2013 — Hydrogen Production and Delivery
Summary of Annual Merit Review of the Hydrogen Production and Delivery Program

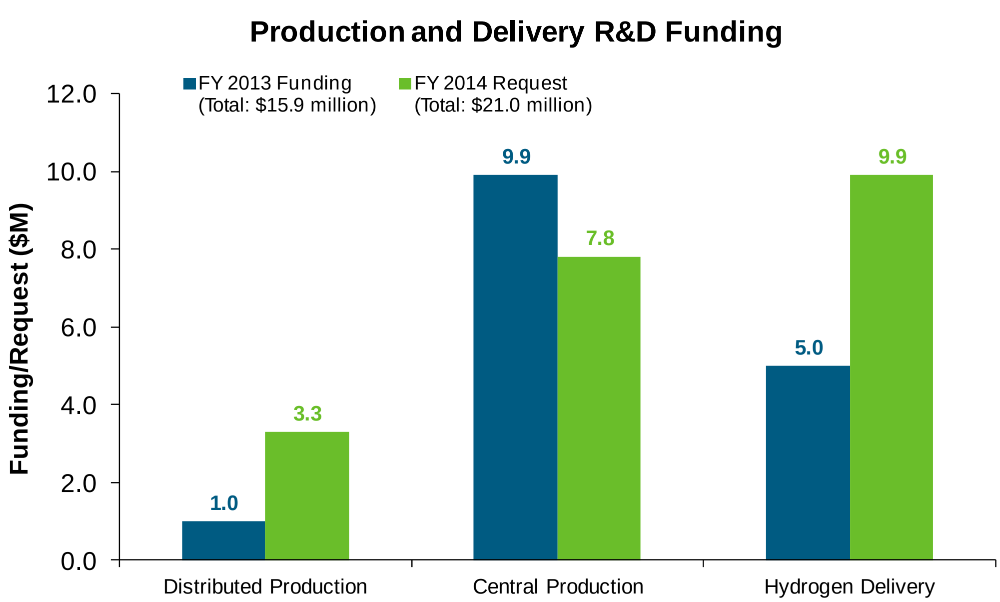
Summary of Reviewer Comments on the Hydrogen Production and Delivery Program:

This review session evaluated hydrogen production and delivery research and development (R&D) activities in the U.S. Department of Energy (DOE) Fuel Cell Technologies Office (FCTO) in the Office of Energy Efficiency and Renewable Energy. The hydrogen production projects reviewed represented a diverse portfolio of technologies to produce hydrogen from renewable energy sources. Production project sub-categories included water electrolysis, solar-driven thermochemical cycles, photoelectrochemical (PEC) direct water splitting, and biological hydrogen production. The hydrogen delivery projects reviewed included R&D for low-cost pipeline materials; pipeline and forecourt compression, including electrochemical and cryo-compression technologies; and delivery cost analyses.

The reviewers recognized the production and delivery portfolios as focused, effective, and well managed, and the projects as well aligned with DOE goals and objectives. Reviewers commented positively on the progress made by the projects in the past year and noted the many beneficial collaborations between project partners and with outside organizations. They also emphasized the need for continued cost modeling of production and delivery technologies to identify and address cost barriers. Reviewers also stressed the need for balance between short-, mid-, and long-term technologies in the portfolios, and for more attention to mid-term goals, targets, and deployments.

Hydrogen Production and Delivery Funding by Technology:

The fiscal year (FY) 2013 appropriation for the Hydrogen Production and Delivery program of the FCTO was $15.7 million. Funding was distributed 68% to 32% between hydrogen production and hydrogen delivery, respectively; this is approximately the same distribution used in FY 2012. Production funding is increasingly focused on long-term, renewable pathways such as PEC, biological, and solar-thermochemical hydrogen production. While this emphasis will continue in FY 2014 as part of the $21 million budget request, it is anticipated that there will also be new R&D starts addressing short- to mid-term technologies in production and delivery. The delivery portfolio emphasis in FY 2013 was on reducing near-term technology costs such as those associated with tube trailers and forecourt compressors, and identifying additional low-cost early market delivery pathways that are viable. This emphasis will continue in FY 2014.



Majority of Reviewer Comments and Recommendations:

Fifteen projects were reviewed, receiving above-average to high scores (3.0–3.6) with an average score of 3.3. The scores are indicative of the technical progress that has been made over the past year.

Biological Hydrogen Production: Five projects in biological hydrogen production were reviewed, with an average score of 3.3. Projects in this area included efforts to improve the performance of algal, cyanobacterial, and bacterial microorganisms that produce hydrogen through splitting water or fermentation of biomass. Reviewers cited a number of achievements, including 1) light-induced hydrogen production by algal cells expressing a bacterial hydrogenase at oxygen levels that suppress the normal algal hydrogen production, 2) effective combination of different methodologies and modifications to improve cyanobacterial systems, and 3) deletion of a metabolic pathway that could compete with fermentative hydrogen production. However, they also expressed concern that there could be difficulty with scaling up these types of systems to industrial scale and questioned the ability of the modified strains to thrive under bioreactor conditions. Key recommendations were to seek collaborations and to identify more specific and quantitative targets for intermediate steps in the different projects for this longer-term pathway.

Electrolysis: Presentations or posters were given for seven projects (including one new Phase I and four Phase II Small Business Innovation Research [SBIR] projects) addressing low-cost, high-performance hydrogen production; renewable energy storage; grid integration (reviewed in the Technology Validation session); and home refueling. Because most of the projects were either just starting or in their last year, or reviewed in another session, only one electrolysis project—an SBIR Phase II project addressing high-efficiency electrocatalysts for alkaline membrane electrolysis—was reviewed in this session. This project received a final score of 3.0. Reviewers praised the efforts to use less-expensive materials to reduce the cost of electrolyzers. However, it was noted that the Ru- and Ir-based pyrochlore catalysts under consideration may not provide enough of a cost benefit when compared to traditional precious metal catalysts. Reviewers suggested reducing efforts in catalyst development in order to focus on other areas of research, such as membrane performance and durability. Carrying out a Hydrogen Analysis model (H2A) cost analysis was also recommended.

Hydrogen Delivery: Five projects were reviewed in the area of hydrogen delivery, receiving an average score of 3.4. Projects were praised by reviewers for good organization, collaboration, and return on investment. It was recommended that all projects update and expand cost and system analysis by adding more factors, gathering more data from stakeholders, and using updated information from the Hydrogen Delivery Scenario Analysis Model (HDSAM) and H2A analyses. Project-specific suggestions for improvements were also made, including improving system engineering (e.g., improvements in welding) and testing (e.g., using extreme conditions) and preparing for demonstration technologies that have reached the appropriate stage of research. The cost analyses were noted as important in determining the potential of the projects for reaching DOE targets.

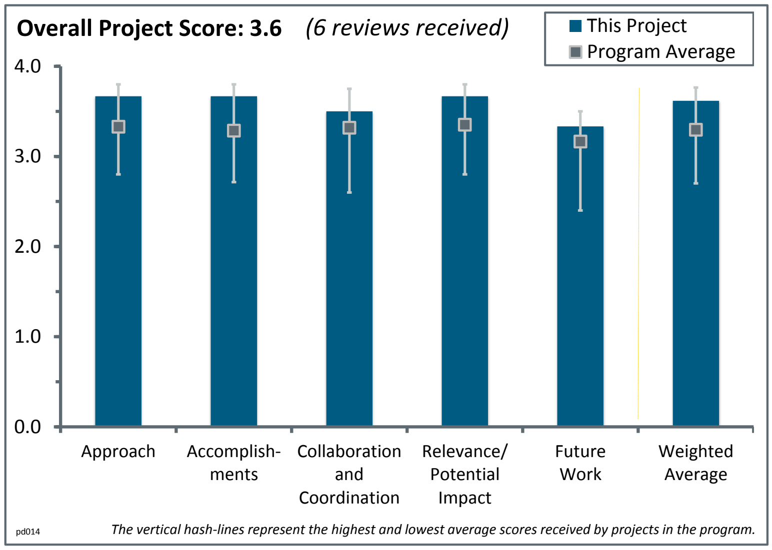
Photoelectrochemical Hydrogen Production: Five oral presentations and four poster presentations were given in the area of materials R&D for solar hydrogen production via PEC water-splitting. Many of the PEC projects are ending in 2013, and most have been reviewed numerous times since their inception. Two ongoing PEC projects were reviewed, receiving an average score of 3.3. Reviewers felt that projects in this area were well aligned with DOE objectives, with a focus on developing the most promising PEC material systems and prototypes. They acknowledged notable accomplishments in enhanced durability in the promising III-V semiconductor materials under investigation in these projects. Projects were rated highly for advancing the state of the art in theoretical understanding and experimental characterization of PEC interfaces, developing innovative surface treatments for extending PEC durability, and effective collaborations with the PEC Working Group. Recommendations for future work included stronger emphasis on demonstrating the extended durability of high-efficiency III-V devices under realistic on-sun conditions, further consideration of alternative lower-cost material systems, and expanded collaborative efforts. Reviewers also noted that continued refinement of R&D priorities based on performance and cost analysis is needed.

Solar-Driven High-Temperature Thermochemical Production: Presentations or posters were given for five solar-driven, high-temperature thermochemical hydrogen production projects—two addressing two-step, high-temperature reaction cycles, and three addressing hybrid (multi-step, including an electrolysis step) reaction cycles. The latter projects are ending in 2013 and were not reviewed. The two reviewed projects received an average score of 3.3. Reviewers praised the innovative approaches and achievements in evaluation of kinetics, analysis of performance requirements, and materials selection and design for the perovskite and hercynite reaction cycles. Suggestions for both projects included increasing attention to reactor design, scale-up and testing, and H2A cost and performance analysis.

Project # PD-014: Hydrogen Delivery Infrastructure Analysis

Marianne Mintz; Argonne National Laboratory

Brief Summary of Project:



This project strives to provide a platform for comparing alternative hydrogen delivery component and system options to reduce the cost of delivered hydrogen. The H2A Delivery Scenario Analysis Model (HDSAM) provides a modeling structure to automatically link and size components into optimized pathways to satisfy requirements of market scenarios and computes component and system costs, energy, and greenhouse gas emissions. The scope of fiscal year 2013 activities included incorporating the SAE J2601 refueling protocol in the modeling of hydrogen refueling stations, evaluating the role of high-pressure tube trailers in reducing refueling station capital, and updating estimates for the hydrogen delivery cost and contribution of refueling station components.

Question 1: Approach to performing the work

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

- This appears to be a robust approach.
- It is excellent that the work centers on use of practical infrastructure that exists or is about to be commercialized.
- The models created to evaluate hydrogen delivery pathways are essential to the effort to evaluate the options for greenhouse gas (GHG) reduction using hydrogen as a fuel. The outreach to industry, technical teams, and other national laboratories is exemplary.
- The development of a rigorous thermodynamic tank fill model will enable a more detailed understanding of the fill process. The use of modeling to examine multiple forecourt configurations has identified promising new options to reduce delivery cost.
- The barriers are well defined along with the partners and the funds necessary to overcome the barriers. There are three national laboratories and industry partners. It is unclear if the team looked at other performance models being developed overseas.
- It is not obvious who sets the priorities for analysis. It is not clear how the model is addressing industry needs.
- It is unclear if there really is a lack of analysis in this area. The industry appears one step further on the way to standardization.

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

This project was rated **3.7** for its accomplishments and progress.

- This is truly outstanding work by the Argonne National Laboratory (ANL) team.
- It is essential to incorporate SAE J2601 as soon as possible; otherwise the results are of questionable value.
- The results of the high-pressure tube trailer work show a clear path to lowering forecourt costs. This project has delivered a very good return for a $300,000 investment.

- The work performed to date is a practical assessment of the industry's progress and the anticipated pathways.
- The supply side may need to be reconsidered as the demand side is adjusted over the next three, five, and ten years.
- Although the industry and stakeholders apparently provided input on the direction of this effort and what delivery options to include, it is unknown (level of certainty) if the investigated delivery pathways will be used by industry. In addition, it is not clear if this pathway is realistic due to the property size of existing gas stations (the footprint available to add hydrogen station equipment) and the separation distances required by building/station codes and standards (set by the National Fire Protection Association).

Question 3: Collaboration and coordination with other institutions

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

- The project team is doing a nice job socializing their analysis with peer organizations and sourcing data from organizations that currently or will soon operate in this space.
- The collaboration between ANL, Pacific Northwest National Laboratory, and the National Renewable Energy Laboratory is excellent. This reviewer attended the DOE-sponsored Hydrogen Compression, Storage, and Dispensing (CSD) Cost Reduction Workshop and therefore may be more aware of the collaboration than the other reviewers.
- There is apparent interaction with other national labs and industry stakeholders, although the role of the other national labs is not always clear. Regarding the hydrogen production companies as industry stakeholders, there should be an effort to approach and include their suppliers (and potential suppliers) to get more reliable cost information.
- It is unclear how much the industry is involved and if it is involved through the U.S. DRIVE Technical Teams. It is unclear what "regular interaction" means.
- This project has limited formal collaboration, but this has not adversely affected the program. Significant work has been done with industrial entities to obtain and validate cost and performance data.
- The team is getting support from the industry and developers to optimize pathways. The modeling needs to be continually revised as markets change to optimize station configuration. The work is based on SAE J2601. However, the SAE J2601 committee may be considering changes in fiscal year 2014.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.7** for its relevance/potential impact.

- The hydrogen pathway work is very important, and the focus on compressor cost and technology is clearly identified by the work of this team.
- This project can help to set concrete priorities for future research and development projects, but it is unclear how this process works.
- Accurate modeling is essential for the program to guide research and ensure that research dollars are spent effectively.
- This work is considered critical to making sure the delivery models are in line and able to optimize equipment configuration as industry approaches the introduction of hydrogen refueling requirements.
- This project is providing the "checks and balances" for technologies and systems being considered to service the fuel cell electric vehicle (FCEV) market. The relevance is very high, and the potential impact will hopefully be in line with the industry's evolution.
- As this is a modeling effort, it will help with decision making, but it is not clear what the industry response will be based on the findings. In addition, it is unclear what the overhead margins are for station equipment because of the small number of suppliers. It is good to see an evaluation of the number of cascade tanks and the effect on station cost.

Question 5: Proposed future work

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

- The future work is necessary.
- The future work matches well with the new areas in the research portfolio.
- This project needs to continue with the analysis phase to consider energy requirements.
- It is not quite clear how the future work is defined nor if there will be any work on the cryo-pump within the liquid delivery options. SAE J2601 is essential, but it is not clear if there will also be recommendations on potential changes to this standard.
- This project should consider the cost of underground hydrogen storage, as it is already becoming increasingly difficult to find properties that can house hydrogen station equipment, especially considering the current small capacity/size of proposed stations compared to what is expected for full commercialization.
- The key issues that need to be incorporated into future H2A and HDSAM model revisions include the following:
  - The large-diameter 160 bar low-pressure steel storage tubes shown in the configuration model are not commercially available.
  - The models show single compressors that can go from 20 bar to 950 bar, and these, too, are not commercially available; hence the need to break compression into two steps from 20 to 500 bar and then 500 to 950 bar.
  - The models show 875 bar as the maximum pressure out of the compressor, but that is not enough to achieve 700 bar fueling. The current technology is 950 bar type with four composite tubes. The models do not yet include the cycle life of high-pressure tubes or methods to optimize the station cost with respect to the tube cycle life. This is more of a factor for steel tubes than composite tubes, but all high-pressure tubes have cycle life “issues.”

Project strengths:

- This project is strong.
- This project has a strong techno-economic analysis.
- This project has a strong scientific partnership and a very comprehensive tool.
- The inclusion of industry and stakeholder input in both the review and focus of the research is a strength of the project.
- The development of the models to analyze hydrogen delivery infrastructure is critical to support the deployment of hydrogen-fueled FCEVs, which offer both zero tailpipe emissions and lower total well-to-wheel emissions compared to any other fast-fill vehicle fuel technology.
- The project should review the model’s analysis and validation to ensure the scenario conditions are realistic and the permutations are in agreement. Refining the tube trailer configuration is providing good insight as to the cost of their use for hydrogen delivery. Physical loss projections may need to be re-evaluated.

Project weaknesses:

- The low level of funding limits capabilities.
- The model is as strong as the data provided by stakeholders.
- This project needs more funding to enable the team to consider all supply options.
- The industry collaboration is not transparent. With regard to that, the industry relevance is also hard to judge.
- This project needs to document and publish the findings and expand the effort model with future technologies.
- The only project weaknesses are associated with some of the assumptions made in the Nexant report years ago, which have been carried forward in the HDSAM and H2A models. This must be addressed in the future work.

Recommendations for additions/deletions to project scope:

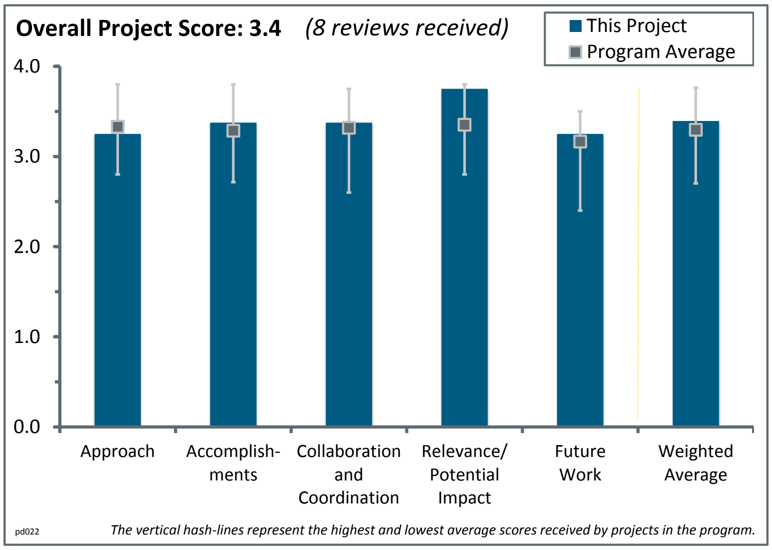
- It is not clear what will happen if the dispensing temperature based on SAE codes changes.
- This project should have stronger technical recommendations towards industry, maybe through a definition of baseline / standard stations. This project should include an ionic compressor and cryo-pump in the analysis. It is not clear if there any considerations for mobile refueling hardware.
- It would be great to see a comparison of the compressed natural gas (CNG) and liquefied natural gas (LNG) fueling pathways to the various hydrogen (and FCEV) pathways. There are a lot of fugitive emissions associated with LNG transfer (over 20% losses between liquefier transfer to tanker, transfer to LNG station bulk tank, and final transfer of LNG to the vehicle). These GHG emissions are not well known and do not (yet) get the same scrutiny as the hydrogen production and delivery pathways.
- The project should look into the cost and economics of underground storage (both bulk and small-scale), including the impact of decreased pre-cooling requirements on the dispensed cost of hydrogen.
- This project should model the impact of the cost and durability of 35 and 70 MPa nozzles (and hoses) on the annual operating cost of hydrogen stations, considering that 70 MPa nozzles currently cost ~$10,000/unit, rebuilds are very costly, and nozzles are not very robust when dropped. The project should compare this to gasoline nozzles (~$300/unit) and CNG nozzles.
- This project should explore if station operators really use a temperature and pressure communication signal to fill hydrogen vehicles.
- This project should explore what ideal station sizes are at different SAE J2601 filling temperatures (economy, efficiency, cascade size, etc.).
- The project should be careful not to get too wrapped up with modeling all aspects of J2601 in different parts of the station system. All stations that fill FCEVs will need to be J2601 compliant, and the current J2601 modeling team already has a hard time modeling this for the revision of the J2601 Technical Information Report (2010).
- This project should consider an evaluation of the annual operating cost at different station sizes (currently quoted operation and maintenance costs appear to be high).
- It is unclear if these models consider continuously running compressors. Apparently, the frequent start/stop events have a significant impact on durability/lifetime, and this could be an option to consider in addition to the economics/efficiency of the number of cascade tanks.

Project # PD-022: Fiber-Reinforced Composite Pipelines

Thad Adams; Savannah River National Laboratory

Brief Summary of Project:

Composite pipeline technology has the potential to reduce installation costs and improve reliability for hydrogen pipelines. Advantages of using fiber-reinforced polymer (FRP) include excellent burst pressure ratings, superior chemical and corrosion resistance, and reduced installation costs with spooling. The goals of this project are to provide test data to support a technical basis for using technology in hydrogen service and to integrate FRP into the ASME B31.12 Hydrogen Piping and Pipeline Code by 2015. This project performed fatigue testing in FRP at various pressures in fiscal year (FY) 2013.



Question 1: Approach to performing the work

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

- The approach was well laid out and seems well designed. The key is getting ASME involved and using natural gas experience to help.
- The program continues to address the technical concerns associated with placing fiber-reinforced piping in hydrogen service, which is being coordinated in parallel with safety, codes, and standards development.
- The contractor performed good engineering practices, fatigue testing under several pressure conditions, and a fatigue cycle test as outlined in the FY 2012 forward work and FY 2013 progress report.
- This is excellent work for the level of funding provided. The scope of the work should be expanded to include a greater number of environmental stressors and conditions, such as moisture, temperature extremes, more flaw sizes, flaw orientation, etc. The work should also be expanded, not only to address how to test pipes but also to figure out how to overcome the shortcomings identified and design better pipes.
- This is a great, clever, low-cost alternative to metal pipes, and it is excellent that this project is concurrently funded with the metal pipeline project, as this is the most pragmatic approach to total success. The approach is to conduct standard fatigue tests of FRP under pressure. This is a well-defined, readily achievable objective, but also may be the key problem with the project. The scope is very limited to ideal conditions and does not completely replicate the extreme conditions that FRP will face when implemented. A key focus of the work needs to be accelerated testing in extreme conditions. Many advantages to FRP are cited, including limited joints, the ability to manufacture it onsite, low embrittlement, etc. A key addition to this list could be safety at puncture from reduced spark ignition. This should be tested against standard metal pipes, as it could be a significant selling point.
- The management of the project is very good. The project is well organized and follows a written FRP live management plan, an important tool for a multi-year project. The goals are credible and aligned with the U.S. Department of Energy goals. The team has managed to keep the project moving forward, despite funding fluctuations, and have identified some engineering issues (e.g., O-ring extrusion). While the ultimate goal of the project is the applied engineering development of a product standard, the project needs to have more scientific depth, especially coming from a national laboratory. It would be valuable if the team added the goal of a peer-reviewed archival publication (more than an ASME report) so their study does not get lost over time.

