogen storage materials.
- Although the project specified addressing issues related to hydrogen storage is its major objective, its relevance to hydrogen storage is limited.

Question 5: Proposed future work

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

- The proposed future work has been planned and modified in a sufficiently logical manner based on the successes and failures of the accumulated data collected.
- The PI provided a generally sound plan for preparing M-B-Si-H phases and characterizing both the hydrogen storage parameters and important structural properties. It is recommended that the project increase collaborative interactions with HySCORE and HyMARC to provide broader and more detailed characterizations. It is also recommended that the Ames team look more closely at the residual gas analyses (RGA) (i.e., mass spectrometry) assessments for the formation of critical gaseous impurities (e.g., B_2H_6, SiH_4, and H_2S) in the hydrogen gas released during reactions and desorption. Detection of these reactive species can be extremely elusive because of their decomposition or reactions prior to entering the RGA sampling chamber, unless the detector is mounted nearby and in the line of sight of the reaction vessels. Without this configuration, the RGA measurements will produce false negatives indicating that the primary causes for irreversible reactors are not occurring. Furthermore, that background pressure of hydrogen can influence the amount of impurity species formed. Finally, the team should look more thoroughly to identify decomposition products that do not contain boron (e.g., LiH) that may be in a nanocrystalline or amorphous form, thus preventing observations via XRD.
- There is good proposed work, but there are questions about moving to Li-based systems because of cost issues. The reason for starting with Li is understandable, but moving to Na, Ca, etc. is suggested.
- The project may offer some insight into hydrogen interaction in hydrogen storage, but its potential application is expected to be small.
- The authors should explore alternative synthetic approaches in instances when mechanochemistry fails to yield the desired product.

Project strengths:

- Mechanochemistry methods provide a powerful and unique means of developing new materials for reversible hydrogen storage that cannot be as easily accomplished in other ways. It is a worthwhile avenue of research for attempting to discover new materials to meet the DOE goals. Ames participants are experts in this area.
- The Ames team has extensive experience and expertise in preparing and characterizing diverse metal hydrides that are very valuable for conducting the tasks comprising this project. As summarized on slide 22, Ames also has a variety of good experimental techniques for preparing and characterizing metallic and complex metal hydrides.
- The project is focused on high-capacity materials that on paper could meet the DOE targets in terms of the gravimetric and volumetric hydrogen densities.
- The project is exploring a previously uncharted area of borohydride compositional space.
- The unique mechanical synthesis expertise at Ames is a project strength.
- The people involved in the project are a project strength.

Project weaknesses:

- The study may be useful for fundamental research in materials and chemistry, but its potential application is not clear.
- The project needs more collaboration with HyMARC.
- Although new compounds can be formed by the mechanochemistry technique, the resulting products are sometimes not single-phase or well understood. More characterization efforts will be needed to sort out what is actually forming in these cases. Also, the high-pressure mechanochemistry activity was slow to be re-established after an accident-induced shutdown, which likely had an adverse impact on the project.
- The project seems to put a good deal of emphasis on mechanochemistry, which was shown to be counterproductive for the synthesis of labile or unstable species. The synthetic conditions and the composition space should be expanded to increase the chance of isolating the desired Si-BH_4 species.
- Because of time constraints, the investigators are forced to take a much too Edisonian approach to their studies. As a result, a systematic structure–reactivity relationship cannot be established. Such a relationship could provide guidance to this otherwise random-walk effort.
- This project has been performed mostly in isolation, without involvement from the HySCORE or HyMARC members (although these interactions are apparently commencing at this time) or the international metal hydride research community. It appears that the only method used (or available) for preparing the various M-B-Si-H materials is via some type of mechanochemistry either with or without the presence of high-pressure hydrogen. Successful synthesis could well require other approaches. Also, there was no indication in the AMR package of conference presentations or publications for the work performed to date in this project.

Recommendations for additions/deletions to project scope:

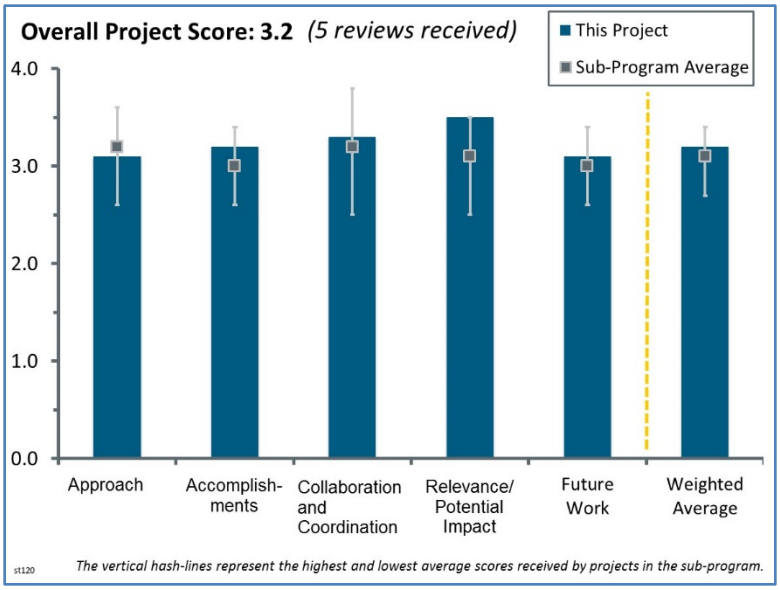
- The future plans for the remainder of the project, outlined on slide 19, are good, reasonable objectives. There are three specific recommendations beyond the more general comments made during this evaluation:
    - The project should search more diligently for volatile species such as B_2H_6, SiH_4, and H_2S using a mass spectrometer with its input close to the reaction vessel, because formation of these species will cause irreversible loss of hydride storage capacities.
    - The project should examine any promising candidate with elastic and inelastic neutron scattering methods.
    - The project should search for nanocrystalline or amorphous phases using magic-angle spinning NMR with the ^{2}H and ^{6}Li nuclei, which permit higher resolution spectra for phase identification compared to measurements of the ^{1}H and ^{7}Li isotopes.
- More product analysis capabilities would be desirable, and more collaborative interactions with HyMARC should help accelerate the results and attain the project goals.
- The investigators should utilize resources available from HySCORE and HyMARC to help them characterize the materials they have generated.
- The project should limit work on Li-based hypersalts.

Project #ST-120: Design and Synthesis of Materials with High Capacities for Hydrogen Physisorption

Brent Fultz; California Institute of Technology

Brief Summary of Project:

This project aims to address challenges related to the volumetric capacity of onboard hydrogen storage systems and the low temperature and low enthalpy of adsorption. Researchers are designing and synthesizing materials with high capacities for hydrogen physisorption. The focus is on graphene rather than activated carbon, as single-layer graphene is a platform with an excellent surface-to-volume ratio. The project will use graphene oxide chemical routes and plasma approaches to synthesize and functionalize the materials.



Question 1: Approach to performing the work

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

- The work is on graphene-based carbons for storage, with the focus on graphene because of its high stability and conductivity. The ability for this material to form the slit pore geometry is deemed optimal for gas diffusion. The approach to tune pore size and add metals (e.g., nanometer-sized Cu) onto the material has demonstrated increased hydrogen uptake capacity (0.015 wt.% near room temperature). Specifically noteworthy are the thermodynamic considerations in the approach to temperature-programmed desorption (TPD) measurements, including the following:
    - The need for absolute hydrogen uptake data for the Clausius–Clapeyron equation to be applied to gain enthalpy data has been established.
    - Constant enthalpy can be achieved with intercalated carbon systems and results in higher-temperature desorption at lower pressures.
- The modification of the chemistry of pores within high-surface-area carbon-based materials is a viable approach to increasing the heats of adsorption. However, this work seems very similar to that of Ted Baumann and Jie Liu during the Hydrogen Sorption Center of Excellence. It would have been beneficial for the principal investigator (PI) to specifically outline the uniqueness of the approach. The use of plasma for carbon modification was also part of the work overseen by Lin Simpson. The team should be specific about how this is a unique approach as compared to past work.
- The approach is to design new and evaluate existing carbon-based sorbents for hydrogen storage.
- The approach and work in terms of the carbon–graphene functionalization is well described, while future new routes for incorporation of Cu are not well described. The Cu is incorporated via Cu salt/reduction using eight different routes, most of which have been completed (slide 16). There are only two more routes to try. There has been little or no difference in the hydrogen adsorption between batches 5, 6, and 7. Slide 18 shows that the Cu has created a ~0.003 wt.% enhancement in the excess capacity. This is a very small difference, and it is questionable whether this difference is beyond the measurement accuracy (however, it is difficult to say without knowing the sample size). An enhancement of ~0.003 wt.% above MSC-30 is a small difference and would also produce a small shift in the isosteric heat of adsorption. The approach beyond the eight batches is not described.
- The work aims to improve the capacity of carbon-based sorbents by assembling materials from graphene or graphene oxide. This approach is meant to control the architecture more carefully, e.g., by creating a slit pore geometry with tuned dimensions. However, there is little evidence of an experimental design to control this. The approach to overcome barriers by functionalization (to improve adsorption enthalpy) appears somewhat speculative, as the synthesis route is less controlled.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- This project addresses the important goal of creating high-surface-area carbon material and increasing the isosteric heat of adsorption. The addition of Cu particles to graphene materials with <10% reduction in surface area is aligned with the goals of DOE. The PI showed that large quantities could be synthesized, which has been a barrier to many research groups in the past. Synthetic reproducibility, in general, was also achieved, as four samples with a small change in the synthetic parameters resulted in materials with very similar surface areas. The amount of progress is good. It seems that the majority of the time for this project has been spent functionalizing the graphene. Although this is a critical step in creating the materials, the work will now be able to focus on the incorporation of the metal. This is the challenging step. The amount of progress seems very good. There are many questions the PI has yet to answer regarding incorporation of the Cu particles, dispersion, the role of the size of the Cu particle, and the effect of any oxide formation and hydrogen diffusion issues.
- This has been an ongoing effort that has yielded results related to thermodynamics, kinetics, and materials design. The researchers have achieved high-surface-area samples that are functionalized with Cu. These materials have demonstrated large hydrogen capacity (0.015 wt.%) at near-room temperature. It would be nice to see, in the future, that the high-surface area samples are tunable (i.e., surface areas of 2,000 m^2/g are achieved and controlled through well-defined processing parameters). Likewise, an assessment of the defect concentration, type, and their role in the hydrogen uptake process would be useful for further improvement of these materials. The stated future goal of changing the metal sites from Cu to Ni is a good one.
- The preparative work on the carbon materials has been very successful. In looking at slide 17, the graph in the bottom left is a little disconcerting. With all the past work the PI has done on metal-modified carbon materials, it is not clear why it would not be expected that one would observe an increase in excess uptake. Copper with multiple oxidation states is primed to undergo some reduction on exposure to hydrogen, or even formation of a surface hydride. The slopes after 0.2 bar seem to match the blank MSC-30 results. It puts this "accomplishment" into question. There should be a determination using TPD instead of a Brunauer–Emmett–Teller (BET) surface area analysis of whether any side reactions occur. The fact that the sample apparently contained 20% Cu also leads to some doubts.
- The team has produced small samples with high surface area that approximately match the capacity of previous carbon systems. The larger-scale syntheses have very low surface area, and the way forward appears to be through collaboration with Cealtech AS. The (small) increased uptake with Cu functionalization is questionable and could easily be attributable to reduction of Cu oxides or other non-sustainable effects. The goal is to improve adsorption capacity (and enthalpy), but only a few samples have been measured (or at least presented), despite many being synthesized. While the team has been active and completed a substantial amount of work, the results indicate that substantial gaps remain between the current performance and DOE goals.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.3** for its collaboration and coordination.

- The researchers have partnered with a Norwegian company, Cealtech AS, which is helping to scale up the graphene production to kilograms per day. Collaboration with the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) has permitted the transmission electron microscopy examination of Cu metal on graphene using high-angle annular dark field imaging (HAADF). This is an optimum approach for examining metals within a carbon background. Further collaboration with HySCORE to examine defects in the graphene from reduced graphene oxide would be beneficial. Particularly, Fourier transform infrared spectroscopy (FTIR) and/or x-ray absorption spectroscopy (XAS) at in situ hydrogen uptake conditions will help determine whether the defects are beneficial to this process. Additionally, the HySCORE collaboration on characterization may help develop benchmarks of defect quantity, which could feed back into processing parameters to further tune defect concentration.

- Collaborations included work with HySCORE, Cealtech AS, and Liox Power, Inc. (Liox). The different roles of Cealtech AS and Liox are not clear. The Pacific Northwest National Laboratory component (HySCORE) is an important collaborator for pursuing the future research of understanding the Cu incorporation. The research team is very capable and will undoubtedly reach out to collaborators when needed to understand the effect of metal incorporation.
- It is suggested that the team work with the Hydrogen Materials–Advanced Research Consortium (HyMARC) and/or HySCORE to get some TPD and possibly diffuse reflectance Fourier-transformed infrared spectroscopy (DRIFTS) experiments to identify whether any side reactions are occurring.
- The role of Liox is not clear in the presentation, and although the role of Cealtech AS in making large quantities of graphene is understandable, it is not clear how this relates to efforts to make specimens in small scale by quite different methods. Cealtech AS appears to be the only option for making high-surface-area materials in larger quantities. Collaborations with HyMARC and HySCORE appear to be limited, although plans to increase these, and especially to seek confirmation of adsorption data, are desirable.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.5** for its relevance/potential impact.

- There are many reasons that this project is poised to affect the DOE Hydrogen and Fuel Cells Program (the Program) goals. Among them is the scale-up reactor design, which, if successful, will open the door to many researchers for examining graphene and its role in hydrogen storage. The researchers are one of the few groups to focus their successful demonstration on room temperature data for hydrogen uptake. The small (0.015 wt.%) but measurable uptake is noteworthy. This “holy grail” approach to adsorption isotherm data collection is commendable.
- The potential impact of determining how pore chemistry could be used to control binding energies without greatly altering sorption capacities is beyond significant.
- This project is investigating the role of metal clusters with high-surface-area carbons. The overall approach of this project enables a careful investigation of the metal–carbon and hydrogen interaction. The previous work has produced large-scale reproducible materials with which to work. The research team has valuable experience to achieve efficient findings.
- This effort is relevant to the overall Program goals. There is an interesting effect of Cu on the hydrogen uptake; however, the origin of this effect is unknown. A more detailed characterization of the chemical state and morphology of the Cu-doped materials is needed.
- The project has potential to advance the Program goals, but the evidence to date suggests this is far from certain. The capacities shown so far are similar to known materials, and any signs of enhancement are questionable.

Question 5: Proposed future work

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

- The proposed future work is a logical extension of the progress made to date. Further details into the plans for how these challenges will be tackled, coupled with descriptions for go/no-go decision measures, would have improved the future plans section of this work.
- The future work proposed is sensible and needed for this project, although some of the strategies are not entirely clear. For example, it is not clear why turbostratic stacking is desirable; it is not clear whether this will improve or diminish the ability to control slit pore geometry and pore dimensions. It is not clear what strategies will be followed to increase and control the distribution of metal functionalization. Validation of adsorption/enthalpy results with HySCORE should be a priority.
- The proposed future work is focused on gaining a fundamental understanding of hydrogen–carbon and hydrogen–metal interactions.
- More specifics on the metal incorporation would be helpful.
- The route forward in terms of metal incorporation and its characterization was not described well.

Project strengths:

- The project represents one of the few that demonstrate small room temperature uptake of hydrogen. The materials system is very promising because it provides at least three properties that could be controlled independently for gaining optimal hydrogen uptake. Those three variables are the (1) defect concentration on the graphene layers, (2) metal sites distributed on the graphene, and (3) surface area of the graphene. Other variables that were mentioned in the work and could be controlled are interlayer spacing for the slit pore geometries. Another major strength of the project is the incorporation of a scale-up processing technology.
- The ability to generate large-scale reproducible carbon materials is critical to the progress of the project. The team has successfully demonstrated this. The team has the knowledge and expertise to proceed down an efficient pathway to incorporate the metal to investigate the isosteric heats of adsorption.
- The project strengths are that it approaches the barriers from a reasonable theoretical basis and explores synthesis from a number of angles to increase chances of success.
- The project is well structured, with a good combination of theory and experiments.
- The collaborations established with Cealtech AS are a project strength.

Project weaknesses:

- It would have been useful to see further details into how the optimization of surface area and metal site distribution could be achieved. This is likely a weakness in the description of the project, rather than in the project itself. There were no major project weaknesses.
- The lack of characterization of materials is a project weakness.
- There is some lack of control over structure and stacking of graphene sheets, as well as their functionalization. Improvements over existing sorbents have not been convincingly demonstrated so far.
- One potential weakness is the limited collaboration with the HySCORE and HyMARC teams, and the project is not fully taking advantage of the theory and experimental tools available.
- The team has tried six different routes to incorporating Cu, and two more listed in the table on slide 16 are left to investigate. There has been little or no increase in the adsorption between three different batches. It is unclear what the approach for incorporating the metal beyond slide 16 will include.

Recommendations for additions/deletions to project scope:

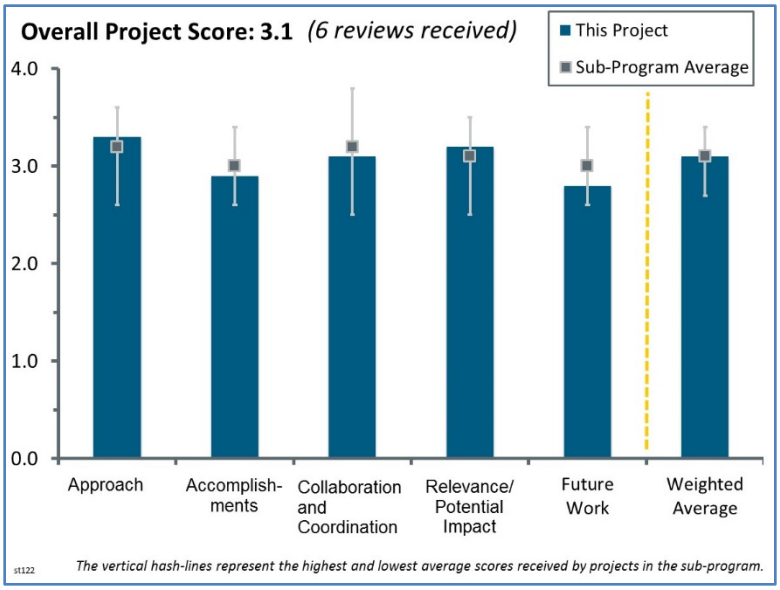
- There does not appear to be a need to significantly alter the project scope. However, it would have been good to see some strategy as to how the investigators intend to go about their efforts to improve their graphene structure and functionalization. Validation of uptake in functionalized samples is a priority.
- Suggested additions are further characterization in conjunction with HySCORE in order to determine the quantity of defects on the graphene. There are no suggested deletions.
- The work on materials with low isoteric heats of adsorption should be discontinued. There should be more focus on identifying materials with a binding energy of more than 10 kJ/mol hydrogen.

Project #ST-122: Hydrogen Adsorbents with High Volumetric Density: New Materials and System Projections

Don Siegel; University of Michigan

Brief Summary of Project:

A high-capacity, low-cost method for storing hydrogen remains one of the primary barriers to the widespread commercialization of fuel cell vehicles. Storage via adsorption is a promising approach, but high gravimetric densities typically come at the expense of volumetric density. This project's goal is to demonstrate best-in-class metal–organic frameworks (MOFs) that achieve high volumetric and gravimetric hydrogen densities simultaneously, while maintaining reversibility and fast kinetics. The approach entails high-throughput screening coupled with experimental synthesis, activation, and characterization.



Question 1: Approach to performing the work

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

- Adsorbents are the best bet to meet the Hydrogen Storage sub-program goals and need to be investigated in a systemic manner, as is being done here. This screening method is an efficient approach, assessing currently known candidates.
- This project seeks to demonstrate MOFs that achieve high volumetric and gravimetric hydrogen densities simultaneously, while maintaining reversibility and fast kinetics. This work combines atomic-scale, experimental synthesis/characterization with system-level modeling. This unique approach enables a broad view for assessing MOF materials. Progress and plans for each area of the project were relevant and well described.
- The approach is to use a combination of theoretical modeling and experiments to explore high-hydrogen-capacity MOFs. The advantage of this approach is the high throughput of the calculations, which allow rapid screening of >100,000 hypothetical MOFs.
- This has been a very successful project since its beginning. It has been a well-designed approach—and has helped enormously in the area. The only concern, which is the same every year, is the use of crystalline density instead of packing density in the calculations.
- The team has developed a nice approach for high-throughput screening of candidate materials through computation, synthesis, and characterization of the promising MOFs and circling back to computation for model validation. On slide 3, it was stated that "the [Hydrogen Storage Engineering Center of Excellence (HSECoE)] developed a 100 bar MOF-5 storage system that approached competitiveness with 700 bar compressed hydrogen." The results that have been presented by the HSECoE do not appear to support this statement. It is not clear whether the Grand Canonical Monte Carlo (GCMC) method is applicable to MOFs with more than one hydrogen molecule attached to a substrate atom.
- The high-throughput screening approach for materials in the Cambridge Structural Database (CSD) probes for surface area (and presumably skeletal density) of prospective adsorbent candidates. As such, this approach relies on a limited number of physical attributes to determine uptake. The metrics that are addressed are based on "total" values inferred from single crystal data. In presenting data this way, any ability to identify adsorption behavior that might suggest design routes for materials of this type is lost.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- This project shows progress in each category with contributions from each collaborator, including synthesis, experimental measurement, and modeling. It is, however, somewhat difficult to distinguish the work completed this year versus the last year. It appears that this year eight new MOFs have been synthesized and three are in progress, numerous adsorption isotherm measurements at various temperatures have been performed, and the hydrogen capacity of 470,000 MOFs has been computationally screened. This project has made excellent progress. This work is in line with DOE goals and provides an important link between structural properties and capacities. The designation of "usable capacities" is an important distinction made in this work. All total volumetric capacities are based on the crystalline volume, which is known to over-estimate the capacity. Future work for the project included densification (of the samples), and it will be very interesting to see these results.
- The researchers have done a very good job, with significant accomplishments.
- Numerous MOF candidates have been screened and the best candidates synthesized and evaluated.
- The project seems to be focused exclusively on high-surface-area MOFs. While this is interesting from a fundamental point of view, it would be useful to expand these studies and put more emphasis on calculating and measuring the isosteric heats of adsorption.
- The team has made very good progress in the past year, having screened nearly 500,000 MOFs computationally and identified more than 2,000 compounds that might potentially surpass MOF-5 by at least 15%. The crystal density is used in this study, ignoring packing effects in a tank. While this is ideal to determine the limits of hydrogen storage, it is more realistic to account for loss (~25%) in volumetric uptake when projecting usable volumetric capacity. It does not appear that this project has the potential to uncover game-changer materials with the necessary capacities to meet the DOE technical targets in system gravimetric and volumetric capacities.
- It would help to use this information to identify any physical principle that could be discerned in order to help those involved in new materials synthesis to benefit from this survey. The metrics that are addressed are based on "total" values inferred from single crystal data, as on slide 14. In presenting data this way, any ability to identify adsorption behavior that might suggest design routes for materials of this type is lost. On the other hand, the GCMC calculations presumably generate what is essentially an absolute uptake value to which is added a gas law contribution. The usable capacity is then presumably calculated at 5 bar pressure. At least, this is an interpretation based on the slide 15 value for NU-100, which has been reported in the past by the group at Northwestern to have a much higher volumetric density than is listed in the table. In any event, all of the usable volumetric values noted here are less than 40 g/L. It is not clear whether this is an intrinsic limitation of materials of this type as far as volumetric density. These are also presumably calculated for single crystal values. While an engineering analysis was done for just a few materials, the improvements to performance appear to be marginal.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.1** for its collaboration and coordination.

- This project shows progress in each category with contributions from each collaborator, including synthesis, experimental measurement, and modeling. The overall project organization is well laid out to incorporate each aspect.
- The project is structured in a way that allows multiple collaborations with experimentalists and theoreticians working in the area of MOFs for hydrogen storage.
- There are strong synergies among the team members but limited collaboration/interaction with other institutions.
- Better use of the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) capabilities should be made to gain a deeper insight into why the better MOFs identified are better.
- Save for system modeling work, the collaborations consist of the prime and subcontract participants.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- This work provides a unique broad view to consider gravimetric and total capacities with structural material properties. The team has considerable expertise and experience in modeling, synthesis, and measurement.
- The effort is well aligned with the DOE Hydrogen and Fuel Cells Program (the Program) objectives. It is desirable to put more emphasis on increasing the hydrogen binding energy of this class of materials, so strategies to accomplish this should be explored both computationally and experimentally.
- This study forms a good overview of MOF adsorbent capabilities, but it does not address achieving materials for higher temperature adsorption. It is not clear how this approach can be modified to address the search for materials with higher adsorption energies.
- This project can enhance its relevance and impact by providing additional insights from calculations at room temperature.
- There appear to be some real limitations as to whether this class of adsorbents will make the substantive improvements to metrics that the Program seeks, because projections on slide 29 show some small improvement to volumetric density. Other issues such as material stability, actual packing density, and conductivity are also in need of analysis/resolution, and it is not clear that these are part of the research effort.

Question 5: Proposed future work

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

- The future work is well defined. Perhaps the project could investigate the possibility of tapping into the Materials Genome Initiative database.
- Some effort should be applied to a deeper understanding of how these MOFs adsorb hydrogen in order to give some insight to those developing new MOF structures.
- The experimental path forward was described as considering the top 20 MOF materials. The project should expand screening to real MOFs in the CSD. Understanding the effect of densification of the material will be important.
- The proposed future work is mostly based on the existing results. It would be desirable to test the effect of flexibility on hydrogen uptake in MOFs.
- This was really the only disappointing part of the project. It would be good to see more specifics about the actual pathways forward—it was too general as to what the actual future work would be.

Project strengths:

- The project is well balanced, with both experimental and theoretical components. The strengths are the high-throughput calculations, which allow many hypothetical MOFs to be screened and their hydrogen uptake estimated even before the materials are synthesized.
- This project provides a unique synergistic view of materials properties and system storage goals. It is a well-coordinated effort involving members with strong expertise.
- The team possesses the knowledge and tools to meet the goals for this project.
- The project is very inclusive of nearly all MOFs thus far identified in the literature.
- The significant amount of data compiled is a project strength.
- An overall assessment of the metrics studied to date is useful. As far as usable volumetric capacity, there seems to be remarkably little to distinguish the properties of these materials from one another.

Project weaknesses:

- The lack of any analytical analysis of synthesized MOFs, which could be achieved through a greater collaboration with HySCORE, is a project weakness.

- As a survey, some physical insight into the properties that have been evaluated would be of value. There appear to be real limitations to this class of materials, and some analysis of why/how this is the case might offer some fruitful directions for future work, rather than just expanding the screening effort.
- The project is focused mostly on high-surface-area materials. There should be more emphasis on increasing the isosteric heats of adsorption, as it is clear that high surface area alone is not sufficient to satisfy the DOE technical targets for onboard hydrogen storage.
- The use of crystalline density for calculations is a project weakness. Possibly more information on improved isosteric heat materials should be provided.
- The go/no-go milestone for identifying MOFs with hydrogen capacities exceeding MOF-5 by +15% falls well short of the capacities required for an MOF to be considered viable for meeting the DOE technical targets.

