2014 — Hydrogen Production and Delivery
Summary of Annual Merit Review of the Hydrogen Production and Delivery Sub-Program

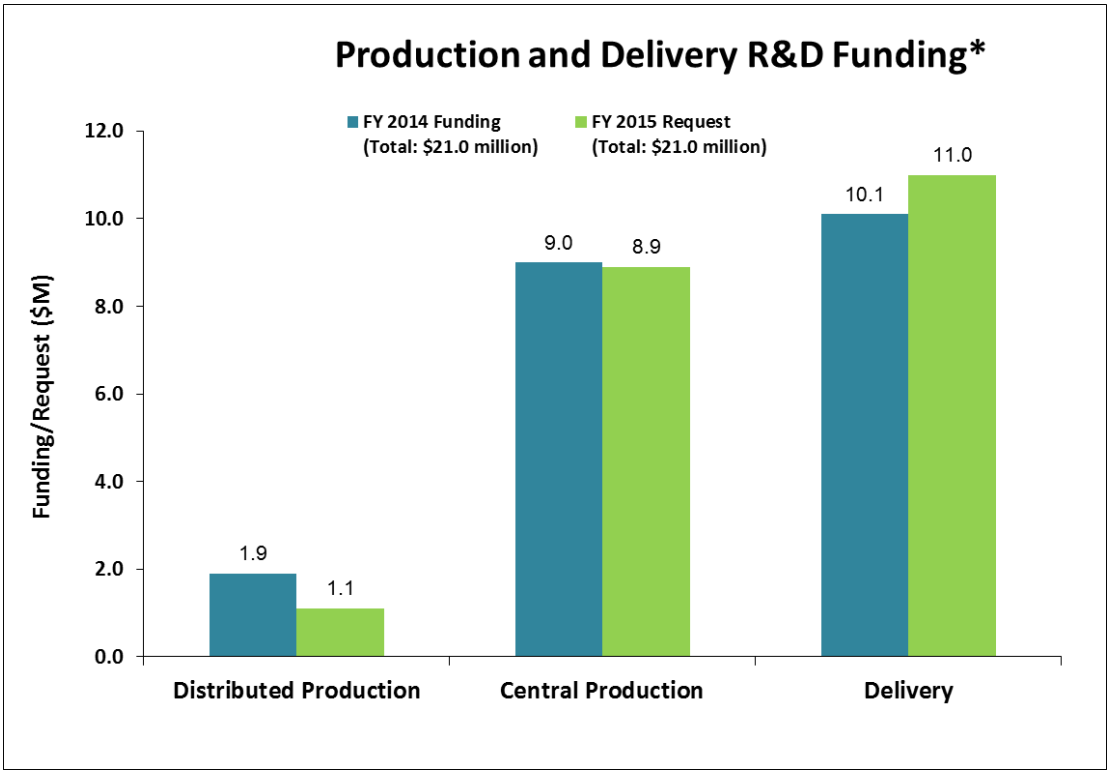
Summary of Reviewer Comments on the Hydrogen Production and Delivery Sub-Program:

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, biological hydrogen production, and hydrogen production pathway analysis. The hydrogen delivery projects reviewed included R&D for low-cost pipeline materials, pipeline and forecourt compression, forecourt storage and dispensing components, and delivery cost analyses.

The reviewers recognized the Hydrogen Production and Delivery sub-program as focused, effective, well managed, and having a clear strategy to achieve DOE goals and objectives. Reviewers commented positively on the high quality of the R&D performed in the past year and the sub-program's engagement with industry. They encouraged continued coordination with the DOE Office of Science and the overall scientific community in leveraging hydrogen research, development, and demonstration (RD&D). They also emphasized the need for continued cost modeling of production and delivery technologies to identify and address cost barriers. In addition, reviewers stressed the need for balance between short-, mid-, and long-term technologies in the portfolios, and for more attention to near- and mid-term goals, targets, and deployments in order to meet the DOE cost goal in 2020.

Hydrogen Production and Delivery Funding:

The fiscal year (FY) 2014 appropriation for the Hydrogen Production and Delivery sub-program was $21 million. Funding was distributed approximately evenly between hydrogen production and hydrogen delivery, representing an increase in funding to delivery relative to past years, when funding was distributed with approximately two-thirds to production and one-third to delivery, and reflecting the current FCTO priority emphasis on hydrogen infrastructure technology development. Production funding is focused on long-term, renewable pathways such as PEC, biological, and solar-thermochemical hydrogen production. While this emphasis will continue in FY 2015 as part of the $21 million budget request, short- and mid-term technologies in production and delivery will be addressed through competitively selected new starts initiated in FY 2014. The delivery portfolio emphasis in FY 2014 was on reducing near-term technology costs, such as those associated with tube trailers and forecourt compressors, and on identifying additional low-cost early market delivery pathways that are viable. This emphasis will continue in FY 2015.



∗ Subject to appropriations, project go/no-go decisions, and competitive selections. Exact amounts will be determined based on research and development progress in each area.

Majority of Reviewer Comments and Recommendations:

Eighteen projects were reviewed, receiving primarily above-average to high scores (2.9–3.6), 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: Three projects in biological hydrogen production were reviewed, with an average score of 3.2. Projects in this area included efforts to improve the performance of algal and bacterial microorganisms that produce hydrogen through splitting water or fermentation of biomass. Reviewers noted that the projects have used logical, rational approaches and made progress in addressing barriers to hydrogen production from biological photolysis and microbial conversion of biomass. In particular, reviewers noted that the algal and cyanobacterial projects are complementary. Reviewers also noted that each project only addresses a portion of the challenges needed for the systems to become commercially viable, and they suggested that the project goals and results be more clearly framed in terms of the "bigger picture." Reviewers also expressed concern about the challenges to scaling up the systems to commercially viable sizes, especially given the complexity of some of the pathways involved.

Electrolysis: Three Small Business Innovation Research (SBIR) Phase II projects in the area of hydrogen production from water electrolysis were reviewed, receiving an average score of 3.2. Projects included efforts to decrease the platinum group metal (PGM) loading of the electrolysis cell electrodes while maintaining performance equivalent to higher-PGM electrodes. Two of the more promising approaches leveraged catalyst technologies originally developed for polymer electrolyte membrane (PEM) fuel cells. Also, one of the projects is focused on the development of catalysts and membranes for alkaline membrane electrolysis, which has the potential to reduce costs for low-temperature electrolyzers. Reviewers praised the progress made toward developing low-PGM, high-performing electrodes. However, reviewers noted that even with the significant reduction in PGM loadings achieved, the impact on the cost of hydrogen, via the resulting capital cost reduction, would be limited. To this end, reviewers suggested that performing Hydrogen Analysis (H2A) model cost analysis would be important for evaluating the ability of the proposed projects to reduce hydrogen production cost. Also, with the success in

developing low-PGM electrodes with high performance, reviewers recommended that more emphasis be placed on durability testing.

Hydrogen Delivery: Six projects were reviewed in the area of hydrogen delivery, receiving an average score of 3.4. Projects were praised by reviewers for their technical approaches and relevance to DOE objectives. Recommendations were made for several projects to expand their economic analyses to ensure that all relevant aspects of mature markets are considered (e.g., the implications of high-volume manufacturing on electrochemical compression costs and the costs of man-ways in storage vessels). Other project-specific suggestions included materials testing (e.g., fluid dynamics testing of joints in fiber-reinforced pipelines) and the development of partnerships (e.g., collaboration with existing refueling station operators to ensure that dispensing hose designs account for real-world fueling conditions).

PEC Hydrogen Production: Two PEC projects were reviewed, receiving an average score of 3.5. 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, such as those based on highly efficient III–V semiconductor materials. Projects were rated highly for advancing the state of the art in theoretical understanding and experimental development of PEC materials and interfaces. In particular, the coordination of theoretical model development with experimental validation work based on spectroscopic results was highly commended. Reviewers also highlighted the excellent collaborative successes of the projects involving the DOE PEC Working Group. Recommendations for future work included re-scoping the work to better match budgetary limits and further expanding collaborative efforts within DOE offices and across R&D agencies to better leverage synergistic resources. Ongoing R&D efforts related to this PEC materials and interface development work will continue through projects competitively selected in 2014.

Solar-Driven, High-Temperature (HT) Thermochemical Production: Presentations were given for three solar-driven, HT thermochemical hydrogen production projects—two addressing two-step, metal-oxide-based, HT reaction cycles, and one addressing a hybrid (multistep, including an electrolysis step) sulfur (HyS) reaction cycle. The projects received an average score of 3.0. Reviewers praised the innovative approaches and achievements in all three projects: the design of perovskite and hercynite reaction materials and the new reactor concepts for the HT cycles, and the membrane and electrocatalyst screening and test apparatus design and construction for the HyS cycle. Reviewers expressed concern about the complexity of the integrated reactions and reactors for all three systems, and they recommended that project emphasis be placed on materials RD&D to obtain the kinetics, durability, and other properties needed to achieve the hydrogen cost goal. Reviewers also recommended continued updating of technoeconomic analysis for the technologies, including realistic assessments of system original equipment manufacturer and capital costs. R&D efforts in these three HT reaction cycles will continue through projects competitively selected in 2014.

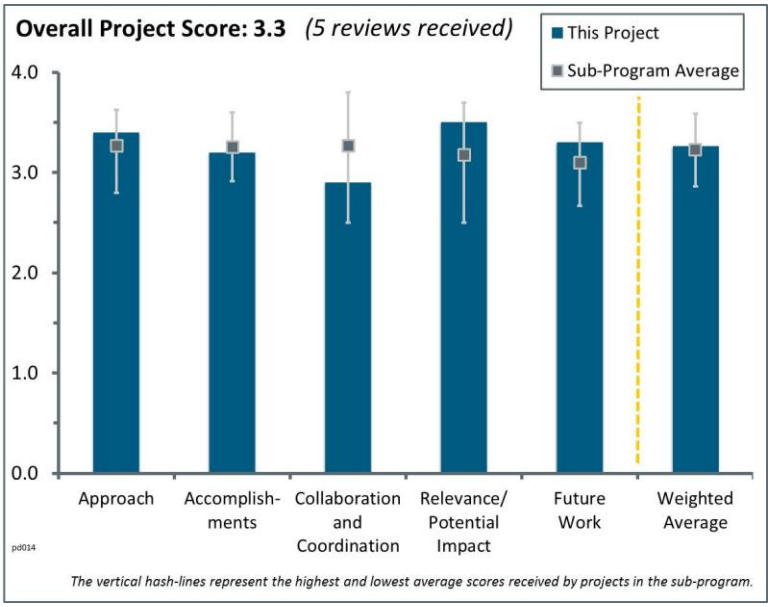
Hydrogen Production Pathway Analysis: One oral presentation was given in the area of hydrogen production pathway analysis. The project received a score of 3.1. Reviewers commended the project team's approach to developing analytical cases studies for PEM electrolysis, which involved gathering information on the state of the art from four electrolyzer companies. The results of the studies were seen as extremely useful, especially in terms of the capital cost breakdown and sensitivity analysis. The reviewers commented that the correlation between the project results and relevant DOE targets should be made clearer. Recommendations included a stronger focus on establishing and documenting specific quantifiable limits achievable through capital and operating cost improvements in hydrogen production pathways.

Project # PD-014: Hydrogen Delivery Infrastructure Analysis

Amgad Elgowainy; Argonne National Laboratory

Brief Summary of Project:

The main objective of this project is to provide a platform for comparing the impacts of alternative hydrogen delivery and refueling options on the cost of dispensed hydrogen. Cost drivers are identified for current hydrogen delivery and refueling technologies, and potential novel delivery concepts are evaluated. Cost modeling for hydrogen refueling stations evaluates high-pressure tube trailers and incorporates the implications of SAE J2601 refueling protocol.



Question 1: Approach to performing the work

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

- This project's approach is outstanding. While the team did not give clear priorities during last year's presentation, this year the priorities were clear and well defined. Through collaboration with industry, the project is focused on the critical barriers and challenges (i.e., lack of infrastructure, tube storage trailer delivery cost, and reliability) that need to be addressed to reach technical objectives along with cost, while managing the component designs. The path/approach looks feasible while supporting existing models and collaborating with industry for input and review.
- This project has a practical approach to evaluating fuel cell dispensing in light of economics. Delivery of analysis data was very effective.
- The development of models based on thermodynamics combined with real-world compression and fueling data has resulted in a rigorous analytical tool, which can be used to accurately predict the behavior of fueling systems.
- The approach, as described, is well thought out and properly addresses key barriers. The project is well organized and feasible. However, the efforts appear to be somewhat narrowly focused (e.g., high-pressure compressed gas as the only pathway for hydrogen delivery). Other pathways and tradeoffs should be at least mentioned and characterized. The tube trailer consolidation and cascade filling approach makes sense—it is known and practiced to some extent in industry—but space limitations at public fueling stations should be addressed in this context.
- It was unclear if shifting the cost upstream to tube trailers meant centralized production or if it referred to the cost of transport.

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 appears to be fully accomplishing its goal. Progress of the analysis should be faster, but this is probably being paced by funding.
- Development of modeling capabilities to optimize compressor size, storage, etc. is a major advancement for the DOE Hydrogen and Fuel Cells Program (the Program). For the first time, tools exist within the Program to optimize infrastructure components to match station demand profiles. Shifting high-capital-expenditure components to terminals to take advantage of economies of scale is a good strategy and an enabler for

hydrogen delivery. The tube trailer consolidation approach is a great way to minimize high-capital-expenditure compression capacity. High-pressure feed enables lower-cost (i.e., fewer stages) compressors.

- The progress toward defining refueling as being capital-intensive helps DOE define its goals and objectives. Information indicates that the compressor makes up 56% of refueling costs. This is a logical result of trying to move capital cost upstream to better share cost with other end users. The Program needs to continue looking at ways to optimize delivery pathways. Collaboration with other industries such as the U.S. Department of Defense (DOD) or the National Aeronautics and Space Administration (NASA) and their hydrogen programs, which were not discussed, is suggested. The project has very interesting plans of moving pressure toward delivery trailers. The project needs to work closer with the U.S. Department of Transportation (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA) Hazardous Materials group to communicate why the high-pressure trailer is needed. This effort may avoid future road blocks. The approach to track the mass, pressure, and temperature of each tube in a tube trailer is an interesting approach to match the delivery needs. A data-intensive balancing effort will be required.
- The stated task of simulation and optimization of the consolidation strategy is completed and well documented. However, a description of milestones and deliverables is not provided. Hence, the progress against targets cannot be judged. The consolidation strategy does provide a solution to achieve DOE goals for hydrogen delivery costs. The results and conclusions are anticipated; there are no surprises. A generic calculation program for public use for designing a cascade system for a given set of input and output conditions would be a useful outcome of the exercise. It would have been helpful to make reference to cost implications of the proposed solution in light of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan (MYRDDP) goals.
- Compressor investment is still needed, so it is unclear how this approach reduces investment cost. There is a tradeoff between additional investment for high-pressure tube trailers and the lower compressor capacity. Further evaluation is needed.

Question 3: Collaboration and coordination with other institutions

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

- The principal investigator has successfully engaged vendors and other stakeholders to obtain data for developing and vetting models. Compressor manufacturers, tube trailer makers, etc. have all contributed to this project.
- The project presented data and experience from industry players. Although the number of collaborators was good, the project may gain additional benefit by seeking more input from equipment suppliers and installation owners.
- The project has good collaboration with industry, but better collaboration with other federal agencies still appears to be lacking. It is unclear what DOD is considering or modeling. NASA also has a hydrogen program, and this project appears to provide no insight as to what NASA is doing. The approach shown using the smaller tubes to store higher pressure was good.
- Collaboration with the Gas Technology Institute is well utilized; their contribution is visible. Collaboration with Pacific Northwest National Laboratory is not readily apparent. Input from industrial gas companies (IGCs) would be useful, as they routinely manage compressed hydrogen transport and delivery and are familiar with cascade filling strategies. No IGC is listed as a collaborator.
- Collaboration was not pointed out very much.

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

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

- This project is the only effort that quantifies the economics and tradeoffs associated with the creation of a hydrogen fuel cell electric vehicle program, especially a program that relies upon commercial investment prior to the public's acceptance of the transportation mode.

- The project has excellent potential to address the cost of dispensing at the station while better utilizing trailing storage applications for early markets. Future cost work is needed for effects of trailers with more storage tubes (e.g., fittings, valves, and plumbing and control sensor control systems) and that impact on the overall cost of tube trailers. The project's very interesting approach aligns well with delivery objectives of the Production and Delivery program.
- High-quality modeling is an essential tool for the DOE Hydrogen and Fuel Cells Program (the Program). Without it, the Program is unable to identify critical processes and components in the production/delivery pipeline. Accurate models also enable cost-effective prioritization of Program activities.
- The work done and the output of this project do provide a useful framework and delivery infrastructure solutions. However, the results are limited to a specific case in this year's efforts. To fully address the goals and objectives delineated in the MYRDDP, the ongoing efforts should focus on providing cost tradeoffs and a broader comparison.

Question 5: Proposed future work

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

- The work planned is appropriate and logical, and it addresses all the necessary elements to provide a more comprehensive analysis and useful output.
- Critical barriers of future work to refine economics of fuel delivery and tradeoff analysis were discussed. The project appears to have excellent collaboration with industry partners.
- The project needs to evaluate the economics associated with tube trailers and tube size. It needs to clearly address redundancy of equipment to determine impact on project economics. The impact of supplying a compressor with products at various pressure levels (i.e., from tubes) is not clear.
- The project is technically focused, but it is unclear what the bigger picture is. It is unclear how this applies for all stations.

Project strengths:

- The analytical work is highly valuable and probably deserves additional funding to accelerate the determination of ideal solution(s).
- The project has excellent potential to address the cost of dispensing at the station while better utilizing trailer storage in the early market.
- The project demonstrates good understanding of issues, analysis capabilities, and access to necessary tools, data, and background work.
- Inclusion of added terminal costs is the logical next step and will help to assess the high-pressure tube trailer concept at a systems level.