- The approach used by the project is indeed a pipeline management plan. The issues of service degradation and design margins have already been addressed, and now the project focuses on quantifying the degradation mechanism(s) in an effort to describe the fatigue life of the structure as a function of hydrogen pressure. The identification of delaminating and fiber cracking is the key to ascertaining fatigue resistance. In this regard, the design of the fatigue pressure versus the cycles-to-failure diagram is an important tool that can help, in collaboration with other ASME codes and standards, to design safe operation performance maps. With regard to the O-ring failure, the association of the failure and extrusion with the asymmetry of the loading seems to set the direction to mitigate the problem, given that any hydrogen effects have been ruled out.
- It appears that over the course of this project, including the work done at both Savannah River National Laboratory (SRNL) and Oak Ridge National Laboratory (ORNL), sufficient testing of commercially available FRP pipelines has been done to allow their proper design and use for hydrogen transport under codes and standards that will now be completed by ASME. It would be better if all the key tests and test results were presented in a concise manner and conclusions drawn as to the acceptability of FRP pipeline for hydrogen transport and whether any additional testing is required. The list of testing categories is provided but with no summary of the results and conclusions. Hydrogen leak rates from FRP pipelines have been measured and appear reasonably low. However, it is not clear from the presentation if acceptable hydrogen leak rates from FRP pipelines have been established and who should set these leak rates. Fatigue testing has been done, but it is not clear if this was done at all the appropriate frequencies and stress levels. In prior years, SRNL developed an FRP life management plan that guides what testing needs to be done. SRNL is writing a very complete report on all the testing that has been done, which should greatly aid the writing of FRP pipeline for hydrogen transport codes and standards by ASME.

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.

- The project's barriers and goals are well defined and are being met.
- Progress appears good, but the real test will be the actual acceptance by ASME, which is a pass/fail point.
- The team accomplishments demonstrated the ability to overcome several technical challenges that were directly targeted at the DOE goals.
- Given the goals stated for the project, the team is making good progress and following their plan. It is not clear how their work affects the cost of pipelines other than enabling an alternative to higher-cost steel. They are definitely on track to meet the standards goal, as evidenced by progress on developing fatigue failure data and their leadership on the ASME B31.12 committee to codify the results.
- This year, fatigue testing was completed on unflawed FRP pipelines that also included metallic joints. The leakage through the joint was identified as caused by insufficient O-ring design and material choice. A remedy was provided but not tested. The team wrote a thorough report on all the testing that has been done in prior years; the FY 2014 testing will be added to the report. This report should greatly aid the writing of the new codes and standards for FRP pipeline hydrogen transport.
- Observing how the project evolved over the years, one can safely state that significant progress has been made. In fact, the design of the initial diagram of the fatigue life of the FRP is a solid indicator of the progress made. The completion of the FRP testing report is another indication that the project's results can be discussed by ASME for codification and the setting of standards. In addition, this report provides a thorough review of the literature and the testing protocols. As such, it constitutes a valuable resource for future advancements in the field of FRPs.
- The project has accomplished its goals, but those goals should be expanded for more rigorous environmental stressors and a wider range of flaw sizes. The response of the composite will be sensitive not only to the flaw size but also to flaw orientation. The latter was not tested.
- It is shocking to see that this project is in its seventh year. It has achieved approximately half the rate of progress that would be expected. It is unclear why the project got to its sixth year before beginning pressurized fatigue testing. Ratings aside, the progress is definitive and demonstrates clear accomplishment towards DOE's objectives of reducing cost while maintaining safety.

Question 3: Collaboration and coordination with other institutions

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

- The researchers are following the most appropriate path to have this work turned into a test standard.
- The team demonstrated good coordination and collaborations among multiple organizations and institutions (e.g., ASME).
- This exhibits good teamwork among project partners that involve industry, government laboratories, and codes and standards.
- The collaboration appears very good, especially with ORNL and ASME. It would be good to have more manufacturers represented, and maybe the direct participation of more natural gas entities.
- Continuous interaction and exchange with ASME is very important for the project's results to be assessed from a technology standpoint. The listed collaboration with ORNL is not clear.
- There appears to be excellent collaboration with ASME on this project, which should greatly assist the writing of codes and standards for FRP pipeline for hydrogen transport service. There appears to be very good collaboration with FRP pipeline manufacturers. There is no mention of collaboration with the DOE Hydrogen and Fuel Cell Pipeline Working Group. This project is a member of that working group and should be collaborating with the other members on a more routine basis.
- This team has built just the right partnerships for the scope and funding level of this project. They have engaged the ASME B31.12 code committee and provide leadership. The team has an industrial supplier for FRP and shares engineering information. They have leveraged expertise in material systems at other federal laboratories. The one concern is that they are working with only one industrial supplier, which limits the diversity of fatigue failure information they are developing. It is not good to develop a product standard based on the system of only one supplier. The project would have to receive more resources in order to expand the testing base.
- There are no partners from academia included in the effort. This is particularly surprising given the potentially large scope of environments the piping will be exposed to, and the relatively straightforward nature of the fatigue tests. University partners could be contracted to accomplish these tasks, and a student could be trained to enter the workforce (win-win). Given the limited budget of this project, though, partnership with academia on a yearly basis may not be feasible. The partners are located primarily in the South. Given the geographical variability of this problem, it makes sense to have partners in other regions of the country. The partnership with ASME is strong and a key benefit. Much of the work completed here is applicable to general FRP use and not limited to hydrogen.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.8** for its relevance/potential impact.

- This is a critical step in providing a hydrogen delivery system.
- Pipelines play a significant role in hydrogen transfer, which has been identified in the DOE Fuel Cell Technologies (FCT) Office goals.
- DOE considers FRPs to be a cost-effective delivery pathway. As such, FRPS are a key technology that needs to be well understood with regard to reliability and safety. The project's results are helping to advance precisely this goal. The same holds for the project's research on O-rings, which are part of the structure.
- If the capital cost of hydrogen pipelines could be significantly reduced, hydrogen pipeline transport could be a low-cost option for hydrogen delivery and help enable meeting the FCT Office's cost targets. FRP pipeline holds that promise. This would be a key enabler of using hydrogen as a major energy carrier with very low-carbon emissions.
- Despite pipeline hydrogen distribution being envisioned as a longer-term hydrogen supply pathway, this fundamental understanding, development, and industry safety acceptance of lower-cost FRP will be valuable in supporting early market initiatives.
- This research is of benefit to general FRP use and is not limited to hydrogen. The development of a new ASME standard for hydrogen use in FRP is highly relevant. A direct comparison of the cost of FRP versus

metal pipelines was not presented and would make the case for relevance simple. It may be that this slide was included in the early years of the project. If not, it is a serious concern that this comparison has not yet been made.
- This project will be important only to the extent that there is a concentrated area of usage that is sufficient to support the investment in a pipeline network. This is likely to be quite far in the future, but it is a good building block. The project is excellent in the long term, but maybe only fair in the short term. The cost reduction will be important, but it is not clear how much FRP will actually reduce overall cost. The installation cost will be lower, but it is not clear what percentage this comprises of the overall cost, including overhead, permitting, rights of way, etc.

Question 5: Proposed future work

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

- The proposed future work is a good plan to enable the use of FRP pipeline for hydrogen service.
- The work proposed is appropriate, but there needs to be more emphasis on optimizing the composite technology to design better pipes.
- The future work identified by the team demonstrates pathways to complete additional fatigue and rupture tests and complete codification into ASME standards.
- Completing FRP codification into ASME B31.12 would be a major accomplishment of this project and is within sight.
- If ASME is convinced that this is an appropriate item to add to their code set, that is excellent progress and should validate the technical approach.
- The team is following their FRP life management plan.
- Research has been proposed to determine the variability in the fatigue data by varying the loading ratio to $R=p_{min}/p_{max}$. This will allow the project to correlate the dependence of hydrogen-induced degradation in terms of parameters whose influence is known to be very important in the field of fatigue and in the absence of hydrogen, and perhaps will help draw conclusions on the nature of the failure mechanism(s).
- The proposed future work is non-specific, likely owing to problems during the early years in appropriately scoping the project. It is not clear what conditions will cause the FRP to fail and what factors primarily contribute to the cost. Identifying these clearly will help to scope the necessary extreme environment tests that need to be conducted and the components that need to be improved. The prevailing approach seems to be “try it and see,” and in the seventh year, that impression is frustrating. The accelerated lifetime tests are very relevant and a logical next step. The additional fatigue testing with Fiberspar absolutely needs to include testing pipe samples in use in various areas around the country, including very different environments. This project should try to find conditions that cause the FRP to fail. Only then can the limits be known that should become standards.

Project strengths:

- This project has a good management plan, leadership on ASME B31.12, and structural design.
- The team exhibited great engineering practices with intensive levels of testing and coordination with ASME.
- Involvement of ASME early in the process to get buy-in was good, along with involvement of Fiberspar and the material testing.
- Integration with standards committees and manufacturers and understanding hydrogen delivery needs and industry are strengths of this project.
- This project has excellent, carefully controlled laboratory experiments. These form a foundation to compare to extreme environment tests. This is excellent work with standards development and the close partnership with ASME.
- This project appears to have outstanding project leadership, and the project team is successfully addressing the previously identified barriers of FRP pipeline for hydrogen service. Based on the work conducted to date, the team recognizes the need for additional fatigue testing and stress rupture testing.
- This project aims to collect the data needed to ascertain reliable and safe operation of FRPs in the presence of hydrogen. The development of the fatigue safety diagrams is a project strength because it helps elucidate

the integrity of the FRPs and therefore their judicious use for hydrogen transport. The proposed approach to develop inspection criteria for the failure of O-rings also serves the project objectives. Overall, the project is focused, and this in itself is a unique strength.

- If the capital cost of hydrogen pipelines could be significantly reduced, hydrogen pipeline transport could be a low-cost option for hydrogen delivery and help enable meeting the Program's cost targets. The FRP pipeline holds that promise. This would be a key enabler of using hydrogen as a major energy carrier with very low-carbon emissions. The team wrote a thorough report on all the testing that has been done in prior years and will add the FY 2013 testing to the report. This report should greatly aid the writing of codes and standards for FRP pipelines for hydrogen transport. There appears to be excellent collaboration with ASME on this project, which should also greatly assist the writing of codes and standards. There appears to be very good collaboration with FRP pipeline manufacturers.

Project weaknesses:

- This project needs deeper material science and archival publications.
- It is not clear if the team considered alternative O-ring materials.
- Hydrogen permeation at different working pressures was not investigated or addressed by the contractor.
- There are too few environmental stressor variations. There is a lack of recognition of the importance of flaw orientation on the mechanical behavior of composite materials.
- The presenter specifically said, "No impact on varying pH was detected." However, slide 26 states that "[in] extreme values of pH some impact could be seen." This direct discrepancy, with a non-specified value of impact, is a concern. The proposed future work is non-specific, which is likely because of problems with appropriately scoping the project in early years. It is not clear what conditions will cause the FRP to fail or what factors primarily contribute to cost. After seven years, one would expect at least a bullet on these issues.
- It would be much better if all the key tests and test results were presented in a concise manner and conclusions were drawn on the acceptability of FRP pipeline for hydrogen transport and whether any additional testing is required. The list of testing categories is provided but with no summary of the results and conclusions. There is no mention of collaboration with the DOE Hydrogen and Fuel Cell Pipeline Working Group. This project is a member of that working group and should be collaborating with the other members on a routine basis.
- By testing only one company's product, it is not clear that the project addressed the potential failure issues of other manufacturers. The project should consider that one company may have specific know-how that another does not. It is not clear if the mechanical fittings will ever be acceptable for direct burial, especially at high pressure and with the test results. There are already some restrictions in this regard in codes, and it is unclear if it is practical in the long term based upon historical leakage and the test results that already show issues. The focus has been as much on the O-ring and mechanical connection as the pipe. While these are needed, it distracts from the fundamentals of the pipe itself.
- The main weakness of the project is the lack of fundamental understanding on how fatigue advances delamination and failure in the presence of hydrogen. This is a weakness because unless we understand the parameters governing this failure mechanism, the project results may be specific only to the pipelines tested under the given flawed geometry and loading conditions. The reference to the fact that a Fiberspar pipe section in Alberta, Canada, meets the factory specifications on burst pressure and glass transition is not rigorous scientific evidence. It is not known whether the loading frequency, the loading ratio, etc. in Alberta are the same as those for hydrogen transport in the United States. The association of the O-ring failure with the material hardness was an unclear point during the project presentation. In fact, the reviewer does not understand why hardness is associated with the extrusion of the O-ring.

Recommendations for additions/deletions to project scope:

- The project's scope and funding should be increased to include more test conditions and flaw orientations.
- A general understanding of the quality of commercially available FRP material would be good for establishing the likelihood of material flaws.
- The project should add research and/or shift efforts to avoiding underground mechanical joints, which are too prone to failure and leakage.

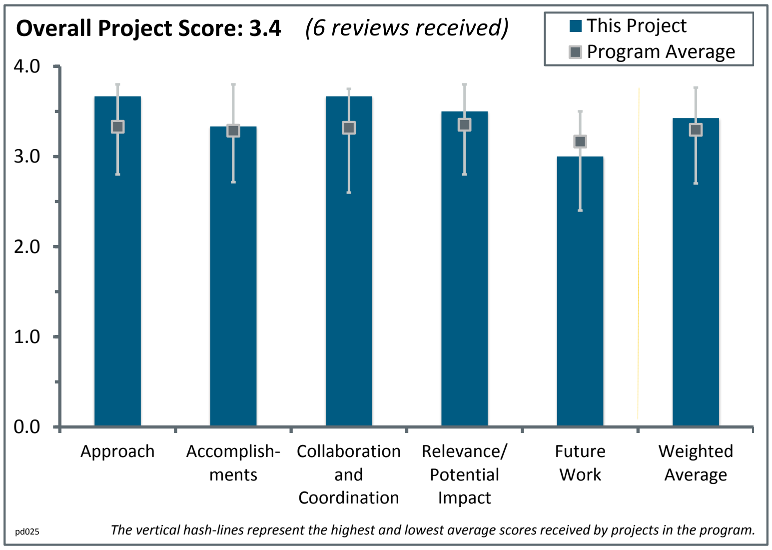
- Hydrogen permeation is a major concern, especially at high pressure. The project team should consider addressing and evaluating hydrogen permeation through the material, especially at mechanical coupling joints.
- With the baseline and ideal laboratory measurements nearing completion, the researchers must find the limits to the technology due to extreme environmental variability. The only way to ensure safety is by carefully locating and quantifying the limits, then making sure the FRP is not installed in conditions that could approach these limits. Modeling should have been completed early on in the project to identify the most sensitive environment sources of degradation. As it stands now, the researchers are stuck with a "try it and see" approach. After seven years, that approach seems unsound; however, the project must go on, given the importance and established investment.
- It seems that third-party damage is an important cause for FRP failure. Hence, a protocol to assess this is required. It is not clear from the project's presentation how a water environment affects the performance of the FRPs. If the presence of epoxy will mitigate the issue, it is not clear what happens if the integrity of the epoxy layer is disrupted. Apart from the load ratio R, the loading frequency needs to be investigated as well.

Project # PD-025: Hydrogen Embrittlement of Structural Steels

Brian Somerday; Sandia National Laboratories

Brief Summary of Project:

This project measured the fracture thresholds and fatigue crack growth of steel hydrogen pipelines to demonstrate the reliability and integrity of steel hydrogen pipelines for cyclic pressure applications. Hydrogen embrittlement was accommodated by measuring fracture properties in hydrogen following the ASME B31.12 design standard. An analytical model was developed to quantify the inhibiting effects of oxygen on hydrogen-accelerated fatigue crack growth, including variables such as load-cycle frequency and oxygen concentration. This model may provide insight into the effects of gas impurities on hydrogen-accelerated fatigue crack growth for mixed natural gas plus hydrogen.



Question 1: Approach to performing the work

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

- This project is making continued good progress on long-term goals. It seems to focus on key items, such as welding.
- Understanding and possibly mitigating the effect of hydrogen embrittlement on steel pipelines is a good objective.
- The team demonstrated good engineering practices, fatigue testing, effects of cracks, crack propagation, and understanding the effects of oxygen on hydrogen embrittlement.
- This was a solid, outstanding all-around presentation of the approach. This is a textbook example of taxpayer funding well spent. Moreover, DOE’s dual-front funding approach of existing technologies likely to carry hydrogen and next-generation technology (another program) is the most pragmatic way to prevent an accident.
- The barriers are discussed and partially addressed. It is not clear whether the research team studied modern X-65 steels or older (1970s) X-65 steels. They do have different microstructures. The project should interface with Oak Ridge National Laboratory (ORNL) in regards to their friction stir welding research efforts. There should also be more work on the migration of oxygen impurities and other contaminants from natural gas that act as a catalyst or a contaminant at the crack tip.
- The focus of this project is to fully understand hydrogen embrittlement in steel pipelines so that they can be properly designed for safety and reliability. The key remaining issues to address in this effort include fatigue crack growth in the presence of gas impurities, such as oxygen, and the nature of hydrogen embrittlement in welds. The project is taking an outstanding approach to researching these issues. It is using state-of-the-art experimental techniques and equipment to measure fatigue crack growth rates under fatigue conditions in the presence of hydrogen at pipeline operating pressures. It is combining this with theoretical models that can explain the observed behavior and testing these models. It is now also using density functional theory (DFT) to predict the impact of various gas impurities on hydrogen embrittlement. The combination of these approaches is providing remarkable insight into the nature of hydrogen embrittlement that will enable appropriate design of steel pipelines for hydrogen transport.

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.

- This is decisive proof of a physics-based model showing validation with carefully taken measurements.
- The team's accomplishments demonstrated several technical challenges that were directly targeted at DOE's goals.
- The accomplishments are good, but there is too much focus on inhibitors that might have limited practical value.
- There is conclusive evidence that low-cost additives to steel pipelines can significantly reduce embrittlement and, therefore, pipeline cost.
- This project strongly supports long-range goals and objectives of the DOE Hydrogen and Fuel Cells Program (the Program). The progress achieved over the past year is discussed. This project will need to expand the work scope to include higher strength and modern steels, including weld consumables and processes that may help meet the future projected cost requirements.
- Considering the funding level for fiscal year (FY) 2013, this project has made excellent progress. It expanded the model being used to predict fatigue crack growth behavior in the presence of gas impurities in the hydrogen. The model predictions with oxygen fit the observed behavior extremely well. This year, the project also included the use of DFT to be able to predict the impact of impurities other than oxygen. Fatigue crack growth rates are now being measured on various parts of welds. The results are remarkably consistent considering the experimental challenge of the non-homogeneities present in welds. This is due to outstanding experimental technique.
- It does not seem like a year's worth of work was done since last year's presentation. A model has been developed, but that should not have taken a year. It would have been good to see greater progress over this time.

Question 3: Collaboration and coordination with other institutions

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

- This is a textbook example of good collaboration and coordination.
- This project has good coordination with a large consortium of investigators. Participation by Dr. Petros Sofronis at the University of Illinois makes this possible.
- The team demonstrated excellent coordination and collaborations among multiple organizations and institutions.
- This project has good collaboration and an open process with others. The key stakeholder is the U.S. Department of Transportation (DOT), and they are engaged.
- The collaboration on research efforts is underway with ORNL and there was some mention of the National Institute of Standards and Technology (NIST). This project needs to look at an expanded model for fracture properties recently developed by NIST-Boulder.
- This project is part of the DOE Pipeline Working Group. This group consists of all of the Program-funded projects on hydrogen pipelines and other organizations. This encompasses national laboratories, Secat, Inc., Exxon Mobil, the University of Illinois, NIST and ASME. This group meets at least once per year to share results and provide insights into each other's work. The experimental work done at Sandia National Laboratories (SNL) is done in true seamless partnership with the theoretical modeling work at the University of Illinois. This partnership is resulting in remarkable data and understanding of the hydrogen embrittlement of steels. The people at SNL and the University of Illinois are also members of the International Institute for a Carbon Neutral Society funded by Japan. This presents the potential for additional collaboration on hydrogen embrittlement of steels being done at Kyushu University in Japan.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This project targets the key weakness of steel pipelines for hydrogen transport.
- Pipeline is one of the most significant methods for hydrogen transport, and this has been identified in Program goals.
- This project will likely lead to economical additives for hydrogen pipelines that inherently limit embrittlement.
- Steel is the material of choice for all existing hydrogen pipelines, so steel is very relevant to industry and the future growth of hydrogen as a fuel; however, widespread pipelines are not needed until the economics of hydrogen can be justified.
- The work described appears to be in line with the project goals and objectives. This work is seen as critical to the Program and could potentially provide significant advancements toward verifying pipeline safety with the delivery of hydrogen. The failure prediction models under refinement have the potential of using other components within the fuel cell system.
- This project will enable the safe and reliable design of steel pipelines for the routine transport of hydrogen under the expected condition of oscillating pipeline pressures. This may be the least expensive method of transporting large amounts of hydrogen long distances when hydrogen is a major energy carrier. The current projected cost for the transport of hydrogen by steel pipelines is too high for rapid and significant penetration of hydrogen as an energy carrier, unless the cost of fossil fuels increases further. It is not clear how the results of this project could be applied to reduce the cost of hydrogen transport in steel pipelines.

Question 5: Proposed future work

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

- There should be less focus on inhibitors.
- This project needs to focus on friction stir welding to determine and demonstrate the lower-cost approach for safely transporting hydrogen.
- The future work identified by the team demonstrates pathways to complete additional fatigue crack growth measurements at both girth weld and seam welds, and additional pipeline steel testing.
- It would be good to see a greater rate of accomplishments from the project by (1) using the model to study other mechanisms of crack growth impeding other species, (2) looking at different steel compositions, and (3) using friction stir welding and studying differences in weld vulnerabilities.
- The future work includes gathering the needed data on fatigue crack growth rates for both girth and seam welds, as well as steels other than X52. It is not clear how the work done to date or the future work might address the high costs of hydrogen transport in steel pipelines.
- The most robust solution to embrittlement problems faced by pipeline operators needs to include a portfolio of remediation steps. The researchers have identified promising passive additives to economically accomplish this goal. A potential extension could include active crack remediation steps, for example, determining at what point during crack initiation the surface can be refinished or coated to remedy the crack to extend pipeline life without replacement. The presence of both oxygen and water could also be an interesting follow-up study.

Project strengths:

- This project targets the key weakness of steel pipelines for use with hydrogen.
- One strength is the principle investigator, who made a very “SMART” (Specific-Measurable-Attainable-Realistic-Timely) presentation.
- This project uses great engineering practices, along with modeling and collaborations with national laboratories and academia.
- This project has good basic research. Understanding the effect of impurities is also useful, albeit maybe not a practical consideration.

- The collaboration across several federal laboratories and agencies provides excellent use of funds and knowledge. Partnering with industry as well as codes and standards committees and groups is seen as a good, sound investment of research and development resources.
- The project is taking an outstanding approach to research fatigue crack growth rates in steel pipelines in the presence of hydrogen, including in the presence of gas impurities. It is using state-of-the-art experimental techniques and equipment to measure fatigue crack growth rates. It is combining this with theoretical models that can explain the observed behavior and testing of these models. The project is now also using DFT to be able to predict the impact of various gas impurities on hydrogen embrittlement. The combination of these approaches is providing remarkable insight into the nature of hydrogen embrittlement that will enable the appropriate design of steel pipelines for hydrogen transport. This project will enable the safe and reliable design of steel pipelines for the routine transport of hydrogen under the expected condition of oscillating pipeline pressures. This may be the least expensive method of transporting large amounts of hydrogen long distances when hydrogen is a major energy carrier. The experimental work performed at SNL is done in true seamless partnership with the theoretical modeling work at the University of Illinois. This partnership is resulting in remarkable data and an understanding of the hydrogen embrittlement of steels.