Recommendations for additions/deletions to project scope:

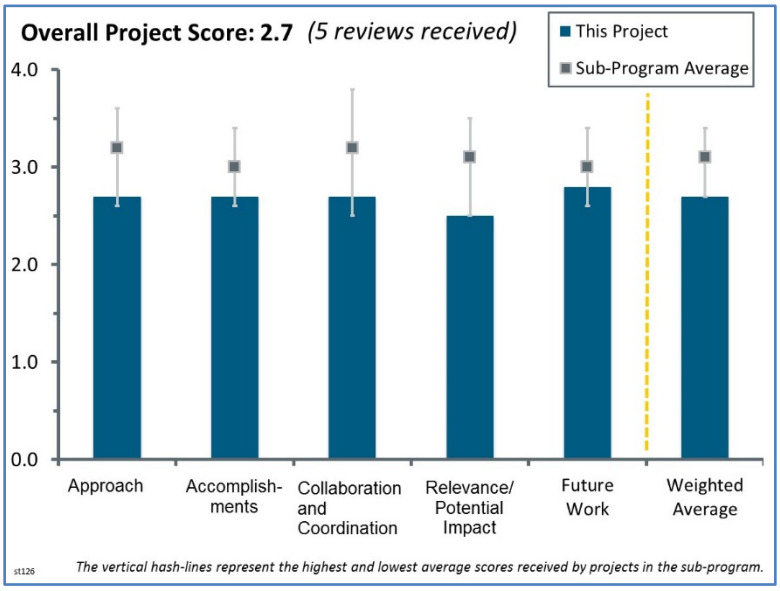
- The recommendation is to focus on narrowing down the list of candidate materials and exploring the temperature effects on hydrogen adsorption to compute and experimentally determine the isosteric heats of adsorption. Another recommendation is to explore the effect of flexibility, because such approaches have shown to have an effect on isotherm shape and overall hydrogen capacity.
- The team should use HySCORE and the Hydrogen Materials–Advanced Research Consortium as collaboration partners to investigate higher isosteric heat MOFs.
- Evaluation of improved isosteric heat materials sets would improve the project.

Project #ST-126: Conformable Hydrogen Storage Coil Reservoir

Erik Bigelow; Center for Transportation and the Environment

Brief Summary of Project:

The project goal is to develop storage systems for compressed hydrogen gas that will provide a cost-effective and conformable storage solution for hydrogen vehicles, thereby reducing the cost, weight, and packaging issues related to conventional high-pressure hydrogen tanks. The target is conformable, lightweight 700 bar gaseous hydrogen storage with around 10% gravimetric capacity. Researchers are aiming for continuous production processes for a storage system that can be extended, once proven at smaller sizes.



Question 1: Approach to performing the work

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

- This approach addresses the introduction of high-pressure hydrogen tanks into existing automotive designs, but new designs may not require conformal tanks when balanced against volumetric and cost considerations.
- The project is rather high-risk based on limitations of suitable liner materials, which must meet requirements for hydrogen permeation, formability, and mechanical properties. It is suggested that a risk assessment and mitigation plan be developed. Perhaps the braided overwrap will require a polymer matrix. It is not clear how that would affect cost, weight, durability, etc. Perhaps this technology is more suitable for compressed natural gas in which permeability is less of a concern.
- In the early stages, there should be a stronger effort on selection of the permeability resin. There should be a much, much greater focus on hybrid construction of the fiber reinforcement (i.e., carbon + Kevlar®), rather than a Kevlar-only solution. This would give less strain for a given pressure and thus partially alleviate the problems with resin brittleness.
- The main barrier is getting the permeability of the liner down to 0.01 g/(hr-kg H_2 stored) from the current 0.05 g/(hr-kg H_2 stored). The researchers do not seem to have a good idea of how they will achieve this. Without this, other components may not help it translate into commercial use. The only workable idea may be to reduce the pressure requirement to 350 bar from 700 bar. Also, the current process does not allow for higher thickness of the liner. Unless they can present a good plan forward to address this issue, this should be a no-go.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.7** for its accomplishments and progress.

- Progress has been made on the resin liner and fabrication approaches. Pressure testing and cyclic results of folded tanks will be critical to assessing the viability of this approach.
- Progress was made to show that the Kevlar braid could meet static pressure requirements and achieve the weight target. A dry braid may not be suitable for fatigue life and damage tolerance protection of the thin, fragile liner.

- The researchers have been able to make conformable tanks, but the permeability testing does not show any progress toward the target of 0.01 g/(hr-kg H_2 stored). They have tested various resins that meet most of the requirements, but resins are not a crucial issue.
- There are some accomplishments, but many challenging tasks remain, and it seems that the project team does not have a viable solution in mind.
- A satisfactory material selection has not yet occurred (fiber composition and resin), so the rest of the effort is on hold until that occurs.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.7** for its collaboration and coordination.

- The team seems to be working well with the inventor and with Texas A&M University, where testing is being carried out. However, the team needs to change the process of manufacturing so it can allow for a thicker liner, which will help it move toward the goals set for hydrogen permeability. Hence, the team needs to bring a process engineer into the collaboration.
- There is good interaction between partners, but the team is lacking a true materials expert.
- Collaboration is sufficient for validation of this technology, but it is not extensive. Collaboration could be enhanced by engaging either commercial tank vendors or original equipment manufacturers (OEMs) to assess market drivers and economic opportunities.
- Some validation of the system-level approach toward the goals is suggested via collaboration with projects ST-001 and ST-100.
- There is no collaboration with industry, vessel manufacturers, or OEMs.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **2.5** for its relevance/potential impact.

- The progress will be excellent if the team can solve the problem of permeability. The strength around sharp corners, which can occur in non-conformal containers, is also a concern that has not been addressed here but will play a big role in commercialization.
- The project is focused on the right area. With the right materials selection, it could be very successful. The project team should get a materials expert (composites, polymers, and fiber reinforcement) on board.
- The project—if successful—has strong potential to provide a useful compressed gas storage (CGS) product form for hydrogen storage, while meeting cost and weight goals. Perhaps the permeability would be less of an issue for fleet vehicles that require refueling each evening. The project needs to establish the value proposition for the technology—even if it does not meet all the current performance goals.
- The project fully addresses only one barrier that is not critical in meeting the DOE targets.
- The presenter claims low vessel cost (ultimate) and low vessel weight (ultimate). However, the presenter did not show any evidence that this will be possible and was unable to explain how this claim will hold. Aside from this, volumetric efficiency is similar to a compressed gas vessel. It is therefore difficult to understand whether this project has a solid rationale.

Question 5: Proposed future work

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

- The plan is appropriate once the previously addressed hurdles are appropriately handled.
- Burst testing of the folded package and abrasion fatigue testing of the folded package will be necessary to assess this technology.
- The future progress hinges on addressing the permeability issue. It would likely be beneficial for the team to test all this for 350 bar and see whether it can meet all the metrics or/and modify the process so it can accommodate a thicker liner.

- The project has numerous risks; a risk assessment and mitigation plan was not presented for future work—although several key risks are identified. The limits of a 0.05" wall thickness for the blow molding process is a limitation that needs to be addressed. Perhaps the team should consider spray coating or infusing the braid.

Project strengths:

- It is an impactful project with good collaboration. It could be a game changer if successful.
- This novel approach seems suitable for mass production and offers extendable storage volumes and flexible geometric packing. Perhaps this class of CGS needs its own performance criteria if it is enabling for certain applications.
- The project has an excellent design concept.
- The project has a good concept for conformable storage.
- Initial results on resin permeability are encouraging.

Project weaknesses:

- The lack of materials expertise in polymers, composites, and fiber reinforcement is a project weakness. The team should get an expert on board.
- The team needs to change direction to address the permeability issue. It should bring in a process engineer or materials scientist who can help the project.
- Concept implementation is challenging because of high pressure, permeation, heating during fill-up, and durability.
- The project fully addresses only one barrier, and it is not critical in meeting the DOE targets. More efforts should be placed on strength and durability of the folded package and less on permeability, which can be addressed later if the concept is sound, because the resin does not contribute to burst strength.
- Most weaknesses have been addressed in prior questions. Another issue is fatigue failure at the end fitting. Even if permeability of the liner is satisfied, there is the likelihood of damage and failure during blow molding, overbraiding, final packaging, and service life.

Recommendations for additions/deletions to project scope:

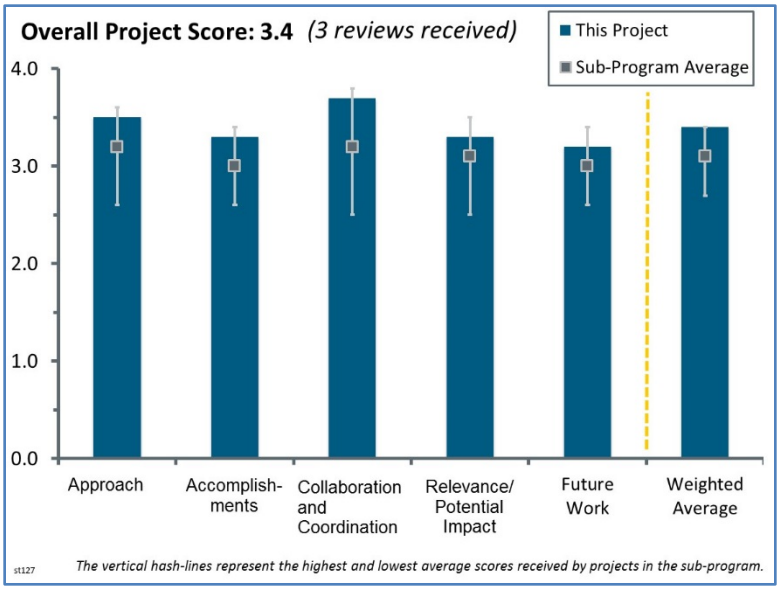
- Fatigue and burst testing of the folded package needs to be completed as soon as possible.
- The team should work with projects ST-001 and ST-100 for project review and setting future priorities.
- The team should reduce the pressure requirement to 350 bar and show that it can be done for three to four different types of conformal containers, instead of spending all its energy to find this for 700 bar. There are many applications where 350 bar will be useful.
- There are many critical tasks that need to be accomplished. It may be best to focus on one, e.g., permeability, and either resolve it or cancel the project.

Project #ST-127: Hydrogen Materials–Advanced Research Consortium (HyMARC) – A Consortium for Advancing Solid-State Hydrogen Storage Materials

Mark Allendorf; Sandia National Laboratories

Brief Summary of Project:

Critical scientific roadblocks must be overcome to accelerate materials discovery for vehicular hydrogen storage. The project objective is to accelerate discovery of breakthrough storage materials by providing capabilities and foundational understanding. Capabilities will include computational models and databases, new characterization tools and methods, and customizable synthetic platforms. Foundational understanding is needed for phenomena governing the thermodynamics and kinetics limiting development of solid-state hydrogen storage materials.



Question 1: Approach to performing the work

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

- The project has a very good, multidisciplinary team. There is good integration of theory and experiment. The team seems to have "gelled" and is working in an efficient, collaborative fashion.
- The Hydrogen Materials–Advanced Research Consortium (HyMARC) team has formulated a comprehensive and well-reasoned approach that is providing a basis for understanding the detailed aspects of the thermodynamics, hydrogen diffusion, reaction kinetics, and interfacial processes operative during sorption reactions in hydrogen storage materials. The approach integrates important elements of theory/ modeling, materials synthesis, and diagnostics/characterization in a framework that is effective and straightforward. The charter of the HyMARC effort is daunting. However, the approach that has been adopted and the team that has been assembled seem to be fully capable of successfully addressing the principal project goals, namely understanding and elucidating the foundational issues and critical processes that control the hydrogen sorption behavior in storage media. Notably, significant improvements in the development and implementation of a more coherent and consolidated technical approach have become apparent over the last year. The approach provides a solid basis for facilitating and enhancing progress on the companion seedling projects devoted primarily to new materials discovery. That being said, it would be helpful if the principal investigator (PI) and his team could provide a more illustrative roadmap that clearly identifies the model systems being studied, provide criteria for their selection, articulate what critical questions will be answered by studying those specific systems, and describe whether and how that work is translatable to more complex and technologically relevant materials. Likewise, a more compelling statement concerning the direction of the Advanced Light Source (ALS) work would be helpful. The ALS activities could be game changers. However, limited beam time and funding resources demand that the most important problems must be addressed first. The identification and prioritization of those projects should be a high priority.
- The approach has been much better explained this year and better justified. The U.S. Department of Energy's (DOE's) "reset" approach of taking a step back to fill in some of the foundational science gaps in our knowledge of materials-based storage remains controversial to some, and it carries some risk, but HyMARC has addressed many of these concerns, and its approach mitigates much of the risk. The HyMARC approach has converged to a reasonable and well-explained strategy to address significant barriers that confront hydrogen storage technologies that strive to eclipse physical storage approaches. The

consortium is clearly focused on developing a more foundational understanding of the thermodynamics and kinetics that control hydrogen release and uptake in complex hydrides, and the controlling features of hydrogen physisorption in adsorbents. Much of the focus of the consortium lies in developing accurate computational models of these phenomena across multiple length and time scales—a grand challenge in itself. The consortium has also done a nice job of improving its definitions of what the characteristics of a good model system are that can then be subsequently used to help in the calibration and validation of computational models. This is an improvement over last year. The approach relies a great degree on seedling projects to add much of the experimental work to provide feedback to the theory effort, so there is some risk involved in having the appropriate topics addressed by seedling proposals and that the right balance of projects is populated via the funding opportunity announcement (FOA) process. It is a challenge for the DOE Hydrogen and Fuel Cells Program (the Program) managers to control this flux, and only time will tell if it can be successful.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- Solid progress has been achieved in this reporting period on virtually all aspects of the project. In a project of this size and scope, it is critical that individual efforts on tasks and sub-tasks do not go "open loop," leading to a random mix of technically interesting but disconnected efforts that are largely inconsistent with the overall project goals. The team has obviously given serious thought to this issue, and it should be commended for ensuring that the individual project elements are coordinated and cohesive. The progress thus far is meeting the DOE mandate for this effort, and together with the initial results on the companion seedling projects, it is on track to address the critical DOE goals for hydrogen storage. The progress is broadly based—solid results have been obtained in theory/modeling, synthesis and nanostructured material development, and advanced characterization. It goes without saying that in a project of this scope, it will be critical to maintain a keen focus on the most demanding issues and to avoid the temptation of pursuing "curiosities" that may be scientifically interesting in their own right but have only minimal impact on the overall project goals.
- Communication of the strategies and goals in such a large consortium effort is critical to the success of HyMARC, and the consortium director has done an excellent job of providing a communication infrastructure that has appeared to bring a focus to the overall effort. As a result, a number of modeling efforts have made substantial progress over the last year, with many models being made available to the at-large community. Also, as a result of the overall more focused communication, there is much better coordination among the experimental efforts to address critical pathway issues in several materials. This is an improvement over last year. HyMARC has also made large strides in bringing on external collaborators that are top-notch and help to fill key capability gaps in the overall technical portfolio of the consortium. A key accomplishment is the rapid integration of the seedling projects into the consortium's efforts, and even though these seedlings are just getting started, they have mostly been actively engaged with HyMARC already in meaningful interactions.
- New insights to the reaction pathway of doped sodium alanate are a major accomplishment.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.7** for its collaboration and coordination.

- An impressive and effective network of collaborations has been developed over the last year. There was some concern at the outset of the project that the overall effort might become too insular. The PI and project team have clearly dispelled that notion and have instituted collaborations with numerous investigators (especially the Hydrogen Storage Characterization Optimization Research Effort—HySCORE) that broaden both the scope and the efficiency of the overall effort. Notable progress has been made on bringing the ALS activities into the project mainstream. It appeared initially that the ALS effort was not especially well integrated into the overall HyMARC project, but that concern was addressed effectively in the last year. However, it cannot be overstated that the ALS effort must continue to focus on the critical issues—this will demand input from the entire project team.

- The development of appropriate collaborations with best-in-class researchers has been very good over the last year. It was apparent that many, if not all, of these collaborations are strategic in filling in a few capability gaps within HyMARC, providing good scientific and technical leverage to the overall effort.
- Very strong collaborations have been developed.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- The Program and the HyMARC project team should be commended for instituting and formulating this project. Although this kind of project generally falls outside of the traditional purview of the DOE Office of Energy Efficiency and Renewable Energy (EERE), it is nonetheless critical to the overall success of the EERE hydrogen storage activity. A comprehensive materials search-and-discovery effort was conducted previously in the Centers of Excellence and in independent projects. However, that work lacked the sufficient foundational understanding required to address critical obstacles in a systematic and effective way. (Of course, without that prior work, those obstacles would not have been so readily apparent.) The HyMARC project is exactly the kind of effort that is needed to truly address the major issues and challenges that underlie the development of new and advanced materials capable of meeting DOE goals for hydrogen storage.
- The relevance to Program goals is very high. As the problems that the project team is trying to solve are extremely rigid because of the very tough technical targets for onboard hydrogen storage, only time will tell whether this novel "reset" approach will pay dividends and the output will provide novel paths forward to materials that can successfully and simultaneously achieve the DOE technical targets. If successful, this approach will have a tremendous impact on the whole hydrogen fuel cell technology area.
- Unlike the individual (or seedling) projects, the core team does not seem to be pursuing high-risk–high-reward research.

Question 5: Proposed future work

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

- The consortium's future plans involve the integration of a diversity of models that cover a span of length and time scales—a rather grand undertaking for a single element, much less for complicated materials such as a complex metal hydride. The consortium has an outline for how this can be potentially achieved, so its future plans are solid in this area. A continued emphasis on maintaining communication across the consortium is a crucial part of HyMARC's plans. Gaining access to local structure/composition characterization techniques such as neutron scattering and light element x-ray photoelectron spectroscopy (XPS) at the Spallation Neutron Source and ALS is a valid tactical approach in the short-to-medium term to provide some key bounding properties as input and/or validation to the computational modeling efforts.
- The proposed future work follows logically from the studies currently underway. It will be important to carefully and thoroughly evaluate the overall hydrogen storage material landscape to ensure that, after more than a year of work on this project, the proper issues are still being addressed. The project must be sufficiently nimble so that the technical efforts continue to focus on the major issues as the project evolves; i.e., as understanding improves, the priorities may change. The project team must be willing and able to work with the Program and its technical teams to adapt to those changes if and when they arise.
- The project could be more impactful if the core participants invested more time in novel/speculative/ risky materials.

Project strengths:

- This is a signature project for the Hydrogen Storage sub-program. The approach has been carefully formulated to address critical technical issues that affect the successful development of hydrogen storage materials. The project team is well coordinated and has expertise in all relevant areas. Excellent facilities

and instrumentation are available, and the core effort is augmented by strong collaborations with investigators in HySCORE and other independent activities. The project provides wide-ranging and solid support for companion seedling efforts devoted to new materials discovery.

- The consortium director has done a commendable job of bringing a set of strong communication plans to the consortium to "glue" the disparate efforts together and maintain the focus on critical path issues. The consortium is pulling together, via internal expertise and external collaborations, a powerful set of characterization tools to address phenomena at the appropriate length and/or time scales. HyMARC has rapidly engaged many of the new seedling projects, and it is likely to have engaged all of them in the near future. It has plans to make these fruitful interactions that should lead to technical advances.
- There is excellent collaboration and good fundamental science.

Project weaknesses:

- It is essential to provide a clear and persuasive argument about how the results obtained in model systems will translate to more complex systems. The successful extension of work from the model systems to materials that are relevant to DOE needs is crucial. For example, it is not clear what specific results from the studies of model systems will affect our understanding of hydrogen sorption reactions in the $MgB_2/Mg(BH_4)_2$ system. If that connection cannot be made in a compelling way, the project team must be willing to make the "mid-course corrections" necessary to maintain the focus on the overall project goals. This is especially important in the ALS studies, given the premium placed on beam time and availability. In addition, there is an often-confusing mix of technical efforts in HyMARC, HySCORE, and independent/seedling projects devoted to theory/modeling of sorbent materials (especially metal–organic frameworks) and functionalization to improve hydrogen reactivity. It would be helpful if HyMARC could take the lead in organizing and coordinating those efforts to ensure that the "right" questions are being addressed in the most efficient way.
- There is still some work to do in continuing to define what the ideal characteristics of model materials are; this would be helpful to maintain focus on the critical path, and it could provide DOE with potential FOA topics. There was not sufficient attention paid in the presentation to the justification or the goals of what the materials studied at ALS were intended to be.
- More emphasis on high-risk–high-reward research would be welcomed.

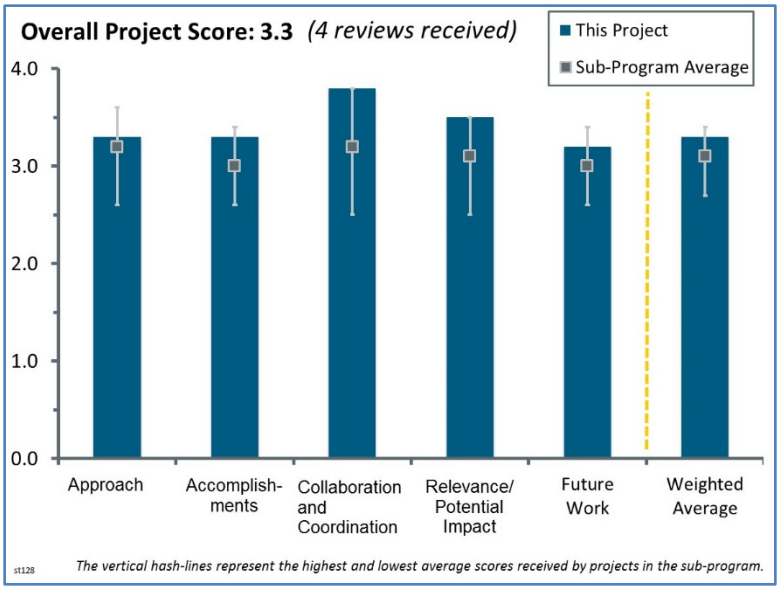
Recommendations for additions/deletions to project scope:

- By and large, the technical team approaches the problems from a materials science perspective; as many of the materials classes being explored rely on chemical frameworks, making and breaking chemical bonds, chemical kinetics, catalysis, etc., the consortium may want to enhance the complementary chemical sciences skill set.
- A very strong research and development team has been assembled—especially in the areas of modeling/simulation, materials synthesis, and characterization. However, the core team seems to lack an individual with in-depth chemical insight into the reactions involving major constituents and additives. Close collaboration with an individual (e.g., staff member, advisor, or consultant) having deep expertise in solid-state chemical reactions and/or reactions of gases with solid surfaces is recommended. As discussed at the Program Annual Merit Review, understanding the role of surface oxidation on the thermodynamics and kinetics of the hydrogen sorption reactions may be crucial to the development of improved storage materials. It certainly seems that this is a "foundational issue," and it is therefore subject to at least more consideration in the HyMARC project. At the conclusion of the HyMARC activity, it is hoped that a definitive statement can be made about the role of surface oxides in technologically relevant materials. Further discussions with the DOE Program management team concerning the level of effort that might be devoted to this issue are recommended.

Project #ST-128: Hydrogen Materials–Advanced Research Consortium (HyMARC) – Sandia National Laboratories' Technical Effort

Mark Allendorf; Sandia National Laboratories

Brief Summary of Project:



This project addresses a lack of knowledge about hydrogen physisorption and chemisorption. Researchers will develop foundational understanding of phenomena governing the thermodynamics and kinetics of hydrogen release and uptake in all classes of hydrogen storage materials. Sandia National Laboratories will (1) provide data required to develop and validate thermodynamic models of sorbents and metal hydrides, (2) identify the structure, composition, and reactivity of gas–surface and solid–solid hydride surfaces contributing to rate-limiting desorption and uptake, (3) synthesize metal hydrides and sorbents in a variety of formats and develop in situ techniques for their characterization, and (4) apply multiscale codes to discover new materials and new mechanisms of storing hydrogen.

Question 1: Approach to performing the work

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

- The various approaches to the diverse and insightful work being performed are well-thought-out. There is a lot of reach in the approach to some work, such as metal hydride improvement and understanding. Some of the work is material-specific; more of it should resemble the grand canonical Monte Carlo work that allows for models to be tied together, rather than be specific to certain situations or materials.
- The approach focuses on energetics (thermodynamics) in sorbents and metal hydrides, kinetics and the effect of nanostructuring and additives on reaction rates, and methods to improve reversibility. The approach is sensible and straightforward and addresses many of the critical obstacles that impede progress in development of improved storage materials. A more detailed statement of how the Advanced Light Source work will support the overall goals would be useful (specific systems and physical/chemical processes to be studied should be included). In addition, in the spirit of creating a "foundational understanding," as discussed at the Hydrogen and Fuel Cells Program (the Program) Annual Merit Review meeting, it would be helpful to augment the approach to include assessing the importance and role of surface oxides in hydrogen sorption reactions in relevant materials. The presence of a tenacious oxide could alter predictions derived from modeling of clean surfaces. A concerted effort to understand and mitigate those effects might turn out to be an important research direction.
- The approach as formulated is quite reasonable. However, it might make sense to dedicate more of the Hydrogen Materials–Advanced Research Consortium's (HyMARC's) time to the development of new experimental techniques and tools, and to studying novel phenomena that can enable the development of new hydrogen storage materials. An example is the exploration of new high-pressure-driven phenomena that are observed and can take place in various solid-state metal hydrogen systems. Such activity(ies) should not target the development of new material(s) as the main goal and may be carried out as a collaborative effort coordinated by HyMARC.
- The project should expand the scope of the effort and support more theory–experiment activities.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- Solid progress was made on model development and validation for hydrogen sorption reactions in metal–organic frameworks (MOFs), hydrogen diffusion, segregation and reaction barriers in model systems, the effect of doping/additives in complex metal hydrides, reactivity of selected systems at high pressures, and improved kinetics in nanostructured systems. In addition, the development and implementation of sophisticated surface diagnostics are providing unique insight into surface characteristics and reaction mechanisms at relevant length scales. The low-energy ion scattering (LEIS) work will be especially important in understanding surface diffusion. However, validation of LEIS using the Ti-doped $NaAlH_4$ system is challenging (and might be misguided), given the fact that the diffusion and reaction processes in this system are so controversial to begin with. The project team must continue to carefully consider how the results will provide a payoff in understanding related processes in more promising complex hydrides. The project has clearly demonstrated progress toward meeting DOE goals. Over the last year, a much more cohesive and coherent effort has emerged. It will be important to rapidly transition from the simpler model systems to more complex materials. A clear and compelling pathway that shows how this transition will proceed would be helpful. This is especially important in transitioning from studies of diffusion rates and mechanisms in PdH(x) and MgH_2 and surface chemistry of Ti-doped $NaAlH_4$ to more technologically relevant materials. Specifically (as pointed out in the future work slide), rapidly extending the molecular dynamics model formalism(s) developed for MgH_2 to more complex systems, e.g., $Mg(BH_4)_2$, is imperative. Although the work on catalytic additives is important and initial results are intriguing, it is important to exercise caution in elucidating mechanisms—especially in those cases in which the additive species might directly react with the matrix elements.
- A great deal of good work was performed in the past year. The modeling work is impressive and will yield great insights into MOF performance without the need for synthesis, as well as the surface diffusion work with the LEIS.
- Accomplishments and progress toward overall project and DOE goals are commensurate with the funding level.
- HyMARC runs many diverse activities that are somewhat scattered over the hydrogen storage space. An updated model in which service-type activities and focused research are better balanced may be worth considering.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.8** for its collaboration and coordination.