Project weaknesses:

- The project has good collaboration with industry, but better collaboration with other federal agencies still appears to be lacking. It is unclear what DOD is considering or modeling. NASA also has a hydrogen program, and the project appears to provide no insight as to what NASA is doing. Future cost work is needed for effects of trailers with more storage tubes (e.g., fittings, valves, plumbing, and control sensor control systems) and that impact on the overall cost of tube trailers. The project needs to work closer with the DOT PHMSA Hazardous Materials group to communicate why the high-pressure trailer is needed. This effort may avoid future road blocks.
- The project has limited results (i.e., lacking cost data). It needs to incorporate practical aspects and narrow the focus.
- The project is progressing too slowly.

Recommendations for additions/deletions to project scope:

- Funding for this project should be increased to accelerate the work, and a communications strategy/plan should be created to disseminate the information to investors, operators, and the general public.

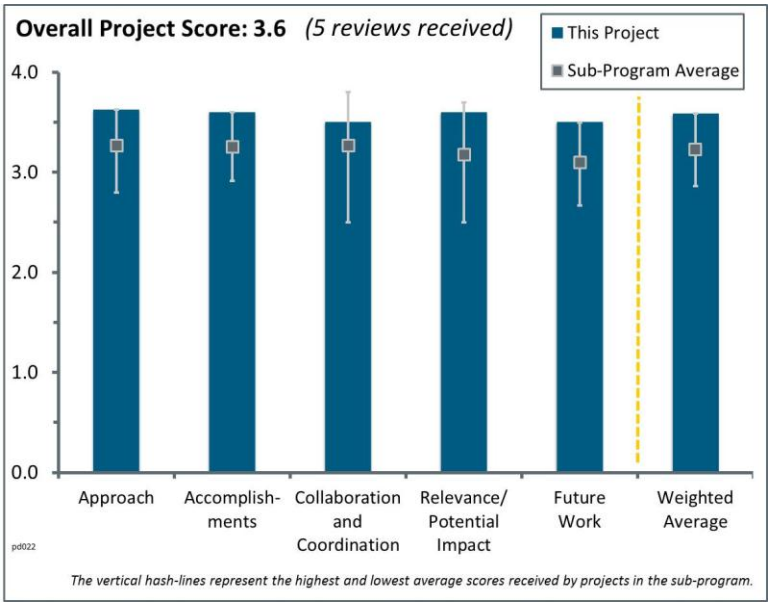
- The project needs to work more closely with the DOT PHMSA Hazardous Materials group to communicate why the high-pressure trailer is needed. This effort may avoid future road blocks. Better collaboration with other federal agencies still appears to be lacking. It is unclear what DOD is considering or modeling. NASA also has a hydrogen program, and the project appears to provide no insight as to what NASA is doing. The project has excellent potential to address the cost of dispensing at the station while better utilizing trailer storage.
- At some point, the costs of extra valving required for trailer consolidation need to be addressed.
- The project should include multiple pathway analysis and provide suggestions/challenges for potential new or modified pathways to enable reaching DOE cost targets.

Project # PD-022: Fiber-Reinforced Composite Pipelines

George Rawls; Savannah River National Laboratory

Brief Summary of Project:

Composite pipeline technology has the potential to reduce installation costs and improve reliability for hydrogen pipelines. This project critically evaluates the current application of available fiber-reinforced pipeline (FRP) product standards and defines changes to the current FRP product standards to meet the ASME Code Methodology to provide the technical basis for using FRP in hydrogen service. The goal is to build a body of data to support codification in the ASME B31.12 Code Hydrogen Piping Code in 2015.



Question 1: Approach to performing the work

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

- Given the level of support and the complexity of the testing involved, the project's approach is optimum. One of the key objectives of the project is to develop information that can be used for the B31.12 codification of FRP pipelines by ASME. In this regard, the project's approach is based on fatigue testing of the FRPs in order to ascertain the life of the pipeline for a projected 50-year operation. Hence, the approach taken to develop the pressure versus cycles-to-failure data shown on slide 9 is most appropriate. In addition, the approach toward pipeline joint development seems to be sound, as there is a proposal for non-mechanical joints. It should be noted that ASME pipeline operators expressed reservations about mechanical joints.
- The project has done an excellent job of developing the information needed for standards incorporation.
- FRP technology provides reduction in number of joints compared to the current steel pipe technology. Mechanical, pH, burst strength, and fatigue life effects on FRP degradation so far show promising results.
- The team is addressing the project goals for providing a basis for the use of FRP as an alternative to steel pipeline and integrating FRP into pipeline code by 2015.
- The future needs for the pipelines are unclear. Variable sizes and lengths may be needed.

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

This project was rated **3.6** for its accomplishments and progress.

- The project accomplishments from last year are summarized on slide 5. These are accomplishments that address fundamental understanding of FRP degradation by hydrogen in the presence of a flaw. Certainly these accomplishments provided the basis to embark on work to study the conditions for extending the pipeline life from 20 to 50 years, which was this year's objective. An additional project accomplishment was the identification of the requirement for a 5% decrease in the fiber stress for the 20- to 50-year extension, which in turn set the pressure levels for testing toward 50-year design life. Given the refueling station demand for 36,500 cycles, the project results indicate safe operation up to 50 years at load ratios of 0.5. This is a key result of the project that is truly significant. Another important result of the project is the finding that the life of the FRP depends on the load ratio. The investigation of this dependence can be taken on in the future. Lastly, the project concluded that increased hardness remediates the extrusion failures of

the O-ring in the FRP connectors, and, in response to ASME's pipeline operators' concerns over the use of mechanical joints, the project investigators came up with three new concepts for fiber-reinforced composite pipelines.

- All of the work is aimed directly at providing a basis for the ASME code. The work shows flexibility in successfully dealing with the desire by the gas supplier to increase design life (and value) from 20 to 50 years. The identification and parallel strategies for resolving the challenges with the FRP connectors are right on task. The codification status (i.e., review stage of the technical codification report) will potentially result in an early achievement of the 2015 milestone around code development.
- A good process is involved. It could be significantly improved by performing the tests with pressurized hydrogen, which is the ultimate use of these results. Over the long run, hydrogen diffusion through the pipe layers is certainly possible and could change the material response. This is a critical element that is missing from the research.
- FRP technology has addressed DOE technical barriers; however, no data on detail cost saving were presented.

Question 3: Collaboration and coordination with other institutions

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

- Collaboration with the ASME is very important. ASME's B31.12 panel is an authoritative body that checks the soundness of the project results toward codification. In addition, the University of Hawaii is involved with the engineering aspects of the pipeline installation. The project is also collaborating with Oak Ridge National Laboratory on economic analysis, but no results were presented.
- There is good technical collaboration, but it was not explicitly indicated which standards committees are bring used and especially what the timeline is for introducing this to the committees and achieving approval.
- Comments from the previous year noted that the team is working with only one company's product, and this seems to continue to be the trend, both with manufacturers and with other institutions. Collaboration is not always necessary, but there seems to be resistance, even upon suggestion to ensure the team is open to a variety of viewpoints. Increased collaboration with academics and pipeline manufacturers would only benefit the project.

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

This project was rated **3.6** for its relevance/potential impact.

- The use of FRP pipelines is a game changer for cost reduction and for installation in situations where steel pipeline is not applicable.
- Codification of the FRPs for hydrogen transport is a key step for hydrogen delivery to refueling stations. Codified FRPs can be used for hydrogen distribution at a reduced cost.
- FRP technology provides reduction in the number of joints compared to the current steel pipe technology.
- This is very relevant but would be greatly enhanced by testing under more realistic conditions using pressurized hydrogen. A lot of the focus was on pressure changes (i.e., R-ratio), but the speaker indicated that a constant pressurization, or at least less cycling, may be more realistic. As a result, diffusion of even small amounts of hydrogen under static, elevated pressure could change the material response.

Question 5: Proposed future work

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

- The proposed work is the work necessary to complete the project.
- Proposed evaluation of the FRP non-mechanical joints is necessary and important. Further work on the variability of fatigue data and the load ratio dependence of fatigue life is also very important. It is stated on

slide 17 that the effect of cycle frequency and variability in the fatigue data will be done in collaboration with Fiberspar. It is strongly recommended that this investigation be carried out independently from Fiberspar. For codification, it is also very important that the Savannah River National Laboratory investigation be carried out independently of Fiberspar. Evaluation of the rupture-stress versus time relationship shown on slide 7 in the presence of hydrogen is very important regarding the estimation of the required decrease of the fiber fracture stress for the 50-year life extension. Currently, the plot of slide 7 does not account for the hydrogen effect on the fiber toughness.

- Future work is on track to meet DOE goals, except there are no efforts on cost analyses.
- Including pressurized hydrogen is recommended.
- Cost analyzes, big picture, etc. are missing. The work should be put into context.

Project strengths:

- This is very important work for the long-term development for hydrogen technology.
- The project has an excellent team and process.
- This project addresses the performance of FRPs toward codification for 50-year operation. This is done in an engineering way through cycle life assessment. The three new non-mechanical joint concepts may turn out to be valuable alternatives to the mechanical joints that rely on the use of O-rings.
- There is a clear path to success, and the project appears to be positioned to complete the work in a timely fashion.
- FRP technology provides a reduction in the number of joints compared to the current steel pipe technology. Mechanical, pH, burst strength, and fatigue life effects on FRP degradation so far are show promising results.

Project weaknesses:

- Some of the proposed joint concepts reduce the internal diameter of the pipe. Choked flow is one of the major effects. (Choked flow is a fluid dynamic condition associated with the Venturi effect.) Additional analyses are needed for each proposed joint concept.
- The data charted in the ASTM D2992 data set for FRP for the data point at >10,000 hr (slide 7) look to be significantly different from the rest of the data, and there is no statistical analysis. There was also quite a bit of discussion during the presentation about the chart in slide 9. It is not clear if there are enough data to support the conclusion on the effect of the R-ratio.
- The project should use pressurized hydrogen. Even small amounts of diffusion over time will change the polymers response. The project has tested the glass fibers under a hydrogen environment but neglected the changes that may occur in the polymer and interfacial properties.
- The project is “too engineering” in nature. Fundamental understanding of the fatigue failure of the FRPs is missing. The load ratio dependence indicates a delta-sigma effect, which is similar to the effect prevalent in structural metallic alloys. If such understanding is pursued, perhaps the fatigue life extension to 50 years will be done in a safe way predicated on true mechanistic understanding instead of performance-based mechanical engineering, which is the current project’s approach.

Recommendations for additions/deletions to project scope:

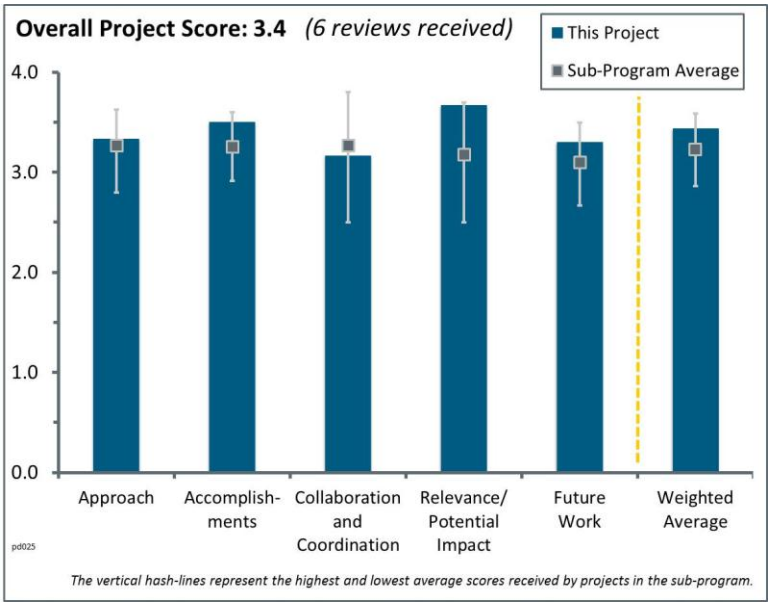
- Additional funding is required for the project to address fundamental fatigue issues. FRPs are such a promising technology for hydrogen transport that they deserve attention and full certification from a fundamental fracture mechanic’s standpoint. The director of the project, George Rawls, understands the issues well and is capable of expanding in this direction, if provided with additional support. The project should dissociate from the FRP manufacturer so that a fully independent assessment of the fatigue life of the FRP pipeline is obtained.
- Additional fluid dynamic analyses are needed for each proposed joint concept.
- Hydrogen testing should be added.

Project # PD-025: Hydrogen Embrittlement of Structural Steels

Brian Somerday; Sandia National Laboratories

Brief Summary of Project:

The purpose of this project is to demonstrate reliability and integrity of steel hydrogen pipelines for cyclic pressure applications. Steel pipeline has been proven for hydrogen delivery under constant pressure, but this project addresses the potential for fatigue crack growth due to hydrogen embrittlement and susceptibility of welds to cracking under cyclic pressure. The project will establish microstructure-performance relationships that will allow steel pipelines to be viable for hydrogen delivery.



Question 1: Approach to performing the work

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

- This is a good study on the weaknesses of steel pipe embrittlement with hydrogen. This has a good movement to study of welds as failure sources. Analysis depends upon fatigue crack growth laws. Perhaps the project should also look at weld failures and techniques for detecting them that are better than the methods used today.
- The presenter addressed barriers focused on safety related to steel pipelines. The project team looked at the welds more susceptible to failures than base metals (based on ASME B31.12 code). They applied basic research to test X65 samples of pipe sections to determine whether there are differences between base metals and the heat-affected zones. Barriers are clear and defined. Targets and testing protocols are well designed. The scope of work is feasible, and several objectives are integrated within tasks.
- Safety, reliability/integrity, and weld susceptibility to hydrogen-accelerated fatigue crack growth in hydrogen steel pipe were recognized and addressed.
- The project is a continuation of recognized work.
- To get the pipe in the ground, data and models on base material and welds are needed to ensure safety and to develop codes and standards. To reduce cost, a better understanding of performance will enable the appropriate assignment of safety factors to reduce waste due to overly conservative design and to implement new pipeline materials. The project appears to be reasonably well integrated with other efforts but should continue to move more in that direction. The approach must include modeling to be successful.
- The stress rate was constant during both increasing and decreasing stress as shown in the presentation (i.e., a linear saw tooth profile). It is not clear whether the stress rate used for the testing is reflective of the anticipated stress rate. It is unclear whether the crack growth rate is affected by the stress rate. The test conditions to answer the question of crack growth rate should reflect the anticipated use conditions. The future work does not include efforts to address either the ferrite and pearlite effect on crack growth or the orientation of the microstructure relative to the load orientation on crack growth, both of which, according to the presentation, show substantially greater importance than any weld effects. The factors that are most impactful to the crack growth are the most important to address in the codes and standards surrounding the use of steel pipe for hydrogen transmission. The presentation did not address the cost of installation. Because the project has ended, this barrier was not addressed.

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 project focused on crack growth from embrittlement and was targeting fatigue growth laws to apply to general conditions. There was a focus on girth weld on carbon steel pipe. This research is vital to existing pipeline companies that deliver hydrogen and future infrastructure for fuel cell applications.
- The focus of the project in the past year was to measure fatigue crack growth laws for hydrogen gas for pipeline steel girth welds. The task was challenging because of the complex geometry, stress state, and gradient of material and microstructure associated with pipeline welds. By applying a creative yet sound scientific approach, the team was able to overcome challenges that confounded the classic measurement method and was able to successfully and reliably measure the susceptibility of the base metal, heat-affected zone, and fusion zone to enhanced fatigue crack growth in the presence of hydrogen. The team also identified that the brute force approach was not enough to solve this complex problem and that a microstructural-based modeling approach is needed to resolve the enormous challenge of reducing the cost of pipeline delivery of hydrogen. Of particular interest was the work to understand the orientation dependence of the performance of X65 base metal, which provides an additional argument for a microstructure-based modeling approach to removing technical barriers.
- Good methodical progress has been made through the issues associated with hydrogen embrittlement. The project used a novel approach to look at fusion zone crack growth rates by reorienting the specimen.
- Active partners are identified and included with sufficient budget to ensure work is completed on time and within funding limits. Results indicate that orientation of base metal shows macrostructure effects. More information is expected from the remaining work.
- Steel pipe technology has addressed most of the DOE technical barriers; however, no data on detailed cost saving was presented.

Question 3: Collaboration and coordination with other institutions

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

- The project shows dedicated effort to revitalize U.S. government relationships, international connections (i.e., Japan), and industry. The project is working with the National Institute of Standards and Technology (NIST) and numerous others. More effort should go into collaborating with current pipeline companies.
- The team expressed the development of a coordination plan to take up the work of the now defunct Hydrogen Pipeline Working Group. The new group, which has apparently been co-authoring a white paper to address the technical barriers associated with “Safety, Codes and Standards, Permitting” and the “High As-Installed Cost of Pipelines” (slide 2), consists of representation from federal laboratories, academia, industry, and standards development organizations. Coordinated and collaborative research in this area is absolutely necessary to achieve the DOE cost-point goals in the desired timeframe because of the limited number of hydrogen test facilities available to produce data. While it is too early to judge the quality and execution of the plan detailed in the white paper, it is reassuring to see a real desire expressed by the principal investigator to collaboratively address the barriers. It was also good to see individual examples of collaboration as demonstrated by the inclusion of such work in the presentation. While it is understandable that a team cannot work with every stakeholder, it was surprising to see only one partner each from industry and academia listed in the presentation. The project could benefit from a wider variety of stakeholder partnerships.
- Industry partners and other institutions are identified collaborators with the work scope and expected outcomes.
- The project has adequate collaboration with others. Perhaps they should be looking at other pipe samples besides those from ExxonMobil.
- There was not any report of the work performed by the International Institute of Carbon-Neutral Energy Research, and apparently no friction stir welded pipe was supplied by Oak Ridge National Laboratory (ORNL).

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

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

- Safely light-weighting steel pipeline is a direct cost savings measure. Understanding the behavior of welds for various material types is critical for the safe implementation of new materials. This work directly supports the development of the codes and standards that will enable the safe implementation of new pipeline materials at significant cost savings.
- Results will be used to quantify the ability to protect pipe materials against fatigue crack growth relationships, which is a safety/reliability issue that needs to be understood to meet the DOE Hydrogen and Fuel Cells Program (the Program) goals and objectives.
- The project is very relevant because hydrogen embrittlement is a serious problem with steel pipelines for hydrogen transport.
- Issues regarding the use of steel transmission pipe are highly relevant and of enormous potential impact to the cost and ability to transmit hydrogen through pipelines.
- The work appears to complement work performed by NIST to increase loading on hydrogen pipelines.
- Steel pipe technology has been around for a long time, and some of the technical challenges are well understood.