Project weaknesses:

- It is a stretch to find a weakness in this project. The difficulty of this project is low enough that a university could accomplish the same work, probably at a lower cost, and train students in the process. This could potentially be a better use of taxpayer funds. If students were trained during the program, it was not mentioned, and they were trained indirectly. The energy labs exist to do the big, dangerous, and expensive work that nobody else can. However, Somerday is doing a better job than most university faculty could, so he is the right person for the job.
- There was a poor rate of progress on objectives in 2013. This project needs to step up progress.
- To better evaluate the effects of hydrogen on crack growth, the principle investigator should look at recent developments in the crack growth models developed at NIST-Boulder for hydrogen-induced cracking.
- As much as modeling is important to gain an analytical understanding of a material's behavior, it still needs to be verified by actual testing. More testing needs to be done, especially on hydrogen dissociation in oxygen-rich environments.
- The focus on impurities acting as an inhibitor is interesting, but it is unclear if it can be used as a reliable method in practical use to guarantee safe performance. Also, the project must consider those impurities compared to SAE J2719 to make sure that they are even possible while meeting the required specifications.
- The current projected cost for the transport of hydrogen by steel pipelines is too high for rapid and significant penetration of hydrogen as an energy carrier using steel pipelines for hydrogen transport, unless the cost of fossil fuels increases further. It is not clear how the results of this project could be applied to reduce the cost of hydrogen transport in steel pipelines.

Recommendations for additions/deletions to project scope:

- This project should accelerate the work on objectives.
- This project should consider alternate welding methods and figure out/recommend a means of lowering the cost of steel pipelines.
- This project should attempt to determine how its results might be applied or extended to reduce the cost of transporting hydrogen in steel pipelines by better pipeline design, alternative steel compositions, or lower-cost welding.
- This project should have a joint discussion with ASME B31.12 code committees, SAE J260, NIST-Boulder, the ORNL friction stir welding research team, and the DOT Pipeline and Hazardous Materials Safety Administration to jointly develop a research and development plan to address the remaining issues.
- A potential extension could include active crack remediation steps, for example, determining at what point during crack initiation the surface can be refinished or coated to remedy the crack to extend pipeline life without replacement. The presence of both oxygen and water could also be an interesting follow-up study.
- Although steel pipelines provide significant advantages over competing technologies, they still require a significant number of girth welds. The welding process needs to be done onsite during the installation, and

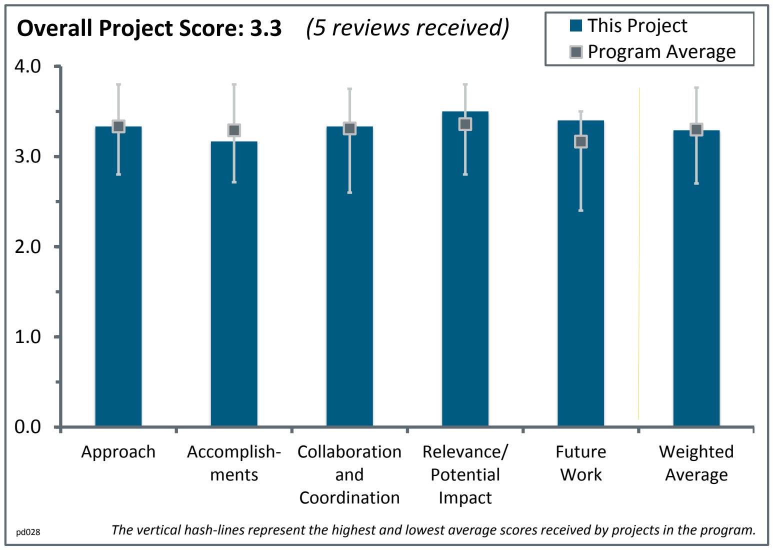
its quality is directly impacted by the environment. More work and research needs to be done to further understand those impacts.

Project # PD-028: Solar-Thermal Redox-Based Water Splitting Cycles

Al Weimer; University of Colorado

Brief Summary of Project:

The objective of this project is to develop and demonstrate robust materials for a two-step thermochemical reduction-oxidation (redox) cycle that will integrate easily into a scalable solar-thermal reactor design and achieve the U.S. Department of Energy (DOE) cost targets for solar hydrogen. The project also develops steady-state and dynamic models of a multi-tube solar receiver to identify parameters controlling receiver efficiency, identify optimal tube/cavity configurations and solar flux input, and quantify the impacts of isothermal operation on receiver efficiency.



Question 1: Approach to performing the work

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

- The project is doing excellent work on an innovative idea.
- This is a good practical approach to developing redox kinetics and materials selection.
- Evaluating the hercynite cycle materials and evaluating the effects of increased pressure and temperature on the reaction rates is a good approach towards meeting the main objectives of this project.
- The project focuses on a key factor to overcome the gap between the theoretical efficiency of thermochemical hydrogen production and the state of the art. A significant part of the provided solar energy is needed to reheat the redox material after water is split to remove the oxygen by working isothermally. This solves another problem of such high-temperature (HT) reactions; thermal stresses are minimized, possibly leading to much longer lifetimes of the components. The concept to identify an appropriate class of oxides and the development of appropriate structures is not likely to be improved.
- The project compared the hercynite isothermal process with the temperature swing performance of hercynite, cerium oxide (CeO_2) and zirconium-doped CeO_2, with a claim of superior hercynite isothermal performance using increased water vapor partial pressure. It is difficult to distinguish the operational or cost implications of this approach. Additionally, the penalty of simultaneous oxygen and hydrogen production was unclear. Isothermal reactor operation was not clearly explained, so it was difficult to discern the benefits or disadvantages of the isothermal approach beyond the claim of superior performance. The focus on isothermal swing process would benefit greatly by better exposition of system-level benefits beyond the material response to HT fluctuation.
- The material advantages of hercynite over modified cerias may be illusionary. The data are presented on a gram activity basis, but the density of ceria is approximately twice that of hercynite, which may minimize apparent activity differences on a volumetric basis. If ceria is both the active phase and support versus the hercynite on inert alumina, less hercynite is in the reactor relative to ceria, which further debits hercynite. One of the proposals for using hercynite in a particle flow reactor is to use atomic layer deposition to coat alumina nanospheres. Particle flow is likely to cause attrition, which would slowly abrade the outer-surface hercynite from the alumina core over many cycles, in addition to the slow loss of material that may result from the reaction cycle. The isothermal reactor performance of hercynite is excellent and represents a true and potentially significant advantage of the hercynite material that should continue to be pursued.

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 has made good progress in understanding redox reaction rates.
- Good progress was presented on this project, including the benefits provided by the zirconium-doped CeO_2 and the effects of the increased water pressure on the hydrogen production rates.
- The demonstration of decent hydrogen production during isothermal cycling and the impacts of operating pressure and temperature performance of the hercynite are encouraging. The 150-cycle activity maintenance of the hercynite material appears promising. Use of the hercynite material in an isothermal reactor system appears feasible.
- Significant developments in performance could be achieved, and some are already reported. The methodology of the project has the potential to overcome key barriers leading to substantially higher process efficiencies and component lifetimes. Therefore the project also has the potential to significantly lower the cost for thermochemical hydrogen production.
- The progress of the hercynite cycle research and development (R&D) and its focus on critical performance metrics has been good. Among the missing ingredients are a system definition and system performance analysis using the Hydrogen Analysis (H2A) version 3 tool. It would seem that the many years of metal oxide thermochemical redox R&D would pay off with understanding and tools, permitting more rapid turn-around of material and system performance metrics.

Question 3: Collaboration and coordination with other institutions

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

- As can be seen from the results, the project has had a great deal of collaboration.
- Each partner serves a unique function and appears able to provide the team with the necessary skills and equipment.
- There seems to be reasonable collaboration between the researchers of this work and both the National Renewable Energy Laboratory and Sandia National Laboratories.
- The collaboration within the project is logical and necessary. By integrating world-leading knowledge on the high-flux irradiation of solar receiver–reactors and on laser-assisted stagnation flow reactors, the project goals seem to be achievable, and the results will be of very high quality.
- The collaboration metrics are outstanding, but the coordination metrics are poor based on the significantly divergent approaches to meeting common program objectives exhibited by the collaborating partners. Some of this is clearly a consequence of maintaining teams without a competitive solicitation of new projects, but the question remains whether the DOE Hydrogen and Fuel Cells Program would be better served by a more coordinated effort.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.50** for its relevance/potential impact.

- This project is very relevant to DOE's hydrogen production R&D objectives for the longer-term central hydrogen production targets.
- The relevance of the project is very high, as it might solve one of the key problems of two-step thermochemical cycles: the intermittent heating between the two steps. The impact in achieving higher efficiencies is therefore significant. Additionally, material issues of HT cycling will be minimized, probably leading to extended lifetimes of the components.
- HT thermochemical systems are incredibly complex, with very demanding operating conditions. This particular thermochemical program appears to offer a two-step isothermal cycle in a fixed-bed reactor, which is as simple as such a system can be. The potential for success appears higher than numerous alternative HT thermochemical processes explored in the past.

- It would have been good to see more progress on reactor design and analysis using H2A.
- Sufficient uncertainties remain for hercynite performance in both temperature swing and isothermal performance that prevent this project from moving into the "outstanding" category. Those uncertainties are largely reflected by operational uncertainties associated with both the emergent reactor design and the degree of simultaneous oxygen and hydrogen production.

Question 5: Proposed future work

This project was rated **3.40** for its proposed future work.

- The proposed plan should enable continued progress and development of the hercynite system.
- The proposed work will add great value to this work, especially the inclusion of H2A analysis for the isothermal redox processing.
- The project has progressed in a logical manner. The future work should include dealing with steam flow variation and modifications to eliminate the variability mentioned. Scale-up issues with packed bed design should be understood.
- The proposed future work is the logical continuation of this outstanding project. The proposed task will make it possible to prepare more reactive particles and to demonstrate the technology under concentrated solar radiation.
- Much of the proposed future work addresses the completion of work reported in this review. However, the proposed future work also addresses the development of material for incorporation in a particle flow reactor. No benefits of this divergent approach were addressed.

Project strengths:

- This project is very relevant to DOE's longer-term hydrogen production pathways.
- The project is carried out by a world-class team of scientists. The partners create a strong synergy within the project. The project is well linked to other projects and teams in the same research area.
- Good data were gathered for developing rate expressions, there was good collaboration between labs and partners, and good work was done on optimizing materials for redox.
- This project has experienced researchers that have developed an effective plan to capitalize on the unique features of the hercynite system, which offers operating advantages over alternative HT thermochemical systems.
- The project is a very innovative attempt at solving one of the key issues to achieving close-to-theoretical efficiencies of thermochemical hydrogen production and reducing the temperature gap between the two steps.
- This project has clear technical proficiency and clear progress toward significant hydrogen production via both temperature swing and isothermal redox of hercynite. High-efficiency cycle performance was estimated. Cycle performance was demonstrated on different test beds.

Project weaknesses:

- Not enough time was spent on reactor design and scale-up. The steam flow variation should have been addressed sooner.
- Hercynite, with its constant reaction back and forth into separate components, may offer integrity challenges that will only be apparent after prolonged HT operation.
- The reactor technology being used is straightforward and probably the right choice for carrying out this project. However, there are more advanced reactor concepts under development that might be suitable to achieve an additional raise in the efficiency of the process.
- This project has inadequate design and analysis (probably due to insufficient funds, but also possibly due to the lack of focus on program objectives). The collaborating partners continue to move along divergent paths, thereby diluting progress toward the program objectives. The justification for simultaneous development of a particle flow reactor was not clear.

Recommendations for additions/deletions to project scope:

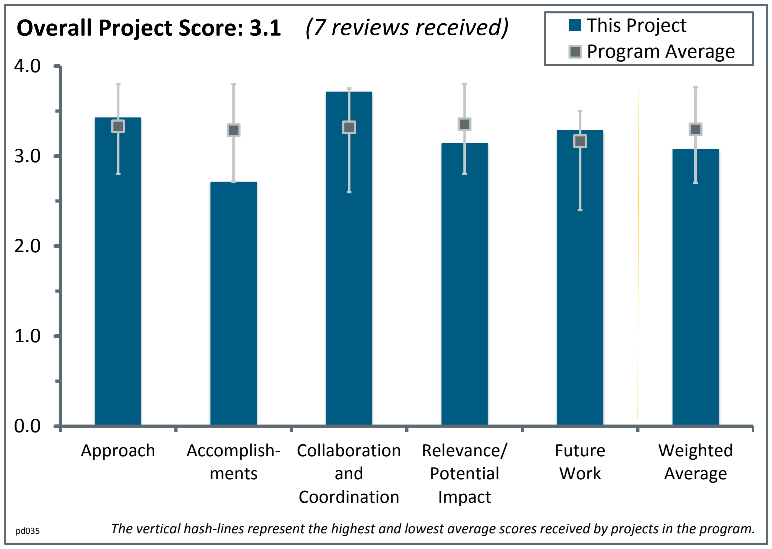
- This project should implement an effective effort in design and performance analysis of a reactor and should work to accelerate the progress toward a cycle performance assessment via H2A v.3. The project should define the benefits/disadvantages of varying water vapor partial pressure to achieve higher performance rates. Also, investments required for implementing a particle reactor flow concept need to be justified.
- The existing connection with other teams should be used to combine all developments in two-step thermochemical cycles as well as on materials on reactor technology.

Project # PD-035: Semiconductor Materials for Photoelectrolysis

Todd Deutsch; National Renewable Energy Laboratory

Brief Summary of Project:

The objective of this work is to develop semiconductor material devices that can split water into hydrogen and oxygen spontaneously upon illumination with a minimum of 10% efficiency. The main focus this past year has been to develop state-of-the-art III-V materials that meet the U.S. Department of Energy's (DOE's) near-term efficiency targets, and to optimize surface treatments for these materials that promote durability.



Question 1: Approach to performing the work

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

- This project has done good work on material evaluation and surface treatments. The team seems to have a good understanding of surface treatment conditions.
- The approach to the work performed in this project is in line with that of the Office of Energy Efficiency and Renewable Energy (EERE) Photoelectrochemical (PEC) Working Group's three-pronged approach to developing efficient and stable photoelectrode materials. Attempting to stabilize highly efficient (but previously unstable) materials is an important area of research.
- As long as the gallium-based III-V tandem electrode is the most efficient PEC system and the only one that has delivered greater than 10% solar-to-hydrogen (STH) conversion efficiency, it deserves a spot in the Hydrogen Production program portfolio, and somebody needs to be working on it. This project is a reasonable mix of developing new materials and optimizing existing ones.
- This group is clearly addressing one of the three major PEC approaches of the PEC Working Group. The project team is candid about barriers to success, such as irreproducible results from metal impurities. The nitridation technique is well-designed and feasible, and the efforts of this group are clearly integrated with others, as evidenced by the Partners and Acknowledgments slides. The project is also taking a multipronged approach to this challenge by studying a variety of aspects in parallel, which is a good research model.
- The National Renewable Energy Laboratory (NREL) continues to focus on improving the durability of their champion III-V semiconductor material. The continued development of these materials is critical to the ultimate success of photoelectrochemical hydrogen production. In parallel, NREL is also giving thought towards how these materials will ultimately look at the system level and is developing the appropriate characterization techniques to further this goal.
- This is a broadly collaborative and coordinated project that has made significant progress in two of the five technical targets in the 2012 Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (MYRDDP). The approach is somewhat diluted by widely divergent pathways and material choices among the partners, with little justification for continuing some of those pathways beyond completing existing efforts to seek incremental improvements/understanding. The two technical targets with significant progress are STH efficiency and hydrogen production rate; both of these advances are based on a single expensive material and device concept. It appears that the approach could be significantly improved by greater investment in the discovery of less-expensive highly photoactive materials and alternative design/synthesis pathways to achieve equivalent progress in hydrogen production cost, solar interface, and electrode cost per TPD (metric tons per day) hydrogen. Such investments could possibly be

implemented without unrealistic funding increases by better focusing and coordinating the many PEC Working Group members.

- The team should look at the economic and environmental sustainability before devoting too much effort to the material. Of special concern is the CO_2 footprint of gallium and indium.

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 primary accomplishment achieved this year appears to be the elucidation of problems with reproducibility in the nitrogen ion treatment of $GaInP_2$ photocathodes, due in large part to help from the surface characterization team at the University of Nevada–Las Vegas (UNLV). Progress was also made in the development of other III-V materials and in setting up an outdoor PEC testing platform.
- NREL has addressed the durability of their electrode materials via the formation of surface nitrides. There was some degree of ambiguity regarding the efficiency of nitride incorporation; however, Dr. Deutsch is now confident that they have identified the path forward via co-implantation with a dilute co-dopant. Due to provisional patent protection, the nature of this dopant was not revealed. An advanced characterization system was prototyped to perform sophisticated PEC measurements under outdoor sum illumination. Publishing a manuscript on standardized PEC testing and reporting is a very important part of the process, as it mandates that independent researchers perform their measurements and calculations such that meaningful information can be extracted to provide effective comparisons between different material classes and fabrication techniques.
- The general PEC hydrogen production program advanced significantly this past year by demonstrating performance and durability feasibility with at least one device and material configuration. This is an outstanding accomplishment and should serve to focus future work on the discovery of similar materials and designs that could surmount remaining barriers to accelerate achievement of program objectives. It is noteworthy that collaborators providing highly sophisticated material characterization and related *ab initio*/molecular dynamics simulations were central to validation of the reported advanced performance. Another achievement in the form of technology-enabling efforts allowed the prediction and demonstration of at least one material corrosion pathway, which could help with the discovery of interface stabilization processes for other materials and device designs. The collaborative project completed its multi-year standardized protocols and reporting methodology effort, which should help to reconcile many other reports of performance.
- This group has achieved a high-efficiency Group III-V PEC system that exceeds DOE’s near-term PEC efficiency targets, but the group has had few advances since the system was first demonstrated in 1998. Their small advances since 1998, especially in surface protection, have demonstrated progress toward DOE goals.
- There has been an impressive improvement in photoelectrode durability via nitrogen doping of the surface through ion implantation. There is some concern about the methodology, though. By imposing an external bias, there may be a cathodic protection effect that serves to reduce corrosion from what it would be in the solar-driven system. That might explain why greater durability was demonstrated at higher current density (i.e., greater applied voltage). Eventually, these results should be corroborated by illuminating the isolated cell and letting the cell voltage and current float as the system evolves. Achieving 24 hours of stability is good news, but it is still well short of the 1000 hours ultimately required. Clearly it is time to push beyond and determine what the new stability limits are. Adding bismuth took 0.06 eV off the bandgap energy. That is better than nothing, but it is not clear how much more can be expected. Perhaps the theoretical justification as to what gains could be expected should be revisited and given more prominence.
- It would have been good to see more work done on durability and on-sun testing.

Question 3: Collaboration and coordination with other institutions

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

- NREL clearly provides coordination and leadership to the other PEC Working Group members.
- The NREL group has very good collaborations with the PEC Working Group, which includes a multitude of complementary expertise, including synthesis, modeling, and characterization.
- This project is actively engaged through synergistic collaborations with a number of partners, especially the PEC theory and surface characterization groups.
- The work done by UNLV was critical to optimizing surface treatment. This is a good demonstration of collaboration in all areas.
- This group definitely interacts with other groups to publish papers on experimental techniques, technoeconomic analysis, and general research. This is clearly evidenced by the Partners and Acknowledgments slides. The group utilizes extensive computational modeling support from one DOE EERE-funded principal investigator and surface characterization from another.
- This is a highly collaborative project and participates in the PEC Working Group that meets regularly to discuss process options and report progress. Inclusion of sophisticated characterization and simulation teams has proven its value and should be emulated, where appropriate, within other Hydrogen Production and Delivery program efforts. Coordination of this effort should be improved to accelerate the progress toward meeting the technical targets in the 2012 MYRDDP. Changing specific tasks among partners in the PEC Working Group could be disruptive and might lead to the replacement of some partners, but the project should continue to seek project constructs that appear to follow the most promising pathway.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.1** for its relevance/potential impact.

- Being able to directly couple solar to water splitting is the key to improved STH efficiency.
- This group is targeting a Type-IV system, which could be cost-competitive with natural gas-derived hydrogen in the long term.
- The work that NREL conducts is extremely relevant to the current DOE objectives for PEC hydrogen production. They are moving the technology forward towards meeting future DOE milestones.
- The project is well focused on program objectives and success in material discovery and synthesis accompanied by device designs. Enabling cost-effective fabrication and manufacturing would provide an attractive option to solar-powered hydrogen production.
- This project is well aligned with DOE's objectives. Even if III-V semiconductors are not ultimately a low-cost hydrogen-generating PEC technology, the ability to achieve high STH efficiency with today's III-V technology is very useful for addressing device-level challenges and stability at high current densities associated with the EERE PEC efficiency targets.
- This project and the PEC program as a whole could be cut tomorrow and have little impact on the foreseeable future of implementing of hydrogen and fuel cell technology. There are many other ways to supply hydrogen more cheaply than PEC. However, most of them exploit nonrenewable resources and do not prepare us for a sustainable energy future. Even within the program, PEC has to share the limelight with solar thermochemistry and photobiology. Nevertheless, DOE needs to bet some money on PEC, and a few million dollars a year on the possibility that technical advances can enable hydrogen production cheaper than photovoltaic (PV)-electrolysis is a worthwhile wager.

Question 5: Proposed future work

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

- The investigators understand what has been accomplished and what the next round of experiments should be.
- The general proposed future work is fine. Although not explicitly stated, there needs to be a narrowed task for applying the good nitriding process to a high-efficiency tandem cell and validating that process by reporting a superior result to the previous 12% STH efficiency from a decade ago.
- Overall, the future work plans are appropriate. Determining if the application of a nitrogen ion treatment to other III-V surfaces (and beyond) should be a priority, as should the determination of Faradaic efficiency during stability tests to alleviate concerns about surfactant interference. Outdoor testing with 10 times the concentration and light-cycling will also be of great use to the PEC community.
- This reviewer did not highlight any decision points but clearly laid out the proposed future work. The breadth of this proposed work is sufficient enough so that if some aspects struggle or become slowed, others can become the focus. This multi-pronged approach is advantageous in that the overall project and goals do not stall.
- The proposed work builds carefully on the success demonstrated this past year and is certainly focused on two of the three undemonstrated technical targets. Nevertheless, some thought should be given to alternative materials should it prove impractical to develop cost-effective synthesis and manufacturing processes to implement designs that could meet STH efficiency targets.
- This project needs to focus more on on-sun trials.

Project strengths:

- The leading PEC cell system for hydrogen production is continuing to improve. It is the flagship project for the PEC program.
- This is a nice, broad approach to understanding materials and surface treatments using expertise from various resources. This project seems to be on track.
- This project has outstanding technical proficiency, outstanding collaboration, outstanding facilities, and outstanding interactions with similar groups that are outside the inner circle of collaborators.
- The team and collaborations are very strong and experts in PEC, and this group has clearly identified a tractable problem to investigate using the wealth of resources afforded to them. Their approach is solid and, should large breakthroughs be discovered, there is a strong chance of realizing a cost-effective and scalable technology.
- The $GaInP_2$ remains the leader of high-performance PEC materials. Primarily through NREL, a wealth of knowledge on using this material for PEC has been accumulated over the past 15 years that is valuable toward further development. The recent results identifying the requisite co-dopant for effective nitriding validates the efficacy of the larger PEC working group towards solving outstanding issues in a collegial manner.
- This project has good synergy between theoretical, characterization, and materials experts. The extensive experience in III-V PV materials and PEC development makes NREL well suited for carrying out research focused on the task of stabilizing high-efficiency photoelectrode materials. NREL's current role as cell test and certification center for the PV field makes it a logical choice to assume this role for the evolving PEC field.