- Numerous beneficial collaborations within HyMARC and with external projects and institutions are evident. Collaborations and interactions with the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) are especially noteworthy. The project team has expertise and experience in all relevant areas. The technical effort is well coordinated, and tasks are synergistic.
- There is a great deal of collaboration on almost every aspect of the work done. This is a great example of use of the consortium set by the group leading it.
- HyMARC has been doing an excellent job supporting external partners and collaborators.
- Collaboration and coordination with other institutions with capabilities outside the current project organizations should be encouraged.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.5** for its relevance/potential impact.

- This project is a key element of the HyMARC project. It is focused on developing a fundamental and foundational understanding of relevant phenomena and processes in hydrogen storage materials. As such, it directly supports the overall HyMARC goals and, in turn, the research, development, and deployment goals of the Program.
- This project has continued to make great strides in developing models, measurement techniques, and test equipment. The discoveries and understanding that have come from this project help develop the fundamental understanding of hydrogen storage materials and technology, and it should continue to do so at this pace.
- HyMARC has been doing a great job advancing progress toward the Program goals and objectives.
- The success of HyMARC is critically important to establishing the capability of handling the evaluation and coordination of hydrogen storage research.

Question 5: Proposed future work

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

- The proposed future work follows the work previously done in a well-thought-out manner and will continue to improve our understanding of the different materials studied. The encapsulation work proposed is particularly exciting, as previous work has shown that this method can increase material resilience when exposed to air.
- The proposed future work is a straightforward and reasonable continuation of the current effort. However, there is no mention of ongoing work on the important role that additives/catalysts might play in enhancing reaction kinetics. In fact, the general topic of reaction kinetics and elucidation of reaction mechanisms is (surprisingly) marginalized in the future work slide (slide 21). It is not clear whether that de-emphasis is intentional. Clarification here would be helpful.
- HyMARC proposed a comprehensive list of future tasks that is extremely diverse. Some focus may be beneficial to the outcome of the consortium's activities.

Project strengths:

- This is an important project being conducted by a strong research and development (R&D) team with expertise and experience in all areas relevant to achieving HyMARC goals. The project approach and work plan are well formulated. Likewise, the combination of modeling, synthesis (including nanostructured materials), and advanced characterization/diagnostics, together with support from extensive collaborations, provides a solid foundation for addressing the critical technical issues identified in the HyMARC project.
- Project strengths include the following:
    - Unique experimental setup
    - High level of technical expertise
    - Openness to external collaborations and joint research activities
- This project has good, strong collaboration and access to some great technology. Though broad in scope, each aspect of the project is focused and has provided productive results.

Project weaknesses:

- HyMARC's scope may need to be further refined and balanced so that service-type activities are complemented by a clearly defined systematic research effort.
- A stronger emphasis on understanding reaction kinetics, mechanisms, and obstacles in complex hydrides is needed. Most notably, greater attention should be given to the role of additives and catalysts in enhancing reaction kinetics. The proposed future work seems to minimize that R&D imperative.

- Most of the project is focused on important areas of study, but pursuing the understanding of materials that may never work at ambient conditions, such as various MOFs, may be a waste of time and resources.

Recommendations for additions/deletions to project scope:

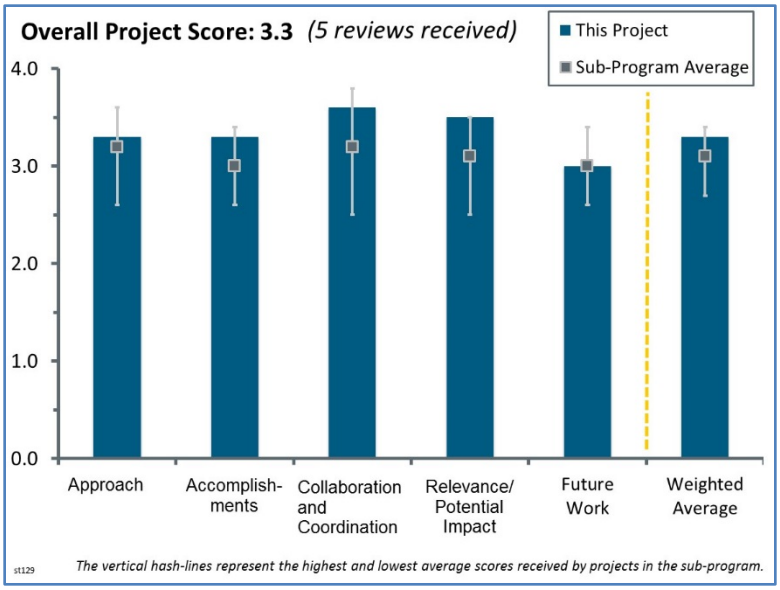
- The addition of an individual (staff member, advisor, consultant, etc.) with a deep understanding of solid-state chemistry, especially hydrogen sorption reactions in complex metal hydrides, would be useful. The insight provided by that individual could help to augment the technical effort and guide the future work in a more efficient and effective way. Discussions with DOE program managers concerning this addition to the project scope are recommended. (This was also suggested by this reviewer in companion reviews of the overall HyMARC and theory/modeling activities.)
- More focus should be placed on MOFs that can operate at near-ambient conditions rather than cryogenic conditions.

Project #ST-129: Hydrogen Materials–Advanced Research Consortium (HyMARC) – Lawrence Livermore National Laboratory's Technical Effort

Brandon Wood; Lawrence Livermore National Laboratory

Brief Summary of Project:

The Hydrogen Materials–Advanced Research Consortium (HyMARC) is providing community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials. HyMARC team member Lawrence Livermore National Laboratory is conducting porous carbon synthesis; x-ray absorption/emission spectroscopy; and multiscale modeling including density functional theory (DFT), ab initio molecular dynamics, phase-field mesoscale kinetic modeling, and kinetic and quantum Monte Carlo (QMC).



Question 1: Approach to performing the work

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

- The scope and depth of the theory and modeling effort in this project is most impressive. The approach combines existing theory and modeling methodologies with new capabilities (under development). The principal investigator (PI) and his team have a solid understanding of the critical problems and obstacles, and they have developed a theory/modeling framework that addresses those problems in a comprehensive way over extended time and length scales. Experimental validation of modeling results is a vital element of the project. That work is being performed in close collaboration between HyMARC and external investigators. The project integrates a large number of disparate modeling approaches in a coherent way.
- The approach is now better explained than last year. Last year, reviewers suggested the project looked more like a U.S. Department of Energy (DOE) Office of Basic Energy Sciences project than an applied DOE Office of Energy Efficiency and Renewable Energy project. The presenter did an excellent job of justifying the more foundational approach, and it was clear that this was well coordinated with the top-level HyMARC approach presented just before this talk. Hence, a tightly focused, better-justified approach has evolved in the last year. This was accompanied by a clearer explanation of which model systems can be useful to provide validation to the computational effort. Quite a stretch goal has been proposed to eventually provide a validated multiscale (length and time) computational model of hydrogen behavior in model hydrides. This is a grand challenge to be sure, and the approach lays out a logical approach to this attempt.
- The modeling approach taken for understanding the science behind metal hydride- and adsorbent-based hydrogen storage is laudable; however, until the models can be translated to produce or direct experimental research toward novel hydrogen storage materials, the outputs of this project are simply non-translatable models.
- The approach is adequate.
- It would be helpful if more experimental validation of computational models could be performed.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- There has been excellent progress in a broad diversity of elements of the computational aspects of this project and excellent signatures of good interactions between the computational and experimental efforts, which is commendable. There has been demonstrated progress in this project in the initial interactions with the new seedling projects in devising logical pathways to address computationally key questions that the seedlings must address. The project has made available to the community spectroscopic and thermodynamics databases as well as the classical potentials derived for interfacial simulations in borohydrides that are important contributors to developing an understanding of key features of hydrogen mobilities in this class of hydride materials. Through its careful computational modeling combined with experimental insight, the project has identified key computational/theoretical aspects of hydrogen adsorption in high-surface-area metal–organic frameworks. These observations and results will help provide support in a computational sense for some of the seedling efforts. The new results on morphology-dependent thermodynamics was fascinating, and it will probably contribute to a better understanding of hydrogen mobility in these interfacial complex metal hydride materials and will support future research in a few of the seedling projects. The influence of strain was explored computationally and correlated with the current experimental understanding of the behavior of hydrides in confined environments, which will also be important in supporting a few of the seedling projects. The project is successful in contributing to the literature; in the last year, the project has generated one publication and six manuscripts that are in the review process.
- The serious challenge of bridging time and length scales and effectively integrating results from different modeling approaches has been confronted directly, and solid progress is being made. A more in-depth understanding has been obtained concerning diffusion and reaction kinetics. These are critical obstacles that have hampered prior work. The initial results on the development and application of a reactive interface nonlinear kinetics model are especially intriguing, and they should pave the way to providing a better understanding of how interfacial reactions and hydrogen sorption fronts actually proceed in a solid. Fully characterizing the interfacial reaction zone ("soup") as well as other amorphous materials remains a research challenge. Overall, the results are having an important impact on the direction of the project, and it remains a successful and critical element of the overall HyMARC effort.
- The project has made specific accomplishments and progress toward overall project and DOE goals.
- The project accomplishments with respect to model development appear to be adequate. It was unclear how the improved models (dubbed as accomplishments) translate to the real world. It is not clear how they are better or why they better. Clarification on these types of issues will benchmark the significance of these accomplishments. There were a number of accomplishment claims such as "predicted phase diagrams of MgB_xH_y..." but no phase diagrams were shown, and there is no experimental evidence of validation via x-ray diffraction (XRD) or nuclear magnetic resonance.
- There are some slow-downs in progress resulting from staffing issues.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.6** for its collaboration and coordination.

- The PI and his project team are working closely with other HyMARC investigators. Also, extensive collaborations with the Hydrogen Storage Characterization Optimization Research Effort (HySCORE), other external institutions, and HyMARC seedling projects are evident. A confirmation of the importance of this work is the fact that virtually all of the PIs of seedling projects state that these modeling and theory efforts are important/critical to the success of their projects. (In fact, a concern is that the Theory and Modeling team will be overwhelmed with requests from multiple investigators.) The project team is well coordinated, and communication among all investigators seems to be open and effective. The PI is fully engaged in all aspects of the project and seems eager to accommodate the theory and modeling needs of the HyMARC team and companion seedling efforts.

- The presentation included many signatures that identify very good collaboration among the theorists and the experimentalists in this project. There is excellent communication and collaboration with many principal researchers in HySCORE and across HyMARC. This project has rapidly developed effective collaborations with several of the new seedling projects and has already demonstrated computational support in several instances. This is clearly a well-led project.
- Collaborations are a major strength of this project.
- Close collaboration with multiple organizations has been established.
- Collaboration within HyMARC and HySCORE appears to be present. The obvious gap is the experimental data to validate the models. Model improvement with no data is at best an academic exercise.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.5** for its relevance/potential impact.

- This project seems to be the centerpiece of the overall HyMARC effort. As such, it is of vital importance to the DOE Hydrogen and Fuel Cells Program (the Program). This project is critical to meeting the goals set forth by the HyMARC team, namely, to develop tools and create a foundational understanding of the phenomena that control the thermodynamics and kinetics of hydrogen sorption reactions in existing and emerging hydrogen storage materials. This is fully consistent with the objectives outlined in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (MYRDDP).
- As a key HyMARC goal is to provide foundational understanding of hydrogen behavior in certain hydrides and in porous materials, this project is highly relevant and has had a high impact on the success to date of HyMARC. If the project continues to be successful and multiscale models are proven to be valuable in showing the way to successful future storage materials development efforts, it will have been highly impactful to the MYRDDP.
- The project strongly supports research and development in hydrogen storage and advances knowledge.
- From a fundamental science perspective, the relevance is high. From a hydrogen storage perspective, the potential impact is low.
- The impact could be improved by aiming for additional experimental validation of models.

Question 5: Proposed future work

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

- The proposed future work is logical and follows in a straightforward way from the current effort. Appropriate decision points and milestones have been identified. It will be important to continue to develop a clear understanding (and compelling narrative) about how effectively the results obtained on model systems will translate to more complex materials. A strong emphasis on enhanced understanding of kinetics and interfacial reactions is encouraged. Understanding the participation of selected additives on reaction rates will also be useful. Specifically, a closer examination of possible side reactions between TiF_3 and MgB_2 is needed. As suggested in the Program Annual Merit Review meeting, Mg might react preferentially with F, thereby defeating the desired additive effect. Likewise, a concerted effort by the entire HyMARC project team to experimentally validate the predictions derived from this project is strongly encouraged.
- The proposed future work follows logically from the progress to date. An area of concern is that the project is apparently understaffed by two postdocs, delaying progress in two areas that may affect the team's ability to keep the future work on schedule.
- Continued improvements to the models are following a logical progression. However, actually validating the models with experiments is missing from the future work. The most challenging aspect of this project, or any other modeling project (e.g., DFT, QMC, and classical molecular dynamics), is designing and performing experiments to validate the models.

Project strengths:

- This project is vital to the overall success of the HyMARC effort. The project is well coordinated, and the scope and depth of the theory/modeling work are most impressive. The PI and his coworkers are highly qualified to conduct the work, and they have formulated a coherent and highly effective work plan that is yielding important results in all areas relevant to understanding the critical processes in emerging hydrogen storage materials.
- The project is highly collaborative both within HyMARC and HySCORE and with the new seedling projects. The project has become more tightly focused and has done a good job in providing for logical justification of the materials it has chosen to explore to develop the appropriate computational models that address key salient features of hydrogen behavior in these complex materials systems. The project is strong and has made significant progress; the list of accomplishments is substantial.
- A high-caliber, well-experienced team is tackling a very difficult problem in identifying the fundamental science behind hydrogen storage materials.
- Collaboration is a project strength.

Project weaknesses:

- Although not a weakness, per se, the dominant concern is that the knowledge gained from the studies on model systems will not translate effectively to more complex materials. The need to explore model systems in order to provide a solid foundation for understanding processes operative in more complex materials is understood and supported. However, it remains a constant challenge for the entire HyMARC team to ensure that representative model systems are selected and that the appropriate questions that will lead to deeper understandings in complex materials are addressed. As currently configured, the project team seems to lack an individual with extensive solid-state chemistry expertise. As the project moves into studies of more complex systems involving multiple reaction pathways, phases, intermediates, etc., the insight provided by such an individual could greatly benefit the overall project.
- The primary weakness is the lack of model validation and the currently untranslatable results to the real world. This level of model development is a very time-consuming effort that often lags significantly behind experiment throughput; therefore, a well-thought-out plan on what material characterization data are required for the modelers and how the models are performed should be a high priority. The models so far have been focused on the end states (i.e., initial and final states of hydrogenation), but none have been focused on the intermediate partially hydrogenated states.
- In a collaboration with Sandia National Laboratories, the work on the role of additives is an important one, but as it currently stands, it may not be well posed. Studying TiX_3 species on model hydride or boride surfaces may not reflect chemical reality. Some work should be done to explore where the thermodynamics of $TiX_3/MgBH_x$ lie; the TiX and MgX bond strengths may be quite similar, indicating that there is a reactive channel that their current model is not accounting for. Similarly, it is not clear whether TiX_3 on MgB_2 is a chemically realistic endpoint of a promoted borohydride. Depending on the outcome of an analysis of the reactivity of TiX_3 in these systems, the team may wish to adjust the experimental approach as well as the computational starting points.
- The project needs to involve more people/institutions.

Recommendations for additions/deletions to project scope:

- The project is well scoped as it stands.
- It is recommended that the project add an individual with extensive solid-state chemistry expertise and experience to assist in guiding the project as it ventures into new territory involving more complex materials and reaction pathways. Discussions with DOE program management concerning this issue are encouraged.

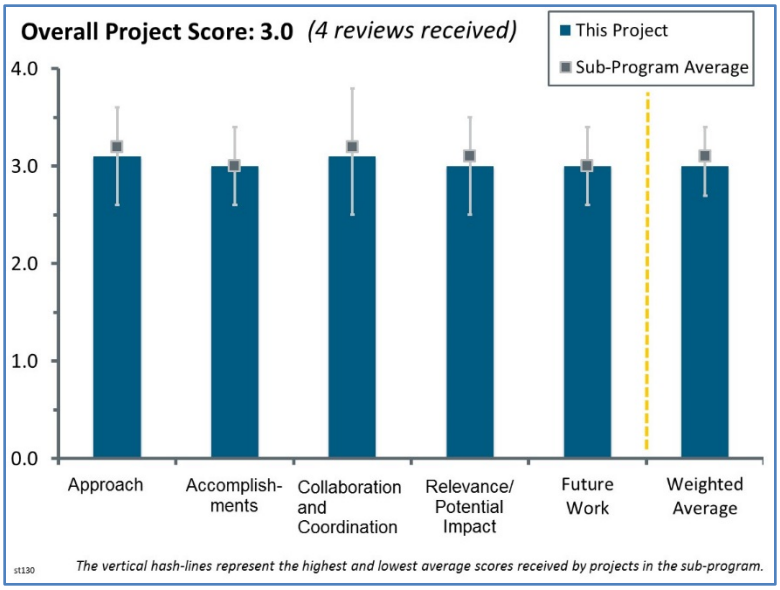
The modeling team needs to sit down with the experimentalists to develop a materials characterization plan on how and what is to be measured to validate the models. With two years in, there should be significant and targeted characterization data available to the modelers; this is especially true given that experimentalists can collect data faster than the modelers can develop models. The modelers should start publishing materials characterization predictions as a function of hydrogenation that can be measured by the research

community, e.g., XRD, infrared, kinetics, Raman, isotherms, heats of adsorption, phase diagrams, and binding energies. This approach offers a broader audience of researchers to validate or significantly improve the models. The ultimate test of a model is the time-based validation of an experiment. HyMARC should recognize that models are meant to be improved, and the first iteration of a model is never perfect; historically, data outlasts models.

Project #ST-130: Hydrogen Materials–Advanced Research Consortium (HyMARC) – Lawrence Berkeley National Laboratory's Technical Efforts

Jeffrey Urban; Lawrence Berkeley National Laboratory

Brief Summary of Project:



The Hydrogen Materials–Advanced Research Consortium (HyMARC) is providing community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable development of solid-phase hydrogen storage materials. Lawrence Berkeley National Laboratory (LBNL) will (1) focus on light materials and synthesis strategies with fine control of nanoscale dimensions to meet weight and volume requirements, (2) design interfaces with chemical specificity for control of hydrogen storage/sorption and selective transport, (3) explore storage concepts, (4) develop in situ/operando soft x-ray characterization capabilities in combination with first-principles simulations to extract details of functional materials and interfaces, and (5) refine chemical synthesis strategies based on atomic-/molecular-scale insight from characterization/theory.

Question 1: Approach to performing the work

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

- The HyMARC team has done a better job this year of ensuring that the participants in all the associated projects are aligned with respect to the overarching goals of HyMARC. In general, this is true for this LBNL project. With additional focus on providing the underpinning knowledge of what contributes to thermodynamics and kinetics barriers in hydrogen storage materials, this project could make real contributions to the model materials available for study and the computational aspects of the project. The characterization efforts using unique Advanced Light Source (ALS) capabilities are impressive and appear to be well posed to make a contribution to the understanding of hydrogen behavior in hydrogen storage materials. The project deserves kudos for dropping a few unpromising lines of research, as was recommended last year.
- The approach is strong and innovative, allowing for materials to be synthesized and characterized quickly and accurately. The completed computational modeling complements the work and allows discoveries to be made.
- Overall, the approach is very good. LBNL should concentrate on providing its excellent user facilities and computational tools to seedling projects.
- It is not quite clear what is meant by the following:
    - "Innovative synthetic routes to metal hydrides and hybrid nanoscale systems to reveal key phenomena governing hydrogen release/absorption and motivate new hydrogen storage materials"
    - "Developing new acid/base concepts to modify the enthalpy of hydrogen binding in sorbents"

  Also, in the light of the actual experiments described in the presentation, it is not quite clear how the following goal is going to be addressed: "Focus on light materials and synthesis strategies with fine control of nanoscale dimensions to meet weight and volume requirements via encapsulation, confinement." It is not clear how the control over stochastic chemical processes (slides 9 and 33–35) can be established.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

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

- There has been good progress made on studies of the encapsulation of magnesium borohydride and in demonstrating enhanced kinetics at relevant temperatures in Mg/Ni/reduced graphene oxide (rGO), and the characterization using in situ techniques, with the aid of computational modeling, hints about the role of partial oxidation of the metal surface. In collaboration with Sandia National Laboratories (SNL), computational modeling efforts have resulted in the ability to predict hydrogen sorption on metal–organic frameworks (MOFs) at high pressures and low temperatures. LBNL has collaborated well with HyMARC in developing pathways to access ALS capabilities and has provided fixtures for in situ studies at ALS.
- The team has made some great progress this year with regard to metal hydride encapsulation and MOF modeling. Most of the work is focused on Mg with the intent being to transition to Mg-borohydride, like the encapsulated rGO work.
- There are good progress and accomplishments overall. While good progress was made on calculating adsorbent properties, the presentation did not include the final selection of two improvement strategies to increase standard enthalpy, which was due March 31, 2017.
- Experimental results leave numerous questions unanswered. The nature of rGO coating is unclear. It is not clear why GO is used to modify water-sensitive Mg-borohydride when pristine oxygen-free graphene in an organic solvent would be more appropriate. These should be addressed soon.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.1** for its collaboration and coordination.

- Collaboration on gaining access to and performing HyMARC experiments at ALS has been excellent, as has been the collaboration between the computational efforts on hydrogen adsorption on MOFs and the experimental validation effort with SNL. It appears that the degree of interaction and collaboration with the graphene/rGO experimental effort is less well integrated with other organizations within HyMARC at this point. In the future, monitoring of the similar effort in encapsulation of hydrides within graphene at Argonne National Laboratory (ANL) (a new seedling) should provide an interesting collaboration.
- There is excellent collaboration with both HyMARC members and seedling projects.
- Collaboration within HyMARC appears to be strong. There seems to be a good network of researchers participating in this work.
- Collaborations are good and do not require further comments.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.0** for its relevance/potential impact.

- The increased air stability in the encapsulated hydrides is a great accomplishment. Work needs to be done to further control the air stability, but the work so far is well done. The in situ observance of hydride formation is also impressive, as well as the MOF model agreement with experimental data.
- The project is relevant to the DOE Hydrogen and Fuel Cells Program's goals and objectives.
- The potential impact of the information that can be ferreted out from studies of hydrogen storage materials using capabilities at ALS could be very high, but only time will tell whether the anticipated information can provide the foundational knowledge HyMARC seeks. The work on encapsulation of hydrides in various graphenes may be impactful if methods are found to control particle size, particle spacing/loading, etc. such that it provides for a useful platform to inform computational modeling efforts in examining nanoscale issues on kinetics and thermodynamics of hydrogen release and uptake. The work on computational modeling of hydrogen absorption in MOFs is impactful in providing an experimentally validated computational model that enables predictions of MOF isotherms. Because there are many complementary

and competing projects in this specific area, the team will need to demonstrate that its approach is powerful and unique.
- There is good potential impact so far in the project, but this type of project and effort needs more time to make more of an impact and should be continued.

Question 5: Proposed future work

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

- The proposed future work follows logically from the current status and includes increased collaboration with at least two new seedling projects. The future work in encapsulation includes size control of the included borohydride; it is too early to tell whether the ANL seedling will come at this from a different strategy, but if so, this activity represents a risk mitigation strategy to get the computational modeling effort a size-controlled model material platform. The future work portion of the presentation could have benefitted from more description of how each model system proposed (Al nanoparticles, $LiAlH_4$, $NaAlH_4$, etc.) fits into the HyMARC scheme and priorities.
- The proposed future work will continue the great progress that is being made. It is encouraging to see that other hydrides will be investigated with the same tools and methods as the Mg-based hydrides. The results of the seedling efforts will be interesting to see.
- A move from the previous year to more complex materials, such as Mg to $MgBH_4$, is promising.
- The team may want to include an effort that can address what the nature of rGO coating is and how hydrogen diffuses through it. It should also address where pristine oxygen-free graphene would offer benefits compared to rGO.

Project strengths:

- The project includes supporting work at the ALS, which allows HyMARC users the opportunity to exercise this unique capability and explore its general usefulness in characterizing the structures and compositions of light element storage materials in situ. If the encapsulation work can lead to size-controlled nanoparticles of specific metal hydrides of interest to the HyMARC computational modeling effort, this would represent a significant strength and the basis of a powerful collaboration.
- The project involves great experimental techniques and processes that allow for new observations to be made. This is a great example to set for HyMARC and the other laboratories working with the team.
- The project strength lies in LBNL's excellent user facilities/capabilities and computational skills.
- Collaborations, which are very good, are a project strength.

Project weaknesses:

- The diversity and number of ongoing efforts is a project weakness, but this is common with large and complex projects and should improve with time and the advent of more seedling projects.
- The project needs to perform more characterization and analytical work on the Al-based hydride so that it can be compared to the current Mg work.
- The encapsulation effort did not appear to be laser-focused on providing an optimal model material platform for HyMARC collaborations, and it could benefit from better integrating with the HyMARC computational team's needs.
- It is not quite clear what is meant by the following:
    - "Innovative synthetic routes to metal hydrides and hybrid nanoscale systems to reveal key phenomena governing hydrogen release/absorption and motivate new hydrogen storage materials"
    - "Developing new acid/base concepts to modify the enthalpy of hydrogen binding in sorbents"

  Also, in the light of the actual experiments described in the presentation, it is not quite clear how the following goal is going to be addressed: "Focus on light materials and synthesis strategies with fine control of nanoscale dimensions to meet weight and volume requirements via encapsulation, confinement." It is not clear how the control over stochastic chemical processes (slides 9 and 33–35) can be established. Experimental results leave important questions unaddressed. It is not clear what the nature of rGO coating

is or why GO is used to modify water-sensitive Mg-borohydride when pristine oxygen-free graphene in an organic solvent would be a more appropriate option.