Question 5: Proposed future work

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

- The proposed future work basically consists of two components: (1) providing a fundamental understanding of fatigue crack growth mechanisms as they relate to the material (the mechanisms would then be leveraged to develop predictive models to reduce testing and data needs); and (2) the use of the learning from the complete body of work in this area to predict pipe wall thicknesses, ultimately translating the science into application. These are clearly the next steps and are the ones needed to deal with all new base metal and welds in new pipelines.
- Future work is on track to meet DOE goals, except there are no efforts on cost analyses.
- The work clearly showed that welds are not the most impactful issues regarding steel piping. The future work should address the pearlite and ferrite effects as well as the orientation of the microstructure. The future work should also address lowering the installed cost, which was not addressed in the project.
- The project goal is to identify macrostructure performance and the material relationships to ensure safe and reliable transport of hydrogen and the best cost-effective means. Future work needs to consider alternative welding approaches under consideration by the pipeline industry (e.g., friction stir welding). The project needs to have models developed that will calculate wall thickness based on realistic operation and inspection parameters.
- The project should show how this information will be used to calculate steel pipe thickness for given conditions for hydrogen transport.
- There is not much detail in the next steps.

Project strengths:

- The team has a clear path to success based on a fundamental understanding of the problem and a deep and thorough understanding of the scientific challenges associated with the problem. Also, the strong collaborative nature of the team is refreshing in an area where other groups seem less focused on actually solving the problem.
- This work is probably vital to NIST and Sandia National Laboratories (SNL). It is filling a void that may not be performed by commercial organizations.
- SNL has a strength in addressing the material-related issues related to hydrogen embrittlement.
- This is a good fundamental approach to the cracking of pipe.

- The remaining challenge is the long-term effects of compression cycling across the large range of current pipeline system materials with temperature changes and modeling required to simulate results.
- Steel pipe technology has address most of the DOE technical barriers; however, no data on detail cost saving was presented.

Project weaknesses:

- No weaknesses were identified.
- So far all the efforts were on addressing fatigue crack growth measurements for pipeline steel friction stir weld in hydrogen gas. In the previous year it was indicated that "there is a framework for calculating the steel pipeline wall thickness required to satisfy the inspection interval based on the measured fatigue crack growth rates in hydrogen gas. Solidifying the wall thickness calculation will allow more definitive assessments of steel pipeline costs." However, a detailed cost framework can be developed in parallel.
- The project did not address the cost of installation issues. A more complete sampling of steel pipe from multiple vendors would have improved this project.
- The project should show how this information will be used to design better pipe for hydrogen transport and should test other hydrogen-exposed pipe.
- While it is clear that the team is headed in the direction needed to address the barriers, it is unclear whether there is sufficient testing infrastructure (i.e., hydrogen test facilities) to perform the number of evaluations necessary to develop and validate the models to safely implement the desired cost savings. Even when taking into account the other facilities that are collaborating with the team, it is unclear that the goals will be achieved without additional test facilities. Outreach, partnering, and education of stakeholders are critical for the adoption of the scientifically based codes and standards that will ultimately realize the maximum savings achievable through this work. Unless pipeline owners and operators feel comfortable with the recommendations (e.g., thinner pipe walls), pipe will not go in the ground, and the savings will not be realized. It is unclear whether pipeline owners and operators are involved in the work.
- There is no collaboration with corporate research and development organizations. It is unclear whether the project team is doing enough to determine the usefulness of research for industries. There is a noted need for relationships with industrial gas organizations.

Recommendations for additions/deletions to project scope:

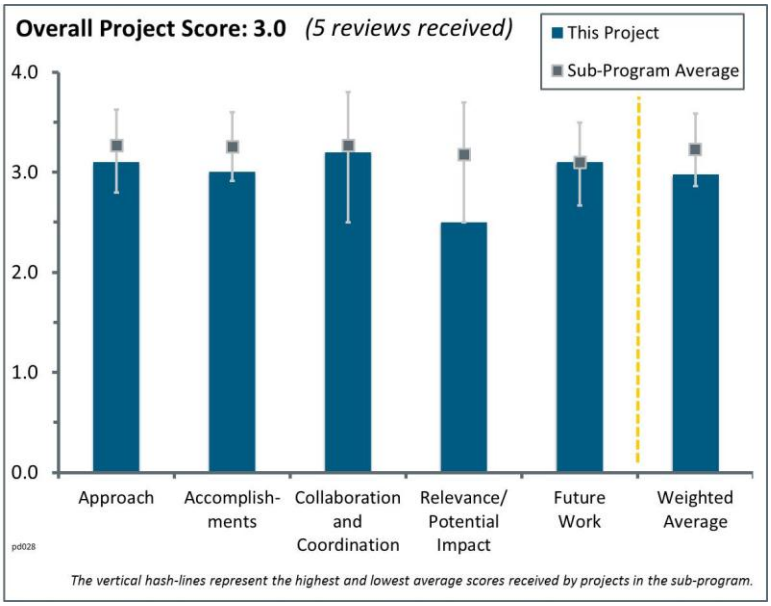
- More testing on fatigue crack growth measurements is required. In parallel, detailed cost analyses are in order.
- If the project is to include addressing the cost of installation, then there should be stronger involvement from a collaborating partner that actually installs pipeline.
- There is a need to have models developed that will calculate wall thickness based on realistic operation and inspection parameters.
- The objective of the project must be determined. It is not clear whether the project is a high-level analytical study to write papers or whether there is a practical objective to make a real impact on existing and future gaseous hydrogen pipelines.
- The project should show how this information will be used for design of better pipes for hydrogen transport; test the fatigue crack growth rates in steel pipe exposed to hydrogen from other sources; look at base metal, heat-affected zone, and weld zone; and look at girth weld with ORNL friction stir welded pipeline steel as planned.

Project # PD-028: Solarthermal Redox-Based Water Splitting Cycles

Al Weimer; University of Colorado

Brief Summary of Project:

The overall objectives of this project are to develop efficient, robust material and operation methods for a two-step thermochemical reduction/oxidation (redox) cycle and to develop a scalable solar-thermal reactor design that will achieve the U.S. Department of Energy (DOE) cost targets for solar hydrogen. Specifically during this year, the goal has been to develop an understanding of hercynite cycle chemistry, multi-tube reactor performance, and redox behavior. Development has also been under way for continuous particle flow reactor and materials concepts with independently controllable redox conditions.



Question 1: Approach to performing the work

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

- The approach is sound, and it is obvious that the researchers are completely engaged and enthusiastic about the work. Work is focused on critical areas and meets the reviewers' comments from 2013, with which the reviewer disagrees in some respects. The idea that spherical particles could improve durability is reasonable, though more development is needed.
- The development of the pseudo-isothermal hercynite cycle is an excellent example of an innovative design to overcome some thermochemical barriers. The founding analysis of efficiency of the pseudo-isothermal cycle is outstanding. The approach to this work is excellent. Barriers to anticipated performance are identified, but the current and future work needs more focus on the most important barriers. Performance is critically dependent on heat recuperation and is so identified in the presentation, but a focused design effort to determine gas–gas recuperation efficiency is not apparent in the presentation. Long-term operational stability depends on maintenance of active particle characteristics with minimal attrition and accretion. These are frequent problematic issues accompanying gas-entrained particle transport systems, and the proposed work does not clearly demonstrate an assessment and mitigation approach to assuring robust long-term operation. The design concept for a particle flow solar thermal reactor is innovative but lacks detail and modeling necessary for assuring transport performance, requisite residence periods, and heat recuperation performance.
- Moving solid materials is extremely difficult, especially at high temperatures and low pressures. Alternatives need to be considered. Examining 1350ºC active materials means the reactor will need to be hotter. This will make the construction harder and will require exotic materials, increasing costs. Materials that operate at lower temperatures are needed, and more focus should be given to their development. How the materials will be moved will increase material degradation. The presenter talked about including binders, etc. This may decrease the degradation, but now less active material will be available for reaction, thus increasing the amount of material that needs to be moved.
- This project focuses on development of innovative solar thermochemical water splitting processes based on metal-oxide redox cycles in general, and a cobalt ferrite/hercynite cycle in particular. The work encompasses fundamental understanding of redox materials and different types of redox cycling (e.g., isothermal and temperature-swing). Isothermal operation is not possible for a pure thermal water-splitting process. The project's isothermal operation is accomplished by cyclically varying the steam composition

for the oxidation and reduction reactions by sweeping the steam from the reactor (using He) prior to the reduction reaction, then reintroducing it for the oxidation reaction. Clearly this is not a pure thermal water-splitting process, and the governing thermodynamics are different and still being worked out. The specifics of the cyclic operation were not clear from the presentation. It is clarified in the technical reference listed in the presentation.

- Generally and normally, progressing fundamental understanding, materials, and process in parallel, as the investigators are doing in this project, is viewed favorably because these aspects are integrated, influence one another, and are needed to assess economics. But in this case it is fairly clear that the hydrogen productivity and kinetics of the materials are the current key limiting factor towards the ultimate objective of efficient and cost-effective hydrogen production. Materials with much higher performance (i.e., likely >10x, possibly 100x) are needed for that, and discovering them should be prioritized if economically feasible hydrogen production is the ultimate objective. However, compared to 2013, there seemed to be much more emphasis on process than on materials. The reason is not clear, but that does not seem to be the more promising path to achieve a practical technology.

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.

- Accomplishments and progress are excellent. The identification of the pseudo-isothermal cycle and its quantitative demonstration assure potential success for thermochemical performance of this concept. Detailed design of integration with a solar interface and analytic reactor performance modeling remain to be addressed so that the capability for this cycle to meet long-term DOE goals can be demonstrated.
- Good progress has been made in analyzing the process and identifying impacts on efficiency, such as heat recuperation, the effect of O_2 removal, and the differences in reduction temperature versus oxidation temperature. Also, the project team came up with an alternative reactor design to overcome limitations of prior designs. However, the technical information on the new reactor presented at the review and provided in the reviewers' files was sufficient to understand what drove the choices and how the new design is potentially better, but not enough to assess the merits of the new design. Maybe the new concept is very recent, and work is in progress. The new design seems related to (or possibly inspired by) fluid catalytic cracker (FCC) reactors—there may be learnings from FCC reactors that could be used in this project, although the materials and conditions are different. Many process hurdles remain, of course, and the new design would have to be confirmed by experiments—likely at first by separate testing of certain critical process portions before an integrated system. But it seems that the materials are currently the critical limitations.
- The researchers have demonstrated isothermal operation, with oxidation and reduction occurring at the same temperature, with different partial pressures of steam during the reduction (i.e., low P_{H2O}) and oxidation (i.e., high P_{H2O}) steps. However, to avoid simultaneous hydrogen and O_2 production and to improve cycle performance, high reduction temperatures (i.e., 1500ºC) and lower oxidation temperatures (i.e., 1350ºC) can be used. This "pseudo-isothermal" version of the process has also been demonstrated at small scale. The researchers' analysis has shown that, as with many of these processes, in order to achieve the highest overall efficiency, heat recuperation is critical. In this case, the steam/hydrogen gas mixture leaving the reactor must be used to effectively preheat the steam flowing into the reactor. In addition, heat recuperation between the oxidized solids and the reduced solids is needed. A ceramic heat exchanger will be needed for temperatures above 1000ºC. Results of a thermal analysis on a multi-tube reactor design were presented. Also presented was a solar thermal particle reactor concept in which the oxidation and reduction processes occur in different vessels, with redox particle circulation between the two. In this system, solar heat is directed at the reduction vessel where O_2 is produced. The reduced particles are then introduced to the oxidation vessel where hydrogen is produced. The redox support particles can be formed by a spray drying process. An economic analysis was also presented.
- Interesting density functional theory analysis was done. The presenter stated tests were done that suggest the reaction mechanism they proposed was correct. However, it was unclear what the evidence was and what tests were done. Moving from a particle flow reactor from the old reactor design may help efficiencies, but it will increase the system complexity. There is good analysis on the cycle life. Now the needed durability is known. It is unclear where the tests for this are. The active material needs to have long-

term testing to verify that it will work. In the new reactor design, the materials will be at high temperatures, reacting and bumping into each other. This will be similar to sandpaper that will rub the material, causing degradation. Doing the cycle testing in a stationary system will not be sufficient; it will now need to be done in a moving system that simulates the reactor conditions. The Hydrogen Analysis (H2A) economic analysis' capital investment costs seem very low. The other assumptions are not listed, so it is hard to tell the reasonableness of the analysis. For example, it is unclear how much spray processing of the materials will cost. The reaction vessels in the new designs may have relatively high operation and maintenance (O&M) costs, especially considering the fluid bed reactor design that was proposed. This needs to be considered.

- New reactor design offers improvements. The improved yields under pseudo-isothermal conditions are encouraging. The amount of active material is a concern. According to the presentation, 1 g of active material yields 0.0002 mol or 0.0004 g of hydrogen. This yield is very low for a commercial process that operates under sunlight. Another concern in this project is the durability of the particles. The use of results from chemical looping combustors (CLCs) may not be appropriate for this project. The reactions are quite different. In the CLC, a metal oxide is used to oxidize C or CO, and the metal oxide is reduced to the metal. The second bed then reoxidizes the metal. The reaction in a CLC has a displacement mechanism, not an O-vacancy mechanism. The potential for attrition of the moving particles appears high, especially at 1500ºC–1350ºC. X-ray diffraction (XRD) is not the "best" technique for assessing particle durability. XRD is not considered sensitive to materials present at 5%–10%. The use of intensity as a measure of sample integrity is very difficult because exactly the same amount of material has to be present in all samples that are being compared. Fines may or may not have the same crystalline structure, and it is expected that the number of fines will change with time. The summary statement that material costs cannot meet the target cost indicates that more work should be focused on establishing the material itself and its durability and cost. Defining symbols and providing yields in understandable units was appreciated.

Question 3: Collaboration and coordination with other institutions

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

- Collaboration and coordination are good. The National Renewable Energy Laboratory (NREL) provides excellent sources of experimental facilities and solar design capabilities. Sandia National Laboratories (SNL) has outstanding system design and analysis capabilities, but this institution is focused on its own competing reactor concept and is unlikely to provide significant support to the design and modeling effort essential to this project. ETH Zurich can and likely does provide considerable active particle assessment. The project would benefit enormously from adding additional collaborative effort in reactor system design and modeling, as well as solar system and interface design work. The presentation mentioned collaboration with "ANU," but this institution was not identified.
- Students are afforded the opportunity of working at NREL, SNL, and ETH Zurich. The potential for cross-fertilization of ideas is high.
- This project was led by the University of Colorado Boulder (CU-Boulder), in collaboration with NREL, SNL, Lawrence Livermore National Laboratory (LLNL), and ETH Zurich. The project supported a large number of graduate students.
- This was lightly touched on during the review, but the partners seem to be working well together. It is not clear who is responsible for new materials innovation and synthesis. Perhaps it is CU-Boulder. Expanding effort and collaboration in this area to accelerate materials innovation should be considered.
- It seems that most of the collaboration involved using others' facilities or asking questions. Increased collaboration would be good for progress. There does not seem to be anyone on the team with practical experience in building commercial systems. There is a university and two national laboratories. A partner with industrial experience would be a good addition.

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

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

- This project provides outstanding support to progress toward DOE Hydrogen and Fuel Cells Program (the Program) goals via the solar thermochemical hydrogen production pathway. Solar-to-hydrogen efficiency potential is high, providing some promise of reduced solar capital cost if heat recuperation can be demonstrated. Concern regarding durability of the active material needs to be addressed as well. The project should be continued with some change in project priorities and with additional collaborative support.
- This work is generally relevant to the overall objectives of the Program. However, this project is an example of high-risk, long-term research that has a low probability of ever being practical. There are so many technical challenges, many of which are acknowledged in the presentation: durability of the redox particles (both in terms of mechanical durability associated with particle transport and in terms of redox effectiveness over a large number of cycles), solar receiver design (i.e., materials and scale-up), heat recuperation at very high temperature, etc. In addition to the numerous engineering and materials issues associated with this concept, the ultimate potential for large-scale deployment of this technology is minimal. Even if the discussion is strictly limited to consideration of purely solar technologies, photovoltaic-water electrolysis is currently available off the shelf with solar-to-hydrogen efficiency of at least 18%. High-temperature steam electrolysis, which is at a high level of development, powered by photovoltaics, and thermally integrated to concentrated solar thermal energy, can achieve a solar-to-hydrogen efficiency of at least 30%.
- The project is extremely ambitious, as there are development challenges for nearly all aspects of the project. The costs associated with the solar field and the reactors are very high. In theory, this project meets the DOE goals, but the challenges are overwhelmingly high. The relevance of the project cannot be properly assessed until particles with the desired redox properties and necessary durability and cost are identified. Preliminary H2A analysis is promising but not complete—the summary statement specifies that tower and materials cost targets have not been met. Materials of construction are still under development and therefore not included in the cost. If atomic layer deposition is required to prepare containment material of varying compositions, costs could be very high. But it is expected that the costs of the solar field and the reactors will dwarf all other costs.
- This is a long-term development area for DOE. The reactor design is extremely complex. Having multiple reactors on the power tower will mean that should one reactor fail, then all of the reactors will need to be shut down.
- As it stands today, the project has poor prospects of meeting the goal of efficient and cost-effective hydrogen production. Here are some broad numbers to illustrate the reason. Given the productivity and kinetics of the current materials, the reviewer estimates to achieve the target of 50 ton/day hydrogen production as mentioned in the review material, the reactor will need to circulate a few hundred tons per minute of solids and have a solid inventory of over a 1,000 tons (solar intermittency is included in these calculations). These numbers are several times those of the largest FCC reactor the reviewer knows of and are likely to require close to $1 billion for just the reactor. (The reviewer used the FCC because it is a solid circulating reactor, with established technology and economics. Also, energy storage solutions will save reactor cost but increase capital requirements for other units.) A number of smaller reactors could be built, but that increases cost by negating economies of scale. These considerations, not even including the cost of the solar tower(s) and the rest of the plant or the challenge of building such a massive reactor(s), led to the conclusion that unless much more productive materials are found, the prospects for economically viable hydrogen production using this technology are poor. For comparison, a 50-ton-hydrogen-per-day steam methane reformer (SMR) plant (quite small compared to a world-scale plant) would likely cost around $100 million. Also, CO_2 capture has been demonstrated at scale with an SMR (e.g., Air Products and Chemicals, Inc., in Port Arthur, Texas). Also, it is not clear what the total capital investment figure of $70 million reported on chart 15 include, but it seems to be much too low an estimate.