Project weaknesses:

- More focus needs to be placed on durability and on-sun trials.
- This project has insufficient investment in alternative pathways in the event of a failure of the current material focus.
- This project should be careful not to overstep milestones and perform experiments that provide a valid assessment of the state of the art.
- It appears that significant time was consumed figuring out the reproducibility issues associated with the nitriding treatment, and it still remains unclear if nitriding the III-V surface is a viable long-term option.

The absence of Faradaic efficiency measurements is a notable weakness of this project, given that its primary objective is to investigate the stability of these materials.

- This group generates hydrogen and oxygen in one vessel and does not report Faradaic yields. As such, the photoelectrodes may be reducing oxygen instead of protons, and thus the observed current and efficiencies may be artificially inflated. Another weakness is the group's use of expensive hydrogen evolution electrocatalysts (i.e., platinum) and oxygen evolution electrocatalysts (i.e., RuO_2). The group must start addressing catalyst requirements and investigate alternative electrocatalysts that are more abundant and could be scaled to the terrawatt scale. The authors should clearly identify when a three-electrode or two-electrode measurement is used, as well as all of the experimental conditions used for each IV plot, including the potential where water splitting occurs.
- At some point, every materials-intensive project needs to have the capability to generate material in appreciable quantities. Although NREL has III-V fabrication capabilities, it appears from the review that this is more of a foundry-type relationship, with limited materials available for PEC. From the 2012 DOE Hydrogen and Fuel Cells Program Annual Merit Review, the proposed future work indicated that there would be an evaluation of dual (stacked/side-by-side) systems that were not highlighted in this review. It is unclear if this was abandoned or completed. In some ways, there appears to be a passivity towards the effort (i.e., NREL will characterize materials that come their way and generally support the larger community). There needs to be a sense of urgency towards finishing the III-V work.

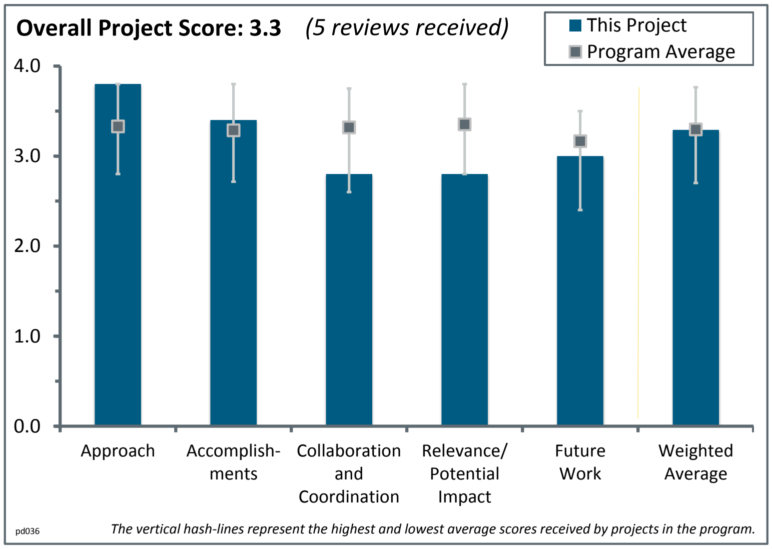
Recommendations for additions/deletions to project scope:

- At this point in the project, there really should be a singular goal. This project should apply all the hard work from the previous few years and fabricate a fully functioning, nitrided tandem that exceeds previous performance metrics. This is important for the overall validation of current and past efforts and gives credibility to the potential for future success.
- While it is certainly a worthwhile venture, too much effort is focused specifically on understanding and demonstrating passivation of a single material ($GaInP_2$) by a single nitridation process (nitrogen ion implantation), a finding that was presented last year. This approach should be extended to other materials to view how universally useful the nitrogen ion treatment may be for III-V materials. Given that investigating stability is a primary objective of this project, accurate determination of the Faradaic efficiency (in the presence and absence of surfactant) and minor corrosion rates should be a priority.
- Evaluating PEC system stability is important, but the stability should also be assessed with day–night variations. The group's proposed on-sun testing should surely include multiple day tests where the system is bathed in hydrogen and oxygen at night. Some corrosion/passivation processes occur under conditions in which the sun is not shining and the PEC device is bathed in hydrogen and oxygen to reverse bias the cell. It is imperative that the project researchers begin to address these issues. As such, they must employ a separator (e.g., Nafion or a very fine, small frit) in PEC measurements to separate their hydrogen and oxygen reaction products. Then, when the sun goes down, they should assess their system stability in the presence of these gases. Another possibly useful condition to evaluate is in neutral pH with a large buffer concentration; there the III-V material should only passivate and not corrode, resulting in a stable electrode.
- This project should continue characterization and simulation studies of semiconductor–electrolyte interfacial phenomena for better understanding of electrochemical and corrosion processes. This project should encourage PEC Working Group members to evaluate the opportunities for closer coordination and teaming for III-V materials discovery and performance testing. This project should also encourage fundamental science agencies to invest in continuing an *ab initio*/molecular dynamics approach to interfacial behavior studies, including development/incorporation of quantum dynamic modeling of energy states in liquids. This project seeks broader collaboration with materials synthesis/fabrication specialists and continues or expands upon relationships with device manufacturing institutions.

Project # PD-036: Maximizing Light Utilization Efficiency and Hydrogen Production in Microalgal Cultures

Tasios Melis; University of California, Berkeley

Brief Summary of Project:



The objective of this project is to improve the sunlight-utilization efficiency of photosynthesis in microalgae by up to 300%, which will improve hydrogen or fuels production in microalgae and cyanobacteria by about the same percentage. Research proceeds on the truncated light-harvesting antenna (TLA) concept, which minimizes the light-harvesting antenna size of the photosystems to prevent early light-saturation of photosynthesis and the associated wasteful dissipation of absorbed sunlight. Genes and associated molecular mechanisms that confer a TLA property in the TLA3 strain of *Chlamydomonas reinhardtii* are identified, and protocols are developed for the targeted truncation of the light-harvesting antenna size in cyanobacteria.

Question 1: Approach to performing the work

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

- The researcher has demonstrated that the gene replacement approach to the size reduction of antenna structures has general applicability in both algae and cyanobacteria.
- The approach has been methodical and step by step. The work in *Chlamydomonas* was carried to completion. The knowledge learned is being applied in the cyanobacteria system in a clear and deliberate manner.
- The identification and cloning of genes involved in truncated antenna size in microalgae and cyanobacteria is impressive. The work accomplished in the Melis lab is impressive and fits well with the work of Weyman et al. The approach is very robust.
- The success of the approach adopted and the techniques applied by this project to address antenna reduction in green microalgae provides great confidence that similar success will be achieved with cyanobacteria. A slide showing Δcpc transformants indicates some change has already occurred. More quantitative information as to the extent of the effect would be appreciated in next year's presentation.
- In 2012 and 2013, this project reduced the antenna size, but it is not clear what the direct result has been.
- In a bioreactor, it was always assumed by the team of principal investigators (PIs) that a family of microalgae is needed across the cross section of the reactor to get the best solar utilization. Therefore, algae in the middle of the reactor would have a larger antenna than those on the exterior surfaces to have the most favorable average solar utilization for hydrogen production. Now it appears that the intent is to produce a monoculture all with the same antenna size. Except for the science, the approach does not show how this will produce the levels of hydrogen needed at a cost that is practical and able to meet any of the targets, or with a higher efficiency. Based on reviewer comments from the 2012 DOE Hydrogen and Fuel Cells Program Annual Merit Review, it appears the approach for stable mutants is to incubate and continuously replace TLA mutants with new strains. It is not apparent this will be an economical approach, and it is not addressed as part of this work or any of the analysis activities.

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.

- The project completed the objective to reduce the antenna size with the potential to improve photosynthetic efficiency. It is not clear if this mutant strain can improve hydrogen yields or system efficiencies to meet the DOE targets.
- Cyanobacteria were successfully modified to eliminate blue receptors of the antennae through methods previously used on algae. Cyanobacteria with reduced antenna size were first produced about 10 years ago, so the general accomplishment is not new.
- The increased utilization efficiency above what was expected is excellent, as is the elucidation of the mechanisms of TLA2 and TLA3 function in the light-harvesting-complex-protein assemblage. The characterization in cyanobacteria is another example of impressive accomplishments.
- This project exhibits commendable progress. Unlike the original green microalgae work, which had well-documented, explicit targets over time that were achieved well ahead of schedule, the targets for the cyanobacteria work are not as obvious. For example, it is unclear if there is a target date for the transformation go/no-go decision. In the absence of targets, this reviewer will assume worst-case timing comparable to the microalgae work. On that basis, this work appears to be on schedule.
- Neglecting the issue of project duration, the accomplishments of the *Chlamydomonas* system have taken this task to completion. The antenna adjustment in cyanobacteria work has begun, and initial pigmentation arguments suggest that the concept is operational. There remains a significant amount of work to be done in the cyanobacterial system. A question is whether the effort is diluted by attempting to explore the extended photosynthetically active radiation (ePAR) concept at the same time.

Question 3: Collaboration and coordination with other institutions

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

- Collaboration and cooperation between the Melis and other laboratories seems strong, and the topics overlap to produce a sum greater than their parts.
- Some collaboration exists primarily on education and supplying strains, but there is no indication of collaboration on the use of bioreactors to determine a more real-life trial on its stability and production capability.
- This project and presentation seem to be pretty much stand-alone. There was not much evidence of actual collaboration or input from collaborators.
- The researcher is capable of conducting the work with minimal input from outside groups, so lower levels of collaboration are not necessarily hindering the project. Nation Renewable Energy Laboratory (NREL) researchers and others are making use of the advances and were described as being offered advice on implementation.
- As was true for the microalgae work, this cyanobacteria project appears to be state of the art with little or no need for collaboration. The beneficiaries of collaboration with this project appear to be other collaborators, not this project.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- This project directly and effectively addresses the "light utilization efficiency" barrier (2012 Fuel Cell Technologies (FCT) Office Multi-Year Research, Development, and Demonstration Plan [MYRDDP], barrier number AN). This and prior work could have a substantial effect on photobiological efficiency of the production of various products in addition to hydrogen.
- Antenna size modification will be necessary in all algae and cyanobacteria organisms to achieve commercial fuel production levels. The technique has general applicability and is not limited to hydrogen-

producing organisms. However, this technique must be combined with significant advances in other aspects of cell modification to achieve DOE hydrogen production goals.
- While hydrogen production is certainly relevant, the rate at which progress is being made argues against the project as being critical to the program. As part of a go/no-go, the PIs should be expected to evaluate the best results that they think will be achieved, and decide the project's ultimate fate based on this production expectation. Assuming an argument can be made to continue, the PIs should estimate how close they are to completion and estimate realistic timelines.
- The PI has stated this work links with other efforts at NREL and the J. Craig Venter Institute, but the PI does not show how they are linked or if any outcome in terms of production yield has been observed. The one data point referenced is from 2010, which used a mutant that had 50% of the control. If that was such a significant yield increase, it is unclear why the lab did not stop there and do more bioreactor testing to determine if it was replaceable. The PI has said this is very time-consuming work requiring many hours of laboratory time. For such an effort, there should have been some attempt to show higher yields and more mutant stability, instead of just stating that six other groups have formed due to this PI's efforts, especially with the laboratory in Australia.
- The lack of fitness evaluations is a concern for the potential impact. To knock out such a large portion of the photosynthesis complex and consider it unlikely to inhibit organismal production is not a scientifically sound approach. Predictions appear to be formulated based on assumptions without testing. To test organismal fitness or assess basic physiological responses of TLA mutants would be simple and inexpensive. Certainly, the collaborating laboratories would be able to do such a test. These are basic and critical assumptions needed to meet the desired FCTO MYRDDP goals. The organisms need to survive and thrive.

Question 5: Proposed future work

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

- The plan is adequate. The question on ePAR remains.
- The proposed cyanobacteria work appears to be very achievable and well focused on barrier AN.
- The general ePAR idea is sound, but the proprietary limits on divulging actual approaches limit the reviewer's ability to evaluate the effectiveness of the idea.
- Most of the future work should be based on determining the stability and replication potential of the mutants in a mass culture situation, before additional genetic mutation work is agreed upon. This project should develop a more accurate predictive model based on hydrogen production levels or efficiencies with the TLA strains.
- The future direction appears to be an assessment of stability and fitness according to the slides, which would address the concerns previously raised by this reviewer concerning lack of fitness evaluations. The PI's response to audience questions regarding organismal fitness and physiological response to TLA was insufficient, which was a concern. If the future studies as indicated in the presentation include fitness and physiological measures (in all four future subtopics), then the score of this reviewer would change from three to four. Assumptions are insufficient to meet the long-term DOE goals.

Project strengths:

- The scientific approach is well thought out and has been adequately conducted. It has taken some time, but the work is perhaps quite difficult.
- This project is tackling big problems of general use to the entire community of photobiological fuel production, not just hydrogen.
- This project completed the proposed work and provided strains to other organizations for testing. A project strength is the multi-culture tests that the PI has said are in progress.

Project weaknesses:

- As new approaches are tried to enhance light utilization in algae and cyanobacteria, collaboration may be useful but potentially limited by the researcher's proprietary concerns.

- There is no direct link to see if these mutants can be integrated into a biological system to produce hydrogen to meet the MYRDDP cost targets and efficiency goals.
- It is taking a long time to come to some conclusions. The estimates of final attainment and percentage of achievement would allow some assessment of whether this project should begin its second decade. It is not clear if the approach will be adequate to achieve the top targets in terms of hydrogen production.

Recommendations for additions/deletions to project scope:

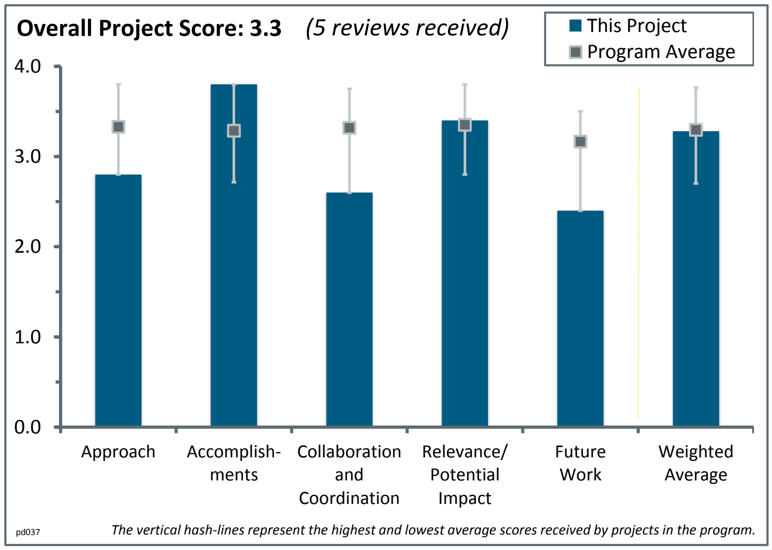
- This project should decide to put ePAR on hold for now, as it appears to dilute the effort.
- This project should complete a thorough characterization of the mutants' ability to survive a mixed culture environment, produce hydrogen with a reasonable yield, and survivability with the wild type in a bioreactor before committing funds for more genetic engineering.

Project # PD-037: Biological Systems for Hydrogen Photoproduction

Maria Ghirardi; National Renewable Energy Laboratory

Brief Summary of Project:

Photobiological water splitting coupled to hydrogenase-mediated hydrogen production has the potential to convert about 10% of incident solar energy into hydrogen. Various barriers have been identified as currently limiting green algal hydrogen production, including the oxygen sensitivity of the hydrogenase enzyme, the competition for reductant with CO_2 fixation and cyclic electron flow, the down-regulation of photosynthesis due to non-dissipation of the proton gradient and state transitions, and the low light-saturation of photosynthesis. The general goal of this project is to develop photobiological systems for large-scale, low-cost, and efficient hydrogen production from water.



Question 1: Approach to performing the work

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

- The approaches utilized have successfully met the project goals in terms of product and timeliness.
- The approach to generating hydrogen production in green algae seems reasonable. The presenters have knocked out the native hydrogenase and added an oxygen-tolerant clostridial hydrogenase (PsaD-CaI). While the rate of hydrogen production is much lower in the mutant system, the mutant is able to generate small amounts of hydrogen in the presence of oxygen.
- This project is well focused on addressing the "rate of hydrogen production" and "oxygen accumulation barriers" (barrier numbers AO and AN from the Fuel Cell Technologies (FCT) Office 2012 Multi-Year Research, Development, and Demonstration Plan [MYRDDP]). In the past, the existence of Task 2 has provided risk reduction and some flexibility. While sulfur deprivation (and its discontinuous nature) appears to be an inferior means of achieving hydrogen production compared to incorporating an oxygen-tolerant hydrogenase, it is unfortunate lack of funding eliminated Task 2 and its work related to the non-dissipated proton gradient and study of the long-term performance of immobilized culture.
- Adding an oxygen-tolerant hydrogenase to the algae is the straightforward part of the project. Connecting this hydrogenase to the cell supply chain so it can make hydrogen is a much harder long-term issue that must be addressed.
- The rationale for pursuing a parallel track with green microalgae is not very clear. Heterologous gene expression is what is being pursued, so the native number and complexity of genes in *Chlamydomonas* should not be a factor, unless gene knockouts are necessary. A better argument would be if *Chlamydomonas* is faster growing, less susceptible to predators/competitors, easier to manipulate genetically, or more robust in outdoor conditions.

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

This project was rated **3.8** for its accomplishments and progress.

- This project completed the milestone on light-dependent expression of clostridial hydrogenase (PsaD-CaI) successfully and on time. This appears to be a technical breakthrough. The assays for oxygen tolerance were well done and showed promising results in atmospheric concentrations of oxygen.
- The successful transfer of clostridial hydrogenase into the algae is impressive. The confirmation of a uniform population using the green fluorescent protein (GFP) assay is well done. The ability of the mutant to produce small amounts of hydrogen in the presence of oxygen is a major achievement. The presenter's plan to boost production by using a stronger promoter is sound.
- The researchers succeeded in putting the oxygen-tolerant hydrogenase into a cell and reported 2% of the rate of hydrogen production of the wild type. Part of this activity was retained in the presence of oxygen relative to the wild type, which is encouraging. This work is foundational and only the first step. Years of additional work in a myriad of areas on cell modification will have to be combined to reach DOE's targets.
- Steady progress has been made with significant accomplishments, such as the CaI transformant and subsequent quantification of light-induced hydrogen photoproduction, and recognition of heterogenous strain communities on GFP plates. The techniques are classical and have been used for some time, but they are not easy, nor are they always readily accomplished. This explains the 12 years invested to produce this sequence of accomplishments.
- Commendably, the project successfully introduced a bacterial hydrogenase into a photosynthetic alga, induced expression, and observed light-dependent hydrogen production in the presence of oxygen. The project recovered a high-producing strain after significant heterogeneity appeared. And, despite cancellation, Task 2 demonstrated continuous operation of immobilized cultures for 1,440 hours, 70% to 90% of the time; however, hydrogen production rates were only 0.5% to 10% of initial rates.

Question 3: Collaboration and coordination with other institutions

This project was rated **2.6** for its collaboration and coordination.

- This project has effectively leveraged Office of Science funds to develop a more sensitive assay; however, owing to budget constraints, partnerships with some collaborators were lost. Long-term partnership with the Melis lab appears to be unaffected.
- This project had to drop collaborators because of a lack of funding. This project started working with a new group in France that has a mutant that shows promise in terms of addressing Task 2 (ATP synthase mutant).
- This project has lost partners because of a funding decrease. The partners appeared to perform valuable functions, and their loss means that useful avenues will not be studied. This project has begun working with a new team in other areas, but not in the area of lost collaboration.
- The loss of Task 2 appears to have reduced the project's level of collaboration and capabilities. The results of this research have been communicated through several publications and conferences (including international conferences).
- The reduction in collaboration is the fault of funding shortages. The reviewer wonders if collaborations are not possible without providing funding. Certainly money "greases the wheels," so to speak, but collaborations with other funded laboratories conducting similar work must be possible. People were presenting such work at the 2013 Hydrogen and Fuel Cells Program Annual Merit Review. The principal investigator (PI) has indicated that conversations with industrial partners are ongoing. Industry people working in the general field of algal photosynthesis would probably be amenable. Some of these musings were effectively addressed by the PI, who indicated potential collaborations with a group in France who are working on a mutant with the same effect as a proton decoupler, thereby addressing some of the issues lost in the Russia collaboration.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- A photosynthetic algae strain that produces hydrogen has much potential and should be pursued.
- The research appears to be at an early technology readiness level, so it is unclear how these research results will translate into larger production scales.
- The relevance of this process to providing hydrogen to hydrogen fuel cell systems is not questionable. Other energy supplies are complicated by their environmental footprint. The utilization of photobiological systems does not suffer the same issues and thus is a long-term solution rather than a “bridge” solution. The PI has addressed the FCT Office MYRDDP.
- This work should identify the issues surrounding photobiological hydrogen production in algae, but in and of itself will not meet the long-term DOE goals. However, this work is necessary if the goals are to be met in the future.
- Acquiring a productive green algae that (1) possesses an oxygen-tolerant hydrogenase, (2) has a more efficient reduced antenna, and (3) is capable of dissipating the related proton gradient would be a significant stride for the biological hydrogen production pathway.

Question 5: Proposed future work

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

- The proposed future work builds on past accomplishments and is the logical continuation of the work in progress.
- The proposed future work, in terms of combining the genetic mutations into a production strain, is the logical next step.
- The work is novel, and the accomplishments are significant. It is also recognized that because the work is novel and the techniques are time-consuming, 12 years of investment is warranted; however, the goals for the future seem less than ambitious.
- The proposed work is a logical extension from the present position. The team needs to sit down and analyze why the hydrogen production rate is so low and how to make the most significant advance. It is unclear what the limiting factor is for hydrogen production in the algal system with the oxygen-tolerant hydrogenase—probably a connection with the cell supply chain. It is unclear if this proposed work maximizes the connection or if other directions are more promising.
- This reviewer did not see a defined plan to improve the recombinant hydrogenase activity, aside from testing the stronger promoter. Furthermore, it will be important to determine if increased hydrogen production will have a negative effect on the cells or if the cells will maintain the promoter/hydrogenase genes over a relevant time scale.

Project strengths:

- This is an excellent team capable of unraveling the issues of hydrogen production in algae.
- This project is well conceived and executed. The challenges and complexity are identified and addressed (e.g., the heterogeneous community on the GFP plates). The lab has made significant contributions to moving this science forward.
- Green algae that can be used for hydrogen production has a lot of promise in the biofuels industry. This project has already achieved a great milestone in generating small amounts of hydrogen in a prokaryotic system.