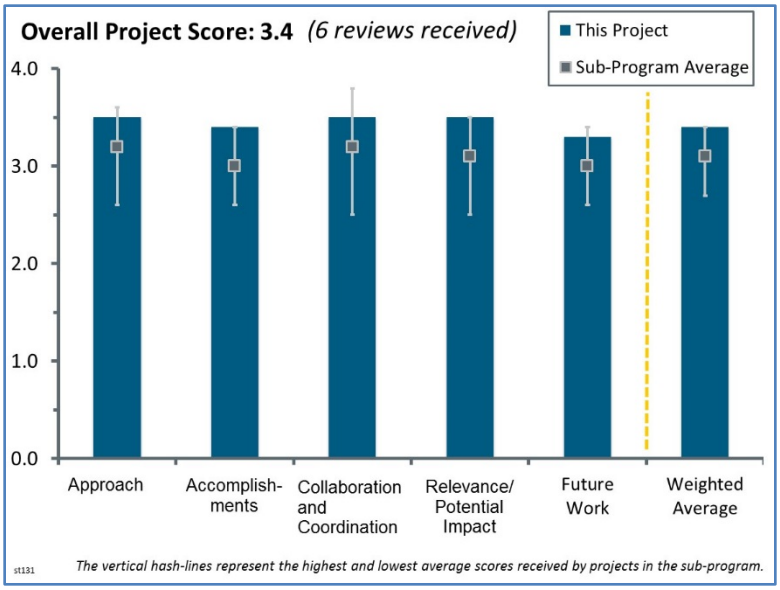
Recommendations for additions/deletions to project scope:

- The scope is more focused than it was last year and is fine as it stands now.
- The project should perform similar encapsulation work and analysis to other metal hydrides to better understand the phenomena involved.
- The project should continue to investigate more complex metal hydrides.

Project #ST-131: Hydrogen Storage Characterization and Optimization Research Effort (HySCORE) – National Renewable Energy Laboratory's Technical Efforts

Thomas Gennett; National Renewable Energy Laboratory

Brief Summary of Project:



This project represents a collaboration between national laboratories to investigate the properties of promising new hydrogen storage materials, and works in coordination with the Hydrogen Materials–Advanced Research Consortium (HyMARC) core team. The National Renewable Energy Laboratory (NREL) leads the collaboration, which includes Lawrence Berkeley National Laboratory (LBNL), Pacific Northwest National Laboratory (PNNL), and the National Institute of Standards and Technology (NIST). The objectives are to (1) develop new characterization capabilities such as nuclear magnetic resonance (NMR) spectroscopy, diffuse reflectance Fourier-transform infrared spectroscopy (DRIFTS), calorimetry, diffraction, and scattering; and (2) validate performance claims and theories critical to the design of new hydrogen storage materials.

Question 1: Approach to performing the work

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

- This Hydrogen Storage Characterization and Optimization Research Effort (HySCORE) project (ST-131) actually has two major components: (1) NREL coordination of sophisticated diagnostic capabilities at NREL, LBNL, PNNL, and NIST to assess candidate hydrogen storage materials from the HyMARC and independent Fuel Cell Technologies Office (FCTO) projects and (2) NREL in-house activities for volumetric capacity determination of adsorbents, hydrogen-pressure-dependent thermal conductivity (TC) measurements of sorbents, and development of a reliable variable-temperature (i.e., ~ 50 K to 350 K) volumetric pressure–composition–temperature (PCT) system. More detailed descriptions of the second category tasks are thoroughly covered in Hydrogen and Fuel Cells Program (the Program) Annual Merit Review presentation ST-014 and will not be explicitly evaluated in this review. Although HySCORE is a multiple-laboratory project, the ST-131 presentation focused on the specific capabilities and activities for NREL, which were mainly to validate hydrogen sorbent properties and storage mechanisms. Hence, NREL, in leading HySCORE, is providing a valuable service to the fuel cell technology community.
- The broad purpose of HySCORE is met by this team. The approach is to tackle characterization related to sorbent materials by offering a broad range of tools, some of which are unique, while also systematically attacking quality control in measurement science. Since its inception, the project has expanded existing capabilities, including TC measurement and PCT analysis up to 200 bar of hydrogen over pressure; interacted with the seedling projects; and performed round-robin tests to ensure reliability of measurements across the hydrogen storage research area. Several of the HyMARC projects, in their presentations, mentioned the need for 200 bar of hydrogen overpressure.
- The approach is logically broken down along lines of materials and techniques. There is little if any duplication of effort. The project contributes critical diagnostic capabilities to the development of storage materials and provides synthetic, theoretical, and characterization capabilities.
- It is a well-designed project that is tightly integrated with the other HySCORE partners.
- The approach, especially developing core capacities with PCT and TC, is very good.

- The primary HySCORE effort appears to have been expanded beyond last year's "relevance" to include the doubling of hydrogen storage energy density from 25 to 50 g/L. The main concern in this regard is that, in addition to the core characterization and validation efforts that were presumably part of the original HySCORE mandate, this may represent a conflict of interest insofar as a materials development effort is not subject to the same peer review process as other projects funded through the FCTO. The attempt at validating theoretical models, especially in regard to multiple hydrogens per metal site, may be of value, but it appears that the modeling effort is based on metal containing catecholates. It has never been clear to what extent the binding enthalpies might be altered when these structures are contained within a backbone structure. These modeling efforts should also take into account the extent to which Mg or Ca might be hydrogenated and/or oxygenated, as opposed to accommodating the molecule via adsorption. The 15 kJ potentials can be relatively high, and at some point, if the technology gets advanced, safety may be an issue. The issue of multiple hydrogens per metal appears to result from a geometric constraint. Even if such an accommodating geometry were possible, it would seem that the rest of the non-metal structure would simply accommodate hydrogen at lower enthalpies, similar to generic carbons, unless the material is such that uniform charge transfer takes place throughout the functionalized structure.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.4** for its accomplishments and progress.

- One of the most noteworthy accomplishments of this work has been the initiation of a round-robin measurement activity that removed 400% spread in volumetric adsorption data among 12–15 laboratories. The measurement spread is now at 5%. These best practices in measurement will be disseminated to the community of researchers who undertake similar measurements. This research has made major contributions in other ways that inform hydrogen storage researchers on best practices (or better practices) in measurement. These other accomplishments include the following:
    - Proving that sorption temperatures could be tuned based on a metal site with a desorption temperature of around 150 K (which is relatively high)
    - Establishing that x-ray photoelectron spectroscopy (XPS) must be used judiciously, because prompt gamma-ray activation analysis (PGAA) led by the NIST group in the team shows deep spectra and showed 2% B doping instead of the 5% B doping reported by XPS
    - Suggesting that 77 K and room temperature temperature-programmed desorption (TPD) data do not tell the whole story and recommending the examination of temperatures where desorption is optimized
- The inter-laboratory round-robin study of hydrogen adsorption with feedback to contributors is a valuable exercise that should improve reproducibility and consistency of reported isotherms. A state-of-the-art theory to predict binding of multiple hydrogens to a metal–organic framework (MOF) metal site is essential for establishing whether this is feasible, especially given prior work predicting very large numbers (up to eight) of hydrogen molecules binding in Kubas compounds. Oxocarbon materials may represent a new strategy for sorbents. The same is true of the derivatized carbon nanotube. The shift of the desorption temperature for the polyether ether ketone (PEEK)–catechol–metal sorbent is remarkable. The material part is heavily weighted toward sorbents.
- Over the past year, the HySCORE partners have made considerable progress on joint work with several HyMARC members by providing complementary techniques for diverse materials ranging from borohydrides to different classes of adsorbents. These efforts have produced new explanations and insights into the hydrogen storage and release processes. NREL has experienced some delays with development of the TC apparatus and the implementation of its variable-temperature PCT volumetric system. However, both are expected to become fully operational within the next few months.
- The effort behind the inter-laboratory measurement studies is of value, and the effort expended by the laboratory in ensuring that the measured data are correctly analyzed is of value to the community. The variable-temperature effort will be important in understanding aspects of the temperature dependence of adsorption enthalpies. The PEEK–catechol data are intriguing. Given the size of the catechol, it is not clear that the pore dimensions of the pyrolyzed PEEK can accommodate the catechol. Perhaps there is a possibility that the catechol functionalization has taken place on the surface of the PEEK and not within the pores of this material. The lack of a low-temperature hydrogen signal in the red trace of slide 12 makes it

questionable whether complete pore blocking has occurred. The calcium oxalate (CaC_2O_4) data illustrate an odd sieving effect. Given the "ultra-microporous" nature of this material, the higher gas kinetic energy appears to be necessary to overcome the small pore dimensions. These are effects of interest pedagogically, but perhaps not for FCTO.
- The work on volumetric best practices and round-robin testing is extremely valuable. The description of new materials (and characterization thereof) was difficult to follow.
- There is good progress on developing characterization tools. Progress on experimental efforts to meet DOE targets was not as promising.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.5** for its collaboration and coordination.

- Some very productive joint studies were achieved from the HySCORE partners with HyMARC collaborators during the past year. A number of mutually beneficial joint efforts are still underway between NREL and its partners on some specific materials such as the MOFs and the metal–catecholate sorbents. NREL leads efforts to define and implement improved protocols on measuring and reporting the hydrogen storage parameters for various classes of materials.
- There is excellent collaboration with both HyMARC and HySCORE.
- The team has been relied upon by HyMARC seedling project partners for accessing unique measurement capabilities, including high-pressure TPD, TC, and PGAA for concentration measurements. Because of the central location of key measurement tools within this NREL team, the characterization of highly relevant sorbent materials systems and the coordination of round-robin measurements by this team are excellent services to the research community. Collaboration with other HySCORE groups is a bit less developed. Because this team works on the experimental and characterization side of the spectrum, it is likely that collaborations will develop naturally with the HyMARC team at LLNL, which leads in computational modeling.
- The collaborations are an inherent part of the HySCORE structure and appear to work well, at least as far as intra-HySCORE collaborations. It appears that the University of Wyoming effort is the only collaboration that was noted, although others are presumably happening with NIST and PNNL.
- Collaborations both within HySCORE and with HyMARC are occurring and appear to be meaningful. It is somewhat unclear how coordinated these are, but they appear to be flowing naturally from the partners' mutual interest and complementary scientific capabilities. Consequently, it does not seem necessary for them to be highly coordinated by the HySCORE leadership. Collaborations with HyMARC should be expanded, particularly in the area of materials development. Because HyMARC is charged with overcoming scientific barriers to materials discovery, the interesting new results for sorbents should be shared with HyMARC so that these can be evaluated in a more general way. For example, the "ultra-microporous" CaC_2O_4 should be considered in the context of both modeling by HyMARC and synthetic method development.
- NREL is an important resource and collaborator for many other hydrogen researchers.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.5** for its relevance/potential impact.

- This project is directly in line with supporting and advancing the Program. Because of collaborative efforts such as this one, years of manpower in measurement are more reliable, and a broad range of scientists has access to specialized tools for sample measurement. This particular HySCORE group is highly regarded for its contribution to the field.
- The project is focused on high-impact problems, such as the binding of multiple hydrogens to sorbent metal sites, the need for highly accurate gas sorption data, and understanding measurement errors and lack of reproducibility. Capabilities being developed will provide resources needed to advance the discovery and development of storage materials. New sorbent materials, such as the PEEK–catechol materials, are

revealing some surprising results that may lead to some completely new strategies for storage. This will no doubt have a substantial impact on the field if the results hold up and further investigations are performed to validate the results.
- Optimistically, the combined efforts of the collaborating NREL and HyMARC teams will lead to more significant characterization, and better validated results will be achieved through more cooperative in situ measurements with neutron scattering, NMR, and DRIFTS studies that complement enhanced PCT determinations of hydrogen storage capacities. Such information should provide critical insights into the various theoretical efforts on identifying and verifying reliable mechanisms for promising hydrogen storage materials.
- The analytical capabilities of HySCORE are critical. The degree of interaction with outside investigators is not so clear and, presumably, subject to non-disclosure agreements, so gauging the full extent of the interactions/impact on materials developments outside of HySCORE is difficult to assess.
- The benchmarking and best-practices work is highly impactful. A better/clearer description of the new materials work would aid in assessing the impact of this portion of the effort.
- There is good progress on adsorbent characterization capabilities and supporting other members to better understand and hopefully be able to predict the hydrogen interactions with materials, but progress in meeting DOE targets is challenging, and the targets should be revised by DOE.

Question 5: Proposed future work

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

- HySCORE has carefully described barriers and challenges and has put forth a plan to tackle those. The future plans seem to be made with consideration of the most promising platform (i.e., broad conceptual base) technologies within the sorbent hydrogen storage materials discipline. The team plans to examine metal site catechol with PEEK carbon absorbent. Broadly, findings related to measurement and materials developments for these particular catechol–PEEK structures could potentially extend to other metal sites on organic sorbent material systems. Other plans include the study of promising sorbent systems that (1) combine N-dopants onto nanocarbon materials and (2) are boron–carbon (BC_x) seeded materials. The team should continue working to find new platform technologies as well as the most promising material systems. The team should also consider developing go/no-go metrics for the decision on which materials systems are selected for study in future years. This idea is slightly different from a go/no-go decision on a material system itself in that a particular gravimetric capacity, volumetric capacity, temperature, etc. would not be the focus. Instead, a go/no-go metric stated by HySCORE would depend on whether the material system represents a material type or a fundamental phenomenon, or answers a particular scientific question (i.e., a platform system). It seems that this is already incorporated into the materials selection process. However, explicitly stating the features of the system and the other types of similar systems that could be affected by the study of it would be useful.
- The proposed future work is logically connected to the accomplishments thus far. Some of the materials accomplishments are pointing to new strategies for sorbents. A plan should be developed with HyMARC to determine how best to move forward with these discoveries.
- The future work will be especially useful if NMR, neutron scattering, and infrared and Raman spectroscopies could be simultaneously utilized to substantiate whether conflicting empirical or model interpretations could be either verified or dismissed for at least one promising system. Greater emphasis on obtaining new candidate materials from HyMARC and its seedling projects should be made, and less effort should be devoted to those systems with hydrogen capacities less than 2 wt.%, even though they could potentially serve as models.
- Future work appears reasonable. More support for current and upcoming seedling projects is encouraged.
- The BC_x work has had a long run, and it is still not clear that the materials (which presumably need to be synthesized as metastable materials in order to achieve high solubility limits) will yield adsorbents of interest. The same argument might be made for the N-rich materials.

Project strengths:

- Project strengths include the following:

  - Outstanding scientific team
  - Excellent capabilities
  - Strong emphasis on problems that matter
  - Effective leadership that is keeping things focused
- Results gained by HySCORE (focused on characterization of sorbent materials) far exceeds what could have been achieved by a single laboratory or small group project. Achieving the objectives to (1) advance instrumentation development and (2) conduct round-robin types of experiments in order to make the best tools and measurements available to hydrogen storage researchers necessitates a team effort of this scale.
- The NREL staff has excellent expertise in characterizing and validating the hydrogen storage capacities for diverse classes of materials. HySCORE members have published a considerable number of journal articles and given a number of presentations. The level of cooperation within HySCORE and with the HyMARC members has increased during the past year.
- The highly collaborative nature of the project is a strength; the benchmarking and best-practices work will have a global impact.
- The analytical capabilities are clearly the strength of HySCORE.
- The development of core capabilities in the area of adsorbents is a project strength.

Project weaknesses:

- As clearly shown in the figure on slide 32, there are no viable sorbents with properties that fit within the desired target box from the former Hydrogen Storage Engineering Center of Excellence. Hence, there is little chance that more in-depth characterization will identify a "golden" candidate that can satisfy these requirements. While a better understanding of currently proposed (but still inadequate) materials is desirable, this does not necessarily translate into making breakthrough discoveries. There is a heavy emphasis on sorbents, with only limited work on hydrides. In part, this reflects the historical development of the research by the component groups. However, HyMARC could benefit from some of the capabilities, and it needs to leverage these to a greater extent. Communication of technical results with HyMARC could be improved. Although the objective of HySCORE is nominally to develop, test, and maintain core capabilities, the materials work (which is quite strong) seems decoupled from HyMARC, which supposedly is tasked with evaluating new storage material concepts and developing tools for the seedling projects to accelerate their work.
- New materials development and synthesis areas seem too broad and need to be narrowed down to a few best prospects soon to meet current DOE targets.
- The new materials work is of uncertain impact.

Recommendations for additions/deletions to project scope:

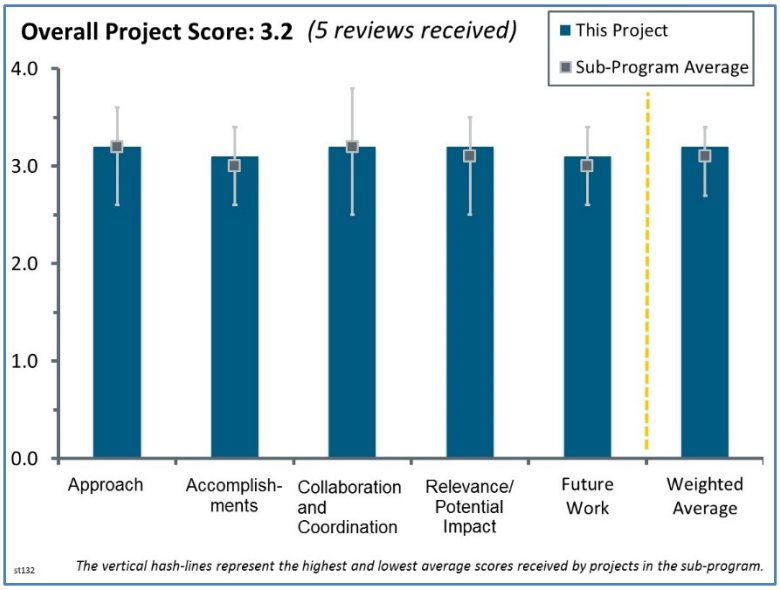
- The level of effort for both HySCORE as a whole and the NREL group is appropriate at this time. It is suggested that less effort be spent on lower-performance "model" sorbents in favor of focusing more attention on conducting complementary capacity and NMR/neutron characterization studies on more favorable candidates from HyMARC and seedling projects.
- The project should narrow down new materials synthesis to fewer higher-potential prospects.

Project #ST-132: Hydrogen Storage Characterization and Optimization Research Effort (HySCORE) – Pacific Northwest National Laboratory's Technical Efforts

Tom Autrey; Pacific Northwest National Laboratory

Brief Summary of Project:

This project is part of a collaboration between national laboratories to develop new characterization capabilities to investigate the properties of promising new hydrogen storage materials, and works in coordination with the Hydrogen Materials–Advanced Research Consortium (HyMARC) core team. Pacific Northwest National Laboratory (PNNL) will focus on nuclear magnetic resonance (NMR) spectroscopy and calorimetry to complement parallel efforts at other national laboratories. The project will also work toward validating claims and theories critical to the design of new hydrogen storage materials that show promise.



Question 1: Approach to performing the work

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

- The approach of utilizing theory to guide and interpret results and experiment to validate theory is powerful when well integrated. This project uses the chemical intuition developed over many years of experience in the area of reacting hydrogen storage materials systems to assist a wide variety of projects within the Hydrogen Storage sub-program. The excellent NMR capabilities that can access realistic temperatures and pressures to extract valuable information on thermodynamics, kinetics, and mechanisms in a variety of complex storage materials is perhaps unique to this project.
- A broadly based research and development (R&D) approach has been adopted. The overall approach builds upon the established expertise and experience at PNNL. The effort incorporates aspects of theory to guide experiments and interpret experimental results and uses experimental work (mainly characterization) to validate theory and to elucidate the details of complex reaction pathways and mechanisms. The approach is sensible, especially insofar as it provides effective support for the complementary efforts being conducted in the companion HyMARC effort (both core and seedling activities). The project also incorporates work on assessing the thermodynamic properties and kinetic processes in promising liquid organic hydrogen carriers (LOHCs)—notably triazine. For the most part, the approach focuses on the important barriers and obstacles that limit the development of hydrogen storage material having hydrogen sorption characteristics that meet U.S. Department of Energy goals.
- The approach makes available the PNNL Environmental Molecular Sciences Laboratory's NMR capabilities needed for the investigations of metal hydrides. The focus on thermodynamics of intermediates is much needed, as these may control the uptake and release kinetics of some metal hydrides. Calorimetry capability is also a valuable tool needed for monitoring phase changes in storage materials and for providing thermodynamic data needed to validate models.
- The approach seems reasonable—providing support for teams developing new materials through unique NMR and calorimetry capabilities. There is good connection/feedback between experiment and theory.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.1** for its accomplishments and progress.

- Good progress has been made on both LOHCs and metal hydrides. Useful recommendations to guide theory and experiments were made. New data concerning thermodynamics of $Mg(BH_4)_2$ intermediates is an important first step to understanding decomposition of this hydride. Experiments using tetrahydro furan (THF) to form adducts (via collaboration with C. Jensen) reveals a discrepancy between theory and experiment concerning thermodynamics of intermediates. Calorimetry experiments validate theory, showing THF binds to Mg more strongly than $Mg(BH_4)_2$ (via collaboration with the National Renewable Energy Laboratory [NREL]). NMR has been shown to be a valuable tool for following formation of intermediates that are amorphous. The team is working with HyMARC investigators to support the development of a phase field model of interfaces.
- All milestones are complete or on track. There is nice progress on liquid carriers and use of solvents to destabilize $Mg(BH_4)_2$. The search for additives or solvates that act to change reaction pathways in a favorable way makes sense. The in situ NMR is useful for tracking intermediates.
- Solid progress has been achieved during this reporting period. The results obtained using in situ NMR to monitor reaction intermediates and products during dehydrogenation of $Mg(BH_4)_2$*THF are helping to characterize the role of additives/adducts on improving reaction rates and selectivity in complex hydrides. The identification of an evolving $B_{10}H_{10}$ product is especially useful (an extension of work reported in 2016). It will clearly be important to understand more fully how the reaction rate varies with THF concentration (especially sub-stoichiometric amounts). This should provide useful insight to understanding the mechanism responsible for the rate enhancement (decreased temperature for dehydrogenation) and changes in product selectivity. The work on the triazine LOHC materials was confusing and, to a certain extent, misleading. At the 2016 DOE Hydrogen and Fuel Cells Program (the Program) Annual Merit Review meeting, the project team concluded, "Triazine not sufficiently stable; future NMR and calorimetry experiments will focus on diazines." However, the project continued to focus on triazine energetics (mainly differences in isomers) during this reporting period. If triazine had been discounted in 2016, it is unclear why so much additional effort was expended on that system in 2017. Some clarification is needed. Overall, the LOHC effort is not particularly compelling (unless the reviewer is missing something). A more definitive statement concerning the motivation and overall direction for the work would be helpful.
- The presenter reported a lot of interesting basic science. However, it does not seem likely that organic storage will produce a material with high hydrogen storage capacity and favorable absorption–desorption performance. The effort related to $Mg(BH_4)_2$ is mainly concerned with the basic polyborane chemistry. It might be useful to initially focus on actual polyboranes and then move to their magnesium salts, which are more complex systems with much more diverse chemistry. The stepwise formation and the decomposition of solvated Mg-borohydride/polyborane derivatives does not add much to the existing knowledge about the behavior of crystalohydrates and other solvent-containing salts. The stability of $Mg(BH_4)_2$ –THF complexes is an interesting observation. However, it is hard to see how THF may promote the formation of $Mg(BH_4)_2$ from MgB_2 , which does not seem to dissolve in THF or to form THF-solvates.
- While the driving force to finish tasks is strong, the work on LOHCs presented did not include much new information beyond what was learned last year, and perhaps more emphasis on the $Mg(BH_4)_2$ system would have provided more useful information via the HyMARC collaboration with the Hydrogen Storage Characterization and Optimization Research Effort (HySCORE), as there is no LOHC work in HyMARC. The work on thermodynamics and prediction of NMR parameters for solvates of $Mg(BH_4)_2$ indicated a good deal of progress and has direct impact on the new HyMARC seedling project at the University of Hawaii. The role of solvates in controlling kinetics and reaction pathways is very interesting and useful to consider in the context of HyMARC's interests in interfacial phenomena in hydrogen mobility.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- There is excellent collaboration across HySCORE and HyMARC, including new seedling projects. Areas of collaboration are broad, including NMR spectroscopy studies of reacting systems, computational modeling of thermodynamics, and NMR chemical shifts, all of which are important to a rather broad cross-section of researchers in the hydrogen storage community.
- The project team is fully integrated with both HySCORE and HyMARC activities (including seedling projects). Collaborations that rely on the extensive NMR experience, expertise, and facilities at PNNL are especially noteworthy. A slide that summarizes the collaborations (who and what) would have been helpful.
- There are strong collaborations with HyMARC and HySCORE partners on focused topics. There is continuing collaboration with the University of Hawaii and the associated seedling project. There is a new collaboration on electrolyte-assisted reactions with the Liox seedling project. A collaboration with the University of Missouri–St. Louis (UMSL) seedling project should be started to provide additional information to UMSL regarding structure and chemistry of N-doped carbons.
- Collaborations are excellent and do not require any additional comments.
- There is a long list of collaborators/teams that could be supported by these resources, but it is not clear how many were engaged in 2016/2017. With the exception of the work done with the University of Hawaii, it appears that most of the work was done within PNNL or HySCORE team. A broader, more substantial list of active collaborations would be expected for HySCORE team members.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- The PNNL project is vital to the overall success of the HySCORE activity. In particular, the unique experimental capabilities (especially high-pressure, temperature-variable in situ NMR, and variable-pressure reaction calorimetry) are powerful tools that are being employed effectively in both the HySCORE and HyMARC work. Likewise, the solid-state chemistry expertise at PNNL is providing useful new insight into important chemical problems being explored in both projects. The PNNL project is well aligned with the Program mandates for hydrogen storage materials R&D.
- PNNL provides access to unique high-pressure NMR capabilities that are needed by the seedling projects and HyMARC to carry out their missions. Variable-pressure reaction calorimetry is another important capability available at PNNL that is not available at other laboratories working on hydrogen storage projects. The computational effort to predict chemical kinetics and thermodynamics of borohydride intermediates is highly relevant, focusing on a class of materials that could be practical if kinetic limitations are understood and resolved. Substantive interactions with some seedling projects are accelerating materials discovery.
- There is an impressive list of capabilities to support materials development, but it seems to be underutilized. The 2016/2017 focus was on relevant systems, liquid carriers, and $Mg(BH_4)_2$. An in situ NMR could be really useful; the ability to track noncrystalline intermediates may be a key piece to the puzzle.
- The work on LOHC has reduced relevance at this time, but the project team's work on the $Mg(BH_4)_2$ system with and without solvates is highly impactful to the HyMARC effort in providing supporting data and observations that contribute to a greater foundational understanding of this important model storage material. This project's work also directly contributes to a new HyMARC seedling effort at the University of Hawaii. Interaction with the HyMARC computational modeling effort brings some chemical science expertise to a largely materials-science-dominated approach. This should allow the team to more rapidly develop computational approaches that get at both chemical and physical behavior of hydrogen in storage materials.
- HySCORE is relevant to the Program's goals.