Question 5: Proposed future work

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

- Proposed future work includes evaluation of redox material and particle stability, continued screening of potential redox materials, improved reactor design, and more detailed techno-economic modeling. These tasks address the major development issues.
- It is good to see increased collaborations are planned. It is good to see that durability tests are included. The design of these experiments must take into consideration the reactor operating conditions (i.e., temperature, pressure, reactions occurring, and high material flow rate). It is strongly recommended that someone with industrial experience in fluidized bed reactors be consulted or included in the experimental design to ensure all considerations are taken into account. The H2A needs to be updated, and it needs to be transparent on the capital costs, operations and maintenance costs, etc. Materials that operate at lower temperatures, have faster kinetics, etc. should be developed.
- The plan has the correct elements but should focus most resources on assessing whether much better materials can be found. More effort in fundamental understanding, synthesis, and testing of materials will be needed and is recommended. The economic basis should be reevaluated and strengthened.
- Proposed future work addresses the critical deficiencies with some lack of clarity in work priorities. For example, the viability of the proposed cycle depends critically on heat exchange in flowing solid particle media and gas–gas recuperation, features that can only be extracted from a detailed concept design with modeling and analysis effort. Some mention of computational fluid dynamic modeling is referenced in the presentation, but a good deal more system design, along with thermodynamic and fluid dynamic modeling, must be done before substantial assessment of heat recuperation will be possible.
- The project is focused on identifying the "best" materials for two-step solar water splitting, which is critical. The redox material represents a potential showstopper.

Project strengths:

- The project demonstrates really interesting and good science and engineering. The execution seems solid. Collaborations seem complementary and effective.
- This is an innovative and potentially promising concept that has demonstrated significant potential to meet long-term Program goals. Available facilities are good to excellent, and project personnel capabilities are good.
- This is innovative, high-quality work, incorporating aspects of fundamental materials science, thermodynamics, and challenging engineering design. The effort is highly collaborative and supportive of many graduate students. Pseudo-isothermal hydrogen and oxygen evolution were demonstrated experimentally at high temperatures.
- It is a very interesting academic study.

Project weaknesses:

- More emphasis should be placed on experimental performance validation, moving toward demonstration of a fully integrated system.
- This project uses a challenging route to the goal of cost-effective hydrogen production. Current materials have low hydrogen productivity and no new leads reported. Solar intermittency increases cost substantially for any given production rate compared to continuous processes, such as SMR. It is not clear how energy storage would help much without new materials, but it would be interesting to see the economic analysis.
- The project is conducted in a university environment with project tasks tailored to meet student and academic requirements in lieu of project programmatic requirements. This deficiency can be mitigated through establishment of significant additional collaborative/teaming strategy to address critical project programmatic efforts that are not aligned with student priorities and/or capabilities.
- The current design scheme requires a large amount of materials to be moved at high temperatures and low pressures. The design will cause a high number of material interactions, which may cause degradation. The materials chosen operate at extremely high temperatures. There is a need for more materials development to discover materials that operate at lower temperatures and have faster kinetics. It was hard to tell whether

the H2A analysis was done correctly because very few details were shared. The high-temperature operation will require expensive exotic materials, and it was hard to determine whether those costs are captured in the H2A. There is no one with industrial experience on the team. There are no companies doing this, but there are processes that are similar, though in less aggressive temperatures. Someone with experience in a similar industrial process would add value to ensure the proposed process is practical.

Recommendations for additions/deletions to project scope:

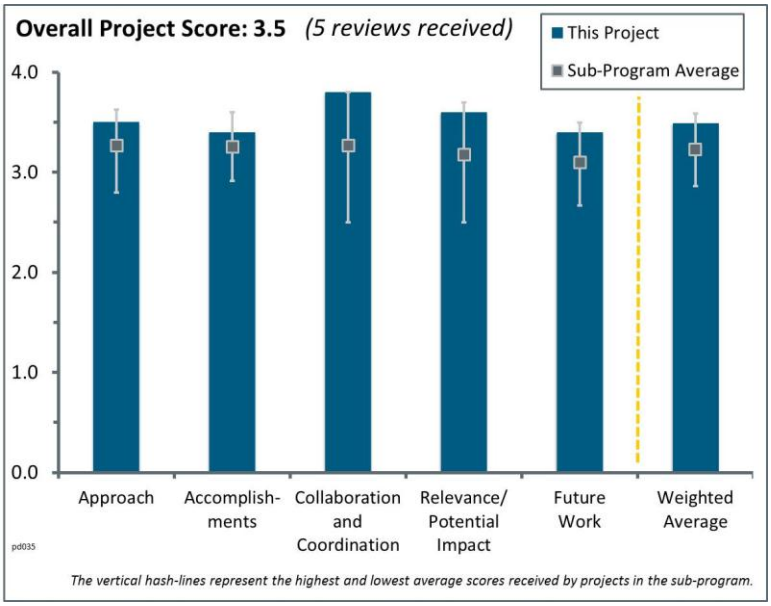
- The energy industry has much experience with reactors that are similar in design to what has been proposed. The researchers may want to engage some energy industry experts to better understand the challenges of the proposed approach.
- The project should establish a collaborative effort with an institution to address reactor design and modeling work necessary to assess gas–gas heat recuperation performance and solids heat transfer efficiency. SNL could fill this role, although the staff members engaged in SNL's competitive reactor design and modeling should be excluded from such additional collaboration. Alternatively, other non-academic institutions could be engaged, such as Argonne National Laboratory or LLNL. In any case, an institution with adequate capabilities should be engaged to accelerate detailed reactor system design, modeling, and analysis.
- Much more focus on better materials and realistic economic assessments is recommended. The project should deemphasize, but not totally eliminate, the reactor design effort. Bigger efforts can be resumed when better materials are found.

Project # PD-035: Semiconductor Materials for Photoelectrolysis

Todd Deutsch; National Renewable Energy Laboratory

Brief Summary of Project:

A long-term objective for this project is to develop a highly efficient, durable material that can operate under 10x–15x solar concentration and generate renewable hydrogen for <$2/kg via photoelectrochemical (PEC) water splitting. Objectives in the current year are to push the boundaries on achievable semiconductor PEC solar-to-hydrogen (STH) efficiency values and to continue development of stabilizing surface modifications viable at high current densities, focusing on III-V crystalline semiconductor systems and stabilization of $GaInP_2$ surfaces.



Question 1: Approach to performing the work

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

- A clearly defined research objective has been implemented and continues to show great promise. The III-V materials class is shown to provide a viable pathway to cost-effective hydrogen production. The focus of passivating the surface against photo-corrosion is showing promise, and the supporting collaborations provide the pathway to the development of a viable material.
- The focus of this team on improving efficiency and durability of existing materials in addition to investigating novel materials is an excellent approach to address some of the main barriers for the PEC Working Group.
- This is a premier group working on high-performance materials for PEC electrodes. The group's extensive experience, thoughtful approach, and innovations set a high standard for the field. The only reason the reviewer did not rate the project as "outstanding" is because the materials work could be strengthened to include a strong failure analysis component to truly understand the physics and chemistry of device degradation, and to utilize processes that are manufacturable for large-scale installations, rather than laboratory tooling. This knowledge will be invaluable to making progress toward the DOE Hydrogen and Fuel Cells Program (the Program) goals. A partnership exists to do this work; however, it is not clear whether it is active enough to serve the needs of the Program.
- The approach to developing high-STH, efficient, durable PEC materials is excellent. The work has resulted in significantly increased operational durability, greater understanding of the mechanisms of degradation, and demonstration of significantly increased STH efficiency. While these metrics still fall short of the requirements for cost-effective PEC hydrogen production, the progress is encouraging. An integrated production concept is presented, although detailed design awaits final selection of active interface materials with effective catalyst formulations, as well as electrolyte formulations that avoid or mitigate electrode fouling. Accelerated progress might be possible upon implementation of in situ observations of operational changes in interface characteristics, such as chemical composition and/or energy states of interfacial active materials. Gross or integrated performance measurements are useful but seldom carry all the information necessary to identify underlying causes of performance changes.
- It is refreshing to see optimization/extension of durability for known materials versus continuing to look at new scattered directions. It is unclear what impact lifetime has on cost projections. A tornado plot would help. There is a good and balanced mix of detailed characterization, modeling, and modification. It is not clear what the practical/achievable scale is. There is good grounding in Pt content, but it is unclear if there is a long-term plan to get around.

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.

- Accomplishments over the past year show excellent progress toward the project goals, which themselves are targeted on the DOE goals. Especially encouraging is the continued advance of interfacial material understanding developed under this project. Faradaic yield measurements are encouraging, although the on-sun experiments showed damaged electrode surfaces, indicating continued work needed for interface protection. The DOE PEC Working Group and Joint Center for Artificial Photosynthesis (JCAP) address very similar goals and could benefit significantly by effective and mutually agreeable collaboration. Such collaboration might benefit from encouragement to both the PEC Working Group and JCAP by DOE Hydrogen and Fuel Cells Program (Program) management. Insufficient data are presented for a firm conclusion, but sonication of fouled electrodes followed by fresh electrolyte appears to accelerate failure of treated samples. The one case presented of electrode performance without sonication and refreshed electrolyte appeared to show reasonably stable operation until termination of the measurements. If this observation is true, then it seems essential that the project identify the causes for rapid failure of cleaned, treated electrodes.
- Significant progress made by this team on this project include the publication of the book on PEC standards, the improvements in durability on the $GaInP_2$ material, and the photoreactor testing.
- The recent progress is encouraging. The dilute Pt/Ru passivation discovery provides a clear research direction to enable a process effective semiconductor for photoelectrolysis. This group continues to be a central leader in photoelectrochemistry, with efforts in both fabrication of high quality III-V semiconductor material and methods for improving the semiconductor durability.
- This project is making notable progress toward its goals; however, the true feasibility of this approach to reduce the cost of hydrogen at scale was not clearly explained. It is not only about the cost of the materials; it is also about the cost of production of the reactors (i.e., large-scale devices), and this has not yet been considered. It is a great accomplishment to keep these materials from dissolving fast, but a clear path to month- or year-long durability has not yet been laid out. It would be very useful if these two points were considered in developing plans for next year.
- The difference in decay on slide 12 between treating and not treating is not clear. There is good identification of side issues, such as Pt fouling, which could have misled results. The setup of the surface passivation test was well thought out. It was very good to see some type of reactor and measurement of H_2/O_2, even if rudimentary. Comments from the previous year were taken into consideration and addressed.

Question 3: Collaboration and coordination with other institutions

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

- Collaboration and coordination with other work and institutions in the PEC Working Group are outstanding and should be seen as an excellent example for other projects to emulate. At the same time, there is much effort outside the DOE/Energy Efficiency and Renewable Energy PEC arena that could benefit from and contribute to the field of PEC research and development if an effective collaborative framework could be established.
- The extensive collaboration of this team with other researchers is an outstanding element of this project.
- The National Renewable Energy Laboratory (NREL) group goes to great lengths to establish and support collegial relationships for the development of this technology. A very close relationship has been established to support the surface analysis effort, which has been proven to have high efficacy with the joint discovery of a passivation method for the semiconductor surface.
- This project is very well connected to key collaborators. The relationships are well leveraged to reach the project's goals. One item the reviewer would have liked to have heard more about is how all the collaborators besides those at University of Nevada, Las Vegas, (UNLV) and Lawrence Livermore National Laboratory (LLNL) are contributing to the work. Also, the UNLV team seems to have broad resources that could be useful but are not really being used for the project.

- UNLV and LLNL collaborations are clear and add important contributions. Roles of others are not as clear and could be further elaborated.

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

This project was rated **3.6** for its relevance/potential impact.

- Given the current state of the art, this project pursues the most promising materials system for practical PEC.
- Relevance and potential impact of this project are excellent. Successful implementation of improvements identified in the waterfall chart would lead to meeting DOE's long-term goals for PEC hydrogen production. The roadmap implicit in the waterfall chart provides excellent guidance to project tasks and priorities. Quantitative metrics for identifying go/no-go decisions are identified in the tasks in the waterfall chart. The project would be improved by estimation of the schedule and cost for meeting these quantitative go/no-go decision points.
- This project is definitely well aligned with DOE's long-term objectives on renewable hydrogen production pathways via PEC water splitting. It is addressing some of the critical parameters to meet DOE's cost target for this technology.
- As shown in the presented waterfall chart, the III-V materials class has a viable pathway to achieving the DOE benchmark for cost of hydrogen production. This material currently presents the minimal risk for achieving these goals. The work being conducted here is highly relevant to achieving the DOE goals.
- The project is an important part of the portfolio, but the general agreement is that commercial PEC is a long way off. There is a need to balance near- and long-term components of the Hydrogen Production and Delivery sub-program portfolio (this is a general comment for the Program).

Question 5: Proposed future work

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

- Proposed future work is to be focused on durability, efficiency, and materials cost. A photoreactor prototype should provide a good basis toward achieving the main goals of this project.
- The continued development of this materials class for durability should remain the primary focus. The NREL group proposes raising the efficiency of the III-V tandem to 25%—a requisite to achieving the cost metric. Alternative, more cost-effective fabrication methods are proposed. Although it is interesting to identify cost-effective alternatives, at this point it is most important to develop the passivated materials.
- Segmented cell characterization will provide value; work to extend durability seems reasonable and is a critical need.
- Proposed future work identifies tasks, but little detail on how these tasks are to be implemented is provided. Task priorities and mitigation or "workarounds" for unsurpassed barriers are a weakness in the project. Optional approaches should be identified for those critical issues that could lead to unacceptable concept performance.
- The proposed future work (slide 22) seems to be too large of a step from where the project is today. This is the correct long-term direction; however, moving to solar concentration and solving all the resulting materials problems without robust options for corrosion protection and system durability and stability seems very challenging. The reviewer would have liked to have seen more of the roadmap laid out.

Project strengths:

- This project has a significant history with, and understanding of, the III-V semiconductor material for PEC hydrogen production. This material offers the best pathway to achieving the DOE goals for cost-effective solar hydrogen production. The expertise with the NREL group and the extended collaborative PEC Working Group results in a formidable team with an unprecedented capability for both theoretical and experimental investigations.

- The concept, approach, team, and collaborators make this a very strong and viable project. Integration of basic materials science into the fabric of assessment and analysis adds great strength to the approach.
- This project is focused on the most promising materials set for viable PEC generation of hydrogen. The understanding of the device requirements is deep.

Project weaknesses:

- The singular weakness with this project is the disconnect with the fabrication team for III-V material. It appears that the material is produced with a foundry-type relationship. It would be better served if the material fabrication was a more integral part of this project, with a shared ownership in the success. The project needs a larger quantity of material at this point of the research effort.
- Planning of future work is deficient in seeking optional paths forward should one or more of the current tasks fail to succeed.
- The chief weakness of this project is in its lack of materials characterization. Good connections exist with the UNLV team, but extensive routine chemical and physical analysis was not reported at the level the reviewer expected. Inductively coupled plasma (ICP) mass spectrometry, which is hard to do quantitatively for alloys, and optical inspection are the main tools—moving beyond them will really benefit the project by revealing the true nature of degradation and the consistency of the structures being built. What is being done now is too qualitative to inform the work at the level needed.

Recommendations for additions/deletions to project scope:

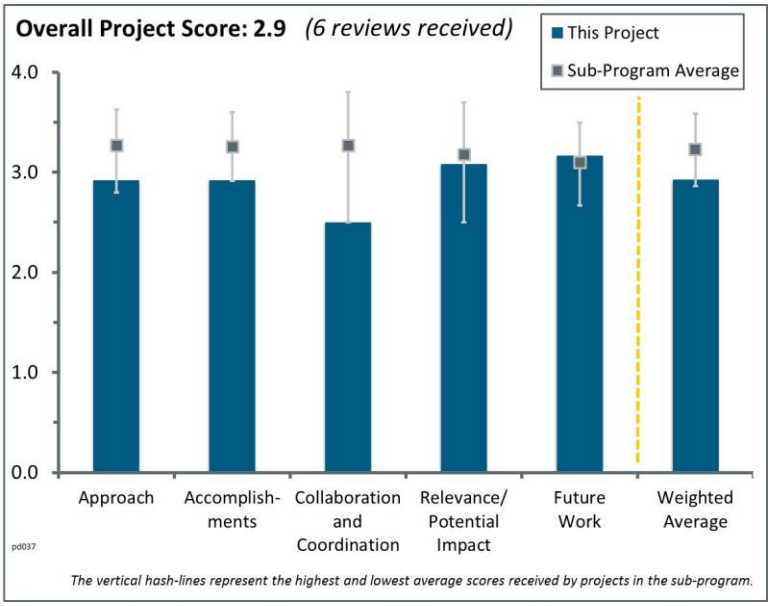
- Additional effort should be added in attempting to make in situ observations of material interface properties under operational conditions. This would be a first of its kind in materials science and could lead to process understanding of extraordinary merit. This is a rich area for instituting collaboration with other programs doing similar work, such as JCAP.
- It is recommend that a plan be made to expand the scope to incorporate new partnerships and, perhaps, new instrumentation for detailed materials characterization. Active partnering to bring in materials innovations as they are published and leveraging work in related programs as appropriate will be beneficial. This is truly essential for the project to meet its goals.

Project # PD-037: Biological Systems for Hydrogen Photoproduction

Maria Ghirardi; National Renewable Energy Laboratory

Brief Summary of Project:

The primary goal of this project is to develop photobiological systems for large-scale, low-cost, and efficient hydrogen production from water. Two specific tasks are being addressed. Task 1 explores the oxygen sensitivity of hydrogenase that prevents continuous hydrogen photoproduction under aerobic, high solar-to-hydrogen (STH) conversion efficiency conditions. Task 2 genetically adds various desirable traits to an algal straining expressing and oxygen (O_2)-tolerance hydrogenase to achieve higher STH and longer durations of hydrogen photoproduction.