Project weaknesses:

- It is not clear whether the project is addressing the biggest issue, versus more tractable issues.
- There does not seem to be a strong plan for increasing hydrogen production and confirming that higher levels of hydrogen will not have a negative effect on the cells.

- This is not a project weakness, but a funding question. It is unclear why basic science, such as this, and all the projects presented during this review period are not funded by the DOE Offices of Basic Energy Sciences (BES) or Biological and Environmental Research (BER). This may simply reflect the reviewer's lack of knowledge of DOE funding decisions and guidelines. The weakness is the speed with which the work is progressing.

Recommendations for additions/deletions to project scope:

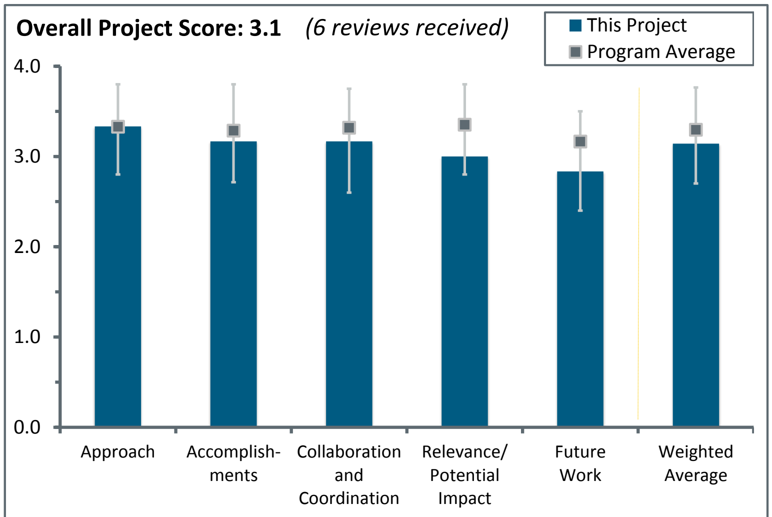
- Additional work should be done to confirm that the hydrogenase system will be maintained over a relevant time scale in a working system. It is unclear how the presenters will confirm that the hydrogenase genes/promoters will not be mutated over time.
- This project should develop collaborations, which will increase the speed of the task accomplishments. The project should explore the physiological constraints of ATP synthase under variable growth conditions and explore the phenotypic variation resulting; identify barriers to hydrogen production over time, which seems to be, in part, strain-specific; and generally push the expectations in the proposed future research.

Project # PD-038: Fermentation and Electrohydrogenic Approaches to Hydrogen Production

Pin-Ching Maness; National Renewable Energy Laboratory

Brief Summary of Project:

The objective of this project is to develop direct fermentation technologies to convert renewable lignocellulosic biomass resources to hydrogen. The project addresses techno-economic feasibility of hydrogen production via biomass fermentation in three tasks. Task 1 uses cellulose in lieu of sugars and optimizes parameters in sequencing fed-batch bioreactors to lower feedstock costs. Task 2 is aimed at improving hydrogen molar yields by developing genetic tools to block competing pathways. Task 3 integrates a microbial electrolysis cell (MEC) reactor with fermentation to improve hydrogen molar yield.



The vertical hash-lines represent the highest and lowest average scores received by projects in the program.

Question 1: Approach to performing the work

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

- The coupled system approach is unique and appears to be advantageous, thanks to unit operational synergies. This approach appears to produce high theoretical hydrogen molar yield and may be more near-term to scale-up compared with photo-biological approaches.
- By including the MEC reactor, the researchers seem to be maximizing the potential hydrogen production. The genetic approaches to creating strains that increase hydrogen production are sound. The assumption that knocking out the ethanol pathway will result in more hydrogen production might not be valid but needs to be tested.
- This program has an effective three-pronged approach: modify conventional bioreactors to address demands of a unique system, alter synthetic organisms to achieve hydrogen production from cellulose, and create a new electrochemical reactor for hydrogen production from the biological hydrogen production effluent. The MEC reactor system appears applicable to biological effluent in general, but it is not limited to hydrogen producers and may warrant its own program depending on advancement.
- The project is well focused on barriers AX, AY, and AZ in the Fuel Cell Technologies Office 2012 Multi-Year Research, Development, and Demonstration Plan, i.e., hydrogen molar yield, feedstock cost, and systems engineering. The potential to attain a yield of 11.6 moles hydrogen/mole sugar is impressive, and the approach being pursued provides confidence that a significant improvement beyond 4 moles hydrogen/mole sugar is achievable.
- The linkage between tasks and where the whole project is going is not clear. Lignocellulose is the apparent target feedstock, but it is not very prominent in the plans. This project is also apparently slow-moving overall.
- The focus of this work should be on the conversion of sugar to hydrogen and all the issues dealing with this fermentation process. Since a great deal of this work is aligned with the U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO), many of the pretreatment issues, barriers, and equipment costs have already been addressed. For example, clean, low-cost, cellulosic-based glucose from an integrated biorefinery (IBR) could be made available cheaply so the research team can focus on the fermentation improvements needed. The equipment like Cellunators^{TM} for optimum mixing and cell disruption has been developed and scaled to commercial size. The processes to remove inhibitors, such as acetic acid and

formic acid, have been implemented and can be applied. These types of technologies can be easily adapted to this application for the fermentation process to be economical.

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 experienced a breakthrough in terms of making genetically tractable *Clostridium thermocellum*. The project appears to have met other milestones on time.
- This project completed some milestones ahead of schedule. This project has many promising tasks and has already demonstrated some. The accomplishments by both the National Renewable Energy Laboratory (NREL) and Pennsylvania State University (Penn State) teams are impressive.
- This project successfully modified the fermenting apparatus for consistent feed delivery. The increase in hydrogen production rate via process variables was a useful demonstration. Last year, the 2013 hydrogen production goal was 4 moles hydrogen/mole glucose; this appears to be the 2015 goal now. Knocking out the formate pathway was a good step in organism modification. The MEC work was an excellent proof-of-principle demonstration.
- The increased hydrogen yield was very good for this approach. This approach may not be reasonable, especially to develop a proprietary plasmid that eliminated the formate pathway. Based on the system economics, by-products are attractive ways to reduce the cost of hydrogen if the yields for the primary pathway are reasonable. Formate can yield other attractive products with a higher value. Based on the molar yields and rate increases on direct fermentation, these seem sufficient for a process system. The complexity of creating plasmids is an interesting science, but it is unclear why it is needed here. It is unclear if the process should focus on fermentation of good hydrogen yields or concentrate on hydrolysis and saccharification. Hydrogen generation in an MEC reactor was very good, but it was not apparent if preliminary economics were conducted to identify barriers the technology must overcome to be feasible.
- Task 1 has resolved an issue with sub-optimal hydrogen production rates by decreasing the fermentor hydraulic retention time, but it will ultimately have to address inefficiencies of handling larger liquid volumes. Task 2 has developed a mutant in which the pyruvate–formate pathway has been knocked out and demonstrated it several months ahead of schedule. The mutant appears to produce significantly more ethanol and marginally less pyruvate than the wild type. Task 3 has begun processing a more realistic wastewater stream and identified issues with protein treatment. Task 3 has devised a very novel approach to eliminate a conventional power source for the electrochemical cell; this effort does not appear to address program barriers as directly as development of the electrochemical cell.
- The progress and accomplishments do not seem major for the project duration. The progress seems slow.

Question 3: Collaboration and coordination with other institutions

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

- The project exhibits good collaboration on all fronts to reduce duplication and increase performance.
- The coordination between NREL and Penn State appears to be excellent. An additional collaboration with a team in Canada did not produce measurable results but was valuable to the presenter in terms of knowledge gained.
- The three different collaborators appear to provide distinct services that will advance the program and enable the accomplishment of the project’s goals. This was the best apparent collaboration of any project this reviewer reviewed that day.
- Task 3 linkage to the fermentative work has improved. The task is beginning to process more realistic fermentation wastewater and identify issues such as higher protein levels than were previously studied. Task 2 is now positioned for greater interaction with Task 1 by providing mutants for testing.
- The collaboration with Penn State is strong and synergistic. It is clear from the results so far that the efforts are well coordinated among the participating institutions. There was good leveraging of the Genome Canada relationship; however, the genetic engineering component may have benefitted from a collaboration with Dartmouth College (Lee Lynd) or Oak Ridge National Laboratory, which are both

proficient in working with *C. thermocellum* due to the Office of Science Bioenergy Research Science Center activity, of which NREL is a participating organization.
- This project seems like three separate projects with not much evidence of collaboration. It is not clear what the groups are gaining from each other.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- The combined approach of bioreactor, genetic engineering, and MEC research is an excellent way to maximize the output of the funding.
- This appears to be a feasible approach for hydrogen production, especially for grid-independent facilities that have a waste or lower-cost sugar stream to make hydrogen. This hydrogen can be used to hydrogenate and produce drop-in fuels, to run stationary fuel cells for auxiliary power units (APUs), or in local vehicle applications.
- Efficient fermentation of a less expensive feedstock through the application of an inexpensive process would be a significant step in achieving DOE targets.
- Owing to the relative ease in scaling and integrating these more "conventional" bioprocesses, it is likely that this approach will yield significant quantities of hydrogen in a shorter timeframe, which will aid in more realistic techno-economic evaluations of how this might affect cost goals by 2030.
- The relevance is likely there. However, the magnitude of the value to the overall DOE Hydrogen and Fuel Cell Program is questionable. Lignocellulose is mentioned but does not appear to be a focus.
- The general idea of producing hydrogen from cellulose is scientifically sound, but it is questionable for practical application. Taking a feedstock that can be readily converted into ethanol, a renewable liquid fuel product of high volumetric energy density at standard temperature and pressure that has an efficient delivery system, and making hydrogen instead with all the concomitant problems that result from a gaseous energy feedstock seems counterintuitive. Unless hydrogen can be produced significantly more efficiently than ethanol, or serve a unique function, it will not happen. Getting extra energy from a biological effluent in the MEC reactor may possess some merit, even if it is hydrogen.

Question 5: Proposed future work

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

- The proposed future work is a logical extension of ongoing research.
- The proposed work is a logical extension of the current progress and should allow the team to meet the project goals.
- The future plans appear to be building upon the progress to date and are likely to address the remaining barriers. The penalties of frequent liquid replacement in the bioreactors in terms of operating expenditures should be examined more closely in techno-economic models.
- The future work needs to be reevaluated for impact.
- This project demonstrated that deletion of the pyruvate-to-formate gene produces more ethanol, leading to a hypothesis that knockout of the ethanol production pathway will refocus the output to hydrogen, which may or may not be valid. This requires testing.
- It is not clear why this project does not focus on the fermentation to produce hydrogen and does not try, with limited funds, to scale the MEC reactor, eliminate the formate pathway, and develop new equipment to feed cellulosic slurries. If this process can produce multiple products and high hydrogen yields, it will have exceeded any of the accomplishments from the biological hydrogen production pathways. Then this project could collaborate more effectively with BETO to reduce or modify existing feedstock processes to reduce cost and improve the yields more.

Project strengths:

- This is an excellent collaborative team that can work together to achieve goals.

- This project has good principal investigators (PIs) and organizations conducting research, and good fermentation yield.
- This project has strong collaborations. It combines multiple technologies to maximize hydrogen production. Overall, this reviewer was very impressed with the work and the level of coordination.

Project weaknesses:

- This project has too large a scope with limited resources.
- This is a very fragmented project. It is unclear what value each piece brings and when each section will reach an evaluation point.
- The MEC reactor could be considered a separate project altogether with its own set of difficulties that may warrant a larger effort once it is past the proof-of-principle stage and the preliminary economic analysis.

Recommendations for additions/deletions to project scope:

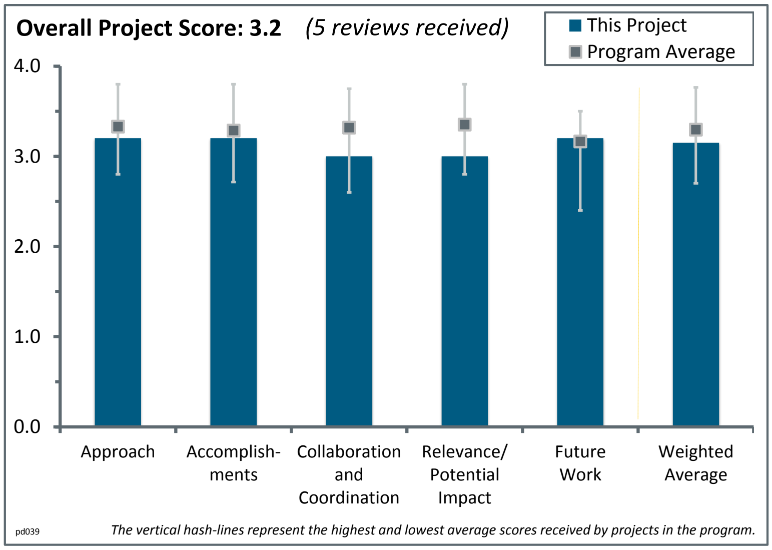
- There should be some firm targets for the project, and each task should be evaluated in light of them. The interactions between the PIs should be strengthened as necessary.
- The presenter stated that there is no competition between biofilm formation and clostridial cells; however, the presenters should include an evaluation of the biofilms in the MEC.
- Instead of focusing on traditional agricultural or woody biomass resources, this project should be exploring the *C. thermocellum* treatment of municipal solid waste and other organic wastes that might be co-located with wastewater treatment plants that may already be considering MEC technologies. This can bypass many feedstock availability issues. Also, since the carbon is supplied at such a low concentration (5 grams per liter per day under current experimental conditions), this technology could be especially amenable to dissolved organic carbons and cellulose from municipal liquid wastes.

Project # PD-039: Hydrogen from Water in a Novel Recombinant Oxygen-Tolerant Cyanobacterial System

Phil Weyman; J. Craig Venter Institute

Brief Summary of Project:

The objective of this project is to develop an oxygen-tolerant cyanobacterial system for continuous light-driven hydrogen production from water. Current approaches to improve the system include (1) developing strategies for increasing expression and activity of the environmentally derived hydrogenase in cyanobacteria by changing the frequency and strength of promoters, testing a novel strategy for expression of hydrogenase, and altering the FeS cluster ligation to increase hydrogen evolution activity; and (2) developing strategies for increasing hydrogenase-ferredoxin interaction through construction of a ferredoxin-hydrogenase fusion protein that maintains activity.



Question 1: Approach to performing the work

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

- This approach is systematic, thorough, clear, and logical.
- The approach is effective and has resulted in several new improvements in hydrogenase activity. Now the project needs to determine if these mutants perform when put into a large mixed colony.
- The presenters have incorporated multiple pathways to increase hydrogen production in the presence of oxygen, including increasing promoter strength, creating fusion proteins, and modifying different sites on the protein.
- This project has begun investigating the more limiting aspects of hydrogen production from cells, connecting the oxygen-tolerant hydrogenase enzyme to ferridoxins. The interaction of hydrogenase with the cell supply chain is a far more limiting factor on hydrogen production than the activity of the enzyme. Hopefully this work will illuminate the supply chain limitations on hydrogen production.
- IPTG induction is likely to be costly on large-scale systems. The project should look at copper-inducible promoters (Himadri Pakrasi). It is not clear why seawater would be the best metagenomic resource for oxygen-tolerant hydrogenases. Also, the screening criteria and rationale for the identification of the clones of interest were not explained to indicate what features in the sequence indicated promising activity. If those sequence features could have been predicted, then rational design of hydrogenases and targeted mutagenesis of the native hydrogenase could have been pursued in parallel.

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.

- These are very good accomplishments to achieve increased evolution of hydrogen.
- This project reached the January 2013 go/no-go milestone earlier than scheduled. The rate of evolution appears to be only a two-fold improvement; however, the hydrogenase activity could be higher when time is not taken into account. The ferredoxin hydrogenase fusion protein milestone appears to be on track.

- The presenters have demonstrated that, by combining extra promoters and a double substitution, they achieved a factor-of-five boost in hydrogenase output that is not oxygen-sensitive. The many different pathways to achieve the project goals have been evaluated, and go/no-go criteria have been clearly defined.
- The project achieved excellent progress, especially in light of the collaboration between Weyman and Maness. The tasks are mostly at 100% complete; those remaining are on track. The scaling-up question remains an issue, but at this basic exploratory stage, it seems a premature question (brought up by previous reviewers). This type of research, though it has applications, is fundamentally basic research and as such cannot be expected to scale up. The quantification of hydrogenase activity, identification of novel "maturation" genes, and other accomplishments are impressive.
- The increase of two times the in vitro hydrogen production from the combined system was nice, but the actual function in the working cell is what is important. It did illustrate how hard the problem of photo-biological hydrogen production actually is. The ferredoxin mutants were encouraging, but it is not clear how the project has gone far along the path of improving "hydrogenase-ferredoxin (Fd) electron transfer to enable 25-fold better Fd docking to the hydrogenase" (it was listed as 20% done). The real performance metric should be enhanced hydrogen production by XY% through this approach.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration with the National Renewable Energy Laboratory (NREL) appears to be fruitful; it led to ferredoxin troubleshooting and improvements.
- This is a good team with excellent principal investigators, and the partners communicated and worked together to validate performance.
- It seems the collaboration between Weyman and Maness has been productive and resulted in exceptional achievements in both projects presented at this review.
- The roles of collaborators were not clearly defined.
- Previously, the program had direct ties to NREL, but the project and NREL's DOE Hydrogen and Fuel Cells Program Annual Merit Review presentations were separated this year with the implication that they still communicate. Researchers from the J. Craig Venter Institute (JCVI) are perfectly capable of pursuing this work, with or without external collaborators, and probably have colleagues with which to discuss approaches at JCVI.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Creating a non-oxygen-sensitive hydrogenase system is very promising and would contribute well to DOE goals.
- Biological hydrogen production is an incredibly complex problem. This work is focused on identifying the issues that surround this problem. This work will not solve the problem directly but must be combined with numerous other advances in cell modification if the problem is to be solved in the next 20 years.
- Oxygen tolerance is critical for biological hydrogen production, and this project has made advances in the science. However, how much of an impact these improvements would yield has not been identified since there is no indication or reference to any economic analysis.
- There are no attempts at scalability, and the work appears to be on the "long-term" trajectory (more fundamental in nature) towards the biological hydrogen production cost goal of $10/gasoline gallon equivalent (gge). This project has "quite a ways to go," as stated by the PI himself.
- The impact on basic science will be significant because of the exploration of promoters, genome sequencing contribution, quantification of hydrogenase activity, and the identification of causal mechanisms. The contribution to hydrogen production looks promising, but at such an early stage, it seems impossible to predict how this will scale up to the production level. It is unclear what the issue will be with strain contamination. It is unclear what will happen to cellular or organismal fitness when engineered for increased hydrogen production.

Question 5: Proposed future work

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

- The ferredoxin coupling and making the final cyanobacterial strain are important and will be addressed.
- The plans build on previous accomplishments, but until all of the modifications are put into a strain, the actual improvement over any of the previous work will not be known.
- The presenters have clearly defined their pathways for moving forward, including the evaluation of promoter strength and using light to drive hydrogen production.
- It is not clear that proximity of the hydrogenase to ferredoxin is the rate-limiting step to hydrogen production. If that is the case, it would be nice to know what the theoretical maximum rate would be to measure progress.
- The future work builds on the lab's success (which is substantial), as well as the work of others, such as Maness. This collaborative atmosphere and previous success bode well for future success. The techno-economic analysis will help identify promising directions and allow those which lack promise to be discontinued, which is a sensible way to mitigate risk.

Project strengths:

- The researchers have the knowledge, skills, and equipment necessary to achieve the project milestones.
- This project is clearly defined by the project goals. The previous results have demonstrated the researchers' ability to achieve their goals.
- This project is well planned, has clear milestones, has achieved some milestones, has productive collaboration, and has abundant resources to work with.

Project weaknesses:

- There seems to be some overlap with the NREL group.
- All the work of this project might make only minimal direct progress toward the ultimate goal of practical biological hydrogen production. Interfacing the hydrogenase with the cell supply chain is difficult and unlikely to be maximized in the near future.
- The project has not considered scaling, and it is unclear if the researchers have examined the fitness consequences of their engineering. Many of the reviewer concerns from last year have been addressed, with the question of scaling up via *ex vivo* to *in vivo* experiments being one example. Many concerns have not been addressed, such as the potential role of additive or pleiotropic gene effects on the desired phenotype. It is unclear if "forward screening" mutagenes is a non-starter. The gene stacking or redundancy may address some of these issues and others (e.g., Muller's ratchet).

Recommendations for additions/deletions to project scope:

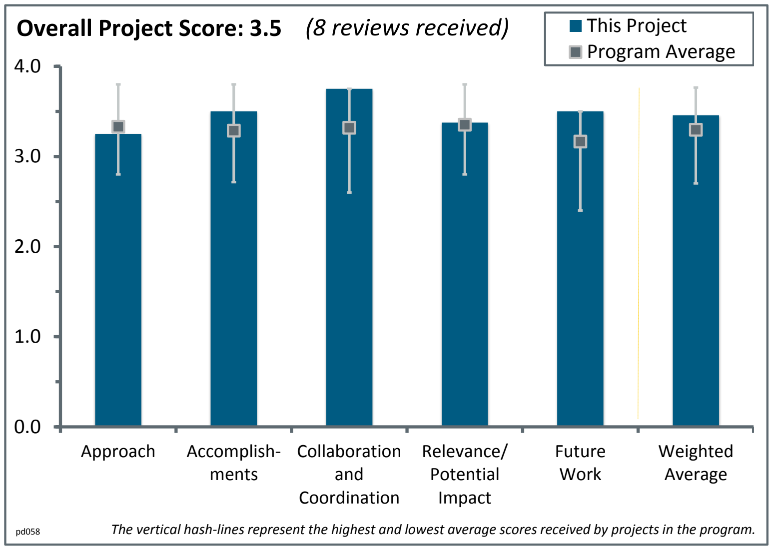
- This project should explore fitness under the parameters that are likely to be experienced by the organism in production.
- It will be important to measure other elements besides gene expression as controls for hydrogenase activities and parameters to modify for better activity. These can include protein folding assays, metabolic pathway optimizations (shutting down endogenous hydrogenases to elevate the relative levels of metal co-factors), optimizing localization of the protein, shutting down proteases, and other bioprocess engineering methods.

Project # PD-058: Characterization and Optimization of Photoelectrode Surfaces for Solar-to-Chemical Fuel Conversion

Tadashi Ogitsu; Lawrence Livermore National Laboratory/National Renewable Energy Laboratory

Brief Summary of Project:

The objectives of this project are to develop a theoretical tool chest for modeling photoelectrochemical (PEC) systems; compile a database of research publications on relevant photoelectrode materials; uncover key mechanisms of surface corrosion of semiconductor photoelectrodes; understand the dynamics of water dissociation and hydrogen evolution at the water-photoelectrode interface; evaluate the electronic properties of the surface and water-electrode interface; elucidate the relationship between corrosion and catalysis; and produce simulated x-ray spectra for interpretation of experimental results.