Question 5: Proposed future work

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

- The future work follows logically from the activities currently being conducted. The future work on the effects of solvates on $Mg(BH_4)_2$ sorption reaction kinetics is especially important. It provides (at least in part) a basis for understanding how adducts and other additives can alter reaction pathways and kinetics in complex hydride systems. The proposed work on physisorption and hydrogen interactions with metal centers and B/N-doped carbons (with NREL, the National Institute of Standards, and Lawrence Berkeley National Laboratory) is intriguing. However, it will be important to compare and efficiently integrate that work with all of the other efforts underway for HySCORE and HyMARC (including seedling projects) devoted to enhancement of hydrogen physisorption by addition of reactive centers to solid-state sorption templates. The proposed PNNL contribution to the HyMARC effort on modeling the "soup" is not stated in sufficient detail; additional information concerning the PNNL work is needed. In addition, a more definitive and compelling statement about the impact of the future LOHC materials work should be provided.
- This project's future plans are very appropriate to approaching HySCORE and HyMARC goals. The proposed future plans include employing unique low-temperature, and perhaps moderate-pressure, NMR techniques to obtain information on hydrogen interactions with so-called doped and undoped adsorbate surfaces or "naked" metal ions, e.g., in metal–organic frameworks. These techniques are a unique contribution to the field and will likely lead to impactful results when incorporated into, or used to validate, computational models.
- Future work plans continue the experiments and theory already underway through collaborations with other HySCORE partners as well as with the seedling projects and HyMARC. The logical next steps are planned for the coming 12 months. The work on N-doped carbons has strong synergies with the UMSL seedling project. Although UMSL is focused on stabilizing metal hydrides within the pores, the need to understand the structure and chemistry of the N dopants is the same for both physisorption and hydride applications. At a minimum, PNNL should be sharing data with UMSL, and preferably, starting a collaboration for some joint experiments. The proposed work to validate the "soup" model is very important for both specific hydrides and in general for understanding any storage materials involving phase changes or reactions at buried interfaces.
- Future work is described in much detail. However, it is designed to address very fundamental questions such as chemical behavior of magnesium polyboranes, hydrogen interactions with metal centers, or B-N in carbon(s). Although this is very useful in the long run, the proposed effort(s) may offer few short-term benefits.
- It is not clear what is planned with the LOHCs. It was indicated that a success will be using calorimetry to optimize catalysis (kinetics), but it is not clear where this is in the future work slides. There appear to be plans to support a variety of different projects this year. More support of activities outside of PNNL and HySCORE is strongly encouraged. For work on solvates, the project should consider estimating hydrogen capacities based on the minimum solvent (or ligand) required to tweak the reaction pathways. Ideally, the solvent acts as a shuttle (not a final stabilizing agent) and therefore can be useful in small quantities (<1 mole equivalent).

Project strengths:

- The project provides vital support to both the HySCORE and HyMARC activities. The contributions derived from the use of the unique PNNL diagnostic capabilities are especially significant. The PNNL team has broad expertise and experience in solid-state chemistry and advanced characterization methods. The team is well coordinated, and strong/beneficial collaborations with related projects are evident.
- The project has an outstanding scientific team with important capabilities not available elsewhere in the Hydrogen Storage sub-program. It has a strong emphasis on high-impact problems.
- The project makes very good use of a quite powerful NMR capability resident at PNNL, and it uses that capability to form strong and appropriate collaborations with a variety of hydrogen storage projects within HyMARC and HySCORE. Coupling this capability with its chemical computational modeling capability lends strength to its technical contribution.

- Project strengths include the broad activity with nice balance between LOHCs, complex hydrides, and sorbents and a good connection between theory and experiment. Although current (active) collaborations are somewhat limited, this group is experienced and well connected. Collaborations this next year will likely increase as more projects get underway.
- The project team and the collaborations are very good.

Project weaknesses:

- This is not a major weakness, but perhaps the effort expended on finishing the LOHC work could have been more effectively spent in accelerating the $Mg(BH_4)_2$ and other computational work.
- HySCORE and HyMARC are complementary, and it may be a good idea to combine them into one larger organization. The research is drifting toward fundamental science with long-term benefits for general materials/inorganic chemistry. However, it is not clear whether its results could be translated into a practical hydrogen storage systems.
- Collaborations with other seedling projects with related work have not been established.
- The technical effort on the LOHC materials lacks a compelling and convincing motivation. Although work on triazine was apparently discontinued last year ("triazine not sufficiently stable, future NMR and calorimetry experiments will focus on diazines"), the triazine effort was resurrected during this reporting period. The overall impact of the work is ambiguous. The project team should provide a more persuasive case regarding future work on that class of materials. The specific contributions of PNNL to the HyMARC reactive interface phase field modeling ("soup") effort should be described in greater detail.
- Previous work seems to be primarily focused on new materials development—LOHCs and improving $Mg(BH_4)_2$ reaction pathways. Based on overview presentations from HyMARC and HySCORE, it seems that these organizations are supposed to support materials development activities at other institutions, not lead their own work. The level of effort dedicated to materials development here seems to be significant—the PNNL group is driving the work, not just providing characterization support. This is really a broader criticism of HySCORE (and HyMARC) in general; its scope/charter does not seem to be well defined. It is expected that HySCORE (and HyMARC) would be developing advanced tools and techniques, not developing new materials.

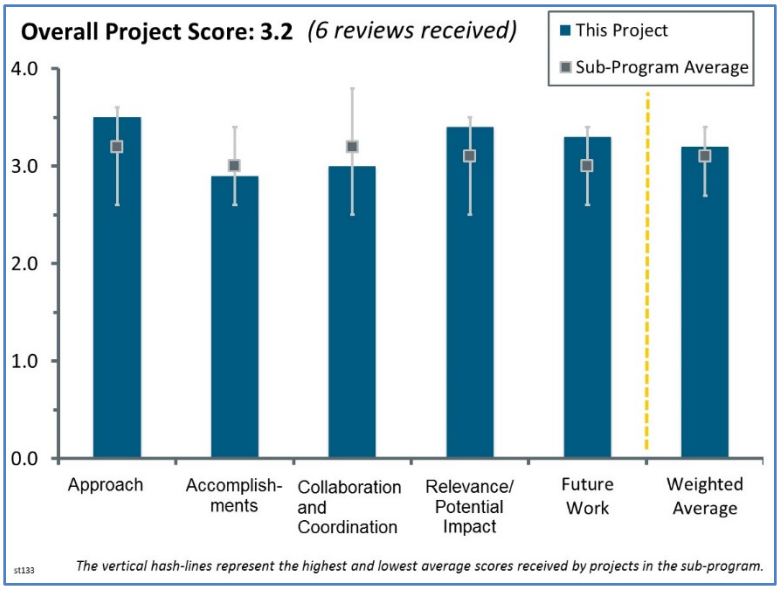
Recommendations for additions/deletions to project scope:

- The scope of the project is appropriate as it stands now.
- HySCORE needs to be better defined. Materials development seems to be showing nice progress, but it does not seem well aligned with HySCORE charter. The materials development part of this project may be better suited to a separate seedling effort (not under HySCORE).
- This recommendation is mainly for DOE. Numerous sub-projects within HySCORE, HyMARC (core and seedling), and independent projects are devoted to understanding whether functionalized templates can lead to enhanced physisorption of hydrogen (higher capacity and larger enthalpy). For example, PNNL is conducting work on understanding the role of metal centers and B/N substituted carbons on hydrogen sorption properties of physisorption frameworks. Although these multiple efforts are not necessarily duplicative, they are (often) similar, leading to a concern that this overall category of technical work is becoming increasingly defocused. It is recommended that careful thought be given to this issue, and steps be taken to clarify and definitively state the contributions of the different projects/sub-tasks to this technical area. This clarification would alleviate the confusion and provide a basis for consolidation of technical efforts where appropriate.

Project #ST-133: Hydrogen Storage Characterization and Optimization Research Effort (HySCORE) – Lawrence Berkeley National Laboratory's Technical Efforts

Jeffrey Long; Lawrence Berkeley National Laboratory

Brief Summary of Project:



This project is part of a collaboration between national laboratories to develop new characterization capabilities to investigate the properties of promising new hydrogen storage materials, and works in coordination with the Hydrogen Materials–Advanced Research Consortium (HyMARC) core team. Researchers will also validate new concepts for hydrogen storage mechanisms in adsorbents and provide accurate computational modeling for hydrogen adsorbed in porous materials. Specifically, Lawrence Berkeley National Laboratory (LBNL) is developing in situ infrared (IR) spectroscopy as a tool for characterizing emerging hydrogen storage materials as well as developing metal–organic framework (MOF) materials that will allow for more than one hydrogen molecule per open metal site that will increase hydrogen capacities for sorbent materials.

Question 1: Approach to performing the work

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

- Assuming that a MOF-based system is ultimately deemed to be a practical and useful medium for hydrogen storage (there is some concern/controversy about that), the approach that has been adopted by the LBNL group is sensible, and the proposed methods for multiple hydrogen binding are certainly intriguing. The project comprises a combination of first-rate experimental and computational/theory work to comprehensively explore candidate systems that may be capable of adsorbing up to four hydrogen molecules on a single metal cation in a functionalized MOF template. In addition, the development and application of high-pressure, in situ IR spectroscopy has been shown to be a powerful method to probe the characteristics of hydrogen binding on metal sites. The approach to developing MOF systems with improved hydrogen-binding properties is novel and builds upon earlier successes demonstrated in the project. However, the application of these techniques to studying hydrogen uptake in calcium oxalate seems to be a diversion. Unless a more persuasive case can be made for further development of calcium oxalate as a useful hydrogen storage medium, it is recommended that work by the LBNL group focus primarily on the MOF systems and catecholate-bound metal cations.
- MOFs are clearly one of the top candidates for successful sorbents. Binding of greater than one hydrogen per metal cation is a strategy that could enable the U.S. Department of Energy volumetric capacity target to be met. The synthetic approach looks feasible and consistent with what this team and others have learned so far. The use of protecting groups is clearly required to enable the reactive sites to remain free of solvents and other species in the pores.
- The innovative approach focuses on binding two to four hydrogen molecules to one metal cation site to achieve high storage capacity at ambient temperature. The use of in situ IR spectroscopy allows for accurate and fast measurements of total gas capacity over a wide range of temperature and pressure.
- The project aims to address important and highly relevant barriers.
- The general approach of this project is aligned with the efforts of the Hydrogen Storage Characterization and Optimization Research Effort (HySCORE) team, although the specific strategies could have been

focused on materials that maximize the benefit of the multiple hydrogens bound to a single metal site. The project did not seem to build on the momentum from last year and pursued other activities.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- Excellent progress has been made since the last DOE Hydrogen Fuel Cells Program (the Program) Annual Merit Review. The technoeconomic analysis is very valuable, particularly because it helps put to rest the stereotype of MOFs as impractical because of cost. Good progress is being made toward creating a MOF with highly under-coordinated metal sites. If anyone can pull this off, it is this group. It is good to see that the high-pressure Fourier transform infrared spectroscopy (FTIR) instrument is finally assembled and being tested. The computational effort made progress in two areas: (1) calcium oxalate, which is possibly a new strategy for creating an effective sorbent material, and (2) binding of multiple hydrogens to metallated catecholates. The results in both cases are encouraging and support continued experimental efforts in these areas. It is good to see calculations addressing solvent effects, which are almost always ignored in modeling of gas sorption by MOFs.
- Following on the success achieved last year on the first demonstration of the binding of two hydrogen molecules on a single metal cation in the Mn_2 (2,5-disulfhydrylbenzene-1,4-dicarboxylate) MOF system, the work during this reporting period has been incremental, focusing on finding ways to increase the density of bound hydrogen molecules and developing more robust platforms for functionalization. Particularly noteworthy progress has been made in the computational/theory studies—i.e., solvent effects, addition of other metals (e.g., Sc^{3+}), and predicted capacities resulting from metal atom insertion. Likewise, the effort to bring the diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) instrument to full functionality should pay big dividends in the detailed characterization of emerging materials. Although it is understood that the calcium oxalate work supports other efforts within the HySCORE project, that effort seems to be an unneeded diversion from the principal goals of this project.
- The team installed the DRIFTS instrument and demonstrated that it was operating within the needed resolution. Good progress was made in computation to understand the solvent effects on hydrogen binding energy in catechols and calcium oxalate. The technoeconomic analysis of MOF production was a nice addition to the scope of the project that was not initially planned for in last year's future work. The crystal density is used in this study for calculating usable capacity, ignoring packing effects in a tank. It is suggested that the principal investigator should clarify this point in future presentations.
- Experimental validation of multimolecule adsorption is key for assessing the validity of this approach. Some thought has been given to manufacturing, and more work needs to be performed to assess the potential technical impact of this effort.
- Assisting with the MOF technoeconomic analysis and de-protection of the Zr-based MOF, BOC-cat-UiO-68, were good accomplishments over the past year. Last year, this project made significant progress in identifying the phenomenon of multiple hydrogen molecules binding to an open metal site. This year, there seemed to be a notable lack of progress in this key area.
- Despite last year's important report on binding two hydrogens per metal site, this year's presentation made no mention of progress toward extending (or demonstrating) that approach on other MOFs. It is not clear whether any other systems were examined. On the computational side, the predictions of the thermodynamics of multiple hydrogen binding to Ca-catecholates and Mg-catecholates were largely repeats of last year's presentation. The Mg-thio-catecholates were added this year, but this is a small addition (only four more calculations). Overall, the quantity of new results presented was well below expectations for an $800,000/year project.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.0** for its collaboration and coordination.

- The collaboration of this project is apparent among the HySCORE effort. It was good that this project collaborated with other entities for the cost analysis.
- There are strong collaborations between the team partners.
- There are only a few strong, good collaborations internal to HySCORE, and none external to HySCORE. The internal collaborations are also limited in that most of the work is done at LBNL (theory by Martin Head-Gordon), with a little joint work with the National Renewable Energy Laboratory. The internal collaboration on theory is very strong. Jeff Long's collaboration with the National Institute of Standards and Technology is presumably ongoing, although this was not mentioned in the presentation. However, there is no mention of any collaborations with Pacific Northwest National Laboratory, the seedling projects, or HyMARC.
- Close collaborations with the HySCORE and HyMARC project teams are evident. However, clarification of how this project relates to the MOF effort within HyMARC and to what extent collaborations are underway would be helpful. In addition, a more complete description of the collaborative effort with Brandon Wood (HyMARC) would be useful. There seems to be considerable overlap between this project and the HyMARC effort—a clearly delineated description of the roles and responsibilities is needed.
- There is good collaboration with the HySCORE effort, but it could be expanded to groups outside of this sphere.
- The level of collaboration is appropriate.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.4** for its relevance/potential impact.

- The LBNL group is at the leading edge in the development of functionalized MOFs for hydrogen storage. Insofar as MOF work in general is deemed by DOE to be a promising pathway to addressing the goals/ objectives of the Program, this project is essential to meeting those needs.
- The work at LBNL is highly relevant to the mission and goals of the Office of Energy Efficiency and Renewable Energy/Fuel Cell Technologies Office (FCTO). Efforts are highly focused on key targets, and the strategies employed hold great promise to meeting unattained storage goals (volumetric capacity and operation at ambient temperature). The new high-pressure FTIR capability and the theoretical models are state of the art. If these can be extended to problems outside those that are the immediate focus of HySCORE, their impact could be great. Perhaps at this stage it is premature to expect a high extent of external use, particularly because the seedling projects were only recently funded.
- The project includes highly relevant objectives to advance the Hydrogen Storage sub-program goals. In particular, the impact of doubling the hydrogen storage volumetric density would be significant, as would increasing the adsorbent operating conditions to ambient temperatures.
- This is a highly relevant project. It aligns well with the Program goals.
- The project objectives are relevant to Program goals and objectives for system gravimetric and volumetric capacities.
- The work thus far is promising, but synthesis is key.

Question 5: Proposed future work

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

- The proposed future work follows directly from the success achieved last year on demonstrating multiple hydrogen binding on metal sites in functionalized MOFs. Attempts to metallate new structures (e.g., catechol MOFs) are fully consistent with the project goals. Likewise, the computational exploration of new MOF systems and new metal sites will be useful for guiding future experiments.

- Proposed future work, both in the synthetic and theory efforts, has its eyes on the prize and is consistent with the approach defined at the outset of the project.
- The proposed future work is well thought out and consistent with the project goals.
- The proposed future work seems appropriate for the remaining challenges and barriers, although there should be additional effort to identify an MOF with improved performance based on the multiple binding site mechanism.
- The future work is on track.

Project strengths:

- The project strengths include an outstanding scientific team with excellent capabilities, the strong emphasis on problems that matter, and cutting-edge synthetic and theory efforts; it is difficult to imagine any group that could address these problems more effectively.
- The LBNL project scientists are recognized experts in experimental and computational development of functionalized MOFs for hydrogen storage. The approach adopted in this project is novel and innovative, and the project builds strongly upon the demonstrated success achieved by this group in prior work. The project is well coordinated, and beneficial collaborations are in place. Solid work is being conducted to validate and employ a new IR spectrometer for materials characterization.
- The project strength is the technical depth and capability of the individuals involved with this effort. The project has an effective balance of computational and experimental activities.
- This is a capable team with a good track record of success. The project is well aligned with DOE goals.
- Modeling of potential multimolecule adsorbent sites with reasonable bonding energies for higher-temperature adsorption and release have been completed.

Project weaknesses:

- Experimental validation experiments are eagerly anticipated.
- This project has no clearly identifiable technical weaknesses. However, the immediate impact on other hydrogen storage projects supported by the FCTO is limited at this stage. Capabilities and tools developed are not being accessed outside of HySCORE. A plan for what to do next if the metalated-catecholate strategy fails is missing.
- There is an issue for both DOE and LBNL/HySCORE: in general, a hydrogen storage concept based on the use of a functionalized high-surface-area MOF that serves as host for metal centers that bind multiple (two or more) hydrogen molecules is not particularly compelling. The approach is encumbered by a notable gravimetric penalty (from the MOF), sensitivity to contaminants (bare metals are highly reactive), limited binding energy for molecular hydrogen (sufficient binding only at low temperatures), and serious questions concerning the efficacy of multiple hydrogen binding. A candid and comprehensive examination of this issue is needed.
- The project weakness is the lack of progression in demonstrating a material that can benefit from the multiple hydrogen molecules on a metal site. The project should have utilized the discovery from the last review to indicate a potential material improvement.
- There were limited accomplishments (poor progress, based on the presentation) in the previous year.

Recommendations for additions/deletions to project scope:

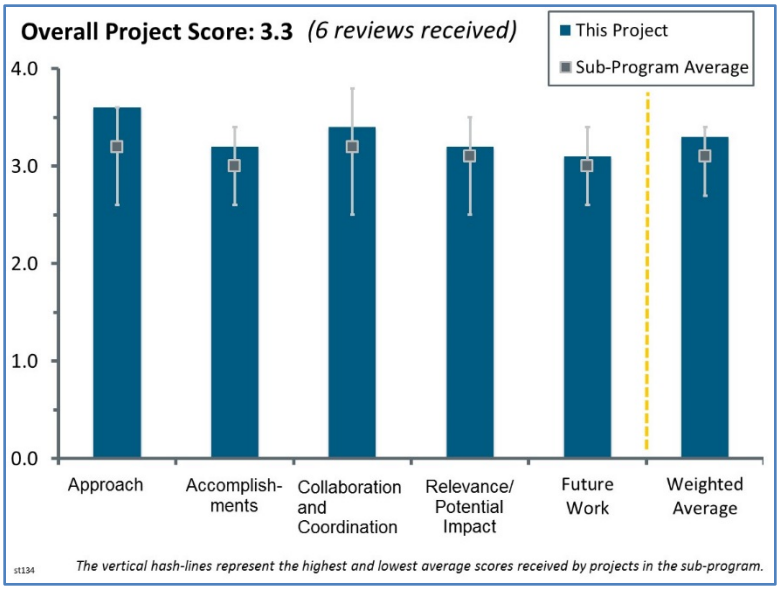
- Volumetric capacities will need to be closely examined to assess attainment of this critical goal.
- The project should focus back on synthesizing and advancing materials that can utilize the multiple binding on a metal site to demonstrate an improvement in material performance.
- The attention paid by the LBNL group to support the HySCORE effort on calcium oxalate is an unnecessary diversion. The focus should be keenly on exploring and improving hydrogen storage in functionalized MOFs. It is recommended that the calcium oxalate effort at LBNL be discontinued.

Project #ST-134: Investigation of Solid-State Hydrides for Autonomous Fuel Cell Vehicles

Joseph Teprovich; Savannah River National Laboratory

Brief Summary of Project:

This project, which is a collaboration between the U.S. Department of Energy and the U.S. Department of Defense (DOD), will develop a methodology that incorporates engineering modeling and analyses to efficiently screen, design, and select storage materials and material systems against cost and performance targets leading to an initial system design for an unmanned underwater vehicle (UUV) application. Project activities include screening of hydrogen storage systems against DOD targets and requirements, a detailed design of a hydrogen storage system for use in an integrated system design, and development of a preliminary design for an integrated UUV platform.



Question 1: Approach to performing the work

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

- The goal of this project is to extend UUV mission length for ocean floor mapping to 96 hours by replacing the auxiliary battery with an 11.3 kg AlH_3 bed for hydrogen supply, an H_2O_2 tank for oxygen supply, and a polymer electrolyte membrane fuel cell to convert the evolved H_2/O_2 to electric power. The H_2O_2 is converted to oxygen via a catalytic cracking process, which releases substantial waste heat that can be captured and transferred with a heat exchanger to the AlH_3 bed to release hydrogen on demand. This is an extremely well-conceived project. The entire system design is elegant, synergistic, and very convincing. The materials selected for this project are highly appropriate, and the methods of testing and evaluation (experiments with a model tank as well as numerical simulations) are rigorous and ensure a high probability of success. The team deserves kudos.
- AlH_3 as a hydrogen storage material for an unmanned aerial vehicle (UAV) is a perfect application of AlH_3 because of its high net usable hydrogen capacity and hydrogen quality.
- The project's excellent work moves prior work into alternative applications that reduce prior unknown risk to design and develop novel applications.
- The approach to this work is very thorough. Using the tried and true method from the Hydrogen Storage Engineering Center of Excellence (HSECoE) to design and develop a hydrogen storage system for a vehicle is smart. It will allow for previously developed methods to be put to the test and used.
- The approach appears to be sound, combining experiments to determine, e.g., hydrogen release in test reactors with design considerations and heat-flow modeling. The project is different from many others in that it is not addressing barriers to develop storage materials but is developing a storage system for a specific application outside the mainstream light-duty vehicle or portable power applications. In this respect, the design of the project is good.
- The stated approach calls for developing a methodology to efficiently screen, design, and select materials and systems for UUV applications.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.2** for its accomplishments and progress.

- The achievements to date are very impressive. The system design is extremely robust and synergistic. All of the calculations for weight, volume, energy and power requirements, heat release, etc. are quite meticulous. Experiments have been conducted to test hydrogen evolution from a laboratory AlH_3 bed with good results. The experiments seem to agree well with numerical simulations for pressure and hydrogen release rate as a function of the applied temperature. The entire research and development protocol is quite sound.
- The project is progressing forward through alternative designs for use in UUVs, pushing the gravimetric and volumetric targets with AlH_3.
- The project has made good progress toward the goals set. Various levels of characterization were performed, and the transient modeling is a great step forward. However, some of the goals do not translate exactly to DOE goals and requirements. This is the nature of the project, as it is a UUV rather than an automobile or ground vehicle. Great progress has been made on both sets of the project's goals, which should be commended.
- This project was not reviewed in 2016, and the presentation this year has combined results over two years. Progress over these years has been good, with results evident from materials screening, system design, and laboratory-scaled testing of prototype reactor performance.
- Accomplishments and progress seem to correlate with the funding level.
- Many accomplishments included in 2017 slides were previously reported in 2016. It is not clear why the Office of Naval Research (ONR) did not fund the project in fiscal year (FY) 2017.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- The collaboration between the team members appears to be well coordinated, with each role clearly identified and focused. There appears to be good communication between the partners on understanding the thermal management issues that have critical effects for control of the two key system components: the peroxide and the hydrogen storage sub-systems.
- The design aspects necessitate collaboration with Navy partners, and there appears to be good communication with this organization. The collaboration with Ardica does not appear to involve much beyond some AlH_3 supply, but there does not seem to be value in greater collaboration. The design and engineering considerations for the storage component seem to be handled within the team, and perhaps the team would benefit from reaching out to others in the DOE Hydrogen and Fuel Cell Program (the Program) who have been involved in the HSECoE.
- Collaboration on this effort between the three parties involved was good. It appears that everyone is contributing to the project and working toward progress as quickly as possible.
- Collaboration with the Navy is strong and directed at a specific application.
- The project lists the Naval Undersea Warfare Center, ONR, and Ardica as partners. ONR provided funding in fiscal year (FY) 2015 and FY 2016. Ardica's contributions were not identified.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- The impact of this project advances the Program into new demonstration opportunities outside of transportation and into the DOD. The cross-collaboration between DOE and DOD helps both departments in demonstrating the benefits of teaming to share cost to advance the respective goals.

- The project has good relevance to the Program by providing a low-power demonstration of a hydrogen storage materials system. This has potential to be a useful demonstration of materials storage as well as a testbed in which systems challenges are addressed as the Program scales to larger hydrogen capacities and more stringent performance targets.
- The project addresses a somewhat niche application for a unique hydrogen storage system for new fuel cell applications. It represents a good example of partnership between DOE and DOD for hydrogen and renewable energy systems.
- Although not relevant for automotive applications, the project has significant relevance and impact for the UUV application.
- This project does help the development of a possibly viable storage material, but it does so in an unconventional manner. Some of the work will not translate directly to DOE work.
- The project objectives are directed to DOD applications and fostering the relationship between DOE and DOD.

Question 5: Proposed future work

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

- The project is clearly focused on the next steps, and the researchers know where their efforts need to be and who is responsible for the team members. The next steps are logical, and they appear to be progressing to their future direction.
- The path forward is to work with the Navy to develop a final design, fabrication, and testing of the prototype UUV system. The current rate of progress ensures high likelihood of the success of this objective.
- The proposed future work is good; however, it does not include any specifics on the development of the system. If there are issues with producing large batches of AlH_3, it is not clear what will happen. Risk mitigation was not covered deeply enough.
- The path forward is not described in great detail, amounting to developing prototypes based on work completed so far. While this is an appropriate near-term goal, there is not too much evidence of planning, risk mitigation, etc.
- The presentation did not specifically identify future work, suggesting that the project will end in FY 2017.
- The project appears to be ending.

Project strengths:

- Project strengths include the excellent system design for the chosen mission; good materials selection; strong, rigorous experimental and computational test protocols; and good partnership between participating teams.
- This project has strong collaboration and the ability to leverage some great work performed by the HSECoE. The modeling effort has progressed well and should allow for optimized system design. Most of the bases have been covered with regard to design and analysis of the system.
- The project has great collaboration, has the right team members for success, and is a good demonstration of storage system design for alternative uses with fuel cells.
- The project chose a good system (i.e., UUV with the Navy partner) to learn and demonstrate hydrogen storage for medium-power applications.
- The team has a wealth of experience and knowledge in modeling metal hydrides. The project demonstrates an ideal application of metal hydrides.
- The credible team is a project strength.

Project weaknesses:

- There are no obvious weaknesses.
- Despite a feeling that this is a good test application, it does not have strong cost constraints and has an unusual system for oxygen delivery that aids hydrogen generation. These aspects limit the more widespread application of the outcomes from this project to others in the Program.