Question 1: Approach to performing the work

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

- This project is well focused on the hydrogen production rate and O_2 accumulation barriers, and it is pursuing these in a rational fashion through a combination of genetic modification and improved and more consistent techniques. The project's work with algae complements work by Pin-Ching Maness with a cyanobacterium.
- The approach to boosting hydrogen production from the O_2-tolerant clostridial hydrogenase using new transformants with introns was a logical next step, even though it did not increase hydrogen photoproduction.
- The outlined tasks contribute to overcoming limitations in hydrogen production, including using a bacterial hydrogenase with less O_2 sensitivity. While the project aims are on task, some of the challenges due to experimental results and personnel changes have led to delays or changes in milestones.
- At a broad level, this project and PD-095 share similar traits, although the details are different. The comments here are almost the same used for PD-095. The approach is clear and seems suitable to the objective as stated, but the objective itself is narrow, and it is not put into the broader context of producing hydrogen in a cost-effective manner. The problem tackled here is only one of the pieces needed to make hydrogen, but there is no information about the relative importance of this piece versus the others (e.g., photosynthetic efficiency). It is perfectly fine to work on a piece of the whole in parallel, but context would be useful to assess whether the whole is worthwhile to begin with. The reviewer appreciates the project's recognition that more steps need to be taken care of (Subtask 2).
- The proposed approach appears logical, but this project seems to have had many changes in scope and milestones that have been postponed. Hence, there is concern that the principal investigator (PI) does not have a clear understanding of what is needed to achieve the proposed goals.
- There appear to be issues with control of gas headspace in the hydrogen production test cell, preventing assessment of the true kinetics of hydrogen production (e.g., Strain 55 cumulative hydrogen production should show steady increase over 30 min).

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

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

- Steady progress continues; the researchers were successful in generating and testing the impact of intron transformants, albeit it is not clear whether this area was adequately pursued because inadequate funding was cited as a reason for working only with constructs of the RBCS2 intron. Perhaps if more funds were available, the same decision would not have been made. Additionally, the researchers made a significant observation that hydrogen pressure buildup in the bioreactor headspace was a contributing factor to hydrogen production, and hence, a simple modification of bioreactor size may significantly improve hydrogen yield.
- There is good progress with genetic engineering of *Chlamydomonas* to demonstrate improved O_2 tolerance to meet 2015 targets. The reasons for greatly decreased hydrogen production in the engineered strain were not clear; it seems that the 50-fold reduction relative to the wild-type strain cannot be due to a reduced Michaelis constant (Km) alone. More scientific discussion is warranted. No publications were reported for the current review year.
- This research has encountered some delays due to equipment (i.e., microscopes) and personnel (loss), as well as encountering a no-go decision. However, it appears to have rebounded from the no-go decision with new ideas and has continued to progress its research.
- The experimental challenges, equipment delivery problems, and loss of personnel have led to a delay or change in scope of milestones. The PI has taken steps to mitigate problems and has implemented new approaches to meeting milestones.
- Qualitatively, it looks like some progress has been made. The reviewer appreciates that this project reports data on hydrogen production, which is a relevant metric. As the authors clearly say in the presentation, the metric is still far from the target.
- There are some new results, but there do not appear to be any major accomplishments during the last year. Much of the truly challenging work appears to have had the completion date postponed.

Question 3: Collaboration and coordination with other institutions

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

- While this project claims no formal partners, it is interacting with the laboratories of Professor Tasios Melis, Dr. Gilles Peltier, and Professor Matthew Posewitz in accessing genetic materials and techniques, as well as obtaining assistance from Professor Patrice Hamel for work related to Task 2 (i.e., acquiring desirable traits). These appear to be unfunded.
- The National Renewable Energy Laboratory team looks strong, but it does appear that the budget supports outside collaborators, particularly with expertise in bench-top photobioreactor design for biohydrogen experiments.
- There is little outside collaboration, and much of it appears to be out of necessity rather than experimental and task design. Work on understanding the reactor conditions for the *Chlamydomonas* is an area that may provide fruitful outside collaborations (e.g., photobioreactor design, etc.).
- There was one unpaid collaboration for the project. According to researchers, there would have been more collaboration if funding had been sufficient.
- The PI commented that the lack of collaborations was due to lack of funds. In response to a previous reviewer's questions, the investigator indicated that unfunded collaborations were continuing. Any existing collaborations were not addressed in the main body of the presentation.
- Collaboration was not really discussed much. There were none for Subtask 1 and "unfunded help" for Subtask 2. It is not clear that the resources are appropriate for success.

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

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

- There were no issues; the research is highly relevant to the DOE Hydrogen and Fuel Cells Program (the Program).
- Photobiological water splitting coupled to hydrogenase-mediated hydrogen production is an important approach to achieving DOE long-term hydrogen production goals.
- The project is in line with the Program goals. Based upon the data presented, the project has the potential to meet the Program goals; however, the current low rates of hydrogen production and the multiple steps needed to increase to fiscal year 2015 (FY 2015) targets and beyond may take longer than outlined.
- If successful, an STH-efficient algae possessing an O_2-tolerant hydrogenase could make a significant contribution to DOE's photobiological hydrogen production goals. Equipment (i.e., photobioreactor) modification to provide more headspace, technique improvements, and crossing with three other strains to acquire desired traits could be a significant move to satisfying most of the 2012 Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan's 2015 photolytic biological hydrogen production targets.
- While this work is interesting, it is not clear how this PI's work has the potential to be high-impact. This could be more a function of the presentation and less a function of the science.
- This is only a piece in producing hydrogen from water splitting by microorganisms. In isolation, it is hard to assess whether even complete success would help the final goal.

Question 5: Proposed future work

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

- Switching to a different plasmid to progress Task 1 is commendable; crossing an O_2-tolerant recombinant with three other strains to confer additional traits in pursuit of increased STH efficiency is very laudable.
- The proposed goals for FY 2015 are excellent, but there are concerns about the PI's ability to meet those goals, given past performance. However, because of the amount of effort already put into this work, it should be seen through to a logical completion.
- The proposed future approach includes many experiments to increase the rate of hydrogen production and is well thought out. There may be risks and challenges that have an additive effect and result in delay of project targets, though.
- The proposed future work seems appropriate for the narrow objective. Resources are questionable.
- More detail on Subtask 1 would be appreciated, specifically with regards to the hypothesis-based approach to (a) identifying current rate-limiting steps and (b) finding and decreasing data variability.

Project strengths:

- The PI clearly understands the Program goals and has designed milestones and tasks to address current barriers for efficient hydrogen production. There are multiple approaches to increasing hydrogen production, and they span many different aspects of the production process.
- Future plans to introduce several new traits in pursuit of improved STH are very laudable.
- The pioneering work that was completed over the past 12 years and the body of knowledge generated will continue to advance similar efforts.
- The team's biology expertise is a project strength.
- Good progress on genetic engineering of *Chlamydomonas* for improving O_2 tolerance under hydrogen production conditions at full sunlight has been made.
- The project has interesting approaches to decreasing O_2 sensitivity and increasing hydrogen production.

Project weaknesses:

- The team could benefit from the knowledge and experience of other experts in the field.
- There may be other steps in the pathway that can limit hydrogen production even if the problem at hand is successfully solved.
- There are concerns about the project's ability to complete stated goals.
- While the multiple approaches to increasing productivity are appreciated, it presents a challenge to the team to optimize production with many variables in play. It could be useful to assess the relative impacts of variables and focus efforts more in that direction. A more thorough description of the biological methods to improve hydrogen production, particularly with respect to the aggressive targets, would have been appreciated.
- The hydrogen production test cell should be redesigned to provide data on the true kinetics of hydrogen production. The project needs a hypothesis-based approach for addressing low hydrogen production to better interpret current data and to identify more specific strategies for proposed future work. Plans are needed for presentation and publication of the work to get feedback from the biohydrogen research community.

Recommendations for additions/deletions to project scope:

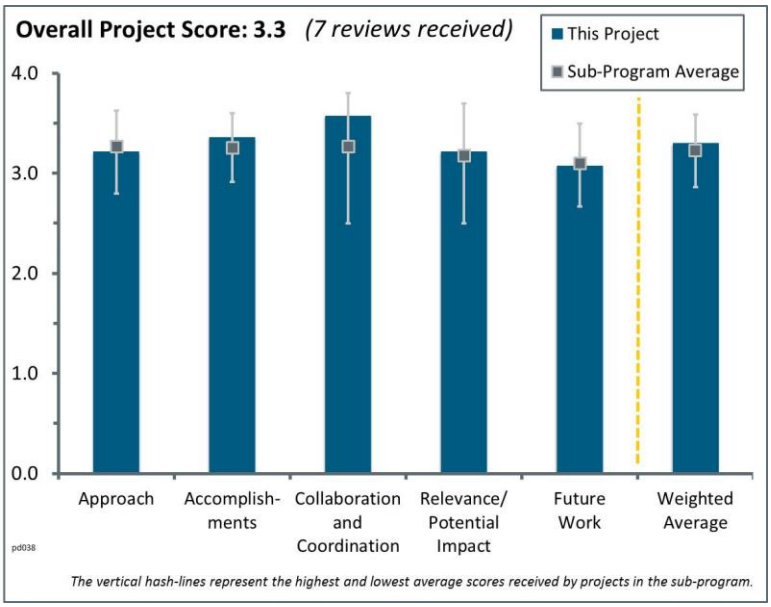
- The PI should consider collaborations to increase the likelihood of success for the project, specifically ideal photobioreactor use/design and organismal engineering.
- The project should consider appropriateness of resources and reassess the potential of the entire pathway.
- The basis of milestone targets is not clear. This research project had a Q2-1 go/no-go milestone of: (1) an initial rate of 11 µmol H_2/mgChl/h, (2) a final rate of 0.06 µmol H_2/mgChl/h for (3) at least 30 minutes, and (4) equal to or >1x (slide 8) or 2x (slide 15) than the final wild type (WT) net yield. It would be useful if such values could be related to DOE targets in some way or simply related to being confidently better than a baseline (e.g., WT) performance.

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

Pin-Ching Maness; National Renewable Energy Laboratory

Brief Summary of Project:

The overall objective of this project is to develop direct fermentation technologies to convert renewable lignocellulosic biomass resources to hydrogen. Feedstock costs are being addressed via bioreactor development using lignocellulose. The bioreactor is optimized by testing parameters, such as lignocellulose loadings, hydraulic retention time (HRT), and liquid volume replacement and frequency, using the cellulose-degrading bacterium *Clostridium thermocellum*. Hydrogen molar yield is boosted through genetic engineering and integration with microbial electrolysis cells (MECs).



Question 1: Approach to performing the work

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

- The programmatic approach is logical and has a clear target.
- The project objectives are focused to address the barriers related to hydrogen molar yields and system engineering. The feedstock cost barrier is partially addressed by projects funded by the Bioenergy Technologies Office (BETO) in other groups at the National Renewable Energy Laboratory (NREL). Some of the cost-prohibitive elements of utilizing lignocellulosic feedstocks (e.g., pretreatment of biomass and removal of acetate in future work) are being studied by BETO projects.
- Trying direct conversion of cellulose instead of sugars to try to lower feedstock costs is an understandable and good approach. An alternative is direct biomass gasification to hydrogen. This approach should be compared to the project's approach to see which pathway has more promise. The tasks of optimizing the bioreactor and of redirecting metabolism to improve hydrogen productivity make sense, but an assessment of what the targets need to be to reach cost-effective hydrogen production would be helpful. It is not clear whether there has been consideration of what to do with the C5 sugars, which are a substantial fraction of the feedstock. Presumably, they are supposed to be used in the subsequent microbial electrolysis step, but clarification would help. It is clear why MEC is envisioned as a way to use a lot of the feedstock unutilized in the fermentation reactor, but it would require more investment.
- The genetic toolkits developed for pathway engineering and generation of *C. thermocellum* mutants were effective. However, the approach would greatly benefit from metabolic flux analysis experiments, which may identify more appropriate targets for metabolic engineering leading to increased hydrogen production and lowered organic acid/alcohol byproduct formation.
- The project is well-focused on the hydrogen molar yield) and feedstock cost barriers by employing a novel electrolytic approach to increasing hydrogen yield and processing lignocellulosic biomass. Systems integration awaits further development and characterization of both the fermentation and electrolytic subsystems.
- The approach continues to be adequate. There is still a long way to go, but the approach may need reconsideration of components to make real progress.
- The three-step approach to increasing hydrogen yield (i.e., optimizing the bioreactor process, knocking out pathways to lactate and ethanol production, and using MEC to convert byproducts to hydrogen) is sound

from the perspective of increasing hydrogen generation, but it is hard to imagine that this rather complex approach will meet the DOE Hydrogen and Fuel Cell Program's (the Program's) economic targets.

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 overall project made a significant amount of progress to achieve stoichiometric hydrogen production from cellulose. There was one publication and three presentations resulting from the work during the reporting period.
- Other than a delay in generating a delta triple mutant, progress appears to be on track.
- Good progress and intermediate accomplishments have been presented, although the project has been going for eight years.
- Many milestones are completed, particularly for utilization of cellulose from lignocellulosic biomass, while many others are on track after delays.
- The results that indicated no lignin inhibition were very strong. The knockout work to generate a strain that contains only the acetate pathway is interesting, and the initial results with the formate pathway knocked out are promising. The Pfl knockout results did not appear to have a significant difference in final production. On slide 10, figures A and B do not seem very different. Slide 10, section C does show an increase in lactate from 10 to 14 hr, but by 22 hr the Hpt knockout is similar. The MEC results in Task 3 were interesting, but apparently there are concerns about scale-up that were raised by another reviewer.
- Progress has been slow but steady. The improvements in lignocellulose conversion due to bioreactor optimization, the unique capability to transform *C. thermocellum*, and the design of a plasmid to knock out lactate production are all significant contributions toward efficient conversion of lignocellulose to hydrogen.
- The project has made very good progress in increasing hydrogen productivity in the bioreactor, but much more is needed. There is good progress in redirecting metabolic pathways to increase hydrogen production. However, the expected improvement from this approach, if successful, is not clear. Clarifying what success looks like and assessing whether it is worth the effort in terms of increased hydrogen are suggested. The 10% improvement suggested in the table on slide 8 may not be large enough. Similarly, while it is clear why the researchers are using MEC and how it increases the overall use of the feedstock towards making hydrogen, it is not clear what the MEC performance target needs to be to make the overall process viable. Whether success in MEC is nice to have or critical, and/or worth the investment, needs to be assessed. Also, clarifying the source of waste heat for MEC in the overall process or, alternatively, defining the needed power to drive the process is suggested. Overall, this project would benefit from a better definition of the integration between the three key pieces: bioreactor, metabolic pathways, and MEC. As it stands, it is not easy to see how improvements in each benefit the whole and how much improvement in each is needed.

Question 3: Collaboration and coordination with other institutions

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

- This project has strong external collaboration.
- The project has strong ties with a biomass feedstock source, Canadian researchers developing genetic methods (with leveraged Canadian funding), and Dr. Bruce Logan (microbial electrolyzer).
- The two principal investigators (PIs) are well coordinated and are working towards the same goal. For the past and proposed future work, further collaboration with NREL scientists working on BETO-funded projects is encouraged to fully utilize their biomass and organismal design capabilities.
- The collaboration with Dr. Bruce Logan is strong and well integrated.
- The collaboration with Dr. Bruce Logan is apparent, as are the in-house NREL collaborations and the collaboration with Genome Canada.
- The collaboration appears adequate.

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

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

- There are no issues; the research is highly relevant to the Program.
- This work will significantly add to the body of knowledge that hopefully will ultimately lead to a one-step process where neither pretreatment nor MEC will be needed to produce the 8 mol of hydrogen or greater yield at the targeted costs.
- The inexpensive feedstock and potential of near-complete conversion to hydrogen make this technology pathway very attractive, assuming rates are adequate to keep capital costs competitive, other efficiencies are reasonable (including identifying the source of the yield reduction when compared to pure cellulose feedstock), and the ultimate system can demonstrate high utilization rates.
- The PIs are focused on addressing barriers to biological hydrogen production that would address the programmatic needs of the Fuel Cell Technologies Office (FCTO). The rates of microbial production, source of sufficient biomass resources, and rate of MEC hydrogen production may be insufficient when scaled up to significantly impact the market.
- Lack of information on the bioreactor/MEC integration and on MEC production rates and power use makes it difficult to assess the overall scheme in terms of cost-effective hydrogen. The data on the bioreactor can provide the basis for some estimates. In addition, the 2020 targets shown on slide 3 need to be addressed. Assuming success in reducing feedstock cost to 8 ¢/lb sugar and in increasing the yield of hydrogen in the bioreactor, then just the biomass feedstock (no capital costs) adds up to nearly $3/kg of hydrogen. Of course the extra production from MEC improves the hydrogen cost because the feedstock is free, but there is not enough information to assess the contribution of MEC to the overall cost. Based on the hydrogen production rates in the presentation and from subsequent discussions with the PI, to achieve 50 tons/day hydrogen production currently, the total bioreactor volume would need to be several 100 million liters. The largest corn ethanol fermenter may be close to 2 million liters today, and three of those are usually used. Either the production rate of the bioreactor is increased almost 100 times, or there is a substantial contribution to hydrogen production from MEC, which is difficult to estimate with the data provided.
- The results of this effort seem to have demonstrated a step forward in the field. There are concerns about the real-life applications and scale-up of the current technology.
- This is still far from being a viable effort, except for niche applications.