Question 1: Approach to performing the work

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

- This project is doing good work, which can provide important molecular insight into the process.
- The approach is broad and attempts to address a wide range of issues regarding PEC systems.
- The molecular dynamic simulation remains an important tool, as it simultaneously addresses the barriers for durability and efficiency. By comparison to empirically derived data, the models can be validated and become more efficient as predictive tools.
- This research is highly complementary to experimental efforts within the PEC working group, which certainly play into the approach of this project. That being said, the overall project approach on slide 6 that illustrates how theoretical/modeling tools are used in modeling PEC systems (and how different modeling tools relate to each other) was not clear.
- The efforts to simulate and computationally model the surfaces of III-V semiconductors under conditions of catalysis are the major thrust. Although commendable, this seems like a gargantuan effort that may be too large of a scope for this project. Notwithstanding, this research is highly integrated with other U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) PEC hydrogen production efforts and supports empirical mechanisms.
- Aligning the project as supporting the National Renewable Energy Laboratory (NREL) effort on III-V tandem electrodes is valid. The advancement of the theoretical methods appears to agree fairly well with the experimental data, but the goal would be to advance its predictive power to where it could advise the experimentalists. It does not look like the capability is there yet.
- Using computational methods along with an understanding of the basic physics involved in PECs could be an important driver of future discoveries. An analog to this is the rapid, wide-scale screening of chemicals for drug discovery used in the pharmaceutical industry. Material screening is important, and if it can be done theoretically and computationally first, this could save a lot of time and money, accelerating the pace of discovery. This approach applied to PEC could help this field become commercially relevant, which it struggles to do at this point.
- This numerical work integrating molecular dynamics simulations using water with density functional theory (DFT)-based semiconductor energy states has permitted first-time description of various phenomena

occurring at the electrolyte–semiconductor interface. The development of $PL_{2,3}$-edge spectra was compared with x-ray absorption spectroscopy (XAS) spectra and provided first-time experimental/theoretical state correlation and confidence in applications of DFT interface state calculations. A hole-trap corrosion mechanism that was proposed from numerical evidence and experimental evidence supported this hypothesis. Currently work is under way for further corroboration that could help find countermeasure treatments to stabilize the interfaces. This project is a collaboration with a much larger effort, but it has suggested some critical pathway solutions that might not have been discovered experimentally.

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

This project was rated **3.5** for its accomplishments and progress.

- This project has done a great job identifying and describing the corrosion mechanism and beginning to understand how to move hydrogen production using various materials.
- Excellent progress is being made for the level of funding received. Elucidating the influence of water structure on photocatalytic mechanisms and photoelectrode stability is of tremendous importance to the PEC field.
- This project has accumulated an impressive number of papers related to PEC. It would be good to see more detail on what exact online collaboration tools are being used to disseminate relevant information to partners. The identification of corrosion mechanisms is an important result, given its detrimental effects on experimental work and progress on PEC material system stability and durability.
- There was a narrow spectrum of objectives commensurate with the funding levels. The project successfully tested the hole corrosion model against data from NREL. The validation of the model against previous NREL data proves the efficacy of these techniques and provides confidence for future results. The project is continuing to build the theory to match the data generated from surface characterization from the Heske group.
- The systems being studied are relevant to present technical challenges in the PEC program. The principal investigator (PI) is looking at implanted nitrogen and “unintended metals,” which are directly supportive of other research projects. The investigator reported fascinating results on the relative ability of InP to transport protons laterally across an adsorbed monolayer of water molecules compared to GaP. It is unclear if those results can be applied to $GaInP_2$, or if that represents an entirely new level of difficulty in computation for which it is too early to tell. The project should also consider why, if the electrode is to perform in 3M H_2SO_4, it is important to have lateral transport of protons across the surface.
- A database of PEC-related research is in development and is currently archiving about 1,200 papers from which relevant information is shared with various PEC projects within the PEC Working Group. The hole-trap corrosion hypothesis has been confirmed by detailed interface characterization at both the University of Nevada–Las Vegas (UNLV) and the Advanced Light Source at Lawrence Berkley National Laboratory. Further confirmation was found through experimental evidence at NREL, and that early work is being expanded in collaboration with the theoretical and material characterization groups. Finally, the simulation of proton transport mechanisms at water–semiconductor interfaces has illuminated catalyst roles in PEC hydrogen release and has identified potential mechanisms for corrosion-resistant properties discovery.
- It is unclear from the Milestones slide exactly how far this project has progressed because the milestones do not contain dates. Notwithstanding, the percentages complete seem rather large, but the body of work seems somewhat scant. This group reports results on proton transfers at interfaces and corrosion mechanisms/attenuation on III-Vs.

Question 3: Collaboration and coordination with other institutions

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

- The collaborations appear to be clear, strong, and beneficial to all parties.
- Good collaboration is shown through technical accomplishments achieved this year.

- The PI is clearly trying to be supportive of PEC efforts elsewhere in the DOE Hydrogen and Fuel Cells Program.
- This project does a good job collaborating with the larger PEC Working Group and more specifically the NREL effort for III-V semiconductor material development and, additionally, the surface characterizations from the Heske group.
- This project has logical and productive collaborations with experimentalists within and outside of the PEC Working Group.
- This group clearly collaborates with others in the PEC Working Group. Recently, they extended their collaborative modeling efforts to copper-indium-gallium-diselenide (CIGS), initiated with the University of Hawaii and the University of Texas (UT), Arlington.
- This project is a wholly collaborative effort within the PEC Working Group, although only a few of the PEC projects have found ways to implement its supporting role. The coordination of theoretical/numerical effort with applied material needs has been outstanding. The additional coordination and collaboration with other theoretical groups has been initiated by this project in hopes of expanding both the level of effort and the numerical tools development.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- Support for the Hydrogen and Fuel Cells Program is relevant to the extent that the entire PEC program is relevant.
- This project helps move PEC technology towards understanding how to improve solar-to-hydrogen (STH) efficiency to the required levels.
- Current state-of-the-art materials do not simultaneously possess both good PEC efficiency and accompanying stability. These types of models are therefore essential for future development.
- The work being performed in this project is of great scientific and practical performance to this field. Further development of these computational tools could be invaluable for achieving accurate high-throughput screening of the stability and photocatalytic activities of photoelectrode materials.
- This group is modeling the catalytic and stability effects of various semiconductors. This research will help support mechanisms in PEC devices, but it is on the fundamental end of the research continuum. This research synergizes well with the surface chemistry team at UNLV and PEC efforts at NREL.
- The objective of developing a theoretical tool chest for modeling PEC systems is important. A sharper understanding of the physical mechanisms involved can help steer experimental researchers in the right direction to arrive at meaningful results more quickly.
- As a stand-alone effort, this project would not provide directly relevant support to achieving the Hydrogen and Fuel Cells Program objectives. On the other hand, coordination of theoretical/numerical studies with applied research and development efforts has resulted in outstanding progress in both understanding and reducing obstacles to PEC. In this sense, the effort has outstanding potential for relevance and a potentially large impact.

Question 5: Proposed future work

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

- It is good to see an interest in transitioning to Approach Two materials.
- The proposed future work is presented but lacks specifics and dates; in addition, there is no mention of decision points.
- The future work is clear and topical. There should be more detail on the public dissemination of the physical model of PEC physics.
- The first three milestones relate to the stabilization of the III-V semiconductor via surface nitriding. The demonstration of durable III-V PEC materials would be a significant accomplishment, and these models may just offer the necessary insight to provide a pathway towards success.

- The proposed projects are appropriate, although the value of investing too much time in investigating CIGS-based photoelectrodes is questionable because of stability concerns. The proposed work on understanding how the water structure and associated proton mobility influence reaction mechanisms is a very timely and potentially important subject, as is the dynamic modeling of photoelectrodes under bias.
- The proposed future work is in strict coordination with the focus, reflecting requested simulations in support of current PEC projects. Continuing validation studies are essential, and these are reflected in the proposed work. CIGS is becoming a central material, and CIGS studies are reflected in the proposed work. The relationship between hydrogen evolution and corrosion is thought to be strong, and the effort is proposed in order to illuminate this process. Modeling interface materials under bias will be a unique achievement with potentially enormous implications to process understanding and control.
- There needs to be more effort on milestones four and five, which are critical in understanding how to push STH levels out and have a robust system. This project should continue to try to understand the GaP and InP variation and mechanism.

Project strengths:

- The project, if successful, may set the groundwork for an accelerated discovery in PEC.
- This is a valid effort trying to adapt *ab initio* DFT molecular dynamics to the semiconductor/electrolyte interface.
- This project fits well with the overall fuel cell strategy. The project is developing a set of criteria to better understand the materials and the selection for PEC.
- This project has outstanding technical capabilities, facilities, and collaborative efforts.
- This research is highly collaborative and completes a strongly synergistic effort between surface/materials characterization, PEC function, and computational modeling/simulation.
- The development of corrosion models continues to improve and compare favorably to the empirical data. As general concepts are developed, they hopefully can be successfully parlayed to other promising PEC materials such as SiC and CIGS.
- The core competency of the PIs in applying *ab initio* DFT and molecular dynamics (MD) simulations to PEC systems is evident, and fruitful collaboration with experimental partners has been established.

Project weaknesses:

- It is important that the modeling effort be widely available and vetted through experimental validation.
- It would be good to see more specific priorities on the future work and where the effort will be focused.
- The computational resources and level of effort are constrained by concerns over funding levels and continuity.
- Some of the proposed future work items are vague, and it seems like this project is pulled in many different directions.
- The predictive power appears great enough to simulate spectra fairly well, but the project may not yet be able to model a PEC system complex enough to explain experimental results.
- The latest results are not as impressive as those in the 2012 DOE Hydrogen and Fuel Cells Program Annual Merit Review report. The modeling effort is commendable, but it seems like a large and complex undertaking that may require additional team members and funding. It may not be worth adding this to the PEC hydrogen production portfolio.
- The scope of this project is well thought out and sufficiently narrow to maximize the probability of success. The models appear to be for binary InP and GaP when they need to be expanded for the $GaInP_2$ system and compared to empirical data from NREL.

Recommendations for additions/deletions to project scope:

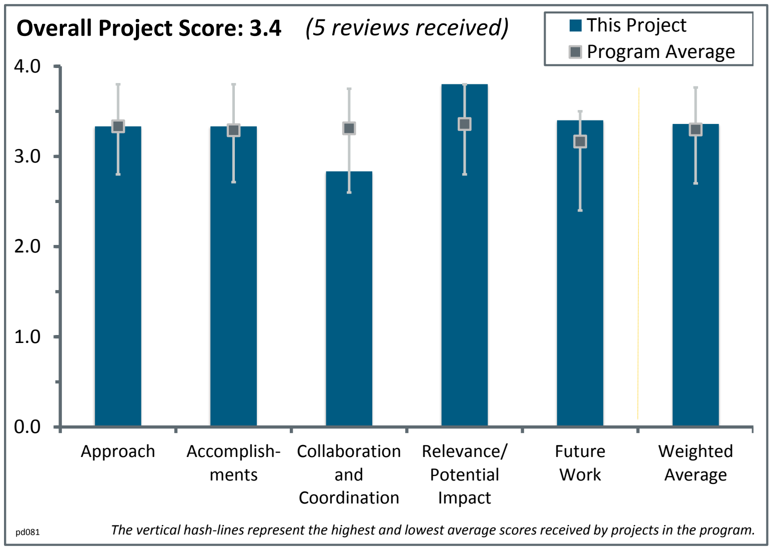
- This project should seek additional support from fundamental research agencies to expand the "influence region" of the simulations and to add quantum dynamics simulations to the liquid phase.
- This project can clearly identify milestone targets and systems to explore. There does not seem to be a clear path for the next step in the studies. Also, this project should include the specific next steps in the CIGS

collaboration. Major technical challenges and the proposed means to overcome them should be clearly spelled out.

- The science behind the photo-corrosion of a cathodically protected surface is quite interesting. As with any model, the efficacy needs to be proven against empirically derived data. This has been met with success for the binary InP and GaP system. There is a real opportunity to develop the theory against real experimental data on the $GaInP_2$ material, and in the short term, this should be a narrow focus. The nitrided surface provides a second opportunity to test the model with a more complex surface structure.
- Although the initial efforts have focused on just a few materials as computational methods are developed and refined, extension of this work across many materials, in conjunction with experimental efforts to demonstrate the potential predicative power of these modeling efforts, would be extremely powerful. This includes trends in surface catalytic activity, susceptibility to corrosion, and energy band alignment. To date, it seems that much of this work has been driven from the experimental side, but as modeling capabilities are refined (as it seems they have been), it would be nice to see the opposite occur. Similarly, close collaboration with experimental efforts to validate modeling results on the surface hydrogen bond network and photoelectrode operation under bias should be pursued.

Project # PD-081: Solar Hydrogen Production with a Metal Oxide-Based Thermochemical Cycle

Tony McDaniel; Sandia National Laboratories



Brief Summary of Project:

The objective of this project is to develop a high-temperature solar thermochemical (STCH) reactor and redox materials for efficient hydrogen production based on a two-step, non-volatile metal oxide cycle. The 2012–2013 objectives include designing and assessing the feasibility of particle receiver–reactor concepts; discovering and characterizing suitable materials for two-step, non-volatile metal oxide thermochemical cycles; and constructing and testing reactor prototypes.

Question 1: Approach to performing the work

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

- The approach seems to be very "Edisonian." The project would benefit from investigating why certain perovskites behave the way they do.
- This project has made good progress on perovskite evaluation of redox kinetics and showed good progress on synthesizing targeted materials.
- The project addresses one of the crucial points for reaching the theoretical efficiencies of thermochemical hydrogen production. The use of a vacuum instead of flushing gases has the potential to achieve real breakthroughs, as well technical benefits, such as reducing the operational cost of the process. The approach to achieve this is excellent.
- The approaches presented in the project, including analysis of the hydrogen production cost using the Hydrogen Analysis version 3 model (H2A), materials discovery, and reactor design, are very effective for accomplishing the project objectives and the U.S. Department of Energy's (DOE's) targets for the STCH hydrogen production pathway in the longer term.
- The materials program is mining perovskites for new high-temperature STCH cycles and has rational scientific design principles to guide the search for useful perovskites. This is an excellent approach that moves away from the simple monometallic or bimetallic phases pursued in the past to find novel materials with optimum properties. The reactor program addressed a variety of issues, but not high temperature reactor operation. The other issues are unimportant if the reactor system does not operate at high temperature. For this reviewer, the materials approach earns a 4, and the reactor approach earns a 2, for an average of 3.
- This project has established a comprehensive approach to achieving program objectives and targets by integrating active materials discovery with receiver reactor design. Both of these tasks were thoroughly justified by outstanding analysis of performance requirements, including overall solar-to-hydrogen efficiency targets, requisite heat recuperation, and material thermochemical activity to meet those targets. The performance testing is either under way or planned for each of those critical issues, and alternative materials and design options have been planned in response to performance testing. A design concept for solar collection and concentration has been developed and offers a relatively inexpensive pathway to prototypical on-sun testing and demonstration.

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.

- More work needs to be done on materials discovery. It is not clear if a low-bed permeability can be maintained as the reactor is scaled up.
- The proposed reactor concept could feasibly solve the issue of avoiding flush gases and, therefore, raise the efficiency of the thermochemical hydrogen production significantly. Through the possible increase of efficiency, it seems realistic that DOE's goals for hydrogen production costs are achievable.
- There was good progress reported on this work. The hydrogen production cost analysis done on this project demonstrated that, for central hydrogen production (100,000 kg/day), the STCH pathway can meet DOE's ultimate cost targets. This project has made good progress on the materials discovery work.
- The materials portion of the program took a major leap forward this year with the discovery of a perovskite material that appears to perform substantially better than the CeO_2 standard with regard to oxygen capacity, oxygen mobility, and lower reduction temperature. The H2A analysis suggests the system is close to the 2020 DOE hydrogen cost target. The reactor system was demonstrated to have sufficient particle transport rates to cycle the process and adequate bed sealing to keep hydrogen and oxygen separate at low temperatures. After five years in the project, it is surprising that high temperature operation has not been demonstrated, although this aspect was described as a 2014 activity. In addition, a moving particle system will exhibit particle attrition; this issue and its impact on reactor system performance have not been studied.
- Outstanding progress was exhibited in receiver–reactor analysis and design, and prototype operational component testing is under way. At least two materials have been formulated for thermochemical activity testing, including one baseline material with enhanced performance via zirconium doping. A large class of perovskites was selected for the materials discovery effort, and the number of potential materials was significantly reduced by selecting materials with three characteristics for further investigation. Forty-five perovskite candidates have been synthesized for screening by thermogravimetric analysis for thermochemical activity and reaction kinetics studies.

Question 3: Collaboration and coordination with other institutions

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

- There is not much evidence of collaboration during this phase.
- This project has good collaboration in the areas of materials discovery and on the economic analysis.
- It seems that the partners are very well connected. A clear synergy exists in the coordination of receiver–reactor development material issues and solar concentrator layout and development. All the tasks jointly used development models that predict the performance of the technology. Based on the presented results, the data used seems to be very reliable, and therefore the collaboration and integration seems to be close to perfect.
- The coordination between materials researchers and between reactor researchers separately appear robust. It is not clear how much interaction there is between the two groups, but it is clear that the new materials will feed into the test reactor program in the future.
- The project exhibits close cooperation with its partner, but the coordination of efforts by the partners is less than outstanding since each is pursuing a different class of materials and each appears to be planning distinct receiver–reactor designs. The partnership appears to be a result of necessity rather than a joint collaborative pursuit of the common overall program objective.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.8** for its relevance/potential impact.

- The costs and work presented are in line with the overall goals of the program.

- This work is very relevant to DOE's research and development efforts and targets long-term central hydrogen production pathways.
- The project has a very high potential to substantially contribute towards achieving the DOE targets for renewable hydrogen production. It is likely that it will lead to significantly reduced hydrogen costs compared to the current state of the art.
- This program addresses the long-term goal of moving to renewable hydrogen sources in the 2020–2030 time frame. STCH approaches have fallen short in the past, and this effort seeks to combine a new reactor system for a two-step metal oxide cycle based on novel perovskite materials to overcome traditional obstacles. Both components of the system appear promising and show evidence that they possess superior attributes to competing STCH approaches.
- Uncertainty remains in terms of the level of perovskite thermochemical performance, but given the success in the materials discovery effort, this project will provide a viable solar-powered thermochemical hydrogen production path. Since perovskites are only one of many other materials options, the overall approach in this project offers considerable promise to achieving the ultimate STCH program goal.

Question 5: Proposed future work

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

- The proposed future work is well conceived as a follow-up to current activities and is well focused on barriers targeted by current work.
- The project is very well focused. The next steps are logical. The project plan seems to be appropriate for effectively achieving the goals.
- The proposed work seems to be reasonable and provides a good plan for addressing the barriers associated with the STCH pathway. The continuation of the materials R&D work plus the sensitivity studies on the cost analysis will be of great value to this work.
- The team needs to focus on more materials discovery. The team seems to be placing too much emphasis on reactor details and design.
- The materials effort has only scratched the surface of perovskite potential, and continued efforts in the area as described in the plan are demanded. The reactor system must be tested at high temperature going forward to look at the effects of particle attrition on system performance and the impact on oxygen release and hydrogen production reactions. Even if the metal oxide changes over time, the physical impact of particles moving through the system and changing must be studied.

Project strengths:

- This project has outstanding technical proficiency, facilities, and project work planning.
- The STCH hydrogen production pathway is highly relevant to DOE's efforts toward longer-term hydrogen production pathways.
- The current materials approach is excellent. The reactor system design promises peak performance. The team appears to have the resources to accomplish goals and is performing well.
- This project is taking a practical approach to reactor design. Good progress was made on the synthesis of candidate materials.
- The project is based on an excellent concept, tackling one of the key factors for reaching very high theoretical efficiencies of two-step thermochemical hydrogen production by avoiding additional gases. The partners are world-leading scientists, and the synergy between them is obvious.

Project weaknesses:

- The collaboration with other researchers in the field is weak.
- This project must demonstrate high temperature operation of a reactor system prototype long enough for problems to develop. The problems may depend on the metal oxide chosen for the cycle.
- The presented simulations are based on solar dishes, which are inappropriate for the proposed technology. The concept of the proposed receiver–reactor seems to be feasible; however, moving parts at very high temperature with a temperature gradient over the moving parts is probably tricky to realize.

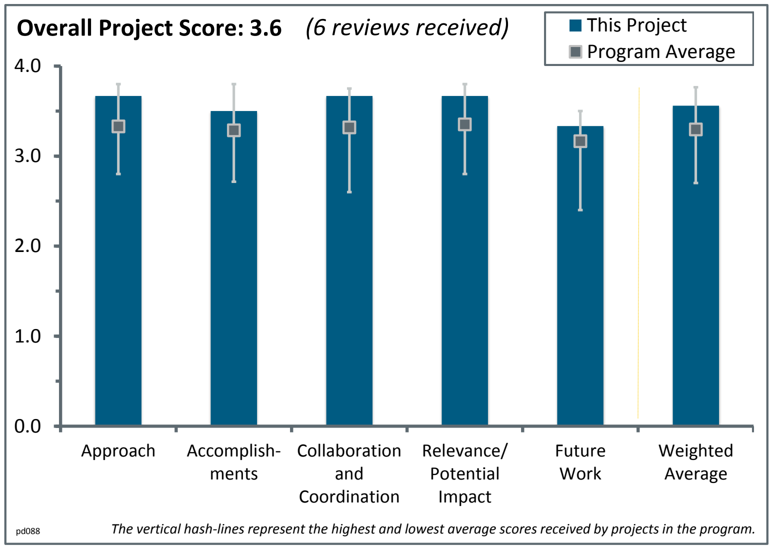
- It seems that maintaining particle size control is very important for the reactor to operate effectively. The durability of the material will be of key importance, as it is conveyed and continually cycled through the reactor. It was not apparent that any testing was being conducted to verify and ensure particle stability of the perovskite material under heat and impact, as will be the case in the actual process as the material moves through the auger.

Recommendations for additions/deletions to project scope:

- The project should make a concerted effort to bring in other institutions and individuals to participate in a broader, well-coordinated effort.
- This project needs significant experimental reactor work at operating temperatures and a probabilistic assessment (using H2A analysis) to see the probability of the project meeting the targets. For instance, in the current assessment, the solar-to-hydrogen efficiency changes from 6.2% to16.7%; it is unclear whether the probability of that actually happening is 10%, 50%, or 90%.
- H2A analysis should be performed for a solar tower/heliostat field arrangement and compared to analysis done for the solar dish scenario. The reflector geometry should be optimized by using ray tracing for a specific location over a full year to maximize the annual output of the system.

Project # PD-088: Vessel Design and Fabrication Technology for Stationary High-Pressure Hydrogen Storage

Zhili Feng; Oak Ridge National Laboratory



Brief Summary of Project:

The objectives of this project are to address the significant safety and cost challenges of the current industry standard steel pressure vessel technology and to develop and demonstrate the steel/concrete composite vessel (SCCV) design and fabrication technology for stationary storage of high-pressure hydrogen. Integrated vessel design and fabrication technology should use commodity materials (e.g., steels and concretes); mitigate hydrogen embrittlement to steels; and develop advanced, automated manufacturing of layered steel tanks.