- The future of the project depends on the viability of a scaled-up production process for AlH_3. The performance of the system will also be dependent on the price of AlH_3. If the small batches produced for testing are used at the system level, it is not clear whether there will be enough funding to sufficiently test the system in operational conditions.
- It would be good to highlight a few more of the risks, such as the thermal management of the system design and the external environment. Once those risks are identified, the team should provide a good explanation on how they are being addressed to mitigate them.
- The material and system are not of interest in automotive applications.

Recommendations for additions/deletions to project scope:

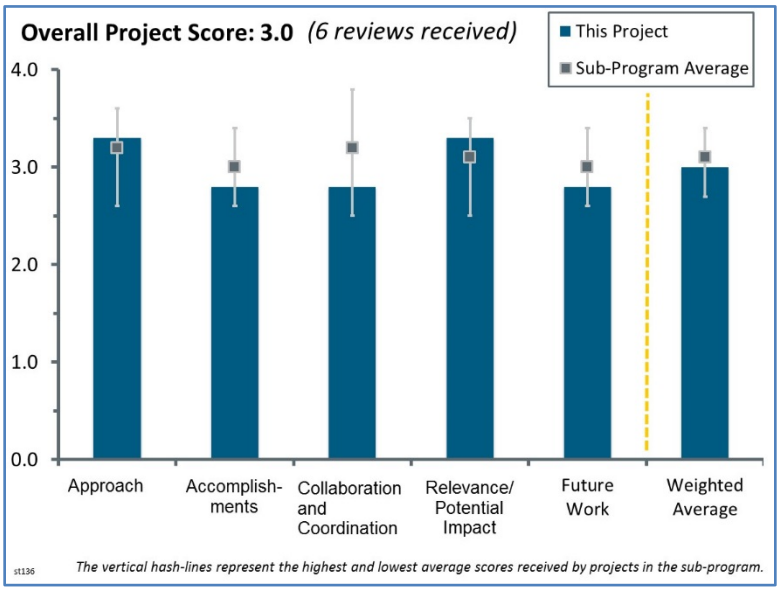
- There are no recommendations; the scope seems to cover everything required for the system and not a bit more.
- The project appears to be progressing well, and it should drive toward a realistic prototype storage system that meets the physical and environmental constraints as quickly as possible.
- The project should continue in some form.

Project #ST-136: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: "Graphene-Wrapped" Complex Hydrides as High-Capacity, Regenerable Hydrogen Storage Materials

Di Jia Liu; Argonne National Laboratory

Brief Summary of Project:

"Graphene-wrapped" hydrides (i.e., complex hydride nanoparticles wrapped by graphene) show promise as a hydrogen storage material. The objective of this project is to produce one or more hydride@graphene composite materials with regenerable and reversible hydrogen storage capacity, targeting total gravimetric capacity greater than 10 wt.% and volumetric capacity greater than 0.055 kg H_2/L. Project tasks include the exploration of new hydride@graphene materials, material characterization and optimization, and development of modeling and simulation capabilities.



Question 1: Approach to performing the work

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

- The approach adopted in this project is unique and innovative. The high gravimetric capacity of $NaBH_4$ makes it an interesting hydrogen storage candidate. However, it has been largely discounted owing to its high intrinsic decomposition temperature. This project utilizes graphene as an encapsulant to significantly alter the thermodynamics and kinetics of hydrogen sorption reactions in nanostructured $NaBH_4$. This novel approach has now made this material a much more promising candidate for practical application. The approach to preparing the nano-encapsulated hydride appears to be scalable. The project team has outlined a reasonable and logical research and development strategy involving synthesis, characterization, and modeling/simulation. Sensible project milestones and a well-coordinated work plan are in place. Extensive collaborations with the Hydrogen Materials–Advanced Research Consortium (HyMARC) are in place to address the critical issues concerning the reaction mechanisms and characterization of sorption reactions in the nano-encapsulated material.
- One of the strengths of this project is the novelty of encapsulating the material to improve the reversibility and the kinetics. Since the techniques and procedures related to this approach are relatively new and therefore untested, this project is a high-risk project, but one very much worth exploring. It is not known how well this technique will overcome the barriers, but it seems reasonable to expect that it just may improve the hydrogen storage technology. It has been a relatively short time since the project started; therefore, most criticisms may be premature. The project could have initiated the modeling work sooner.
- This project is a follow-up on the remarkable finding that composites of $NaBH_4$ and 14 wt.% added graphene will undergo complete and reversible dehydrogenation. The basic approach of the project is reasonable, including verifying the initial observations and exploring graphene composites of other complex hydrides in hope of identifying a practically relevant material.
- The project is nicely focused, the barriers are clear, and the needed integration with other partners is exceptional.
- The project's focus is on $NaBH_4$ (10.6 wt.% hydrogen maximum). The team is trying to demonstrate 8 wt.% reversible. Therefore, there is not much room for error. In published work with collaborators at Shanghai Jiao Tong University, the project team demonstrated 7 wt.% hydrogen. To get to 8 wt.%, they will have to have higher loading of $NaBH_4$ in the graphene. It is surprising, given the demonstrated success

with $NaBH_4$, that the team did not choose to work with $LiBH_4$ or $Mg(BH_4)_2$, where there is much more room for error. It is not clear if there is something special about $NaBH_4$. It is unclear whether the approach works with $LiBH_4$ or $Mg(BH_4)_2$. If true, it might be more interesting to understand the apparent failures and how to overcome them.

- The principal investigator (PI) presented a good approach. While there are some limitations, the concept of encapsulation of materials to enhance hydrogen sorption is a viable pathway forward. However, this work does seems to overlap extensively with the work done and reported in the literature by Jeff Urban in HyMARC. That work encapsulated magnesium in various polymers and graphene sheets with the same net result of being impervious to various gases. While the approach to encapsulation from solution as presented was a great new approach, the significance of the research is lost, considering those previous publications in *Nature Communications*. Finally, one would expect that upon cycling, the expansion/contraction, along with the site heating, will be detrimental to any applicable long-term application.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.8** for its accomplishments and progress.

- Impressive results were obtained on hydrogen sorption reaction temperatures and (de)hydrogenation rates. The temperatures observed for hydrogen release from the nano-encapsulated $NaBH_4$ samples are still high, but significant improvements over the bulk material are evident. Important new results on ReH_2/DeH_2 cycling have been obtained, especially on the regeneration yield. The promising initial results provide confidence that further improvements in the use of catalysts/additives and optimized graphene–hydride ratios in the graphene-wrapped systems will be forthcoming. It will be important to develop a more comprehensive understanding of the mechanism(s) and rate-controlling processes operative in this nanostructured system.
- The researchers have shown excellent progress concerning the $NaBH_4$ wrapped in graphene. The material performance was clearly shown, and the researchers have done a good job explaining their strategy going forward, based on their initial results to attain the DOE goals.
- Given the relatively short time since the project started to this current review, criticisms may be premature. Promising results have been obtained but suffer from the lack of completeness. For example, the PI claims that good hydrogen yield occurs during dehydrogenation, but the graphs on slides 10 and 12 show a significant degradation occurs with each cycle. It is unclear what the nature of this degradation is. The PI should have acknowledged this issue and described the efforts to understand more. The top micrograph on slide 6 shows just how good the encapsulation is, but it is unclear if it is really representative. The lower micrograph shows particles either sitting on a carbon substrate or perhaps sandwiched in between sheets of carbon. It is unclear how the audience is expected to tell the difference. It is also unclear what percentage of the particles are encapsulated. The kinetics appears to be sluggish, as it takes significant time (several hours) to both dehydrogenate and rehydrogenate. It seems that $NaBH_4$ may need re-evaluation as a good candidate for storing hydrogen.
- There does not seem to be a significant amount of work that has been accomplished in the first year, compared to what was presented in the initial kick-off presentations. If there is indeed a formation of sodium hydride as presented, it infers that the mechanism is not as straightforward as presented. Slide 12 seems to indicate a hysteresis that occurs is quite significant. In addition, the high temperatures at which hydrogenation occurs do not seem applicable or have any significant improvement on past work in this area of $NaBH_4$. It would be good to see a more detailed evaluation of this with a more appropriate mechanism. In addition, it is surprising that the hysteresis was not worse on the site heating of graphene during hydrogenation. With the expansion and contraction expected in these materials, the extent of "edge" encapsulation materials and an evaluation of the efficiency of encapsulation would all seem to be very important to investigate/report. A simple transmission electron microscope (TEM) scan before and after hydrogenation cycles is essential, and is surprising by its omission. Finally, the recent nuclear magnetic resonance (NMR) results in the additional slides make absolutely no sense. It is unclear how the boron peak can disappear.

- There is something amiss with the results that have been obtained to date. The claim that $NaBH_4$ and 14 wt.% graphene will release 9.1 wt.% hydrogen to give NaH and B is clearly false, as the stoichiometric maximum is only 6.9 wt.%. In addition, the infrared results, which supposedly demonstrate the production of NaH, clearly show that a B-H stretch persists at 430˚C. The NMR results are the most disconcerting, as the dehydrogenated product does not contain a resonance for elemental boron or a boride. In fact, the results contain no ^{11}B signal at all, as if the boron has disappeared, only to reappear when the material is rehydrogenated.
- This is a new fiscal year 2017 seedling project. The team was able to make another batch of $NaBH_4$@graphene and reproduce their previous work with Shanghai Jiao Tong University, published last year in *Advanced Materials*. It is not very apparent what material was new. It was also unclear whether higher loading was new. It would have been more insightful to compare with the new work. It was unclear whether loading or particle size was different.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.8** for its collaboration and coordination.

- Close collaborations with HyMARC, the Hydrogen Storage Characterization Optimization Research Effort (HySCORE), and external institutions are evident. This cooperation is clearly augmenting and supporting the Argonne National Laboratory-led project and is leading to rapid progress on most project tasks. The project appears to be well coordinated, with clearly defined roles and responsibilities for participating organizations.
- There seems to be extensive and very worthwhile active collaboration with HyMARC, and other necessary collaborations are in the planning stage. The researchers appear to be leveraging these outside resources well.
- The project is working well with both HyMARC and HySCORE.
- Professor Ge at Southern Illinois University has good background on computational approaches to hydrogen storage materials. Asking HyMARC for assistance to understand mechanisms is a big ask. It will be valuable to get more scoping work accomplished by Professor Ge to make this a more reasonable request.
- Almost all of the collaborations appear to be at a very initial stage with no substantial progress made. It is unclear whether this is caused by a lack of initiative, a lack of resources within HyMARC, or some other reason. It is also unclear if the Southern Illinois University work was initiated because the HyMARC resources were unavailable. This may be an issue outside the control of this PI; it may be a larger issue that needs to be addressed at a higher level.
- The project suffers from a lack of expert collaborations. Help from HyMARC and/or HySCORE is clearly needed to sort out the many irrational results that have been obtained.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- This is a high-risk, high-payoff project that is an archetype HyMARC seedling. The approach is innovative, and the initial results are promising. It is an important addition to the HyMARC project portfolio. The project directly supports the goals/objectives of the DOE Hydrogen and Fuel Cells Program (the Program).
- One of the bottlenecks for practical use of complex hydrides is slow kinetics for hydrogen uptake and release from carriers that have the "optimum" thermodynamic range for reversibility. The proposed work is investigating approaches to enhance kinetics of hydrogen release from complex hydrides to address this bottleneck.
- This project's high degree of novelty may lead to real advances toward the DOE goals, and it is definitely worth pursuing. It is also a high-risk project because of the several unknowns with this new approach. When the novelty and high-risk considerations are combined, it reduces the likelihood of making an impact, but the project still has high potential.

- This project appears to be at the cutting edge of using new innovative composite materials to accomplish the Program goals and objectives. There is clearly high relevance and impact.
- This project targets developing composite materials that will enable hydrogen cycling of high-hydrogen-capacity complex hydrides. However, the actual relevance and eventual impact of the project is questionable, as it targets achieving reversibility below 400˚C rather than at polymer electrolyte membrane cell relevant temperatures.
- Encapsulation/confinement is a viable pathway to improving kinetics of hydrogen adsorption on hydrides. However, while this research is interesting, it does not seem to have a pathway toward achieving the DOE goals.

Question 5: Proposed future work

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

- The proposed future work is clearly stated and follows logically from the present studies. Very little information has been provided concerning the hydrogen sorption reaction mechanism(s). Elucidation of mechanisms and rate-controlling processes should be important topics for work in the near future. This will undoubtedly require an even closer collaboration with the HyMARC core team. Several other questions also should be addressed. For example, it is unclear whether carbon in the graphene wrapping is an active participant in the sorption reaction processes. It is also unclear whether other encapsulants (e.g., aerogels) are as effective as (or more effective than) graphene. It is also unclear whether data are available on the dependence of sorption temperatures and the ReH_2/DeH_2 kinetics on the hydride–graphene ratio.
- Future work proposed is well thought out and tries to expand the project toward the most useful composite materials.
- The proposed future work and go/no-go's all seem reasonable.
- It was a little disappointing to see many slides on accomplishments came from work that was published in the peer-reviewed literature before the project was initiated. The team shared four bullet points on future work. It is understood that they have a go/no-go decision point milestone before the next Annual Merit Review, so their first bullet was to increase the storage capacity in $NaBH_4$@graphene through optimizing the hydride–graphene ratio. There may not be room to do this if they are currently at 86% $NaBH_4$. The second bullet was to improve kinetics, which would not be critical at this point. Showing the approach works for more than just $NaBH_4$ should be a higher priority. It is a surprise that this seems to be delayed to Phase II. If the project does not make the go/no-go decision point milestone because of a focus on $NaBH_4$, it would be a shame. The third bullet is to improve fundamental understanding of mechanisms through computational modeling. Experimental data on other complex borohydrides may provide some additional insight to help focus the approaches on specific mechanisms in the modeling tasks.
- It seems like the real project goal should be to optimize the encapsulation's effectiveness. This may involve the hydride–graphene ratio but is more than just that. It is unclear what the other parameters are that can be explored to enhance the effects of encapsulation. Looking at catalysts to improve kinetics is key, but the team should not linger too long on trying to fix $NaBH_4$. It is unclear whether it is more effective to search for better or "more suitable" hydrides. Fundamental understanding through modeling is essential and is an important component for future work.

Project strengths:

- This is a novel and innovative technical effort that has the potential for high payoff. The project team has demonstrated solid progress in the first project phase. A well-crafted future work plan is in place, and strong connections with HyMARC core team members are facilitating project success.
- Novelty is the project's best strength, and the concept appears to be promising. The project approach may overcome barriers that hinder hydrogen storage technology. The team has strong teaming with HyMARC planned, which should be highly beneficial.
- The graphene wrap idea is highly innovative since it addresses some property shortcomings of more conventional materials. In addition, the idea can probably be successfully adapted to different hydrogen storage compounds.

- This project shows very exciting results for $NaBH_4$. The pressure-composition isotherm (PCT) curves in the published paper show that the equilibrium pressure may be in a desirable target area.
- The strength is the new technique for material encapsulation.

Project weaknesses:

- The (de)/(re)hydrogenation temperatures are still very high and far outside the range of acceptance for fuel cell applications. Overcoming that obstacle is a major challenge, and it seems unlikely that, without tremendous success on implementation of the future work plans/ideas, those temperatures will be reduced to acceptable levels. That remains the dominant challenge for the project team.
- It is not clear whether this approach works for other borohydrides or if it is unique for $NaBH_4$. According to the team's published paper, $NaBH_4$@graphene is "unstable" at 40°C, which could be a problem. TEM pictures show a lot of apparent empty space. It is not clear what the volumetric density is or what the error bars are for the cycle measurements. It was interesting that from cycle 3 to cycle 4 the capacity dropped by 3% and from cycle 4 to cycle 5 it increased by 2%. It is unclear whether the increase is real or within the measurement error. Maybe the materials should be cycled under hydrogen for longer time periods and/or at higher temperature.
- It is hard to tell enough about such things as ultimate material costs. Additionally, there is still some degeneration of material upon cycling, so it is not clear if this can ever be improved enough to be commercially feasible.
- The edge effects, volume contraction/expansion, and formation of side products were not addressed in this initial presentation.
- The degradation seen with cycling is not addressed adequately. This project had a slow start with collaborations.
- The project suffers from a lack of expert collaborations. Help from HyMARC and/or HySCORE is clearly needed to sort out the many irrational results that have been obtained.
- This project has obtained several irrational results.

Recommendations for additions/deletions to project scope:

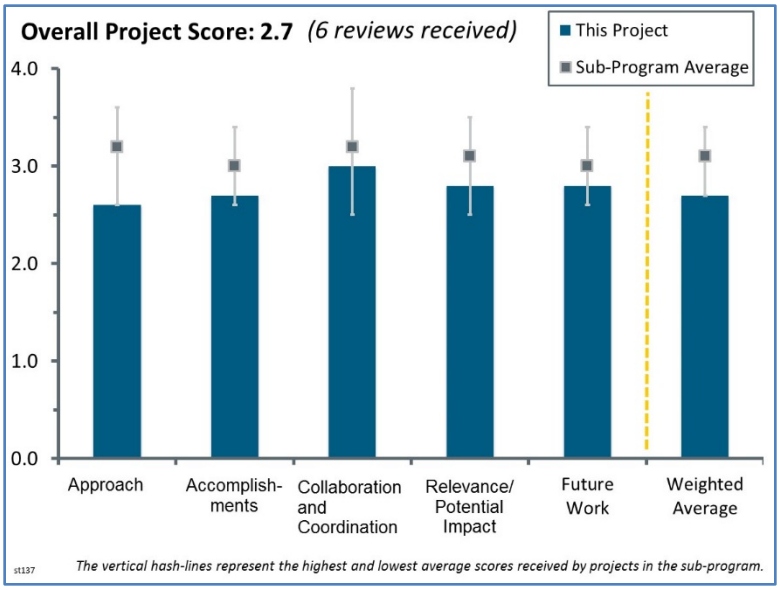
- The ^{11}B NMR data for decomposition of $NaBH_4$@graphene published in the team's *Advanced Materials* paper show the formation of $Na_2B_{12}H_{12}$ after one cycle of hydrogen release. It is also interesting that the published NMR data look different from the ^{11}B NMR data provided in the presentation. As $B_{12}H_{12}$ formation is occurring, it would be interesting to investigate a lower temperature for hydrogen release to see if $B_{12}H_{12}$ can be avoided. The kinetics would be slower, but it might help reach the milestone of 8 wt.% over the promised number of cycles. The team could also learn important information about the equilibrium pressure with more PCT experiments.
- It would be valuable to have some early explicit effort to look for the optimum hydride that would benefit from encapsulation. Maybe this has been done implicitly, but it was not reported on explicitly. Phase II has some effort mentioned. However, it is not clear what the nature of that effort is or if it is an exploration by modeling or measurements. The former would be able to cover much more ground faster and easier with more and longer cycling data. Exploration of the degradation mechanisms seen should be done in order to understand the degradation.
- It would be interesting to determine somehow whether the graphene is mainly providing a means to create tiny reactor vessels for bulk hydrogen storage materials or whether is there an additional alteration of the bulk thermodynamic properties. In addition, one reviewer pointed out that the formation of closo-borate-type clusters is evident in the NMR, which might explain the slow degradation with cycling and might put a limit on the reversibility over extended cycling. This should be investigated more closely since it has an impact on the entire project and might steer the researchers toward non-borohydride-type materials in future efforts.
- The weight-percent hydrogen that can be cycled by $NaBH_4$@graphene should be independently verified. The infrared studies and, more importantly, the ^{11}B NMR studies should be repeated at HyMARC or HySCORE facilities.
- The project needs more characterization after cycling and new mechanisms that explain the formation of sodium hydride.

Project #ST-137: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: Electrolyte-Assisted Hydrogen Storage Reactions

Channing Ahn; Liox Power

Brief Summary of Project:

Most hydrogen storage candidates with high capacities and appropriate themodynamics for polymer electrolyte membrane fuel cell use contain multiple solid phases that must nucleate, grow, and be consumed during cycling; the presence of these multiple phases hinders kinetics. This project seeks to address the kinetics of multiphase hydrogen storage reactions by exploring the use of electrolytes and/or electrochemical approaches to "solubilize" or promote diffusion of reacting species.



Question 1: Approach to performing the work

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

- The novel concept of using electrolytes to decrease the kinetic barrier is well conceived. If the concept is applicable, the researchers predict the reduction of the kinetic barrier down to 4 kJ/mol, enabling charging and discharging at a temperature well below 80°C. This likely assumes that diffusion is the major kinetic limitation, as it is for electrochemical reactions in which there is a negligible chemical barrier for electron transfer. On the other hand, complex hydrides require the breaking of B-H bonds to release hydrogen or the breaking of H-H bonds to recharge the material. The homolytic bond strengths of B-H and H-H bonds are on the order of 400 kJ/mol; therefore, a "catalyst" to overcome these thermal barriers will likely be required.
- The project is outside the box but worth the effort to see if there is a viable path forward. It appears to be well integrated with and designed around the current status quo efforts.
- The approach seems reasonable for what the project is trying to accomplish.
- The electrolytes and complex hydride systems selected are reasonable and worthy of study. However, it is unclear how the systems under study could be modified into systems that meet the gravimetric density target.
- The use of a liquid electrolyte to assist in hydrogen storage reactions is a unique idea. However, in looking at it in more detail, it seems the large activation barrier to the electron tunneling of charge between the two species, as shown in slide 6, will be difficult to overcome. First, it would seem that the solvation sphere would still be a barrier instead of an aid. The only apparent benefit would be more uniform heating of the sample in a slurry, but the bulk diffusion and structural changes that occur were not fully addressed. The slide also shows an ideal case of a sphere. It is doubtful that any of the species in this work would have such a uniform shape, and it may be even less of a point-to-point contact than depicted. Also, on slide 10, the ideal case is very misleading with the calculation. It assumes no activation overpotential, which is expected to be quite large for a material undergoing significant volume changes. The eutectic molten salts is an intriguing idea, but it would be preferable to see the investigation of some ionic liquids (i.e., room-temperature molten salts) instead (slide 15). The use of the other solvents, while informative, did not seem to be relevant to the project. Overall, the approach and progress to date are very disappointing, even though it is still early in the project.
- This project is focusing on assessing the idea of electrolytes to overcome kinetic barriers in metal hydride materials. It is a lower technology readiness level concept evaluation that may not ever be a viable

approach to developing materials that can meet the light-duty vehicle targets. A simple assessment using the tools developed by the Hydrogen Storage Engineering Center of Excellence acceptability envelope should be performed to assess the feasibility of this idea.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.7** for its accomplishments and progress.

- The project has only a few months under its belt. From what has been reported so far, the number and impact of preliminary results is more than satisfactory.
- This is a recently started, fiscal year 2017 seedling project that is making progress toward understanding the limitations and potential advantages of the approach.
- The presentation was diffuse, making it difficult to evaluate how much progress has been made. The principal investigator (PI) seemed to be saying that ethers were found to undergo significant decomposition at 200˚C. It is unclear if the dehydrogenation of $Mg(BH_4)_2$ in the presence of ethers will be studied further. It was shown that the kinetics of the dehydrogenation of MgH_2/Si is significantly improved in the LiI:NaI:KI eutectic; however, it is unclear whether weight percent reported includes the eutectic and whether this system is reversible in the eutectic.
- While the project is new and is just getting started, no significant accomplishments were presented. It may be unfair to have it evaluated at this point.
- This is a new project, so ranking the accomplishments is difficult, or perhaps even premature.
- While the project is quite early, it was still disappointing to see so little progress. In reality, there will be no well-defined answer until further work is completed.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.0** for its collaboration and coordination.

- Collaboration with HRL Laboratories (HRL), the Hydrogen Materials–Advanced Research Consortium (HyMARC), and the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) provides a firm grounding in modeling and experimental expertise.
- The investigators have reached out to the HyMARC team, and it is expected that more interactions will be forthcoming.
- The strong team brings together expertise in different fields from Liox, HRL, and the California Institute of Technology (Caltech).
- There is not significant collaboration yet, but this is mainly due to the short age of the project. The collaborations are scheduled to occur in the near future, which is reasonable.
- The project will collaborate with Caltech for nuclear magnetic resonance spectroscopy, with HySCORE, and with HyMARC. It is unclear which capabilities in HyMARC will be useful, and the role of HRL in the collaboration is unclear as well.
- The project has been underway for only a short time, but plans for collaboration with the HyMARC core seem to be very underdeveloped.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **2.8** for its relevance/potential impact.

- The project as laid out shows high relevance and potential impact.
- One of the bottlenecks to utilization of complex hydrides for fuel cell electric vehicle applications is for charging and discharging hydrogen. The proposed work investigates the use of electrolytes (or solvents) to enhance the kinetics by decreasing the activation barrier to diffusion.

- This project addresses the key issue in the development of complex hydrides: improvement of kinetics. However, the relevance and eventual impact of this project are questionable, as the weight incurred by the use of electrolytes is completely ignored. The project is perhaps more relevant to the development of batteries than hydrogen storage materials.
- Electrolyte-mediated hydrogen storage reactions may offer advantages in the release of hydrogen but may be negated by the increased diffusional resistance (accompanied by a very low hydrogen solubility) of hydrogen through the electrolyte—assuming, of course, that the reaction will be reversible. Currently, there are no known materials that will meet the gravimetric capacities, so the addition of an electrolyte only reduces the capacity.
- While the idea of understanding the ability of electrochemical-driven systems to overcome kinetic barriers in higher-gravimetric-capacity materials could be valuable to the overall Hydrogen and Fuel Cells Program achievements, it is not certain that this concept can ever be a viable approach.
- The potential impact is significant, but unless the researchers are able to find viable ionic liquid systems, it will be very difficult for the project to be successful.

Question 5: Proposed future work

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

- The team recognizes the need to discover more stable solvents, even with a goal of working at lower temperatures. The team has been working at low concentrations (0.1 M) with limited success. It will be beneficial to investigate higher concentrations of borohydride. The project should increase hydride concentration by a factor of 10 and decrease solvent by a factor of 10. A slurry or paste will provide significantly higher gravimetric density and should reduce solvent decomposition and be more aligned with the components of a battery that is being used as an analog for enhanced kinetics (e.g., 40% active material + 12% electrolyte). The use of solvents will increase rates of diffusion, but the presence/need of a catalyst is likely to be critical and should be explored in future work.
- This was hard to assess since the project is in the early stages, but the presenter appeared to have a coherent vision of the future plans.
- It will be interesting to see whether the project can find a material that demonstrates the initial properties and capacities that would allow this concept to be viable.
- The proposed future work will quickly determine the viability of the project.
- The proposed future work (milestones and go/no-go) has a very low bar of around 1 wt.% hydrogen. It is unclear what materials the project is focusing on, e.g., MgH_2, $Mg(BH_4)_2$. The potential for gas phase contamination should be a concern.

Project strengths:

- This is a unique and intriguing approach to a difficult problem. It pushes the boundaries of what has already been tried.
- This is a well-respected team of hydrogen storage researchers.
- The team has a strong understanding of fundamental hydrogen storage limitations.
- This is a strong team of experts looking at approaches to enhance kinetics.
- John Vajo, Channing Ahn, and the strength of the HRL collaboration are project strengths.
- This is a world-class team of co-investigators.