Question 5: Proposed future work

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

- Future work is the logical extension of past successful work by existing collaborators.
- The proposed future work is well thought out for the three tasks presented. More information regarding Task 4 would have been appreciated.
- It will be exciting to see whether blocking both lactate and ethanol production pathways significantly increases hydrogen yield.
- The proposed work should continue to advance this interesting project. There are concerns about the ability to knockout all but the acetate production pathway. The cell seems to favor other methods, as demonstrated by the increased ethanol production. Leaving only one of four pathways as a formate pathway could overwhelm the cell and result in other unintended mutations.
- Metabolic flux analysis is needed. It is unclear how the process flow diagram can be simplified. The project may benefit from collaboration with a chemical engineer.
- It is not clear that the proposed work on the bioreactor and the metabolism has the potential to achieve the DOE goal of cost-effective hydrogen production. This point should be clarified. The role of MEC in the overall process and its integration with the bioreactor should be clarified, as should its potential to lower hydrogen cost. Also, the power and size requirements of MEC should be quantified in a manner consistent with the bioreactor (e.g., using a common basis for the amount of feedstock processed and the consequent

bioreactor effluent fed to MEC). The fate of the C5 sugars should be clarified (e.g., whether they are utilized in MEC) in order to understand the overall efficiency and cost of the scheme.

Project strengths:

- Consolidated bioprocessing organism work is good and has demonstrated that lignocellulosic materials can be used for hydrogen production. The successful knockout of the formate-producing enzyme suggests that knocking out the ethanol and lactate pathways will increase the yield of hydrogen.
- The project has clear goals, has made very good progress, and is likely to continue to yield interesting results.
- There is good progress on bioreactor and MEC. There is impressive genetic work.
- The pioneering work to develop a plasmid that can transform *C. thermocellum* to knockout the lactase dehydrogenase competing pathway is a key strength of the effort.
- Cheap feedstock and high hydrogen yield are two project strengths.
- The project is making good progress towards achieving stoichiometric hydrogen production from cellulose.

Project weaknesses:

- It appeared that the presentation did not provide feedstock and electrode cost data to compare with the 2012 FCTO Multi-Year Research, Development, and Demonstration Plan 2015 targets.
- Some of the goals for knockout strains may be overly ambitious.
- From a process engineering perspective, the flow diagram is cumbersome and complex, requiring two bioprocess-based subsystems.
- There was a lack of discussion of other metabolic engineering that could be performed to increase hydrogen and acetate production. Mitigation strategies for potential deleterious consequences of knocking out the lactate and ethanol pathways were also not discussed. Techno-economic analysis for this project needs to be considered, particularly around feedstock cost. The cited 2011 cost from previously funded BETO work may be out of date considering new cost projections of $80/dry ton of biomass and the new pretreatment method proposed for the feedstock. Additionally, comparison of current hydrogen production methods with fermentation and MEC would be critical. It was unclear from the presentation what, if any, separations methods are being tested or will be tested for cleaning up the fermentation effluent before introduction into the MEC. Separations could be critical to successful future commercial implementation of this technology.
- Integration of bioreactor and MEC is unclear. The impact of genetic work is unclear. Overall, it is not clear what the targets for success are and if they are achievable to meet the DOE goal of cost-effective hydrogen production. Little economical assessment was done.
- After 10 years of effort, there is still no technoeconomic analysis that validates that this is a viable approach.

Recommendations for additions/deletions to project scope:

- It may be possible to think more imaginatively about this project. Right now, two subsystems are needed for the process to work. It may be possible to integrate these two systems in a way so that the carbohydrate is converted directly to hydrogen in a single bioreactor system.
- The project should look into the newly reported one-step lignocellulosic-to-hydrogen process using *Thermoanaerobacterium thermosaccharolyticum* M18 to see if the claims are credible and if the findings offer any important insights.
- This project could be more cost-competitive with a better understanding of the yield and rate of hydrogen production during fermentation, as well as characterization of the remaining solids in the fermenter. Many biorefineries use the remaining lignin after pretreatment and hydrolysis for combined heat and power, thus reducing their energy costs and greenhouse gas emissions. Understanding the quality and impact of utilizing the remaining lignin may be a new positive for implementation of this project. Separations and clean-up technologies should be addressed as part of this proposal. Perhaps instead of tuning the anodes to tolerate protein, etc., removing contaminants or fouling agents before adding the fermentation effluent to the MEC should be considered. The positive and negative impacts of separations methods should be considered within the context of a multi-step process.

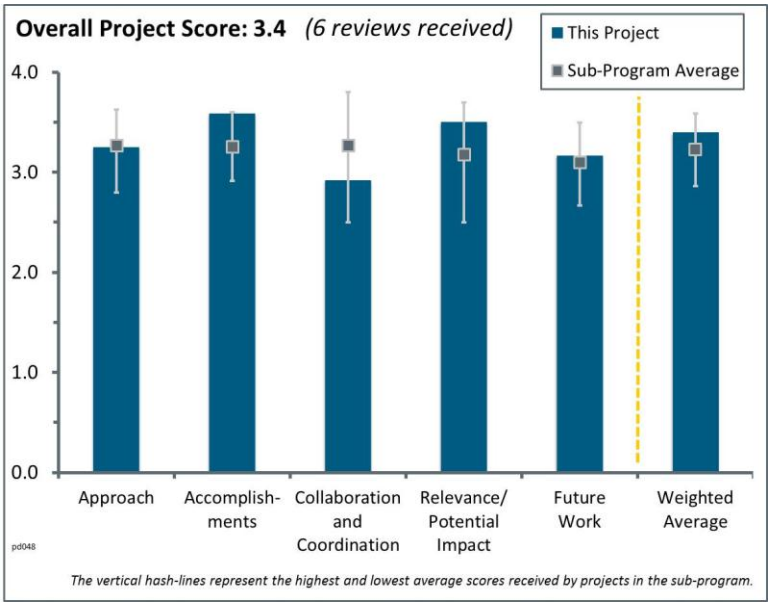
- There could be improved optimization of directed evolution of cells to improve efficiency.
- The project should clarify targets needed for success and whether they are achievable with the current organism and process; do some overall process modeling/engineering work to clarify integration of the bioreactor with MEC to assess synergies and potential; and enhance the economic analysis.

Project # PD-048: Electrochemical Hydrogen Compressor

Ludwig Lipp; FuelCell Energy, Inc.

Brief Summary of Project:

The objective of this project is to provide highly efficient, reliable, and cost-effective hydrogen compression between 6,000 and 12,000 psi through development of a solid state electrochemical hydrogen compressor (EHC). Development of an efficient EHC will increase reliability and availability of hydrogen over current mechanical compressors and eliminate the possibility of lubricant contamination, as there are no moving parts. The project strives to reach compression efficiency at 95%, which is expected to significantly reduce hydrogen delivery costs in the long term.



Question 1: Approach to performing the work

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

- FuelCell Energy has a great approach to the issue of developing a hydrogen compressor that does not use mechanical compression features. This technology also reduces the susceptibility to contaminants.
- Aggressive work to cut costs and increase pressure for electrochemical compression has been well thought out and implemented.
- The approach to this effort has been outstanding.
- The general approach has led to steady gains in hydrogen flux, cell efficiency, hydrogen compression, and cost reduction. Any future research should include process optimization studies based on key parameters, such as current density, membrane thickness, and operating temperature (i.e., optimizing conductivity vs. hydrogen back diffusion).
- Reliability, cost, and efficiency were identified as barriers, and the current project is addressing all of these.
- The project is a little weak on details of how improvements were achieved. It is understood that there is competition-sensitive information in the details, but the general thought process, analysis techniques, design principles, etc. should be discloseable.

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

This project was rated **3.6** for its accomplishments and progress.

- The move to a higher-surface-area cell is being pursued aggressively. Durability tests represent a significant milestone. Achieving 30-3,000 psi compression with a 185 cm^2 EHC stack is also a great milestone.
- Lifetime data, tests to >12,000 psi, and scale-up demonstrate the technical viability of this EHC. By increasing the current density and cell active area and reducing the cell part counts, the team has demonstrated a 60% capital cost reduction since project inception. However, to determine commercial viability, the team should also provide an economic evaluation that compares the cost of EHC to mechanical hydrogen compressors.

- The project has a clear strategy to overcome each of the barriers (i.e., higher cell area, higher current density, and lower part count to reduce capital cost). Cell improvements will increase efficiency and operating life.
- Good progress has been made over the term of the project. There are good results on membrane electrode assembly activity. The team needs to describe the benefits of having electromechanical compression over mechanical in more detail. There was some mention, but the team should stress the benefits for project recognition. There was good description of cost reduction, but the assumptions for volume manufacturing were not stated.
- Impressive gains have been made in efficiency and performance, but pressure capability is a little misleading. It is unclear to what pressure this design has been proof tested and how that relates to the International Organization for Standardization (ISO) standards for operating pressure.
- The scale-up of the prototype has been very successful.

Question 3: Collaboration and coordination with other institutions

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

- This technology is being developed by two strong contributors that are working well together. The EHC offers significant benefits specifically for those that want to implement tri-generation systems.
- The partnership of FuelCell Energy with Sustainable Innovations appears to be an effective collaboration with contributions from both partners.
- Clearly there is a close collaboration with Sustainable Innovations, but no other partners are on the project.
- FuelCell Energy has one collaborating partner to assist in EHC stack development efforts. It may be beneficial to partner with research institutions that can assist in optimizing the membrane technology for high-pressure applications.
- There are only two collaborators.
- The project is collaborating with only one partner. Working with more may allow for faster and better progress.

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

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

- The power cost demonstrated for EHC appears to be less than that of mechanical compression alternatives, and EHC offers operational benefits over mechanical compression: no moving parts, no required maintenance, and no potential for contamination of the hydrogen stream, and it promises significant operating cost savings.
- The compressor cell has utility for many applications; it could use additional focus in the DOE Hydrogen and Fuel Cells Program (the Program) portfolio either as a standalone or with electrolysis.
- Hydrogen compression is high-cost and unreliable. This project has high relevance.
- The degree of compression needed as well as the life, cost, and efficiency are all highly relevant and impactful to the goals of the Program.
- The project is related to the development of an electrochemical hydrogen compressor, which has the potential benefit of reducing the cost of hydrogen compression for various hydrogen-producing technologies.

Question 5: Proposed future work

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

- The description of the future work is exactly what will be needed to overcome the barriers still facing this technology.
- The proposed taller stack is the next step, and this work should be funded.

- Continued cost-reduction and efficiency improvements may make electrochemical compression viable.
- The proposed future work appears to be focused on continued life testing and scale-up to larger multi-cell stacks that can achieve higher throughputs. Optimizing the membrane and the process operating parameters should be considered prior to scale-up.
- Endurance tests should be continued for longer hours. The project should develop a multi-stack of EHCs to demonstrate larger production of hydrogen as needed for site refueling.
- The goal of scale-up is important, but there are no details on how this is to be accomplished and what the critical issues are expected to be. It is unclear why this project needs DOE funding. The project needs to describe the fundamental challenges.

Project strengths:

- The project strengths include the zero-maintenance compressor system, no concerns about compressor fluids contaminating the hydrogen stream, zero-noise compression, and the ability to work well with low suction pressure.
- Both partners have strengths to address the barriers to use of this technology. The presentation clearly showed the progress made during the project, which is a strong indicator of the effectiveness of the project team.
- Strong results and progress were demonstrated.
- The project has the potential to reduce capital cost and downtime as compared to mechanical hydrogen compressors.
- A big strength is that few parts are needed for high-pressure compression of hydrogen.

Project weaknesses:

- Commercial feasibility may require high current density operation to reduce capital costs.
- An essential part of the cost reduction is to address manufacturing methods to produce the EHC parts in greater quantity and at lower cost. The manufacturing methods may affect the cell/stack design.
- Cell variability is a weakness. There was no demonstration of larger-scale production from multiple stacks.
- There was a lack of detail in approach and analysis. There was no response on reviewer comments from last year. It is unclear if this project was reviewed last year.

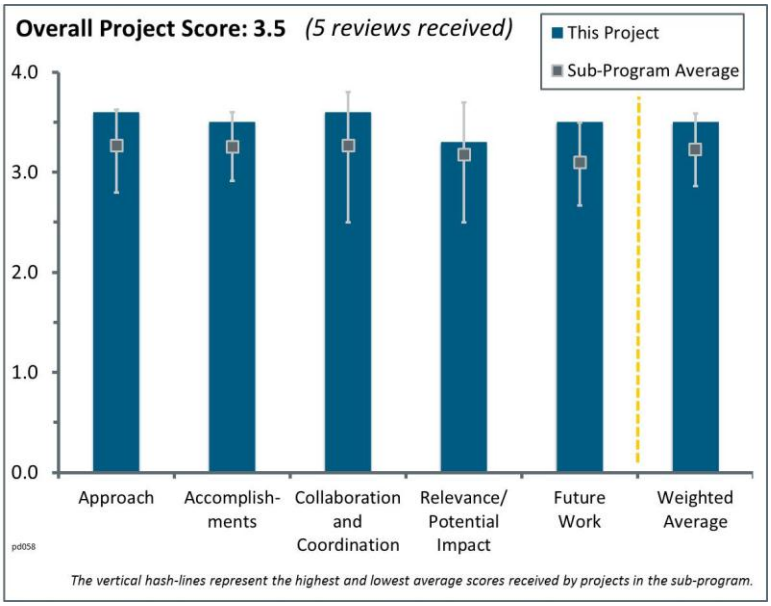
Recommendations for additions/deletions to project scope:

- The project team is on a good course. Further cell and stack improvements to both improve efficiency and reduce cost would have been a good addition to the presentation. Also, a comparison to the three-stage mechanical compression not only in efficiency but also in cost would be helpful to focus the project on areas of technology improvement relative to the mechanical compression alternative.
- The project should include project compression energy that will be required to go from 200 to 12,000 psi.
- The electrochemical hydrogen compressor development effort should be optimized before scale-up. An economic feasibility study comparing EHC technology to other compression technologies is advisable to understand commercial feasibility.
- Cell variability should be attached to ensure uniform current use. A multi-stack production system should be developed to make larger quantities of hydrogen.

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: (1) develop a theoretical tool chest for modeling photoelectrochemical (PEC) systems, (2) compile a publications database of research on relevant photoelectrode materials, (3) uncover key mechanisms of surface corrosion of semiconductor photoelectrodes, (4) understand the dynamics of water dissociation and hydrogen evolution at the water-photoelectrode interface, (5) evaluate the electronic properties of the surface and water-electrode interface, (6) elucidate the relationship between corrosion and catalysis, (7) provide simulated X-ray spectra to the University of Nevada, Las Vegas (UNLV) for interpretation of experimental results, and (8) share research insights with PEC Working Group members.

Question 1: Approach to performing the work

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

- The approach to this seriously underfunded effort is excellent. Important aspects of electrode corrosion and transport processes at the electrode–electrolyte interface have been identified. The collected database of materials properties and PEC processes has provided important insights into observed behaviors of various PEC components. In spite of limited resources, the project is aligned with other efforts that will ultimately provide improved tools for even more detailed investigation of the chemistry and dynamics of hydrogen evolution in PEC systems.
- This group is performing high-quality theoretical work on topics relevant to the Hydrogen production sub-program. It is well connected to experimental programs and to the scientific and technological communities, so its projects are appropriately targeted. The reviewer gave it an excellent rating, rather than outstanding, because it would benefit from refocusing on fewer projects and addressing them more deeply than is currently possible.
- The approach taken by the researchers on identifying the electrode properties that effect electrode stability integrated with the results and work done at both UNLV and the National Renewable Energy Laboratory is an excellent approach towards the main efforts of the PEC Working Group.
- The Lawrence Livermore National Laboratory group is responsible for theoretical work relating to the surface at the semiconductor–electrolyte interface. Using density functional theory simulations, models are being developed that help explain current issues with the surface corrosion for the III-V semiconductor material. The research provides value towards allowing the materials to achieve the U.S. Department of Energy (DOE) benchmarks for durability.
- Within the provided budget, the scope is probably all that can be managed, but it would be good to get past the schematic of “stick in a beaker” for PEC. It is not clear how this will ever get past a bench cell level. No one has done system modeling—it is unclear if this is planned. There is a good connection/linkage between characterization and performance.

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.

- Keeping the limited budget in perspective, DOE received outstanding value from this research. The science was expanded, a product of three archival papers was generated, and the understanding and capability for these models may offer predictive efficacy for the development of future materials.
- Accomplishments have been outstanding. Progress toward improved capability is excellent, although resource limitation inhibits the kind and rate of progress needed to keep pace with overall PEC objectives.
- Several publications in fiscal year (FY) 2014 have resulted from the ongoing efforts of this project in addition to enabling the development of a novel PEC hydrogen evolution reaction (HER) model.
- This team is performing excellent work with very few resources. However, it is not clear if all the work will help overcome barriers. At this point, the main levers are understanding and eliminating failures due to corrosion, which means understanding mechanisms, and this is where theory can really help. The papers presented as accomplishments focus on HER mechanisms and III-V/water interfaces, which are already known to be inherently unstable. This focus seems to be off the main path to success given the resources available. The proposed work from this year and 2013 include critical path work, but it does not seem that the team has the resources to make the progress it wants to (the team pointed this out on the slides).
- Accomplishments include steps toward thorough fundamental understanding and broad application/data compilation.

Question 3: Collaboration and coordination with other institutions

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

- Collaboration and coordination with other institutions are outstanding and an essential ingredient of this project.
- There is a good existing network, as well as recognition of a skill gap and work to bring in new partners.
- This team is very well connected with active and appropriate collaborations.
- The team has a significant collaboration with the PEC Working Group.
- This work was conducted as part of a larger collaborative effort to understand the issues with surface degradation of the semiconductor material. Although the project is most likely budget-constrained, it would be interesting to include the copper-indium-gallium-diselenide (CIGS) system for modeling.

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

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

- The reviewer gave the project high marks for working in areas of relevance to the broad technical needs for the PEC program, but it is not focused or large enough to have the impact it should. A step back to consider a restructuring of goals for this project could help.
- The project clearly aligns very well with DOE's Hydrogen and Fuel Cells Program for the PEC hydrogen production pathway by focusing on some of the critical barriers, such as materials efficiency and durability.
- Relevance and potential impact on PEC progress are excellent, especially in light of the general strategy of the PEC Working Group. Resources are inadequate for concerted code development and validation effort that could lead to breakthroughs in understanding the microscopic dynamic processes of corrosion and photolysis, so it is not possible to assert the level of impact that might accompany this effort.
- The project is working toward thorough fundamentals and linkage to device; toolset development should be applicable for a range of projects.
- These models will provide great value if they can be predictive and help direct the nature of the materials fabrication—e.g., hydrogen diffusion is better for the InP compared to the GaP. It is not clear how this knowledge can affect the development of the semiconductor surface.