Question 1: Approach to performing the work

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

- This project is a very novel use of a combination of technologies (concrete and steel) to deliver a cost-effective storage system. There is a good focus on reducing the cost of the complete system.
- The approach the project team is taking is excellent. The long study and cost analysis phases seem to have allowed the project to develop such that the next phase (that includes fabrication) will benefit from findings that the team has developed over the past two years. The approach to developing an ASME code case is very good.
- The technical approach is excellent, but the presenter and project could make a stronger reference to the fact that layered steel tank technology is already in use at refineries for gaseous storage, per the presenter's feedback during the question and answer session. He addressed hydrogen permeation through different layers and venting this hydrogen off (low quantities at near-atmospheric pressure). Although the interior storage volume is currently calculated at room temperature, the project should consider what the realistic capacity is when system tanks are in operation in an underground concrete set-up, which is most unlikely to operate at room temperature. Compared to above-ground storage, this is a much more stable environment that could have a positive impact on the cost of hydrogen dispensed due to the decreased requirements for pre-cooling.
- This project covers low- (160 bar), moderate- (430 bar), and high- (820 bar) pressure storage operating regimes and efforts that should be focused on addressing industry needs within the range of moderate- to high-pressure storage. There were also a wide range of vessel designs, and it is unknown if site fabrication is required for the largest (564 kilogram) design.
- This project is an excellent and novel, low-cost concept for stationary storage. Since the material cost is often the most sensitive parameter, significant attention must be paid to minimize the use of expensive materials. Although this was considered—for example, in Cases One through Three—no effort was made to consider varying the steel wall thickness by component. For example, the steel layer in the center shell of Case Two does not need to be as thick as the heads. A slide showing simply how much money could be saved from varying the wall thickness in lower-stress regions of the structure should be presented. The "leak before failure" approach is much appreciated. Joule-Thomson expansive heating of hydrogen through small leaks/cracks needs to be considered, as this has been a cause of explosions.

- In regard to installation at the station, there are excavation issues, costs inclusive of excavation, and installation code cases. It is unclear what the value is in terms of station footprint reduction, how leakage through the permeation barrier gets measured, and if leakage is monitored throughout station life. It is also unclear what the process is for end-of-life remediation/disposal and if this is a mild or significant issue. Other issues that need to be better explained include the cycle life of the vessel; lifetime cost effects; the benefits this reinforcement method has over other techniques, such as carbon fiber wrapped Type-I vessels; and how much additional cost savings are projected or available to offset other station costs. The material permeation tests will contribute value beyond this project.

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

This project was rated **3.5** for its accomplishments and progress.

- The manufacturing cost analysis was very good and seemed complete.
- This project has clear accomplishments towards the objectives of the project.
- This project appears to have made consistent and continuous progress over the past three years. The project is on track to initiate scaled prototype testing. This is a textbook example of taxpayer dollars well spent.
- This project has made good progress so far on the development of the system. The project needs to move quickly to demonstrate the system’s proof of concept with inert gas and then hydrogen.
- The fabrication complexity and the cost of the layered vessel should be better understood. This project needs to establish details regarding a step-by-step manufacturing process for layered vessel design. More clarity is needed on the mock-up vessel design that will be used for the demonstration program, and the expected cost of the new vessels should be benchmarked against the cost of commercially available steel and composite ASME storage vessels.
- The biggest cost is vessel heads. It is unclear what is being done to address this in lieu of discarding 30/70 and if there is there any room for further cost reduction. The project should consider if the manway can be eliminated in favor of cameras or other probe-type inspection techniques. The project should also consider how manufacturing techniques can be improved to reduce the pre-stress part of the process. This project has excellent designs for experiments with hydrogen permeation tests.

Question 3: Collaboration and coordination with other institutions

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

- The collaboration and coordination requirements were met.
- This is a great assembly of contributing expertise partners. It is good to see Oak Ridge National Laboratory did not try to do this solo.
- There seems to be a good coordination with the project partners, and the approach to develop an ASME code case is very good.
- All collaborators appear to play a valuable role, but it is not completely clear what the contribution from the Department of Transportation (DOT) was besides funding, as the qualification approach to the storage vessel was not explained.
- This project has included professional organizations that regulate standards (ASME, DOT), academia (University of Michigan), and businesses representing a range of sizes.
- This project does not include collaboration with existing ASME vessel manufacturers.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.7** for its relevance/potential impact.

- This project is key to reducing the cost of stationary hydrogen storage, and it is projected to surpass the DOE objectives.

- The research and development activity involving innovative high-pressure ASME storage vessels is required to achieve long-term DOE cost targets in the area of storage.
- The hydrogen storage on the forecourt is a key cost to reduce in order to achieve the DOE goals outlined in the roadmap. This project focuses on one of these key barriers.
- The reviewer is looking forward to the outcomes of 2013 and 2014 activities, as the results show clear progress towards the targets. The potential of this product is clear, even if it was only that the lessons learned became available to manufacturing companies.
- The total weight of the storage system, the cost and practicality of shipping the complete vessel system, and the cost of site work if the components are shipped to the site for integration all provide some reservations.
- The project has made a very good effort at meeting cost goals. The opportunity to further reduce costs is important, as other station elements are cost-challenged. The impact on station footprints may be good but needs further reviewer comment and valuation. The project should focus on finding out what the impact is of the full cost, including installation, testing, maintenance, station model cost and the percentage of overall cost reduction, and the possible offset of other station costs. The project should also discuss the cost impact of using manways versus alternative vessel inspection techniques, the reliability of manway seals, and the inspection requirements. According to the oral presentation, approximately 25% additional cost was added to the header for a manway. The project needs to provide more detail on hydrogen interlayer collection and venting. It was unclear how the millimeter-sized holes were arranged, how this affects cost, and if there is an optimum arrangement. In terms of manufacturing cost mitigation for pre-stressing, it was unclear if and how volume and automation will reduce the cost.

Question 5: Proposed future work

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

- The reviewer is looking forward to seeing the results from the demonstration of the mockup SCCV design.
- This is a good plan for work for the future. This project should make sure there are no thermal effects that may interfere with the layered concept as a result of differential thermal stresses.
- The completion of the engineering design of mockup SCCV is necessary to move the vessel concept to the demonstration phase. A go/no-go decision point needs to be considered before any technology validation is conducted.
- This project has a clear path towards technology demonstration and transfer. It would be good if a location and demonstration project partner could be lined up before the next DOE Hydrogen and Fuel Cells Program Annual Merit Review (AMR); otherwise, the project should be expected to be delayed in 2014/2015.
- This project needs to address installation in more detail, from the code case to installation costs to benefits/problems. This project needs to comment on cycle life and lifetime costs and create a detailed manufacturing plan.
- The only limitation preventing a rating of four here is the lack of concrete plans for the prototype testing phase. For example, it was unclear if a site and primary contractors have been selected. There was a general lack of specifics on future safety analysis, which is key to the successful implementation of the vessels.

Project strengths:

- This is a simple concept for storage that has great potential to reduce the cost.
- The cost of hydrogen storage appears to be quite competitive with conventional storage technologies.
- This is a practical focus on low-cost and common materials for reinforced high-pressure storage, coupon diffusion testing, and scale-up of the test plan.
- The project involves a novel approach to hydrogen storage, and the project team has followed a methodical approach throughout the project development.
- This project has excellent communication of the cost and potential for improvement. The low-cost enabling technology and careful consideration of cost and failure mechanisms up front are strengths.
- The use of common materials shortens the typical station storage equipment delays due to long lead times of more exotic materials and the availability of manufacturing equipment. Project strengths include the proposed underground storage instead of above-ground storage, as well as involvement of well-established

industry. This project should be testing and prototyping actual equipment and material resourcing, not only modeling and making assumptions.

Project weaknesses:

- This projects needs to move to demonstration testing.
- This project should focus on a single vessel, including demonstrations.
- The cost and weight of shipping the complete storage system seem to be prohibitive.
- There is no narrative presented for installation costs, and an installation code case is not presented.
- There is a lack of consideration for variations of steel wall thickness in a given tank section (shell or end caps). More careful analysis of the safety hazards posed by small tank leaks is needed.
- With a wide range of storage volumes proposed, it is unclear if these vessels are planned to be shop- or field-fabricated, or a combination. The cost analysis should extend beyond the vessel design and should include the total cost from manufacturing, site installation, and ongoing operation and maintenance.

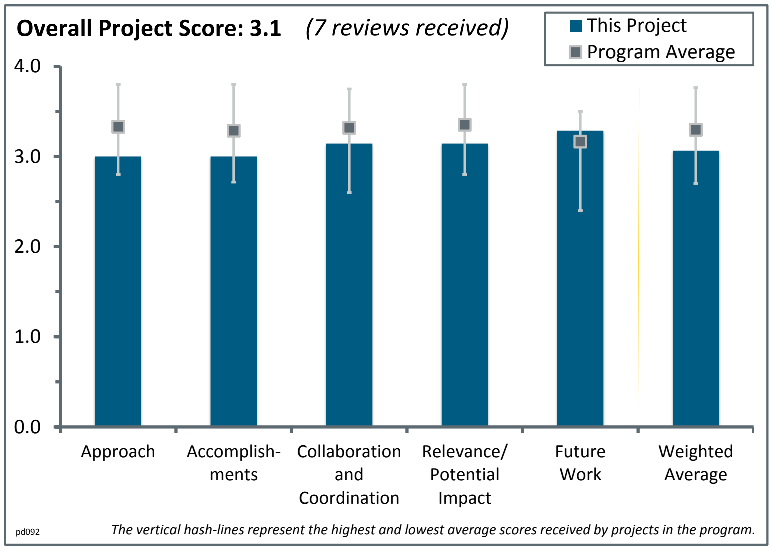
Recommendations for additions/deletions to project scope:

- There are no changes recommended for this project.
- This project should focus in the area of high-pressure (820 bar) storage.
- This project should consider an installation cost study and installation code case manufacturing plan detail.
- This project should consider a potential for variations in steel-wall thickness in a given tank section (shell or end caps). This project should include an analysis of flammability risks posed by small tank leaks. This project should also include identifying a test site for a prototype system and identifying contractors to move into a prototype development phase.
- This project should consider a smaller-size storage tank as well as a future economical option, as there is a limited variety of options in the market for smaller–capacity-size hydrogen stations. The lead time for typical FIBA Technologies tanks is significant and is limited by a minimum purchase order amount. These could also be used for renewable energy storage in the form of hydrogen. The project should consider smaller-size storage tanks in a “multiple tanks together in concrete” setup/demonstration. For the 2014 evaluation on the feasibility of material operations, this project could add a small layer of hydrogen-impermeable polymer on the outside, between the concrete and steel, to create a sufficient barrier to hydrogen, resulting in a manageable hydrogen vent stream. This could allow for increased use of lower-cost steels in more layers. For cost quotes, this project should consider requesting quotes for 1, 5, 10, and 100 steel vessel shell/head units. It is not clear if DOE targets for this project assume hundreds of units.

Project # PD-092: Rapid High-Pressure LH2 Refueling for Maximum Range and Dormancy

Salvador Aceves; Lawrence Livermore National Laboratory

Brief Summary of Project:



Hydrogen refueling is limited by onboard heating and power and capital at the station. A high-pressure liquid hydrogen (LH_2) pump can resolve the refueling challenges, as liquefaction is accomplished upstream and onboard cooling is not required. The LH_2 pump provides rapid fueling at a high density and low power use, and it makes cryogenic refueling practical. This project verifies LH_2 pump performance up to 350 bar by determining LH_2 fill time, onboard density, refueling efficiency, and Dewar boil-off.

Question 1: Approach to performing the work

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

- This project has a good approach to deliver cryogenic (cryo)-compressed hydrogen for refueling.
- This project demonstrates other methods of compression. The project partnerships include several industry partners. The design uses several simple mechanical advantages in cryogenics and thermal dynamics, allowing the total system to reach its performance targets. At the end of the project, a higher pressure is still required to address the technology gaps identified by the DOE Hydrogen and Fuel Cells Program (the Program).
- The team is doing nice work, and the application is justifiable. It is recommended that the project bring in other vehicle manufacturers to bolster the commercial relevance of the team's efforts.
- Although the presentation was not on target, the research approach likely is, and it is the role of the reviewers to differentiate the two in this case. Whether they are ready or not, Dr. Aceves has the responsibility to present an unbiased comparison of cryo-compressed hydrogen technology so that U.S. researchers may understand the benefits that researchers abroad have been pursuing for years. In order to do this, it is recommended that the project make the following changes for future presentations: (1) Immediately present a figure showing a plot of cryo-hydrogen fueling technology cost versus hydrogen density (add in the cost of liquefaction as a secondary point of reference). No other technology comes close on density. Questions remain about how the capital and operating costs compare and the eventual cost floor for the technology. (2) The project should break the system cost down by component to understand where the money needs to be spent and (hopefully) why the project is investing in the high-pressure pump. (3) After the project knows where the potential for improvement is, the researchers should make a pitch for what they are specifically doing and how this is distinctly different from other prior work, such as BMW's. (4) The project should then showcase the progress/accomplishments.
- The approach is unclear. This may be owing to the project title and the lack of a brief description of the envisioned processes.
- The concept is to fuel vehicles with high-pressure LH_2 to enable reliable, fast, low-cost refueling of hydrogen fuel cell electric vehicles (FCEVs). The Linde LH_2 pump technology being investigated appears to be state of the art and designed to minimize hydrogen boil-off. This is a good approach to charging high-pressure LH_2. The question is whether charging LH_2 is the best approach to fueling FCEVs. On a well-to-wheels (WTW) basis, liquefying the hydrogen consumes a lot of energy. This energy use results in a relatively low WTW energy efficiency and emits a lot of CO_2, unless the energy is sourced from an

electricity grid with low carbon emissions. A low-carbon-emission grid in the United States is, at best, a long way off. This approach to hydrogen refueling also results in a variable amount of hydrogen in the tank at the end of refueling, depending on the temperature, pressure, and amount of hydrogen in the tank at the start of refueling. Vehicle owners may not accept this situation. The approach to the testing the Linde LH_2 pump appears to be appropriate. The Linde LH_2 pump system appears to have the potential of a 1%–3% hydrogen boil-off loss from the pump and additional boil-off from the LH_2 storage tank. A 3% loss of hydrogen at the refueling station, after liquefaction, has a significant detrimental impact on WTW energy efficiency and cost. When the presenter was asked about this, it was suggested that the refueling station would also have high-pressure gas delivery. The boil-off would be captured and compressed for high-pressure gas delivery. This solution would solve this problem but would require both delivery systems at the refueling station and a hydrogen fuel cell vehicle fleet that would want both types of refueling. This is a lot to ask.

- The cost viability is ignored and should be included. This is a good technical plan, but the presentation does not tell why this is important and what is being done, other than what industry could already do. The building of a refueling system is important for demonstrating the technology, but the work does not show what is being done differently and what obstacles are identified and being worked on to be overcome.

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.

- This project is doing well and has much potential to satisfy DOE’s objectives.
- The accomplishments and progress of the pump are very good, but it is unclear when there will be actual H70 data available.
- This project has made good progress on using both Linde and BMW technologies to address an issue important to DOE’s hydrogen delivery technology team goals.
- The site for the installation has been prepared, and a section of hose has been successfully tested and approved for use. This seems like a very modest level of accomplishment after 1.5 years.
- Waiting on construction should not be a limitation; it is an opportunity to complete significant planning, modeling, and independent subcomponent validation. Careful planning could increase the number of minor accomplishments during the laborious construction phase.
- Thermal dynamic models indicate the mechanics will allow the cryogenic pump to meet the performance metrics. In March 2013, BMW started construction of the demonstration facility, presumably with DOE funds. Commissioning of the station will be completed shortly before testing the actual conditions. This is an excellent approach to proving the theoretical approach and ensuring project completion while also ensuring the safety of operation at industry partner locations.
- Since the past year’s scope was primarily about building the infrastructure for the future work, excellent progress was made in building the fueling station. The tests are evaluating a simple piece of equipment (the pump) and not really an improved pump design. There was no cost-effectiveness evaluation.

Question 3: Collaboration and coordination with other institutions

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

- These partners are quite knowledgeable in this area.
- This area deserves more attention; otherwise, the project represents government funding to help one foreign vehicle manufacturer, which ultimately will not work.
- This project has done good work with their partners, but there is no indication of which partners are addressing issues to make a better system.
- Although two industry heavyweights and a composite company have been included, no connection with academia was made. The United States is disastrously low on graduates trained to handle and design components for cryogenic hydrogen. This is an opportunity to begin fixing that problem.

- Working with BMW to construct refueling facilities that use cryogenic hydrogen to validate this ability is an interesting approach (i.e., 80 grams per liter density). This will provide reliability data that currently do not exist. Operators will be able to gain many data points for use when optimizing future stations.
- There is excellent collaboration with Linde, who developed this LH_2 pump, but this is the only collaborator. The project lists Spencer Composites as a collaborator, but it is not clear what the company's role in this project is.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.1** for its relevance/potential impact.

- This project is in alignment with the project goals.
- Past modeling efforts indicate the facility will meet the projected targets. Facilities construction and demonstration will validate the concepts and allow future concepts to be economical and be fully tested with the baseline station requirements.
- The "good"" rating was awarded for the promise of the technology, not for the presentation. The problems with the presentation can be summed up by relevance. The prior research completed by BMW and others clearly shows the relevance. However, the progress on this work has not independently contributed anything that differentiates this work from the prior work, aside from pressure-testing a stainless flexline at cryogenic temperatures.
- Without identifying the technical barriers that this station will be used to address and overcome, it is difficult to see what new technology will be developed.
- It is not totally convincing that LH_2 dispensing is a practical solution for FCEVs, but it is much too early to make that decision.
- With the exception of BMW, it is not clear if anyone is seriously thinking of having LH_2 on board. However, an inexpensive and robust cryo-pump is relevant. It would reduce pressurization costs by at least partially pressurizing the hydrogen as a liquid prior to vaporization. Vaporization on board in the vehicle fuel tank may be a challenge because of the material properties of the various building materials.
- The concept behind this project is to fuel FCEVs with high-pressure LH_2 to enable reliable, fast, and low-cost refueling. Charging LH_2 to the vehicle does result in lower-cost refueling stations. The question is whether charging LH_2 is the best approach to fueling FCEVs. On a WTW basis, it takes a lot of energy to liquefy the hydrogen. This also adds substantially to the cost of the hydrogen (about $1/kg).The energy use results in a relatively low WTW energy efficiency and emits a lot of CO_2, unless the energy is sourced from an electricity grid with low carbon emissions. A low-carbon-emission grid in the United States is at best a long way off. Most car manufacturers developing FCEVs intend to commercialize using 700 bar gas storage on the vehicle. This approach is less costly, more energy-efficient, and lower in carbon emissions than a cryo-compressed LH_2 system on a WTW basis—although it has much lower volumetric efficiency for storage on the vehicle. This approach to hydrogen refueling also results in a variable amount of hydrogen in the fuel tank at the end of refueling, depending on the temperature, pressure, and the amount of hydrogen in the tank at the start of refueling. Vehicle owners may not accept this situation.

Question 5: Proposed future work

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

- This is a good plan to demonstrate technology at the lab.
- It is outstanding as long as the fuel is to be transferred into the vehicle as a gas.
- Funding should be continued and, if possible, increased to maximize the testing program.
- This is a good solid work plan, but more emphasis is needed on overcoming the identified technical obstacles, and a cost model is critical for the program direction.
- No clear justification was made for the need to make new density measurements or a complete performance characterization of the pump. If the entire point of the project was to extend this system for operation at higher pressures, it is unclear why the project waited to construct the high-pressure vessel.

- The design will allow for future technologies to be integrated simply. Running the system provides answers to reliability. High-pressure cryogenic dispensing will allow longer vehicle ranges as a result. However, boil-off losses for cryogenic storage are still quite expensive. It is unclear how the future work reduces boil-off losses.
- The work plan calls for constructing and assembling a complete system to test charging LH_2 using the Linde pump in a vehicle-type cryogenic vessel. Temperatures, pressures, flow rates, and power will be measured. This will first be done at 350 bar and then with a system designed to be capable of 875 bar. This is a good plan, but the experimental set-up may not be able to accurately measure the boil-off of hydrogen, which is a key issue relative to the success of this approach for fueling FCEVs.

Project strengths:

- The pump design is a strength of this project.
- This project provides added value to longer-range vehicle performance.
- This project uses some commercial, near-developed technologies to apply to the Program.
- The partnerships and the speed and efficiency with which the project is being conducted are strengths of this project.
- This is a solid extension of the prior research completed overseas. Given the difficulty and scale of the project, it is appropriately located.
- The Linde LH_2 pump technology being investigated appears to be state of the art and designed to minimize hydrogen boil-off. There is excellent collaboration with Linde, who have developed this LH_2 pump, and Spencer Composites, who are expert at building cryogenic pressure vessels.
- This project will demonstrate the capability of cryogenic refueling and address specific technology gaps and issues identified by the Program. The facility design will allow for future advancements in cryogenic refueling technologies. System components are designed and built with a higher rating then what is currently available to allow for higher densities during future component refueling demonstrations.

Project weaknesses:

- The project too closely replicates the work of foreign manufacturers of FCEVs.
- The facilities could have been constructed with future operator training classrooms available.
- It is unclear if this project is in sync with the industry's plans for refueling. If it is not, a re-scope may be warranted.
- There is a lack of identification of future technical obstacles that will need to be addressed. There is also no cost model.
- There is no demonstrated use under the conditions needed by the Program. It is unclear if the seals on the pumps will survive the 850 bar conditions.
- This project's weaknesses include communicating the project's relevance, planning ahead for efficiency, and identifying/pairing collaborators in academia with the appropriate sub-projects.
- The concept behind this project is to fuel FCEVs with high-pressure LH_2 to enable reliable, fast, and low-cost refueling. Charging LH_2 to the vehicle does result in lower-cost refueling stations. The question is whether charging LH_2 is the best approach to fueling FCEVs. On a WTW basis, liquefying the hydrogen consumes a lot of energy. This also adds substantially to the cost of the hydrogen (about $1/kg).This energy use results in a relatively low WTW energy efficiency and emits a lot of CO_2, unless the energy is sourced from an electricity grid with low carbon emissions. A low-carbon-emission grid in the United States is, at best, a long way off. Most car manufacturers developing FCEVs intend to commercialize using 700 bar gas storage on the vehicle. This approach is less costly, more energy-efficient, and lower in carbon emissions than a cryo-compressed LH_2 system on a WTW basis—although it has much lower volumetric efficiency for storage on the vehicle. This approach to hydrogen refueling also results in a variable amount of hydrogen in the fuel tank at the end of refueling, depending on the temperature, pressure, and amount of hydrogen in the tank at the start of refueling. Vehicle owners may not accept this situation. The Linde LH_2 pump system appears to have the potential of 1%–3% hydrogen boil-off loss and additional boil-off from the LH_2 storage tank. A 3% loss of hydrogen at the refueling station, after liquefaction, has a significant detrimental impact on WTW energy efficiency and cost. The experimental set-up may not be able to accurately measure boil-off of hydrogen, which is a key issue relative to the success of this approach to

fueling FCEVs. When the presenter was asked about this, it was suggested that the refueling station would also have high-pressure gas delivery. The boil-off would be captured and compressed for high-pressure gas delivery. This solution would solve this problem, but it would require both delivery systems at the refueling station and an FCEV fleet that would take both types of fuel. This is a lot to ask. The site for the installation has been prepared. A section of hose has been successfully tested and approved for use. This seems like a very modest level of accomplishment after 1.5 years.