Project weaknesses:

- The team will find a solvent that will enhance the dehydrogenation rate, but it is unclear what this will provide in the grand scheme of hydrogen storage for automotive applications. The increased diffusional resistance of hydrogen through the electrolyte for the reverse reaction (i.e., hydrogenation) will be problematic.
- This is a great approach to investigate kinetics but a long shot to meet gravimetric targets. There is no planned computational work. It would be interesting to ask for theory assistance to calculate the barrier for

hydrogen release from MBH_4 to make MB + $2H_2$. If the barrier is high and not a diffusion limited process, the risk could be mitigated through HyMARC for assistance with theory and potential catalysts.
- It is not clear whether the electrolyte-assisted approach will actually work. Although tantalizing, there is no consensus concerning success from the early data presented so far.
- This project has a very soft Year 1 go/no-go. There is high potential for the project to drift off into irrelevance.
- This is probably not a viable concept that can meet the light-duty vehicle system targets in its current conception.

Recommendations for additions/deletions to project scope:

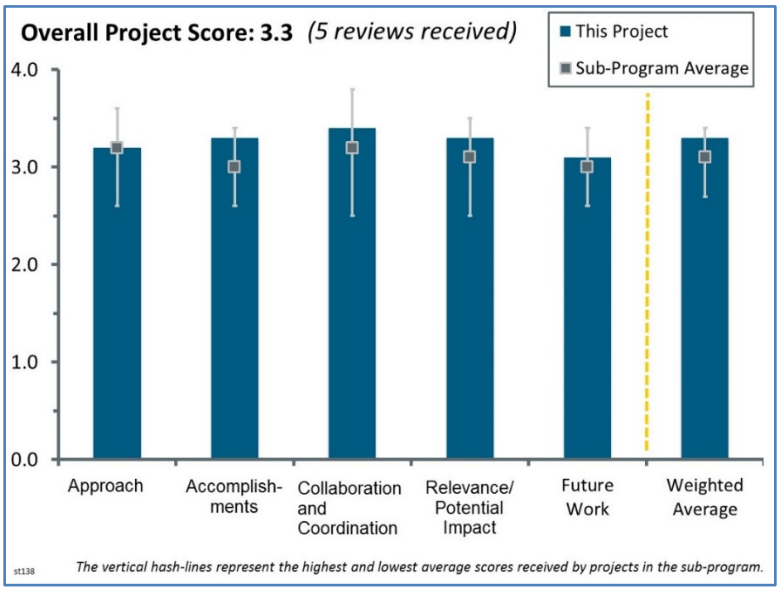
- The PI should place more emphasis on investigating the various possible eutectic salt mixtures. Also, the project should expand the scope to investigate the effects of particle size on performance, since the theory suggests that the mechanism is surface-area dependent.
- The project direction and goals need to be better defined.

Project #ST-138: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: Development of Magnesium Boride Etherates as Hydrogen Storage Materials

Godwin Severa; University of Hawaii

Brief Summary of Project:

The objective of this project is to synthesize and characterize magnesium boride etherate hydrogen storage materials that are capable of meeting the U.S. Department of Energy's performance targets. The project will synthesize magnesium boride etherates using ball milling and heat treatment techniques, study hydrogenation of the materials using variable pressure and time, study and optimize hydrogen cycling of the materials, and develop theoretical models.



Question 1: Approach to performing the work

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

- This is a nicely described approach that appears to derive from earlier observations that the kinetics of dehydrogenation of $Mg(BH_4)_2NH_3$ were enhanced over the parent compound, $Mg(BH_4)_2$, but that unfortunately released some ammonia and formed stable BN compounds that could not be rehydrogenated. This appears to have provided the inspiration for this current project. Rather than employing ammonia as a ligand to enhance kinetics, the project has proposed using ethers as ligands to enhance the kinetics of de/rehydrogenation. This work thus addresses a potential solution to one of the vexing problems with the $MgBH_x$ system that generally suffers from very slow kinetics of dehydrogenation and rehydrogenation at practical temperatures. This project's approach is well designed in that it examines reversibility of the ether system and incorporates computational modeling appropriately. The chemistry appears highly feasible, and there is good overlap with efforts within the Hydrogen Materials–Advanced Research Consortium (HyMARC) and the Hydrogen Storage Characterization Optimization Research Effort (HySCORE), both experimentally and computationally. Multiple pathways to synthesis of the target species are employed, which is a good risk mitigation strategy.
- An intriguing and innovative approach is being employed to improve hydrogen storage properties in the $MgB_2/Mg(BH_4)_2$ system. The participation of etherate adducts in the hydrogen sorption reactions in the magnesium boride system has been shown to greatly enhance the reaction kinetics. The approach employs a combination of synthetic methods, detailed characterization/diagnostics, and theoretical studies (HyMARC collaborations) to demonstrate improved hydrogen sorption properties and to understand the underlying mechanism(s). A detailed and compelling work plan is provided. It provides confidence that the critical issues will be successfully addressed and a promising new material will be developed.
- Given the Fuel Cell Technologies Office (FCTO) commitment to Mg-B-based systems, this effort offers a path toward reducing dehydrogenation temperatures and possible rehydrogenation using various solvents, probing both dehydrogenation of a range of borohydrides that appear along reaction pathways and also concentrating on the rehydrogenation of MgB_2.
- The overall approach is clear and encompasses two different ways to enhance the kinetics of Mg borohydride materials by synthesizing MgB_2 etherates: reactive ball milling and heat treatments from Mg borane etherates, and MgB_2 in presence of ethers. The milestones do not appear to plan for feedback on the synthesis. Future work includes investigations of the mechanism and understanding kinetics of reactions;

however, this may require changes in the synthesis (i.e., concentration of tetrahydrofuran [THF] (slide 5), particle size, etc.). From the milestone summary, it appears that all synthesis is 95% complete. It seems surprising that all synthetic efforts will be completed in the first quarter. Instead, identifying what works and investigating it further would improve the outcome of this research. The THF etherates have proven better than the others, so focusing efforts on this system will provide exciting results, as the team appears to have decided.

- Other metal etherates have been examined, but not MgB_2. This project can see if there is some potential here.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.3** for its accomplishments and progress.

- The project has made very good progress quickly. The researchers have explored the stability of MgB_2-THF complexes in collaboration with the computational capability within HyMARC that helps to elucidate the structures and energetics of complex formation. In parallel, they have succeeded in developing, demonstrating, and characterizing the products from a nice chemical synthesis of the diboride-THF complex, in addition to a "heat and beat" brute force approach. This work has identified that the THF complex of the diboride is chemically stable to above 400°C, whereas polyethers decompose at temperatures less than 200°C. As the presence of THF in the complex diminishes the gravimetric hydrogen capacity of the complex, the researchers are in the process of determining whether substoichiometric THF complexes may be prepared, thereby reducing the gravimetric penalty of adding THF. Most importantly, the project has been able to demonstrate with quite high confidence, using a variety of characterization techniques, that the complexes may be hydrogenated at high pressures (1000 bar) but moderate temperatures of 300°C. This work has employed good collaborations in computation, characterization, and high-pressure hydrogen capabilities resident within the HyMARC and HySCORE consortia.
- Solid progress has been achieved on synthesis and characterization of strongly coordinated MgB_2 etherate species. Reaction of ball-milled MgB_2-THF with hydrogen at high pressure has shown that the system can be hydrided, producing $Mg(BH_4)_2$ at temperatures as low as 300°C. This is a particularly noteworthy result that provides an important motivation for continuing this work. Interesting and potentially important information concerning the reaction mechanism has been provided from molecular dynamics modeling conducted in collaboration with HyMARC (Wood, Kang, et al). The results suggest that the interaction of the MgB_2 surfaces results in stabilization of the Mg-exposed surfaces. Direct bond formation between MgB_2 and THF molecules could be a vital aspect leading to enhanced hydrogenation kinetics.
- Accomplishments include the synthesis of MgB_2 etherates by two routes: heat treatment of MgB_2 and THF, tetraglyme or dioxane, and by MgB_3H_8-THF. Currently, ball-milled MgB_2-THF samples show greatest promise at 300°C hydrogenations. This work has produced the exciting result for the first time of the formation of a significant amount of beta-$Mg(BH_4)_2$ at 300°C, through evidence via thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and x-ray diffraction (XRD). This shows important progress toward the project and DOE goals.
- There is good progress so far, especially in synthesizing materials.
- The work described represents less than six months of effort into this project, but the principal investigator has had a longer timeline of experience in studying this system. For the study of MgB_2, the layered nature of the material appears to be problematic, with the greatest possibility for reaction taking place along the edge of these structures. There are presumably reasons during MgB_2 formation that involve free energy minimization that presumably yields a high aspect ratio of basal to edge plane morphologies, even though the opposite is preferred. The only alternative in this case is to be sure that the MgB_2 has a small overall morphology. The successful hydrogenation of MgB_2 with THF, albeit at high pressure and temperature, points to possibilities for more moderate hydrogenation.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.4** for its collaboration and coordination.

- Close and highly beneficial collaborations between the University of Hawaii (UH) project team and numerous other investigators, most notably the HyMARC core team, are apparent. These collaborations have been vital to the rapid progress achieved thus far. The reliance on fruitful collaborations to accelerate progress and inspire new research and development (R&D) ideas has been a hallmark of the work by the UH investigators. This project is no exception.
- Collaboration in this project is critical. HyMARC provides characterization of samples by XRD and TGA/DSC and hydrogenation of samples, and the National Renewable Energy Laboratory will do temperature-programmed desorption (TPD). Correlating theoretical work supports the stability and observation of the bond formation between MgB_2 and THF. This is a very collaborative effort with a large portion being done outside of UH.
- This project has meaningfully and very quickly taken advantage of multiple capabilities ranging from computation to diffraction to high-pressure hydrogen synthesis and off-gas analysis resident within the HyMARC and HySCORE consortia.
- This work has a fairly high level of integration with HySCORE (Pacific Northwest National Laboratory team) and HyMARC (Sandia National Laboratories team), and has presumably been aided by some of the computational work at Lawrence Livermore National Laboratory.
- Collaborations were mentioned, but the presentation was not that obvious as to exactly how and where the collaborators were involved. The collaboration should be more evident as the project proceeds.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- This is an excellent high-risk, high-payoff seedling project that is being conducted in close collaboration with the HyMARC team. The $MgB_2/Mg(BH_4)_2$ system has emerged as one of the only metal hydride systems that has the potential to meet the DOE targets for hydrogen storage. The principal obstacles (mainly kinetics) to the successful development and use of this material in practical system applications are being directly addressed in this project. The project is tied closely to the overall HyMARC goals and objectives, and it directly supports the HyMARC mission and the FCTO Multi-Year Research, Development, and Demonstration Plan goals.
- This work is highly relevant to Hydrogen and Fuel Cells Program goals in that the project is exploring pathways to enhance the kinetics and reversibility within the MgB_xH_y system. This work is likely to determine the role that complexing ligands play in enabling the observed, enhanced kinetics that may provide guidance to allied computational and experimental efforts and inspire other ideas and approaches to achieving kinetically facile, reversible high-capacity hydrogen storage in materials. If this project can elucidate pathways to minimizing the amount of complexant while achieving high rates of de/rehydrogenation, this will be very impactful on FCTO R&D goals.
- This project provides important work to address the capacity and kinetics for hydrogen storage using magnesium boride etherates. The project goals are consistent with DOE targets for capacity, kinetics, and cyclability. The project go/no-go decision is to demonstrate >7 wt.% hydrogen uptake by a MgB_2 etherate at <300°C, 700 bar, 48 hours, and reversible release of >2 wt.%. The final milestone for the "dehydrogenation of one hydrogenated MgB_2 etherate" is somewhat unclear as to whether there is a capacity associated with this.
- This project in the time available probably has only a small potential in developing a high-capacity storage material, but it has a good potential to add to the understanding of hydrogen interactions in materials.
- This project is in its early stages, and it is difficult to tell whether it will meet the aggressive go/no-go target.

Question 5: Proposed future work

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

- The proposed future work follows naturally from the current studies. The reviewer fully supports a strong emphasis on the MgB_2-THF system as stated by the project team. Likewise, a focus on characterization using the range of techniques outlined in the presentation should provide critical information that will be needed to facilitate progress. The computational work on size-dependent stability of MgB_2 clusters is intriguing. It should provide information to guide future experiments. At this point, only limited information has been provided concerning the mechanism for hydrogenation enhancement. As stated in the presentation, elucidating the reaction mechanism and understanding the rate-controlling processes in the $MgB_2/Mg(BH_4)_2$–etherate system will be an important future direction. It will undoubtedly be facilitated through extensive collaborations with the HyMARC core team. However, it seems apparent, based on comments made at the presentation, that more insight concerning the mechanism is available than was provided at the review. It is to be hoped that details will emerge in future DOE Hydrogen and Fuel Cells Program Annual Merit Review meetings and technical team reviews. It will also be important to clarify how the hydrogenation characteristics vary with the mole ratio of THF:MgB_2, especially in samples containing substoichiometric amounts of THF. Results from those investigations may have important implications in understanding the enhancement mechanism(s). The ability to achieve significant rate enhancements with reduced quantities of THF also has positive impacts on the overall gravimetric capacity of the system.
- A logical progression of R&D tasks is proposed as future work. Given the high quality of the team and its high-quality collaborations with HyMARC and HySCORE, it is very likely that significant progress will be made. Given the experience of the team, one can say with confidence that if additional R&D challenges arise in the future, the researchers will be able to navigate around or through them.
- Future work suggests understanding the mechanism of kinetic enhancement by etherates. This will be studied using TPD, but it is unclear what parameters will be studied. Hydrogen cycling will also be investigated. This will provide important materials performance characterization to optimize cycling in these systems.
- As with all of the seedling projects, a lot of effort is being asked of the investigators to be completed in a short time.

Project strengths:

- The project team comprises recognized experts in the field of complex hydride chemistry and hydrogen sorption reactions. Extensive collaborations (especially with the HyMARC core team) are being used effectively to augment the overall R&D effort. A solid work plan is in place, and the future work on this project will undoubtedly provide important new information concerning the efficacy of the promising $MgB_2/Mg(BH_4)_2$ system for practical storage applications.
- This is a highly collaborative effort with HyMARC and HySCORE in areas that will have impact on the success of the project. The researchers have quickly made very good progress toward their goals. A nicely balanced set of synthetic strategies are employed to mitigate any risks that may arise due to problems in the synthesis of materials. The team has tremendous strength in performing chemical synthesis, chemical characterization, and interpretation of results in this materials system.
- This work has provided the hydrogenation of ball-milled MgB_2-THF at 300°C. The team presented the first evidence for the formation of a significant amount of beta-$Mg(BH_4)_2$ at 300°C (through evidence via TGA/DSC, FTIR, and XRD). The project provides a promising route forward and has a team with strong expertise.
- There is clear evidence that an approach such as this will be necessary to promote lower-temperature cycling of Mg-B systems.
- Materials synthesis is a project strength.

Project weaknesses:

- Reducing the (de)hydrogenation temperatures at practical pressures to values commensurate with fuel cell operation remains a daunting challenge. Although excellent progress has been made using the etherate adduct approach, there is a long way to go. A clear pathway to achieving sorption characteristics at practical temperatures and pressures is not apparent.
- The approach of having all of the synthetic work in the first quarter limits the findings of this project. Instead, feedback from the characterization should provide thoughtful synthetic routes forward. For example, the future computational work includes size-dependent stability and morphology of MgB_2 clusters and particles. This sounds like important work; however there is no apparent plan to incorporate this feedback into the synthetic work.
- Too much work is being tasked to discern a proper mechanism, with limited time to accomplish the work.
- The project would be helped by more computational modeling collaborations.

Recommendations for additions/deletions to project scope:

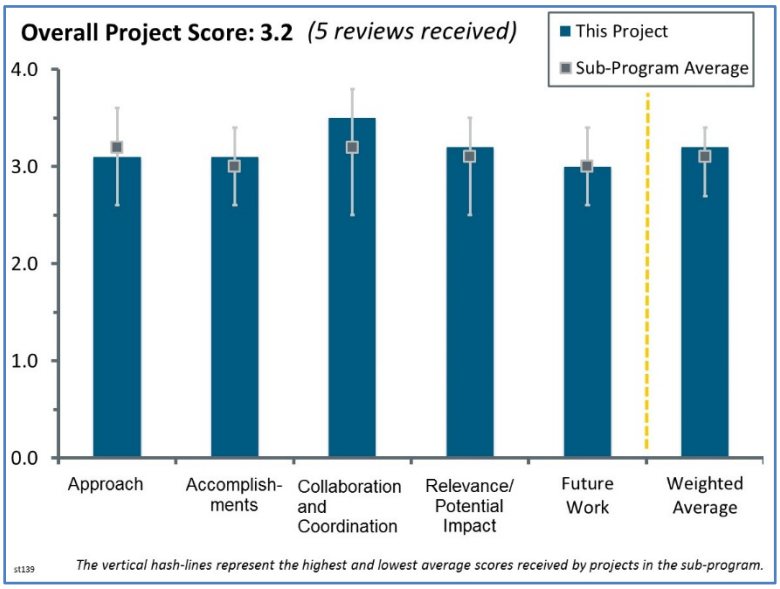
- It could be useful to explore how catalysts/other additives might affect the hydrogen sorption kinetics in the MgB_2–etherate system. The project team might consider adding that to the future work plan.
- It is a well-balanced project as it stands. No additions or deletions to the scope are recommended.
- Feedback-driven synthetic work is recommended.
- More interactions with the HyMARC modeling team are encouraged.

Project #ST-139: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: Fundamental Studies of Surface-Functionalized Mesoporous Carbons for Thermodynamic Stabilization and Reversibility of Metal Hydrides

Eric Majzoub; University of Missouri–St. Louis

Brief Summary of Project:

The objective of this project is to utilize the surface chemistry of the hydride/active-framework interactions to design functionalities that allow the use of unstable complex hydrides for hydrogen storage. Project tasks include demonstration of (1) Lewis acid–Lewis base interaction between aluminum in aluminum hydride (alane, AlH_3) and pyridinic nitrogen in nitrogen-doped carbon nanoframeworks, (2) differences between functionalized and non-functionalized carbon nanoframeworks, and (3) reversibility of aluminum hydride de- and re-hydriding.



Question 1: Approach to performing the work

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

- An approach for altering kinetic barriers and thermodynamics of emerging hydrogen storage materials through the use of high-surface-area functionalized support frameworks is novel and innovative. The approach may be also applicable to modifying reaction rates in other related chemical systems. It is not entirely clear why alane was selected as the initial test system for this work. Even with the benefits attendant to a functionalized nanostructured template, the prospects for reversibility and high cycling yield for alane are remote. It seems that incorporation and characterization of a complex hydride that has more promising properties would be more desirable (although the reviewer, by admission, may be missing something here). That concern notwithstanding, the approach is solid and provides confidence that promising results will emerge. There remains some concern about ambiguities that might arise from the possible retention of tenacious solvent molecules after the infiltration process. The project team is undoubtedly aware that great care must be taken to ensure that the solvent is removed or, at the very least, fully accounted for.
- The project approach is directed at exploring the influence of nanoconfinement of model metal hydrides on the thermodynamics and presumably kinetics of de/rehydrogenation. The strategy is to prepare functionalized nanoporous carbon frameworks, where the functionalization is anticipated to provide the necessary sorbent–sorbate interaction to stabilize small clusters of hydride within the nanoporous environment. Each portion of these strategies comes with significant characterization challenges, and the project approach addresses them in order. The team has already utilized some of the capability of the Hydrogen Materials–Advanced Research Consortium (HyMARC) and the Hydrogen Storage Characterization Optimization Research Effort (HySCORE) in the characterization of some of the project's initial materials and is exploring additional collaborations with these consortia. As such, the project supports the goals of HyMARC to develop the foundational understanding of what the nanoscale confinement features are that may affect important hydrogen storage parameters such as the thermodynamics and kinetics of hydrogen release and rehydrogenation and the influence of nanoscale on phase behavior, among others. The approach of this project includes a significant materials characterization effort, as elucidating whether the metal hydrides chosen for study are indeed nanoconfined or simply

deposited on the outside of the porous host framework. This is a challenge, and the approach is designed to ferret this out in the short term.

- The approach is to study the formation of high-surface-area materials—up to 1,650 m^2/g (in a nanoporous carbon)—and to insert hydrides (AlH_3 and $NaAlH_4$) onto the pore walls. Since nanostructuring hydrides is known to alter the thermodynamics of the material, this work will experimentally reveal these altered thermodynamic pathways.
- The altering of the kinetics and thermodynamics of hydrides through confinement in carbons and other nanoporous materials has been explored by a wide number of research groups over the past 10 years. While various levels of success have been achieved with complex hydrides, no successes have been reported for AlH_3. This is primarily due to the difficulty in preparing alane-composite materials. The approach of infiltrating base adducts of AlH_3 is reasonable and worthy of investigation. However, the approach of infiltrating $NaAlH_4$ with the hope of then converting it to AlH_3 is at best dubious. It is unclear if it was a simple slip of the lip when the principal investigator (PI) stated that the rationale for the selection of N-doped graphene as a host is that "N cannot be hydridized." If not, the PI should consider the structure of pyridine.
- Lewis acid–base reactions make sense for alane stabilization. Previous work on $LiBH_4$ suggests it could work, as there is strong interaction between borane and N (in N-doped C). It is not clear whether the targets can be met with this system.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **3.1** for its accomplishments and progress.

- Early work shows success in preparation of the nanocarbon materials. Slit pore structures are formed and were confirmed using Brunauer–Emmett–Teller (BET) surface area analysis. $NaAlH_4$ and AlH_3 have been inserted into these pore structures. Preliminary data have revealed some issues that the PI is investigating: (1) oxidation occurring during transfer into measurement equipment, (2) solution nuclear magnetic resonance (NMR) imaging to reveal the structure of the alane and solvent, and (3) formation of AlH_3 on regions outside of the pore wall (likewise, the crystalline phase of this AlH_3 is not easily determined). It is very early in the performance of this research, and the early successes of isolating the relevant carbon material and insertion trials are highly commended.
- The project is quite new, and the researchers are already making good progress. They have employed several materials synthesis schemes designed to explore how to selectively incorporate most of the metal hydride within the nanoporous host. The team is doing the necessary initial characterization work to answer the key question as to whether the metal hydride has or has not been selectively infiltrated within the porous host. This determination requires careful characterization to distinguish "inside" versus "outside," and the researchers are making good initial progress here. As their discussions with HyMARC and HySCORE proceed, perhaps additional characterization approaches will arise that address the difficult question of whether the metal hydride is "in" versus "out."
- Good progress was obtained on demonstrating proof of concept. Further work is clearly needed to unambiguously assess whether alane is really in the pores and whether the majority of the AlH_3 molecules are in direct contact with the walls of the pores. NMR characterization was especially effective in isolating and identifying phases present in the functionalized materials. X-ray photoelectron spectroscopy (XPS) was useful in confirming the existence and bonding environment of N in N-doped carbon frameworks.
- All milestones appear to be on track. The team is focused. There has been good progress, especially with synthesis and characterization of two types of N-doped carbons and infiltration of alane. There is significant NMR work to investigate where AlH is going.
- Given the short time that this project has been underway, it is understandable that not much progress has been made. However, it appears that the project is becoming sidetracked by trying to dig evidence for low-level infiltration of $NaAlH_4$ "out of the weeds" rather than focusing on developing methods for higher levels of infiltration.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.5** for its collaboration and coordination.

- Beneficial collaborations are ongoing with investigators from the HyMARC core team, the HySCORE team, the National Institute of Standards and Technology (NIST), and the National Institute of Advanced Industrial Science and Technology (AIST). These collaborations have facilitated rapid progress on understanding the interactions between reactants and the functionalized C frameworks. The project is well coordinated, and the roles of external collaborators in reinforcing and supporting the effort are clearly stated.
- Collaborations on NMR with the University of Washington (Professor Conradi), the NIST Center for Neutron Research (Udovic), and AIST (Japan) for pair distribution function are already underway. There are planned collaborations with Sandia National Laboratories (SNL) (through HyMARC).
- A graduate student from the University of Missouri–St. Louis has already spent significant time at SNL working with HyMARC scientists on characterization and some work in the SNL high-pressure hydrogen reactor. The university also has had another graduate student spend time at NIST performing neutron scattering experiments via the HySCORE collaboration. As this project relies very heavily on advanced characterization, a greater breadth and depth of collaborations with the two consortia will likely ensue.
- The PI has assembled an excellent team of collaborators and appears to be establishing strong collaborations with the HyMARC core.
- The list of real collaborations (domestic and international) is excellent. The project is making good use of consortium resources.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- This project combines, in a clever way, two fundamental areas that are prevalent in hydrogen storage research: (1) designing high-surface-area materials and (2) nanostructuring hydrides to alter their thermodynamic performance. Discoveries in either of these two areas will have broad-ranging impacts on sorbent materials for hydrogen storage researchers and on metal hydride and complex metal hydride researchers. It is likely that, through the HyMARC and HySCORE collaborations, novel measurement methods will also be developed. This project is poised to have large impacts on advancing the DOE Hydrogen and Fuel Cells Program (the Program) goals.
- The use of functionalized nanostructure templates as framework structures that may facilitate enhanced reaction kinetics in complex hydrides is novel and has potentially broad-ranging utility. This seedling project is an important element in the overall HyMARC portfolio; it directly complements and is supported by related work by the HyMARC core team. If the project is successful, the payoff could be large. It directly supports the goals/objectives of the Program.
- This project's strategy is to explore whether functionalization of nanoporous space can lead to enhanced hydrogen storage properties (e.g., thermodynamics, kinetics, and phase separation) by controlling the host–sorbate interaction to control the nanoscale features of a model metal hydride. If successful, this project will help to inform the community and HyMARC and support HyMARC's goals of developing a foundational understanding of key barriers to practical hydrogen storage materials.
- In many respects, alane represents an ideal solution to the hydrogen storage challenge. The major drawback remains its inability for direct recharging. This project is another installment in the quest to develop a direct alane synthesis. However, the relevance of this project is significantly reduced by the lack of even a suggestion of a viable path toward eventually producing a material with gravimetric hydrogen density that would meet the DOE targets with positive results being obtained.
- Although work is currently focused on alane, surface-functionalized nanoporous carbons could be more broadly useful for hydrogen storage. Careful synthesis and characterization work being performed here could be useful in other projects. Overall, it is difficult to see how this effort will have a significant impact on meeting the Program's goals. Even if successful, weight and volume penalty associated with a functionalized scaffold will likely result in a system that falls short of targets.