Question 5: Proposed future work

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

- Proposed future work is excellent and is focused on identifying efforts that could further illuminate the processes of corrosion, hydrogen evolution, and other processes affecting electrode durability and the dynamics and chemistry of interfaces under operational conditions.
- The proposed work presented by the principal investigator is clearly defined and should provide significant progress towards achieving the main objectives of this project.
- The proposed development of a quantitative PEC HER model would be very interesting, and the ability to apply this model to a variety of materials might prove its value. It will be important to model the system as close to reality as is possible, which would require the semiconductor operating in the presence of light.
- Key descriptors for electrode durability are a good focus.
- This team is well focused on the right actions but is too small to do them—the team pointed this out clearly.

Project strengths:

- The tools and expertise brought to the PEC hydrogen production effort by this project are outstanding and add to the strength of the entire PEC effort. Continued dedication by the project members in spite of little prospect of receiving needed funding increments is admirable.
- The team has excellent technical strength and deep understanding of what theory can bring to this very important and challenging technical area.
- The project brings a great deal of science to the greater effort of development of semiconductor materials for solar photoelectrolysis. The insight these models provides should help shape the direction of research.

Project weaknesses:

- The models to date serve as a more ancillary research effort, helping explain past issues with materials durability. If sufficiently developed, these models may offer predictive power, helping shape the future experimentation—of course, this would require a greater monetary investment.
- It is too small and spread over too many topics to work as intended. This is a result of a genuine desire to contribute, not poor planning, but the end result is that effectiveness is compromised.
- This project is severely underfunded. This is a DOE Program Office problem, not a project problem.

Recommendations for additions/deletions to project scope:

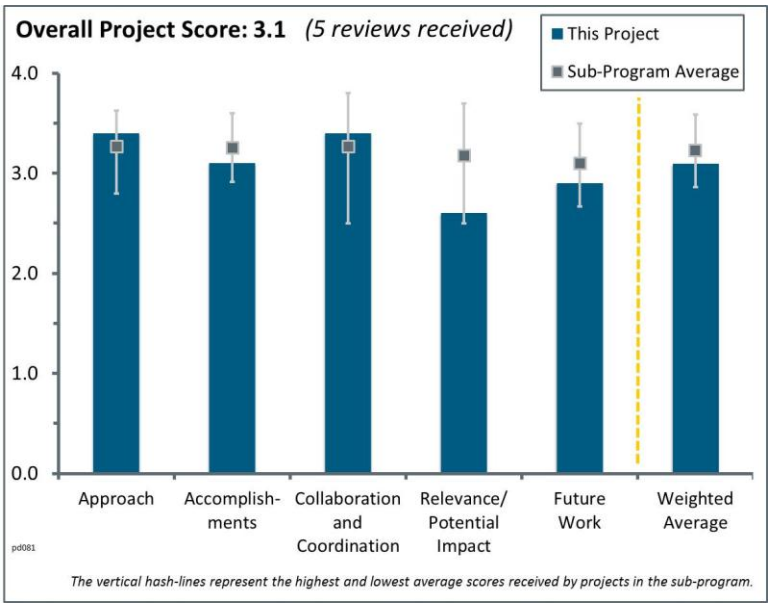
- It is recommended that the work be replanned to have at least one activity be critical mass. The most important thing to understand is corrosion mechanisms of passivated surfaces (N implant with metal impurities).
- The Surface Validation Team should invest adequate resources to enable development and implementation of studies of interfacial transport, chemistry, and energy states of PEC materials under operational conditions. A necessary element of this would entail continued development of in situ capabilities for atomic- and molecular-level experimental characterization of interface materials under operational conditions. This particular project should make every effort to establish broader ties with the semiconductor and catalyst communities in hopes of stirring interest and acquiring resources essential to the Surface Validation Team's ultimate success.

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

Tony McDaniel; Sandia National Laboratories

Brief Summary of Project:

This project's goal is to develop a high-temperature solar-thermochemical reactor and redox materials for efficient hydrogen production based on a two-step, nonvolatile metal oxide cycle. Objectives in 2013/2014 include discovering and characterizing suitable perovskite materials for two-step, non-volatile metal oxide thermochemical cycles; developing particle receiver-reactor concepts and assessing feasibility; and constructing and testing a reactor prototype.



Question 1: Approach to performing the work

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

- The general approach of material selection in tandem with reactor design and performance modeling is an excellent example of process research and development (R&D). Thermodynamic modeling and framing of high-level system performance in terms of active material properties is an outstanding approach to candidate material identification and selection. The focus on technical barriers to solar thermochemical hydrogen (STCH) performance is outstanding as well.
- The approach is excellent but extremely ambitious, as it includes system analysis, materials discovery and characterization, and reactor design and development. If successfully completed, a two-step solar-driven water-splitting cycle will have been discovered, which offers significant advantages over ZnO and CeO_2.
- The speaker was very enthusiastic, and it appears that the people working on this project are involved and excited.
- This project is focused on the development of a two-step solar thermochemical process for hydrogen production based on the metal oxide redox cycle. The cycle is based on concentrated solar energy for high-temperature heat addition at ~1500°C and heat rejection ~1300°C. Improved cycle performance is achieved with low pressure during the reduction step (vacuum reduction). A cascading pressure design has been proposed with multiple reduction chambers for this purpose. The predicted levelized cost of hydrogen production is dominated by capital cost, so high efficiency is critical. Achievement of U.S. Department of Energy (DOE) cost targets requires a large decrease in capital cost and a significant improvement in solar-to-hydrogen (STH) efficiency compared to the 2015 case. Cycle performance is also dependent on achieving good gas-to-gas and solid-to-solid heat recuperation at high temperature (HT) (~1400°C), although this requirement can be reduced or eliminated with high-performance perovskites.
- As with the other STCH project (PD-028), this one combines materials improvements and process development. In general this is a good approach because materials and process are integrated, influence one another, and are both needed to assess economics. But, as for PD-028, it is fairly clear that the hydrogen productivity and kinetics of even the current materials Sr- and Mn-doped LaAlO (SLMAs) are the key limiting factors for the ultimate objective of efficient and cost-effective hydrogen production. Materials with much higher performance (likely over 10x, possibly 100x) are needed for that, and discovering them should be prioritized if economically feasible hydrogen production is the ultimate Hydrogen and Fuel Cells Program objective. It is good that the project in 2014 continued to search for better materials, but much more will be needed to achieve a practical technology.

- The high-throughput material screening is well done. Solid material movement for long periods of time is extremely difficult. Being able to move the material at HT and under low-pressure conditions is a significant risk.

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

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

- Accomplishments reported for this project are outstanding, while progress is somewhat tempered by failure to find a perovskite with better performance than SLMA. Nevertheless, the search parameters have been changed as new understanding evolved, and the researchers believe success is much more likely in the near future. The project demonstrated enhanced reduction under low oxygen partial pressure and determined that operation under vacuum conditions would be more cost-effective than use of an inert sweep gas. The new cascade design for the reactor enables much lower-pressure operation for reduction enhancement while reducing vacuum operating costs. Reactor design innovation for these improvements is outstanding. High-flux mirror testing was completed but may not be important for implementation in the redesigned reactor concept. Scheduling tasks in coordination with needed results would be a better way to proceed.
- Progress on materials discovery was satisfactory to fair. On other aspects, progress was excellent, especially for reactor design and secondary screening test development. The Hydrogen Analysis (H2A) analysis required another slide to justify huge reductions in capital costs with time. Over 85 materials have been synthesized, but only one SLMA was identified as promising. Very clever work that screens materials for their redox properties based on their enthalpy and entropy properties was described. One sentence on page 12 says that the researchers are confident that a perovskite can be found that will achieve the DOE 2020 STH efficiency target, indicating that the SLMA found and the others that appear promising are not sufficient. A better approach is needed to identify potential materials before synthesis and testing. The amount of material needed to produce one mole of hydrogen or two grams should be defined in clear terms. The molar ratio of hydrogen to steam in the outlet gases needs to be specified to get a feel of the amount and number of moles of active material needed to produce a mole of hydrogen. Then the durability has to be determined. Definitions of symbols should be included. For example, efficiency of gas–gas recuperation was not defined. The case for reducing capital costs by 50% in five years was not made. The ultimate cost target of about $2/kg is achieved with a 75% decrease in capital and operating and maintenance costs relative to the 2015 case. Again, the reviewer was not convinced that such a large cost reduction was possible.
- The project's attempt to build on the SLMA success to find better perovskites was appreciated. However, although no direct measurements were presented, it does not appear that hydrogen production and kinetics were improved vs. SLMAs. Finally, on the subject of materials, although it would be good to reach the goal of about 20% STH efficiency, this should not be the only target, as the economics, while affected by efficiency, depend on many other considerations, including hydrogen productivity and kinetics. Good progress has been made in analyzing the process and identifying impacts on efficiency, such as heat recuperation, effect of O_2 removal, and differences in Ttr vs. Tws. Also, the project should come up with an alternative reactor design to overcome limitations of the prior design. It is nice to see the process model and how it was used to identify how to achieve the desired efficiency. Again, as for materials, efficiency is only one figure of merit; other considerations should be added to understand whether the performance can achieve the goal of cost-effective hydrogen production. And of course, the process must be demonstrated, but it seems that materials development is much more important at this stage.
- The project team has identified a perovskite material that exhibits improved water-splitting cycle performance compared to CeO_2 and ferrites. Additional perovskite candidate materials have been screened. Even higher-performance material is needed in order to achieve the desired solar-to-thermal efficiency. A system analysis has been completed for a 100,000 kg/day central-receiver-based STCH production plant based on the redox concept. An engineering test stand has been designed to evaluate the HT vacuum reduction process.
- It is not clear why a delta of 0.3 yields uncommonly large hydrogen yields. It seems that any material with a delta in this situation would make the amount of hydrogen described; therefore, it cannot be uncommon. Achieving the 0.3 delta may be difficult, but that is different from uncommon. Having identified the

material properties is good, but this should have been done at the project inception, not the middle. Since the rate was determined, a cycle life should have been included in the target material properties. Operating the reactor at low pressure is a significant risk and will be more difficult than the presenter believes. It is not clear what will happen if the cascade reactor does not work. The H2A analysis needs to be included, and the assumptions need to be transparent.

Question 3: Collaboration and coordination with other institutions

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

- Collaboration is outstanding. Students conducting research at Sandia National Laboratories (SNL) have a great opportunity to use "real" equipment. Ideas generated at the two institutions give better integration of ideas. Continuing to work with Professor Nathan Siegel is a big plus as well, as he was involved early on in the development of the particle reactor.
- Collaboration and coordination with other institutions is good in this project. The collaboration with the University of Colorado has enabled continued progress toward that institution's goal, but the collaboration has not added significantly to advances in this project. The two institutions are pursuing competitive concepts, and the lack of value-added to this project is no fault of this project institution. At the same time, collaboration with the Colorado School of Mines has added value to the synthesis and screening of perovskite candidates, while solar field and interface design is facilitated by collaborations with Bucknell University.
- Collaborations are working on the right things and seem to be well integrated.
- This project is led by SNL with collaborators from Bucknell University (solar interface), the Colorado School of Mines (perovskite screening), and the University of Colorado.
- There are a lot of partners, but it is not clear what their contributions were. Partner roles should be better defined.

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

This project was rated **2.6** for its relevance/potential impact.

- The promising results of preliminary investigations of real materials within the context of developed thermodynamic models and theoretical studies indicate for the first time that STH efficiencies targeted by the hydrogen production sub-program goals are achievable by STCH concepts. This is an outstanding achievement that deserves recognition.
- This supports the long-term goals for the Hydrogen and Fuel Cells Program.
- Restricting consideration to purely solar-based hydrogen production, STH efficiencies of at least 18% can be achieved with commercially available technology using state-of-the-art photovoltaics providing power directly to conventional water electrolysis units. With high-temperature steam electrolysis (HTSE), which is at an advanced stage of development (technology readiness level 5), an STH efficiency of at least 30% should be achievable using concentrated solar heat for the required HT heat addition (at 800°C instead of 1500°C) and state-of-the-art photovoltaics, even without system integration/optimization. This efficiency is three times higher than the 2015 case associated with the metal oxide thermochemical cycle and higher than the ultimate efficiency predicted for the concept. Furthermore, the materials challenges associated with this process are not to be underestimated. These comparisons beg the question of whether this technology is the best STH technology to pursue.
- Much like PD-028, as it stands today the project has poor prospects of meeting the goal of efficient and cost-effective hydrogen production. Although there were impressive advances with the SLMA materials compared to Ce oxides, the current productivity and kinetics of the materials would need significant improvement. The reviewer estimates that to achieve the target of 100 tons/day hydrogen production mentioned in the review material, the reactor will need to circulate something like 500 tons/minute of solids and have a solid inventory of over a 1,000 tons (using data on SLMA from 2013 and optimizing contact time for smallest solid circulation; also, solar intermittency is included in these calculations). These

numbers are several times those of the largest fluid catalytic cracker (FCC) reactor that the reviewer knows of and likely require on the order of $1 billion for just the reactor. (The reviewer used the FCC because it is a solid circulating reactor with established technology and economics). A number of smaller reactors could, of course, be built, but that increases cost by negating economies of scale. These considerations, not even including the cost of the solar tower(s) and the rest of the plant or the challenge of building such a massive reactor(s), led to the conclusion that unless much more productive materials are found, the prospects for economically viable hydrogen production using this technology are poor. For comparison, a 100-ton-hydrogen-per-day steam methane reforming (SMR) plant (sizeable but not a world-scale plant) would likely cost around $200 million. Also, CO_2 capture has been demonstrated at scale on SMR (Air Products, Port Arthur, Texas).

- The potential impact is uncertain. Reducing H2A costs to meet DOE's target appears unrealistic at best. The H2A results show a nearly fourfold decrease in total costs from 2015 to 2020 and a corresponding 50% decrease in capital costs. Reductions of this size typically require miracles. Cost increases for a project of this magnitude over a long time horizon are more likely. Therefore, the relevance of the project is in question because meeting DOE's ultimate cost target is unlikely.

Question 5: Proposed future work

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

- Proposed future work is outstanding and comprehensively addresses R&D tasks for new material discovery, reactor design and demonstration, reactor integration with solar thermal energy, and characterization of active material stability under operational conditions. These are all essential tasks for success by this project.
- Proposed future work includes continued materials screening, integration of multiple thermal reduction chambers into the engineering test stand, and design of centralized tower and field configurations. The proposed work represents a logical progression.
- It is good to finally see durability tests. The team has enough data at this point to know how many cycles the materials need to achieve. They should have presented that information. Moving the active material will increase the degradation. The durability tests need to take into consideration the reactor conditions, including material movement, in order to be relevant. The active materials still operate at very high temperatures. Materials that operate at lower temperatures while maintaining fast kinetics need to be discovered.
- The future plan has the right elements, but the team should focus the project on new materials. Also, the economic analysis should be strengthened.
- Materials represent a potential show stopper; more effort should be focused on materials. The future work described does not contain an innovative method to screen the huge composition space prior to synthesis. The screening method based on thermogravimetric analyzer results should reduce the work load. It is necessary but not sufficient. Future work includes implementing a durability testing protocol for redox active materials. This is critically needed but will be difficult. X-ray diffraction (XRD) was proposed as a method but will not be sufficient. XRD cannot be used to identify crystalline materials present at 5%–10%, as it is not sufficiently sensitive. XRD does not detect non-crystalline materials. A combination of XRD and Rietveld analysis, as well as surface area measurements, may be useful.

Project strengths:

- The professional credentials of the team are excellent, and each of the team organizations has significant experience in the work they will undertake. The facilities of all organizations are superbly equipped to undertake the proposed work. The proposed work, along with identified risks and remediation efforts, the facilities, and their alignment with the work, all combines to make it highly probable that the project will meet or exceed its promised objectives.
- The concept is very innovative. Significant contributions to the perovksite materials database have been made. Techno-economic analysis has been utilized to identify critical threshold operating points and efficiencies needed to meet ultimate DOE levelized cost requirements. A concept for integration of a cascading pressure design for low-pressure reduction has been developed. Many graduate students have been supported by this work.

- The project has good science and process innovation. The project has the right elements in place: materials discovery, process development, and economic analysis.
- The project has a good approach on materials discovery and good progress on goals.

Project weaknesses:

- This is a challenging route to the goal of cost-effective hydrogen production. Current materials have low hydrogen productivity. Solar intermittency increases cost substantially for any given production rate compared to continuous processes such as SMR. It is not clear that energy storage would help much without new materials, but it would be interesting to see the economic analysis
- They have a very complicated reactor system. They still have not presented durability data. Moving solids around at the rates, temperature, and pressure is extremely difficult, and the presenter seemed to downgrade the challenges. The active materials reaction temperatures are still very high.
- Aside from the redox material, many significant materials issues must be sorted out to make this concept feasible. For example, it is not clear what the reactor material is for operation at 1500°C.

Recommendations for additions/deletions to project scope:

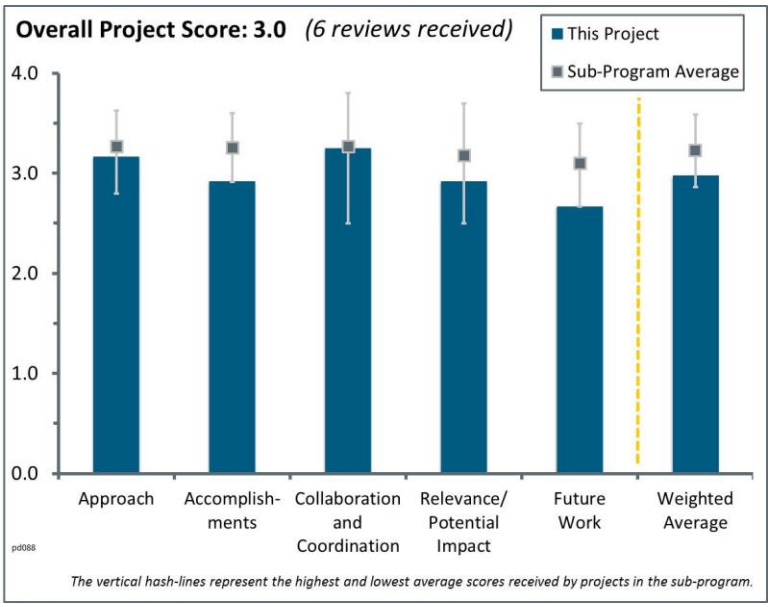
- Effort to characterize interface materials before and after thermochemical cycling and before and after reactor system cycling might prove useful in characterizing and/or resolving material durability issues.
- More emphasis should be placed on experimental demonstration, eventually leading to a fully integrated hydrogen production system.
- Increasing the focus on better materials and realistic economic assessments is recommended, and more details should be provided, as currently there is not enough information to assess the robustness of the reported cost of hydrogen. The project should deemphasize, but not totally eliminate, the reactor design effort.