Recommendations for additions/deletions to project scope:

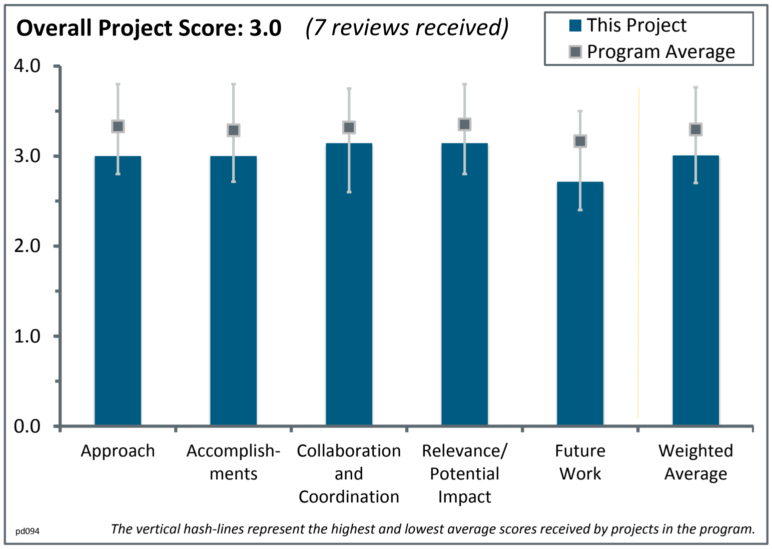
- There are no recommendations at this time.
- This project should add specific technology gaps and a cost model.
- The project should add a variety of other FCEV manufacturers.
- This project should test at scale at the laboratory when the shakedown is complete.
- This project needs to resolve the fueling process questions and test the pump for H70 systems.
- A sensitivity study could have been conducted using simple, first-order models while construction was under way. This analysis would have directed the future project scope and helped with reviewer confidence. As it stands now, there is not enough information to make an accurate recommendation for additions or deletions to the project scope. One accomplishment mentioned was the pressure validation of stainless flexible tubing. It was not made clear why this line must be flexible instead of a relatively easy solid line. One issue with flex tubing is flow-induced vibration due to vortex shedding around the corrugated tube sections. This vortex shedding can cause fatigue and premature failure (the National Aeronautics and Space Administration has studied this for filling shuttle tanks). This test did not consider flow-induced vibration or fatigue testing of the tube under pressure. This problem should be considered in future analysis, given the criticality of this component.

Project # PD-094: Economical Production of Hydrogen through Development of Novel, High-Efficiency Electrocatalysts for Alkaline Membrane Electrolysis

Katherine Ayers; Proton OnSite

Brief Summary of Project:

The objectives of this project are to demonstrate high activity of reduced noble metal content pyrochlore catalysts for oxygen evolution, optimize catalyst composition and microstructure, form and characterize new anion exchange membranes and demonstrate acceptable conductivity for electrolysis, process promising membrane and catalyst materials into membrane electrode assemblies (MEAs), scale up to a relevant stack active area and height, and operate in a relevant environment.



Question 1: Approach to performing the work

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

- The reduction in noble metal catalysts for electrolysis is a good approach, and the focus on materials cost reduction is very good. A Hydrogen Analysis (H2A) would have been very helpful to see if the materials cost savings outweighed the performance losses and the additional cost of including a gas diffusion layer (GDL) and other components.
- This is a very solid overall approach to the program, especially since much time is spent motivating the role of pH and the catalysis challenge. Few groups can make this link as logically, given Proton OnSite's experience. This is very well motivated. It would be good see a little more fundamental effort on understanding the low surface area.
- Alkaline membrane electrolysis is a promising approach to developing lower-cost electrolyzers since non-precious metal catalysts can potentially be used. This project is taking an excellent approach in developing electrocatalysts for the alkaline environment and integrating them into alkaline membrane cells, leveraging Proton OnSite's experience in membrane-based electrolyzer assemblies.
- The approach is valid. Development of the catalyst along with the membrane is a concern (there is little work shown here, though), but the interfaces between the catalyst and the ionomer are not in the scope. It is assumed that no work on the catalyst layer is required in moving from polymer electrolyte membrane (PEM) to alkaline exchange membrane (AEM), yet the nature of the catalyst has changed. Some focus on porosity, etc., would be helpful in Phase II.
- The approach has followed the routine proof-of-concept route through Phase I, which is good. Phase II needs to be reconsidered. The key drivers for product acceptability through manufacturing and commercial deployment should be considered at this point, and the Phase II approach should be adjusted based on addressing the critical tasks first. For example, if the noble metal choice and level will never be commercially viable, there is no sense in trying to optimize the existing catalyst.
- The approach to the project is fairly broad, particularly for such a limited funding level. The inclusion of catalyst studies, membrane studies, and system studies are relatively independent and do not allow for prioritization of the areas of highest concern. A pyrochlore class of catalysts should be compared to other catalysts, such as platinum and silver, to properly address performance improvements. For most electrolysis applications, the catalytic over-potential is more important than the capital cost of the catalyst.
- The approach of an alkaline electrolyzer with an AEM has the potential to reduce electrolyzer costs. The main issue with AEM electrolyzers is membrane durability. Membrane durability (without carbonate recirculation, which decreases performance) should be the main focus. Durability tests need to be longer (at

least 1,000s of hours and probably at least 10,000 hours for commercial electrolyzer products, but Proton OnSite should have durability targets). It is not clear what is new in the catalyst development work, as the catalysts described were reported in the early 1980s. It is not clear what advantages these catalysts have over the nickel-based catalysts used in alkaline electrolyzers or other known non-platinum group metal (PGM) catalysts that can be used in alkaline electrolysis. It is not clear what barrier or need the catalyst development work is addressing.

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.

- For the scale of the project and the time spent, this project appears to be very productive. This is a very well-managed set of activities, some rather scientific and some engineering, yet they are well integrated into one program.
- Progress has been good thus far, and timeliness has been demonstrated. Whether the end product of this proof-of-concept stage is viable is a question that needs answering. The world's supply of iridium is not so great that this approach makes sense for the future. If this is so, then the project should stop now and use the models developed to find better, more viable catalyst choices.
- The initial electrolyzer results are encouraging. The membrane durability shown is with carbonate recirculation, which will decrease conductivity and performance and may add additional costs in hydrogen cleanup. Durability without CO_2 should be shown. The surface areas of catalysts are low and need to be increased. The D-band orbital theory model is questionable. Activity mostly follows surface area trends. Comparing the activity of catalysts with orders-of-magnitude difference in surface area leads to considerable uncertainty. Variations in area-specific activity for materials with the same metal-adsorbate repulsion (V^2) is as large as the variation between materials with V^2=4.45 and V^2 = 5.13.
- The researchers have developed active electrocatalysts and were successful in integrating them into MEAs. This is directly in line with their objectives. However, so far the catalysts are all precious-metal based, which limits the potential for cost reduction in using alkaline membrane cells versus the more conventional acidic membranes. However, the results on the precious-metal based catalysts still represent an important stepping stone. The researchers showed that their MEAs are better than existing AEM electrolyzers. It was unclear, however, if this improvement was due to better MEA fabrication or better catalysis. While it is clear that the catalysts are active for water oxidation, no comparisons were made to known state-of-the-art materials using standard three-electrode electrochemical techniques such as rotating disk electrodes. Comparisons along these lines would have been helpful to assess the progress on catalyst development, which is a major component of this project. Regarding the theory component of this project, it was not made evident if and how it was helpful in catalyst development.
- The down-selected pyrochlore would appear to be $Pb_2Ru_2O_7$. This should be a stated accomplishment. The benefit here is to reduce the cost of hydrogen production, but that value is not clearly stated here.
- The results reported are impossible to fully attribute to a Small Business Innovation Research (SBIR) Phase I award and the low level of funding being reviewed. The results show the high potential promise of a system based on anion exchange with carbonate as the conducting ion.
- Ruthenium and iridium are not inexpensive catalysts. It seems that their use would negate some of the cost savings of not using platinum. The addition of a GDL would also negate some of the cost savings. The overall objective was to determine if there was some cost benefit to going to an alkaline system, yet there was no cost analysis to show that this was the case. Using the carbonate form of the membrane was very clever. The loading was high for the anode. On slide 15, the project claims good stability with carbonate recirculation, but there are not enough data presented to support this. It is not clear if the current was held constant. These systems need to run for thousands of hours, so 130 hours is not enough to say it is stable. However, for Phase I, a 130-hour test is about all that can be done given the time constraints. This shows a step in the right direction and reason to be optimistic, but it is not enough to justify saying it is "good."

Question 3: Collaboration and coordination with other institutions

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

- Collaboration with the Illinois Institute of Technology (IIT) seemed to work very well. Proton OnSite did a good job leveraging the DOE Advanced Research Projects Agency – Energy project.
- The collaboration between Proton OnSite and IIT is working extremely well; it is clear that they are working closely and synergistically with one another.
- Proton OnSite has brought in other parties to add value to the program and augment their skill sets. For a program of this size, the level of collaboration is outstanding.
- For a small award, there is a limit to the extent of collaboration possible. IIT is a reasonable partner for catalyst development.
- Collaborations between Proton OnSite and IIT appear to be working well. This project may benefit from collaboration with AEM fuel cell projects at Los Alamos National Laboratory and the National Renewable Energy Laboratory being funded by the Fuel Cell Technologies Office.
- The extent of collaboration with IIT on membranes was not clear. If the membrane is one of the key limiting features, then IIT should be quite actively involved in resolution.
- Pyrochlore synthesis is at IIT. Some characterization with regard to structure would suggest an involvement of someone at Oak Ridge National Laboratory, for example. Phase I should involve optimization of the structure and interfaces to improve efficiency and demonstrate durability.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

This project was rated **3.1** for its relevance/potential impact.

- As AEM electrolyzers have promise in lowering stack costs, this project is highly relevant with significant potential impact.
- The project seems adequate at this stage, although many choices are yet to be made.
- Focusing on capital cost is not as large of a driving factor as focusing on increased efficiency. The system has shown the potential to address both, but only capital cost was called out in the overview slide.
- The motivation makes the overall relevance of the program very clear. Still, there is some question about what will really be required to displace the PEM technology at Proton OnSite, including additional research and development and engineering efforts. For this to be a completely successful project, that investment would be more than offset by market growth. It seems somewhat unlikely that will happen over the next five to ten years. Nevertheless, as a piece of DOE’s portfolio, this is very relevant work.
- The approach to reduce the capital costs is very relevant. For the smaller electrolyzers, which may be used in the near term, capital cost is a larger portion than electricity cost, so this has some advantages. The lower operating current, compared to PEM electrolyzers, will require a larger stack size increasing the amount of materials required. PEM electrolyzers are operating at two to three times the current density. So even if the cost of titanium is eliminated and a less expensive membrane, compared to Nafion, is used, the overall stack cost may not be decreased substantially. The AEM system will likely have a larger footprint than a PEM system; however, it is becoming evident that the stack is one of the smaller components in a hydrogen generator.

Question 5: Proposed future work

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

- This project is focused on the right things. It would be good to see a more fundamental look at the low surface area of some candidate catalysts, slide 10.
- The future work seems appropriate. An H2A cost analysis should have been done in Phase I as a justification to move to Phase II, and long-term tests need to be done. This project should plan on using water and moving away from the carbonate stream in Phase II, which is needed for this project to be successful.

- The proposed future work is in line with improving AEM electrolyzer performance; however, it would have been good to see more attention paid to the integration of non-precious metal catalysts, since avoiding precious metals is a primary motivating factor for alkaline membrane electrolysis.
- The proposed future work addresses electrolyte stability issues, electrolyte performance issues, and a system trade-off study, which this reviewer considers more important than catalyst development work for AEM electrolyzer systems.
- The Phase II plans are vague. It would be good to know more about tuning the ionomer and membrane. There is little evidence of real collaboration with Tokuyama here.
- This is an area that should be aggressively addressed with straightforward techno-economic rigor. The key limiting features should be identified and addressed first and aggressively. Optimization seems premature. Noble metal pyrochlores are not likely to be a real solution, for example.
- Out of the four future work items presented on slide 18, three are of high value (investigating AEM properties, performing trade study, and product cost analysis). Further work into catalyst development is of low concern/priority, but for the work done in this area, proper comparisons should be made (platinum, iridium, ruthenium, and silver on anodes; platinum and others on cathodes).

Project strengths:

- The demonstration of real electrolyzers is good.
- The approaches are methodical, which should allow for a positive outcome.
- This project is well motivated, is well managed, has good collaboration, and is very productive.
- This has the potential to reduce the capital cost of electrolyzers. It has the potential to use a non-precious metal catalyst.
- This project explores new, potentially interesting approaches to hydrogen production that allow for cheaper materials to be employed.
- This is an excellent team of researchers, combining catalyst development efforts with integration into MEAs and devices. This project has had early success with the development of high-performance AEM electrolyzers.

Project weaknesses:

- There are no significant weaknesses.
- This project has a strong focus on catalyst development.
- The plans for optimization seem premature. Some techno-economic stage-gating of a simplistic type should be employed to help direct Phase II work.
- Pyrochlore characterization is limited. There is no discussion of the electrode/electrolyte interface (perhaps in Phase II). There is no real collaboration with the membrane/ionomer supplier.
- Establishing working devices based on precious metal catalysts is an important stepping stone; however, it would have been good to see more results on non-precious metal systems. While the MEAs performed well, it was not made clear how the inherent activity of the electrocatalysts developed in this project compare to state-of-the-art, known water oxidation catalysts. It was not made clear how the modeling component of this project has helped in the development of catalysts.
- There should be an H2A analysis on the hydrogen cost of this new technology. The replacements for platinum are either expensive (iridium or ruthenium) or toxic (lead). Durability tests in a relative environment need to be done. The researchers are eliminating some costly materials from their system, but they are adding components (GDLs); increasing the materials required since the stacks will need to be bigger to produce the same amount of hydrogen compared to a PEM, due to the lower operating current; and increasing the complexity (need to monitor and control carbonization), so the cost benefits may not be realized. The project should have reported on the catalyst loading per electrode area.

Recommendations for additions/deletions to project scope:

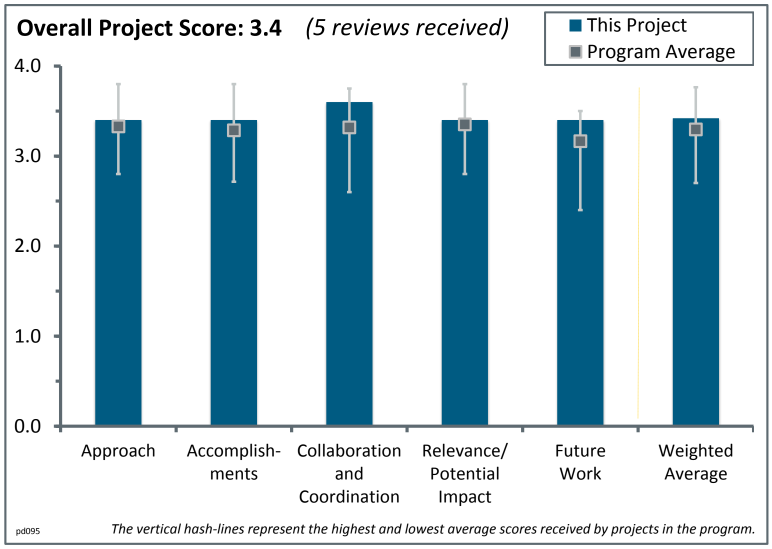
- It is difficult to comment without seeing the Phase II proposal.
- There should be a focus on why certain materials exhibit low surface area.

- This project should reduce the catalyst development work and focus on the membrane performance and durability issues.
- This project should remove the catalyst development and focus on the other three areas highlighted in the future work.
- This project should do an H2A analysis. The researchers need to do the cell- and short-stack testing in a relevant environment to better understand carbonization mitigation.

Project # PD-095: Probing Oxygen-Tolerant CBS Hydrogenase for Hydrogen Production

Pin-Ching Maness; National Renewable Energy Laboratory

Brief Summary of Project:



Photolytic microbes such as algae and cyanobacteria co-produce oxygen with hydrogen. The oxygen inhibits the activity of hydrogenase, the enzyme responsible for hydrogen production. The objective of this project is to develop a robust oxygen-tolerant cyanobacterial system for light-driven hydrogen production from water while increasing system durability. The long-term goal is for the system to be oxygen-tolerant for eight hours (during daylight hours). The first task of this project probes hydrogenase maturation machinery in the oxygen-tolerant Casa Bonita Strain (CBS) of *Rubrivivax gelatinosus*. The second task transfers the oxygen-tolerant CBS hydrogenase and its maturation genes into a *Synechocystis* host that has had the native genes for hydrogen production removed.

Question 1: Approach to performing the work

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

- This project has successfully utilized classic approaches, such as quantitative real-time polymerase chain reaction (RT-PCR) and cloning, which are challenging and yet have been repeated successfully in the principal investigator's (PI's) laboratory. The methodologies are well designed and integrated exceptionally well with the research being conducted by other labs and collaborators.
- This project appears to be well focused on the "oxygen accumulation" barrier (barrier AN) of the Fuel Cell Technology Office's 2012 Multi-Year Research, Development, and Demonstration Plan (MYRDDP). The approach appears to be effective as a new set of maturation genes has been discovered and has been incorporated into gene expression studies.
- The approach to identifying robust hydrogenase activity in CBS and moving it into cyanobacteria is sound.
- This is a good approach, especially the use of a better promoter. There is still no good analysis that links all the laboratory results to a production model that provides some guidance to reviewers on how laboratory accomplishments will lead to a more economic system. This project uses good science, but there are many different approaches at different levels of development, and there is no clear path to having them get integrated and result in a stable mutant.
- NiFe hydrogenase is a logical gene candidate that expresses in the production host because of a long half-life (>21 hours) in air. The pursuit of maturation proteins is also a very logical target for heterologous gene expression. However, the rationale was not explained clearly, and it is unclear why the growth assay is a good proxy for HypE1 and E2 hydrogenase activities.

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.

- These are good accomplishments in terms of meeting the milestones for individual CBS improvements.

- This is a very impressive set of experiments, results, and publications. The PI's group appears to have tested all assumptions and results. Thus, the work is accomplishing tasks, is generating novel scientific findings, and is on task to accomplish future goals.
- Task 1 milestones appear to have been completed on schedule while adding the newly discovered set of maturation genes to the study. A milestone of Task 2 has been completed ahead of schedule while achieving an order-of-magnitude improvement above the milestone's target.
- The RT-PCR gene expression study of the hydrogenase operon (hypE1 and E2) milestone for January 2013 was completed on time. Gene integration and expression in the production host milestone was completed on time. Identification of a strong promoter (psbA) that will improve gene expression milestones was completed on time.
- The presenters have successfully transferred the Hyp1 genes. They have also discovered a second hygrogenase system (Hyp2), which is being evaluated. The evaluation of the stronger promoter has been completed. The presenter referred to milestones due in May 2013 (the current month) as being "on track." If the milestones were to be completed by the end of the month, it is a concern that they are, in fact, behind schedule. It would have been good to have a clearer outline of the milestones due in May 2013, detailing their actual status.

Question 3: Collaboration and coordination with other institutions

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

- The project was able to leverage low-cost (no-cost) expertise and services (genome sequencing and annotation) from partners to achieve better understanding of the system.
- The collaborations with others in the field indirectly and directly are smart. The PI seems to have a "big picture" concept of what needs to be done in the laboratory to coordinate well with other labs and achieve the larger goal of the MYRDDP.
- The collaboration with Michigan State University (MSU) and Pacific Biosciences is well defined and productive. The collaboration with the J. Craig Venter Institute (JCVI) is not well defined in terms of how the projects are different enough to warrant individual funding.
- The project appears to have strong collaborations with JCVI (Task 2), MSU, and Pacific Biosciences (Task 1). Research has resulted in multiple publications and presentations (including a joint international symposium) run over the past year by National Renewable Energy Laboratory and JCVI team members.
- This project has good collaboration, but it still appears that all of the laboratories are working in parallel, not in combined research and development efforts. Each laboratory is working towards its own objectives, but no single laboratory is integrating all the work.

Question 4: Relevance/potential impact on advancing progress toward DOE research, development, and demonstration (RD&D) goals

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

- If successful, this work will result in a photosynthetic hydrogen production system, which should be very valuable to the renewable energy community.
- Successful acquisition of a cyanobacterium with an oxygen-tolerant hydrogenase would be a significant step towards achieving MYRDDP targets.
- The potential impact of identifying and characterizing mechanisms related to growth profiles and hydrogenase production is critical to understanding how to control hydrogen production while maintaining viable and productive organisms. This fundamental and basic research can be far-reaching.
- This is still one of the biggest barriers for photolytic microbial hydrogen production. However, these approaches all need to be integrated into a single mutant to validate that this approach will work for a complete production strategy.
- The project has made progress towards improved hydrogenase activity for hydrogen production. But the R&D appears to be very early in terms of technology readiness levels; it is unclear at this point whether this project principally supports reaching the $10/gasoline gallon equivalent cost target for biological hydrogen production.

Question 5: Proposed future work

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

- The proposed work is a logical extension of ongoing efforts.
- The proposed future work is rational and well integrated with previous work and the work of collaborators.
- The presenters have a clearly defined pathway to move forward and produce results that will support DOE missions.
- The plans build on accomplishments, but the project should spend the time to assemble a mutant with all the hydrogenase improvements to validate that the process will work as planned and that it can be modeled.
- The continued work on CBS hydrogenase is novel and should bring new contributions to the field. The *in vitro* hydrogenase activity assays will be key for further optimization of oxygen tolerance.

Project strengths:

- This is a good team of researchers and facilities.
- This project has strong collaborations with external groups and a multi-pathway approach to the work.
- The addition of private partnerships should help facilitate progress towards commercial goals and cost targets.

Project weaknesses:

- There is possible redundancy with the JCVI group.
- There are parallel paths to improving oxygen tolerance and increasing hydrogen yield, but nothing has been integrated.
- This project has not tested the redundancies the researchers found. These redundancies would seem to have impacts on fitness due to energy inputs, and it would be an easy test.

Recommendations for additions/deletions to project scope:

- This project should ensure the fitness phenotype is addressed.
- Gene expression is one factor that can lead to low enzyme activity, but so can inefficiencies in protein folding. It is suggested that a near-term experimental objective should include comparing the heterologously expressed protein in *Synechocystis* with the native protein isolated from *Rubrivivax* (if it is possible to scale up) in a circular dichromism assay to see if protein folding might be a limitation. Alternatively, the detection of protein aggregates, inclusion bodies, or truncated proteins on western blots using antibodies raised against different regions of the enzyme can help the project direct further optimization efforts.