Question 5: Proposed future work

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

- The future work is specific, logical, and in line with the project's stated goals. The PI should give some ideas on how these nanosized AlH_3 molecular islands will be stabilized (i.e., not transform or agglomerate) once the structures are formed.
- The future work is a direct and logical extension of the current studies. Identifying and implementing an efficient and unequivocal method for infiltrating reactants into the porous framework remain serious challenges. Although this is clearly recognized by the project team, a detailed strategy that will be employed to fully infiltrate the frameworks has not been provided. The use of ^{15}N labeled N-doped carbons for advanced NMR studies should be especially effective in helping to understand the details of binding and (possibly) transport of reactant molecules and whether the template atoms actually participate in the sorption reactions.
- The future work proposed follows on logically from the current status. A key short-term challenge remains in developing synthetic approaches to selectively sorbing the metal hydride within the nanoporous space and providing concrete characterization of the interaction. It seems that this must be accomplished prior to initiating the rather expensive ^{15}N labeled nanoporous host experiments. The inability to gain selective infiltration of metal hydride into the pores might result in materials wherein a mixture of "in" versus "out" convolutes the interpretation of results, hindering future progress.
- Models/estimates to predict the amount of loading (best case scenario) would be a good idea. Previous work has shown large amounts of amine required for one alane. High-pressure experiments should be interesting. It may also be worth looking into what happens to aluminum after dehydrogenation. For this system to work, the aluminum will need to remain near the N and not nucleate Al particles. This should be a priority once infiltration levels are optimized (overloading reduced).

Project strengths:

- A strong research and development team having expertise in all relevant areas is conducting the work on this project. Extensive and highly beneficial collaborations with HyMARC, HySCORE, and AIST are providing solid project support. A clear work plan has been formulated, and initial results are promising.
- The project is well connected to other efforts and nicely engaged with HyMARC/HySCORE partners. N functionalized C to stabilize alane is a neat idea, and capabilities developed under this effort could be useful in other projects. The effort is showing nice progress.
- The project, if successful, will offer a new paradigm in hydrogen storage materials design by nanostructuring the hydrides into isolated islands (a few molecular units in size) that are attached to the pore walls.
- This is a good team with excellent capabilities that is working with a good approach. The project is beginning good and important collaborations with HyMARC and HySCORE consortia.
- An excellent team has been assembled.

Project weaknesses:

- There are no major weaknesses of this project.
- The project has the overly soft Year 1 go/no-go milestone of just showing any degree of rehydrogenation of the infiltrated Al. This opens the door to paths to this project getting lost in the weeds: (1) a frequent problem in 27 Al studies of alane hydrogenation is that the signals for alane and aluminum oxides are in the same region, thus low levels of oxidation can be interpreted as low levels of hydrogenation—this could easily occur in the rush to clear a go/no-go decision, and 2) low levels of hydrogenation could be occurring only on the surface of the infiltrated Al. This is perhaps interesting but far from anything of value to the Program goals.
- The reason for selecting alane as the principal test vehicle for the functionalized carbon framework approach is not entirely clear. It would be useful if this issue could be clarified, and reasons for selecting alane over other (possibly more promising) alternatives could be articulated. Also, identifying and implementing efficient ways to infiltrate reactants into the framework without introducing unwanted

contaminants remains a daunting challenge. Additional detail should be provided concerning a proposed strategy for efficient reactant infiltration.

- A potential weakness lies in determining with high confidence how much of the metal hydride material is sorbed within the nanoporous space versus how much is adsorbed to the external surface. This may convolute the interpretation of experimental data going forward.
- It is hard to imagine how this approach could ultimately meet targets. Even with a small amount of C, one N would need to stabilize multiple AlH_3 units in order to get close to 5.5 wt.% (2020 target).

Recommendations for additions/deletions to project scope:

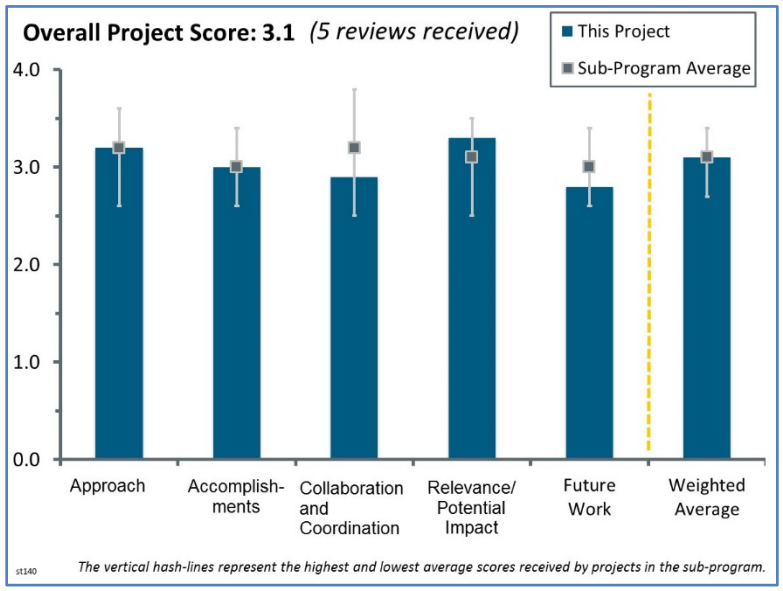
- The scope is appropriate at this stage of the research.
- It is probably worth making a rough calculation to see what the minimum realistic C and N contents are in these scenarios (it is hard to imagine more than 1 N per AlH_3, but maybe there is evidence out there). Based on this estimate, it is unclear what the likelihood of meeting targets is. It would be especially interesting/ useful to know what happens to Al after dehydrogenation. It is not clear if it stays put (near N) or nucleates an Al particle. It seems that any hope of reversibility will require the Al to stay near the N.
- It is unclear whether alane is the best choice for illustrating the power and impact of this approach. The project team is encouraged to consider other possibilities that may be more promising. (This should be done in consultation with the HyMARC core team and the DOE Program office.)
- The project's emphasis should be on finding methods for high levels of alane loading and useful levels of Al hydrogenation.

Project #ST-140: Hydrogen Materials–Advanced Research Consortium (HyMARC) Seedling: Developing a Novel Hydrogen Sponge with Ideal Binding Energy and High Surface Area for Practical Hydrogen Storage

Mike Chung; The Pennsylvania State University

Brief Summary of Project:

This project seeks to develop a new hydrogen sponge—a microporous polymer—that can simultaneously exhibit a hydrogen binding energy greater than 15 kJ/mol, a specific surface area greater than 4,000 m^2/g, and material density greater than 0.6 g/cm^3. A new class of boron-containing polymers with specific boron moieties and repeating microporous morphology will be designed, synthesized, and evaluated. Molecular simulation and advanced structural characterization will be conducted to support scientific understanding and further development of polymer materials.



Question 1: Approach to performing the work

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

- The project's goal is to develop a new class of materials for sorption of hydrogen gases. These materials boast a 4,000 m^2/g surface area. Of particular interest is the ability to tune the pore sizes using boron additions onto the structure. An additional level of nanostructure design is achieved by changing the organic (-R-) spacer groups. Given the success of BC_x materials as sorbents with tunable binding energies (tuned by the B substitutions), organoborane polymeric structures is a next logical step for hydrogen storage research.
- The approach is worth pursuing: making a high-surface-area/porous polymer with enhanced binding that exposes these boron-doped sites that achieve the theoretical DH_{ads} values needed for room-temperature storage. The benefits of a material such as this and the motivation behind the approach are listed in the presentation.
- B-containing systems have long been sought as a means of minimizing the mass of adsorbents while perhaps offering higher adsorption enthalpies. As opposed to substitutional B in graphitic-like structures that have limited B solubility, this effort offers an alternative based on molecular design approaches.
- The approach looks reasonable. However, a high probability exists that the developed materials may not meet the expectations because of chemistry limitations (i.e., inability to obtain the desired structures) or low concentration of active hydrogen absorption sites in the polymer.
- This is a high-risk, high-reward project. The major risk centers on achieving a well-dispersed, high loading of B.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

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

- Current achievements in the project (six months in) include (1) some monomer and polymer synthesis and characterization and (2) preliminary hydrogen characterization using isotherms. Clearly, the time spent working on the project is a major hindrance to having greater accomplishments at the moment.
- The principal investigator (PI) has a long history of organoborane synthesis. For this project, several synthesis routes have been undertaken, and the organoborane structures have been verified using Fourier transformation infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). Pore sizes have been determined using Brunauer–Emmett–Teller (BET) surface area analysis, leading the PI to declare some compositions as "no-go" because pores are too small. Plans for altering the synthesis chemistry (i.e., adding -R- linkers) to increase pore size are underway.
- The following refer to project accomplishments:
    - Two samples appear to have been synthesized and evaluated. While it is understood that synthesis efforts are difficult, there does seem to be some indication that, at least from a pore dimension standpoint, one material, B-PBS-300, has dimensions of relevance even though the surface area is small. On that basis, this is the system that should be the object of focus.
    - The data on slide 18 is problematic, as the difference between 0°C and 25°C data is much larger than one would normally expect. The curves also have unusual kinks.
    - There was an inference during the presentation that appropriate charge transfer along the CH chain is effected through an unterminated B, but during the question-and-answer session, it was less clear that this might be the case. If an unterminated B is necessary, this would be a fairly unstable material. It would be useful to have this clarified.
    - Thermal conductivity of these materials also needs to be considered. At 15–20 kJ/mole, substantial heat generation during hydrogenation would be expected. Polymers as a class of materials have limited conductivity, and this should be addressed at some point.
- This is a relatively new project. Progress to date has been satisfactory.
- It is not clear what the hydrogen absorption sites are that might allow the developed polymeric materials to meet performance expectations. The reaction course and the absence of B-H groups in the polymer before its heat treatment need to be addressed. The PI should provide evidence of boron's influence on the C=C bonds that may support the claim about enhanced absorption of hydrogen by unsaturated fragments of the polymeric framework.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.9** for its collaboration and coordination.

- Excellent collaborations with the Hydrogen Materials–Advanced Research Consortium (HyMARC) and other partners are worth noting.
- There is satisfactory collaboration at this early stage.
- Collaborative efforts with the HyMARC/HySCORE teams have begun with BET, and surface area measurements were performed at Sandia National Laboratories (SNL) (Stavila). Other plans to collaborate with teams include computational research (with Lawrence Livermore National Laboratory) and adsorption isotherms (with SNL and NREL). The PI should consider other useful characterization tools that could be accessed, including x-ray photoelectron spectroscopy (XPS), which would inform about the electronic structures of the C and B species. X-ray absorption spectroscopy (XAS) could likewise be considered for giving similar information.
- The collaboration for uptake measurements really needs to take place with one of the HySCORE team laboratories that have expertise in adsorbent measurements. While NREL is listed on the collaboration slide, there was no mention of NREL involvement with this effort.
- It is still early in the project, but further collaborations with HyMARC are needed to speed up the characterization and theoretical understanding.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.3** for its relevance/potential impact.

- This project, if successful, will have an impact on the field of hydrogen adsorption onto lightweight materials. There are many efforts underway in the topic areas of (1) nano-BCx, (2) tailored nanopore geometries for sorbent materials, and (3) tailored nanopore geometry for insertion of hydrides. Success of (and findings from) this project will have an impact upon many researchers in (at least) these three areas.
- It was suggested during the presentation that a B-PBS-300 material had been prepared with a 2,600 m^2/g surface area. This would be an almost ideal surface area for this effort if validated.
- The project, as formulated, supports progression toward the Hydrogen and Fuel Cells Program goals and objectives.
- There is potential for high impact. The project is focused on relevant goals.
- Items that are perhaps of most immediate interest are:
    - Regarding maximum surface area, the PI clearly sees the difference between high surface area and low material density of metal–organic frameworks (MOFs) and the ideal material, but he needs to consider this in the context of volumetric capacities for his actual materials.
    - The project should develop methodologies such as scattering or positron annihilation spectroscopy to determine the porosity characteristics, especially the dead porosity.
    - It is unclear how much and what the speciation of active boron sites is. It is not clear whether polymer processing changes this distribution on heating. It is unclear whether the conjugation is better for the adsorption of hydrogen and whether it can be controlled. It might be difficult to distinguish B versus C=C as active sites. Perhaps a non-boron containing material should also be studied.

  Better isotherms are needed.
    - The temperature dependence of the uptake is not terribly encouraging. It seems to lose capacity very fast over 25°C. The project should work with NREL to get better isotherms and look at the uptakes at lower temperature using temperature programmed desorption (TPD). The B-PBS-300 should also be looked at to see the pore size dependence.

  Overall, the largest weakness in this approach is that the spatial density of boron seems small compared to the carbon scaffolding. It is unclear whether these materials can really reach DOE's goals. More theoretical efforts are needed here.

Question 5: Proposed future work

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

- The proposed future work is logical and has clear go/no-go decision points for the material systems. Because the HySCORE team program offers many materials characterization tools (beyond temperature programmed desorption), the PI should consider inclusion of one or more of them.
- Future work may benefit from adding tasks that address mechanism(s) of chemical transformations that take place during the preparation of polymeric materials and the chemistry/structure of hydrogen absorption sites.
- The use of any electron microscopy approach for observing micropore morphology would be pointless. These materials would not be stable under an electron beam and would suffer from both ionization and knock-on damage. Pore morphology is still best performed using BET/Horvath Kawazoe (or variant) approach.
- The presentation lacks details related to proposed future work, and perhaps working closer with HyMARC leadership can help speed progress.

Project strengths:

- The project really builds upon the PI's strength in boron organic chemistry and the promise of the BCx material systems to tune hydrogen binding energy to make a new polymer for hydrogen sorption. The tunability of the pore structure and the content of B, as well as the high efficiency and seeming ease of reaction, makes this project ideal for development of novel hydrogen storage materials.
- The approach is worth pursuing: making a high-surface-area/porous polymer with enhanced binding that exposes these boron-doped sites that achieve the theoretical H_{ads} values needed for room-temperature

storage. The benefits of a material such as this, and the motivation behind the approach, are evident and interesting.
- This appears to be an interesting class of polymer materials that are application-specific.
- Collaborations are certainly the project's major strength.
- The technology could be a breakthrough, if successful.

Project weaknesses:

- It is not clear what the hydrogen absorption sites are that might allow the developed polymeric materials to meet the performance expectations. Reaction course and the absence of B-H groups in the polymer before its heat treatment need to be addressed. The PI should provide evidence of boron's influence on the C=C bonds that may support the claim about enhanced absorption of hydrogen by unsaturated fragments of the polymeric framework.
- The largest weakness in this approach is that the spatial density of boron seems small compared to carbon scaffolding. It is not clear that these materials can really reach DOE goals. More theoretical efforts are needed here.
- The PI has not considered all available characterization tools that would be accessible through the HySCORE team.
- There are high risks. This is a challenging system.

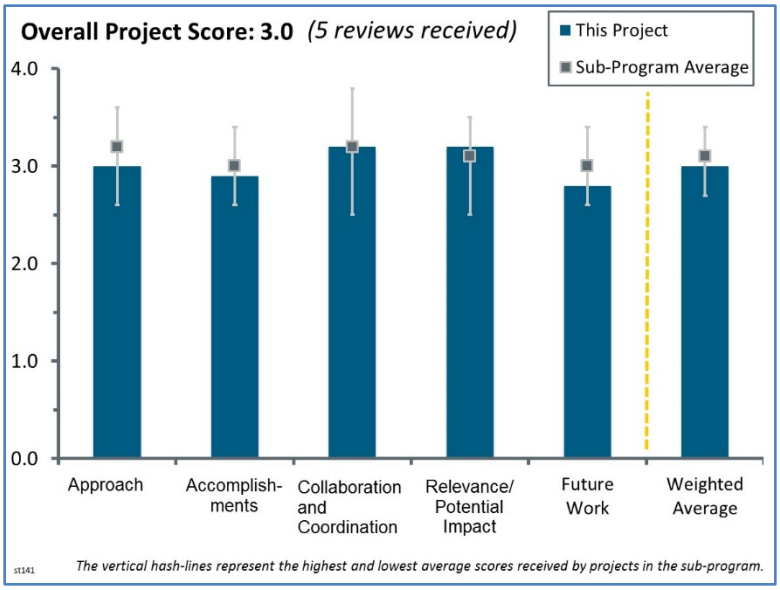
Recommendations for additions/deletions to project scope:

- XPS would be useful for understanding the binding environment and concentration of B in the final structures. Since XPS is a surface-sensitive technique, other techniques that yield similar data might also be accessible (e.g., soft XAS at Lawrence Berkeley National Laboratory is able to reach the B K-edge).

Project #ST-141: Integrated Insulation System for Automotive Cryogenic Storage Tanks

Barry Meneghelli; Vencore

Brief Summary of Project:



The project applies integrated cryogenic tank development approaches and novel technologies developed by NASA's Cryogenics Test Laboratory (CTL) to build an integrated subscale insulation system prototype demonstrating the DOE dormancy targets for a 100-liter cryogenic hydrogen storage tank for fuel-cell-powered automobiles. The approach leverages models developed by Savannah River National Laboratory (SRNL) and applies materials, technologies, and a system-level methodology developed by NASA's CTL to deliver a state-of-the-art advanced cryogenic storage tank concept for fuel-cell-powered vehicles. This approach addresses and mitigates the shortcomings of current multilayer vacuum insulation systems, including improved performance under soft vacuum conditions, for overall higher performance and durability.

Question 1: Approach to performing the work

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

- With a more general title for this new fiscal year (FY) 2017 project, "Integrated Insulation System for Automotive Cryogenic Storage Tanks," the primary focus is actually on assessments of methods to reduce heat leaks into the hydrogen storage volume of Type 3 and Type 4 vessels. Improved thermal management of these vessels, for both cryo-compressed hydrogen and cryogenic adsorbents, is very important in order to extend dormancy periods and minimize undesirable hydrogen venting. Key aspects of this project include modeling and simulation of various tank configurations and alternative insulating methods, which is being performed at SRNL. Thermal testing on various components and subscale vessels will be conducted mainly at the Kennedy Space Center (KSC) facilities. These measurements should provide valuable experimental results of predicted performance for different insulating designs and materials. Since only limited information is available in the general literature and past DOE Fuel Cell Technologies Office projects on options for cost-effective thermal management, this project should provide significant insights into whether thermally efficient cryogenic hydrogen storage systems can be made more practical and less expensive for vehicle applications.
- A system-level approach was used, which addressed the concerning issues. The project is well designed and had different cryogenic systems to characterize the heat loss and thermal conductivity.
- The use of both modeling and prototype testing is important to addressing the issues of dormancy in tanks. The experimental work can validate the model, and then the model can be used to identify the primary heat leakage pathways and where additional research must be done to meet the DOE targets. The model may also elucidate the areas where additional research will not yield significant improvement.
- The approach of this project is not clear regarding addressing the issue with vacuum stability. It is helpful to have a system approach, although the project does not have a specific plan to improve vacuum stability. The project work seems to be focused on the characterization of the current status rather than developing an improved approach. The project should not have included or considered Type 4 for this effort.

- The authors chose 0.1 Torr as the design vacuum quality, and this election seems artificially low. It is not clear why the authors selected this value. In reality, composite resins are quite volatile and will raise the vacuum pressure to higher values.

Question 2: Accomplishments and progress toward overall project and U.S. Department of Energy (DOE) goals

This project was rated **2.9** for its accomplishments and progress.

- Good progress has been made toward the goal. The project has good systems in place for measurements through its cryogenic series.
- Since this project started in FY 2017, most progress has been in the development and implementation of cryogenic hydrogen system designs and intensive thermal performance modeling. Both thermal insulating aerogels and prototype reduced-scale Type 3 vessels have been provided by team partners (i.e., Aspen Aerogels and Hexagon Lincoln, respectively) for laboratory assessments. Initial test results were reported at the DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR) for the thermal conductivities of several aerogels, and preparations are apparently in progress to test thermal properties of the vessels shortly. It is currently too soon to compare the results of these first tests with model predictions and to the DOE targets. Presumably, sufficient information will be available by September 2017 to hold a decisive go/no-go review on whether improved thermal isolation can be achieved. On the other hand, one aspect that was only briefly mentioned during the AMR presentation/slides was related to the outgassing behavior of the insulation materials and vessel walls on degradation of the thermal isolation behavior with both time and temperature. This issue does merit close scrutiny.
- The project is relatively new. As a result, the accomplishments include only data mining, obtaining insulation materials and tanks, and initiating the development of a model. One concern is that the insulation materials identified to date from Aspen Aerogels do not meet the targets selected. The insulation materials need to be much better than what has been evaluated to date, especially in light of the challenges in maintaining vacuum on the system.
- This project is relatively new, although it still should have made further progress based on the extensive experience of NASA in the area of cryogenic insulation.

Question 3: Collaboration and coordination with other institutions

This project was rated **3.2** for its collaboration and coordination.

- The collaborators on this project are one of its strengths. By involving insulation and tank manufacturers and NASA with its experience in cryogenic storage, the project should be able to pull in the right expertise to address issues and identify opportunities.
- There appear to be very cooperative interactions among the technical partners of this team, especially on design and modeling of the cryogenic vessels and insulation requirements. The NASA/KSC testing program is being provided suitable and representative materials and prototype vessels from the partnering commercial vendors. Presumably feedback from the thermal modeling simulations and laboratory tests is being provided in return. However, there seems to have been little or no direct contact with several outside organizations (i.e., the relevant research groups at Lawrence Livermore National Laboratory [LLNL], Argonne National Laboratory, and BMW) that have been heavily involved in cryo-compressed hydrogen prototypes.
- The project collaboration among the partners is good, although the project would benefit from collaborating with institutions involved in developing cryo-compressed systems, such as BMW and LLNL.
- The project needs to collaborate more with cryogenic tank and balance-of-plant equipment manufacturers to find out where heat losses need to be further reduced.

Question 4: Relevance/potential impact on supporting and advancing progress toward the Hydrogen and Fuel Cells Program goals and objectives delineated in the Multi-Year Research, Development, and Demonstration Plan

This project was rated **3.2** for its relevance/potential impact.

- Very high thermal isolation of the cryo-compressed or cryo-adsorbed hydrogen contained within storage vessels is crucial for extending dormancy and overall efficiency of these tanks. Performance levels are improved by using insulators with very small thermal conductivities, as well as minimal outgassing that would reduce vacuum levels that lead to thermal shorts. Highly insulating materials that are also inexpensive would enhance volumetric and gravimetric densities and lower total system costs.
- The project addresses a highly relevant topic related to vacuum stability, which is needed to advance the feasibility and robustness of a cryo-compressed hydrogen tank concept. This project should keep focused on the key barrier of vacuum stability and provide solutions with this impact, rather than being distracted by other efforts.
- There is a significant need to validate the DOE technical targets relative to dormancy with cryogenic hydrogen storage. This work may be able either to confirm the validity of these targets or to guide DOE in the development of new, more reasonable targets.
- Improved thermal insulation under a rough vacuum is a key problem for cryogenic hydrogen storage. This is a problem in desperate need of a solution.

Question 5: Proposed future work

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

- The team provides a reasonable and realistic plan to assess some critical components via laboratory testing, along with completing a full-scale design with an optimized configuration that should minimize thermal leaks into the storage volume. Fabricating and testing a subscale prototype vessel designed with these features would be an excellent goal before the FY 2018 AMR. Detailed comparisons with the thermal modeling predictions for the specific prototype vessel will be especially important to validate whether practical cryogenic hydrogen storage can be achieved.
- The future work was well-planned and -articulated.
- The future work provides general tasks but could include specific steps toward improving the vacuum stability.
- It is not clear what components are going to be tested, other than insulations in the cryostats. It is unclear whether there are plans to select and evaluate structural components such as support rings and penetrations. The future plans should have been better described. There are also plans to update the system based on cost. It would seem that efforts should be made to achieve the required dormancy before ruling out components because of their cost. It would be beneficial to discuss how the model and experimental work will interact as part of the project's proposed future work.
- In slide 13, the authors marked a "sweet" region in pink where the thickness requirement can be met. However, for the expected vacuum quality (pressure >0.1 Torr), there is nothing that can deliver the necessary insulation power. When the presenter was asked about it, he said that the plan was to ask Aspen Aerogels to deliver an improved insulation that would meet the target at the necessary conditions. This is, however, a very difficult proposition since there are fundamental reasons why insulation performance decreases with vacuum. It seems, therefore, that the team is depending on Aspen Aerogels to deliver a miracle for this project to succeed.

Project strengths:

- The team assembled for this project brings diverse, high-quality expertise to bear on the thermal management issues for cryogenic hydrogen storage systems. The thermal design and modeling capabilities at SRNL continue efforts that were part of the recently finished Hydrogen Storage Engineering Center of Excellence (HSECoE) program, while NASA/KSC and Vencor provide the capability for intensive experimental testing of cryogenic components and prototypes. The commercial partners Aspen Aerogels

and Hexagon Lincoln manufacture appropriate cryogenic insulating materials and hydrogen storage tanks. Hence, separate skills and capabilities have been assembled for this project. This is a strong technical team to identify and evaluate better insulation materials and configurations for cryogenic hydrogen storage.
- The project strength is the access to NASA's previous material test information and cryogenic test equipment. The SRNL system modeling and previous experience as part of the HSECoE is also a strength.
- This work is definitely needed if DOE is to continue to consider cryogenic hydrogen storage as a viable alternative to pressurized gas storage.
- Project strengths include good methods of characterization of heat losses and good progress on milestones.
- This is a good team of insulation experts.

Project weaknesses:

- While the technical team is quite strong for investigating issues for the development of improved cryogenic containment systems, the inclusion of the organizations Energy Florida and IBT for commercialization and marketing activities seems premature at this stage. If there is a useful role for these organizations, it should be better explained.
- The project weakness is that this project does not have a clear concept to resolve the main barrier of vacuum stability. This project also has a weakness in the area of partners with direct experience with cryo-compressed tanks.
- It would help to break down the system sensitivity of each component. This project needs more collaboration with the end users.
- There is not a clear plan to address the outgassing of Type 3 or Type 4 tanks in an effort to maintain the required vacuum to achieve the low heat leakage.
- This project seems to depend on Aspen Aerogels' developing a whole new insulating material to meet this target. This seems very difficult and most unlikely.

Recommendations for additions/deletions to project scope:

- The team assembled for this project brings diverse, high-skill expertise to bear on the thermal management issues for cryogenic hydrogen storage systems. The thermal design and modeling capabilities at SRNL continue efforts that were part of the recently finished HSECoE program, while NASA/KSC and Vencor provide the capability for intensive experimental testing of cryogenic components and prototypes. The commercial partners Aspen Aerogels and Hexagon Lincoln manufacture appropriate cryogenic insulating materials and hydrogen storage tanks. Hence, separate skills and capabilities have been assembled for this project. This is a strong technical team to identify and evaluate better insulation materials and configurations for cryogenic hydrogen storage.
- The project should make connections with organizations that have cryo-compressed tank experience to gain lessons learned rather than conducting their own characterization. The analysis of dormancy in the past has shown that physical insulation is unable to meet the dormancy and volumetric density targets. Therefore, this project should acknowledge this past analysis and focus on vacuum insulation rather than physical insulation. The recommended target insulation thickness of 23 mm should be reduced since it is significantly higher than existing cryo-compressed demonstration systems.
- It seems that the modeling is unnecessary. The effort should be focused 100% on finding the magical material that falls within the pink zone of Figure 13.
- The project should use its system to analyze different cryogenic systems and work with DOE laboratories that are doing plenty of analysis in this area.