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 objective of this project is to address the significant safety and cost challenges of the current industry standard steel pressure vessel technology by developing and demonstrating steel/concrete composite vessel (SCCV) design and fabrication technology for a stationary storage system of high-pressure hydrogen that meets the U.S. Department of Energy (DOE) technical and cost targets. SCCV technology integrates modular hydrogen storage system design, composite steel/concrete storage vessel for cost reduction, novel inner steel vessel design to eliminate hydrogen embrittlement, and advanced fabrication and sensor technologies for cost reduction and improved operation safety.



Question 1: Approach to performing the work

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

- Oak Ridge National Laboratory (ORNL) has proposed a novel approach for hydrogen storage using steel vessels and concrete. The approach uses bi-metal layers of stainless steel to prevent/reduce hydrogen embrittlement and pre-stressed concrete to provide strength for pressure containment, which is truly novel. The project now needs to better understand the issues associated with using and installing such vessels. The project needs to include these issues as part of the approach.
- The approach to diffusion experiment is simple and elegant. The team is addressing cost barriers toward the target and making good progress.
- The methodical approach was sound, and the methods on proving the viability of the design and manufacturing process required were also good. How and where this technology from a practical hydrogen forecourt station perspective could be used was not presented, and this prevented a 4.0 rating.
- The approach looks very practical.
- The principal investigator (PI) has taken a reasonable approach to the problem.
- The authors state that a secondary advantage of reinforced, pre-stressed concrete is protection against third-party damage. However, this is more compelling than their claimed primary advantage. The tension elements must stress the concrete and then supply additional stress to augment the strength of the internal bottle of steel. This means that not all of the strength can be used for containment.

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

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

- There is good progress to date. The project now needs to address the issues associated with installation and how the orientation and installation will affect the competitive cost of the storage system.
- Preliminary work aimed at fabrication has progressed well. It is not clear how fabrication costs are determined. Hydrogen permeation rate data show good results for layered design.

- As many of the prospective refueling stations will have space considerations to account for, it appears that with the reinforced concrete these vessels will take up more space than conventional storage vessels. Cost analysis is impressive and well documented and would present an option for significant cost savings for forecourt storage in stations with space. The hydrogen permeation mitigation technology with the weep hole is a novel approach that would prove to be a significant safety improvement along with cost, as shown in the PI's tables. The fabrication technique and proven results of the stir welding process are impressive.
- Concrete is the key to the approach, yet no physical work has been done with this material, despite an ample budget. Instead, the authors have patented an instrument for fatigue testing of metals, which was not a goal. Patents are generally more useful for consumer or industrial products produced in large quantities (in this case, the SCCV tanks) than for a specialized low-cost scientific instrument.
- It is not clear if there has been much progress since 2013.

Question 3: Collaboration and coordination with other institutions

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

- The project has made excellent use of collaborative partners. ORNL has organized a group of subject matter experts who have made the project a success to date.
- There is broad collaboration between multiple parties, and this is proven within the presentation and is exemplary. This is clearly demonstrated by the PI.
- The project team has performed good work in lining up collaborators.
- There is strong collaboration evidence.
- The partnership with MegaStir is substantial and productive. The other partners/interactions seem superficial. In particular, it would have been good to see a publication with University of Michigan utilizing their listed competency, high-performance concretes. The California Fuel Cell Partnership would be an excellent partner; however, there is no evidence provided of their level of interest.
- It is not obvious that ORNL has collaborated with entities other than those immediately required to design and fabricate the test vessel.

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

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

- The project addresses storage needs and cost barriers with available materials and fabrication techniques.
- Hydrogen storage for stationary use is a major cost factor requiring a breakthrough to make hydrogen delivery and storage more cost-efficient. This project provides a technical option for helping reduce the cost of storage.
- Stations are now funded and being built in California. Less expensive storage, or at least the prospect for it, would significantly accelerate the rollout.
- The relevance of this type of technology is unclear because of the physical space required (more than existing technology); a layered inner vessel will require welding, which will add to manufacturing cost—not decrease it. The potential impact is also unclear and has not been effectively communicated by the PI. The project should be compared to existing high-pressure storage for which there are significant data available. From a multi-year research, development, and demonstration plan technical and cost target perspective, the work done by the PI works to meet these targets as written—but in practice, the space consideration of real stations, especially in most early adaptation scenarios for station deployment, will be in high-traffic urban areas where space is an issue. The addition of a significant concrete reinforcement will—while perhaps lowering cost—compound the space issues.
- The reviewer fails to see the relevance of the concept in comparison to established fiber-wound storage technologies. There were no references to National Fire Protection Agency standards regarding setback distances. It is unclear whether this project will offer advantages over a standard tank.
- The projected costs are no better than existing costs for Type II steel tanks.

Question 5: Proposed future work

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

- The fact that the project is evaluating new welding technology for multi-layer strength is appreciated.
- The next phase work seems ready to reduce to practice.
- The proposed work seems good. The project should add significant work to prove the concept for greater than 700 bar pressure storage.
- Economics need to be rigorously investigated and compared to existing technologies to ensure that concrete reinforced tanks have real potential to be competitive. Fabrication and installation costs need to be fully understood for these more complex tanks.
- For future work to include a manway, a cost analysis should be done to see if the extra cost of the manway will make this storage option uneconomic with competitive storage options.
- It is not evident that a manway is useful. Progress in imaging in the visible and infrared, together with developments in robotics, should counter the need for direct human observation and exposure. It would be preferable to see tests on multiple small mockups.

Project strengths:

- The project team had a strong technical presentation. Well-presented and technical assumptions and approach are sound. The cost analysis approach was well presented. The project has the potential to provide a significant low-cost option for stations without space considerations. The PI has a clear understanding of the technology and its technical merits (and challenges).
- The welding of the multi-layers is a project strength.
- Less expensive, large-scale storage is critically needed. This is an important topic that needs to be solved.
- The project's application of existing technology to address the need for low-cost storage is a strength.
- A strength the project offers is a unique proposal using two media (steel and concrete) to provide low-cost hydrogen storage.

Project weaknesses:

- The project should continue to explore the cost effects of installation and orientation of installation, as well as the cost effects of a manway.
- Nondestructive examination for layered-up welds has not been presented (assuming 100% x-ray for head-to-shell joints), and some leak testing or magnetic particle exams for the layer welds would also be helpful for the project. What is/has been done, what would be done to the proposed technology, and how this affects delivery and cost was not presented by the PI. The cost of the manway is unclear. Engineering sense says this could add 10%–15% to the overall cost because of required construction techniques. It is unclear how the expected cost reduction is to happen—meaning is it unclear whether it is from improvements in manufacturing efficiency or economies of scale. This is the question across the spectrum of low- to high-pressure storage.
- There is a lack of relevance to the fuel cell electric vehicle market.
- The case for concrete is not well articulated. It should be possible to explain this more plainly. A complicated spreadsheet and calculation, while necessary, is not complete in itself—an interpretation is needed.

Recommendations for additions/deletions to project scope:

- An estimate of the cost for a small mockup and comparison of the actual costs of fabrication would be more convincing support for the concept than detailed modeling.
- Cost analysis of installation should be added.
- The project should examine other methods to fabricate heads—a significant cost. Perhaps it is possible to fabricate and inspect without a manway (a cost improvement). Transportation to the final installation site should be addressed—the steel model shown on page 19 may exceed common International Organization for Standardization (ISO) container dimensions for intermodal transport; it will be an oversize load. The

ISO container outside floor dimensions are 8 ft by 20 ft/40ft. Please address any installation site corrosion issues—it is not clear if paint is enough. It is not clear how to protect diffusion paths from closing up as a result of moisture and corrosion.

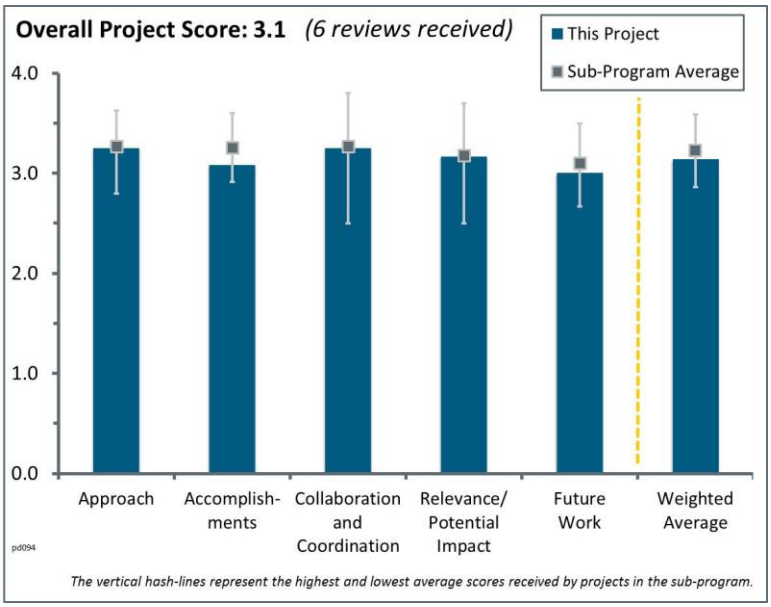
- Addressing delivery and supply chain issues would be great, as early/midterm adoption of the proposed technology will require better delivery and strong supply chain streamlining. Finding ways to simplify the layering technology and reduce welding present in hydrogen affected areas will be important. Further in the high-pressure case, the welding of the "ends" or covers for manways will be a key challenge to the technology. In many and most hydrogen applications, welding in these high-pressure applications is frowned upon and even forbidden. How the welded area responds and holds up to cyclic conditions must be analyzed. For the proposed work for fiscal year (FY) 2016 and beyond, the project should study how the large physical size will affect the utilization of this type of technology in forecourt stations deployment. Underground storage is a good idea—but perhaps not practical in most station scenarios in the near midterm. Of critical importance is demonstrating this technology's capabilities on greater than 700 bar storage. It is unclear if it scales up well or if the welds hold up. It is unclear how cyclic conditions will affect the technology (perhaps in FY 2016 and beyond).
- In this reviewer's opinion, project funding should be discontinued, since it does not address onboard storage.

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 objective of this project is to demonstrate a technology pathway to reduce the cell stack capital cost and resulting hydrogen production cost of alkaline membrane electrolysis. The approach is focused on synthesizing a stable oxygen evolution reaction catalyst to enable low-cost flow fields for reducing the cost of anion exchange membrane operation.



Question 1: Approach to performing the work

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

- This highly innovative project is focused on the development of anion exchange membranes (AEMs) for water electrolysis. These membranes are an alternative to polymer electrolyte membrane (PEMs). They are conductors of OH-ions, rather than H+ ions. A typical AEM is composed of a polymer backbone with tethered cationic ion-exchange groups to facilitate the movement of free OH-ions. The potential advantages of this technology include the use of stainless steel bipolar plates instead of Ti, and lower-cost catalysts. The AEM material candidates include polysulfone, polyphenylene polymers, and others. The catalysts under consideration are in the pyrochlore family, including $Pb_2Ru_2O_7$ (lead ruthenate). These catalyst materials have been shown to support fast kinetics for the O_2 evolution reaction and are stable in alkaline solutions. They are also amenable to production as nanoparticles. Membrane and catalyst development are major thrusts of the work. A porous Ni gas diffusion electrode (GDE) has also been developed.
- The 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 and integrating them into alkaline membrane electrolysis cells. The main issue with AEM electrolyzers is membrane durability. Membrane durability (without carbonate recirculation) should be the main focus.
- The approach is well-reasoned, starting with catalyst and membrane development and ending with electrode development and testing. The catalyst approach is investigating ABO(6-7) pyrochlore materials. The A constituent is Bi or Pb, and the B is Ru and Ir. The reviewer wonders whether there is more of the catalyst space that could be explored with rapid throughput screening similar to the approach used at The Joint Center for Artificial Photosynthesis (JCAP). Proton Onsite should ask itself if Bi, Pb, Ru, and Ir are really the best materials for the job and what it would take to explore the space further. Determining the potential value in doing so is also important. The integration approach is laid out logically and contains a vision for a product at the end.
- It appeared from the discussion that progress has been made on each task in the past year. The future work plan was explained in a reasonable fashion.
- The approach is reasonable in light of the long-term nature of this project. However, this project addresses a very small fraction of the total hydrogen cost pie, and its impact is inherently limited.
- Alkaline membrane electrolysis was proposed as a means to reduce capital costs associated with polymer electrolyte membrane (PEM)-type electrolysis. For example, replacement of Ti with stainless steel for the flow fields will reduce capital costs. However, based on the information in the presentation, many aspects of the alkaline membrane electrolyzer need to be modified or replaced, such as membranes, catalysts, and

electrodes. Corrosion is an issue, and degradation mechanisms need to be investigated. So while capital costs for one aspect of the cell should decrease, other costs may increase. Electricity costs represent 65%–80% of the total costs of hydrogen in PEM electrolysis as discussed in the talk by Dr. Colella (PD-102). In addition, this talk also demonstrated that future stack costs are expected to be less than half of the current stack costs. Therefore, the focus of the work on reducing capital costs does not appear warranted.

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

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

- Significant progress is made in all fields of work. The stable anode GDEs in the AEM cell are especially impressive.
- The project has accomplished good progress with the catalyst and membrane. If ultimately successful, this project has the potential to overcome some of the limitations of PEM electrolysis. The durability test to date does not seem to include the entire electrochemical package, only the membrane with the default Nickel/Cobalt catalyst. It would be good to have a durability test with the proposed final, total electrochemical package. It is important to understand the system and cost implications of using carbonate in the electrolyte, unless the performance can be improved without it. It is far better than using KOH but may not be as simple as PEM.
- It was a good talk. Proton OnSite's results are impressive. The catalyst investigation was minimal, but this was dictated by priorities and reviewers' comments from last year. Several types of membranes, alternate polymers, and undefined materials from Sandia National Laboratories (SNL)/Los Alamos National Laboratory are being investigated. Characterization work is ongoing, but it appears that the membrane choice has not been finalized. In general, the temperature stability of hydrocarbon membranes is relatively low. A durability test using Proton Onsite's electrode, a commercial membrane, and an Illinois Institute of Technology (IIT) anode catalyst showed stability for 200 hours, but cell voltage was higher than the goal, while the current density was lower. Nevertheless, this represents progress. No details were provided for the efficiency calculations for the alkaline membrane electrolyzer vs. the PEM electrolyzer. More details and better definition of the take-home message on each slide are needed for non-experts to fully appreciate the work.
- An AEM bench test stand has been developed. Stable performance of an AEM and ionomer in the electrode layer has been demonstrated. Lead ruthenate oxygen evolution reaction (OER) catalyst activity has been shown to be superior to IrO_2, using the rotating disk electrode method. The performance of this catalyst has also been demonstrated in-cell. Cell efficiencies as high as 79% (at 200 mA/cm^2) have been achieved using an experimental alternate catalyst. Membrane development activities include anode and cathode binder synthesis. Stable gas diffusion electrode behavior was demonstrated in-cell using a porous nickel GDE. The performance effect of carbonate in the feedwater has been quantified. Carbon ingress from atmospheric air is a potential issue. Stack design and flow modeling has been performed. Degradation mechanisms are not well characterized.
- The project successfully synthesized a higher-activity catalyst. However, the project team appears to be behind schedule in accomplishing milestones, including initial ionomer composition screenings, a cost/strength material assessment of alkaline compatible stack materials, and electrode fabrication.
- The limitations to the current technology still seem formidable. Although a plan is in place to make further progress, the progress should be greater than it is.

Question 3: Collaboration and coordination with other institutions

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

- The project is making good use of SNL, IIT, and fundamental Advanced Research Projects Agency-Energy (ARPA-E) work. Perhaps some of the activities discussing hydrogen embrittlement evaluation could be helped by working with the materials group at SNL's Livermore, California, location. That may make the evaluations unnecessary, or they may be able to limit the choice of candidate materials. Also, the team should investigate working with JCAP on catalyst screening.

- Collaborations between Proton OnSite and IIT appear to be working well.
- The project team included industry, national laboratory, and university participants. The project was led by Proton OnSite, with collaborators from SNL and IIT. Proton OnSite provides cell and stack design, system, and testing expertise. SNL has supplied AEM materials based on work performed under an ARPA-E program. IIT is investigating alternate polymer membrane materials.
- As this project deals with a technology concept that is longer term, broader collaboration with multiple skill sets may be beneficial at this stage of the development.
- The interaction with the IIT partner was included in the discussion but could have been further explored. Work with SNL was not clearly developed.
- There was insufficient information to provide a higher grade, but collaboration was shown to exist, and partners are well coordinated. It would have been helpful if the institution doing the work was identified.

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

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

- The relevance of the project is good. One of the important issues facing PEM electrolysis is the capital cost of the system. This project has the potential to lead to a step-change in system cost. It takes a variety of novel approaches at all of the most-costly pieces of an electrolysis system.
- Successful completion of this project does have significant potential value in demonstrating the exploitation of the technology.
- The project is targeting the main challenges of the hydrogen production targets for electrolysis: reduction of the high amounts of expensive anodic platinum group metal catalysts currently needed and reduction of electrolyzer capital cost by eliminating expensive materials such as Ti separator plates and Ti current collectors.
- Increasing efficiency and reducing capital costs will advance progress towards the hydrogen economy. These attributes are critical to meet the goals defined by DOE. However, the best case calculation for efficiency that was presented is not sufficient to meet DOE's target, primarily because of the electricity costs (see the PD-102 presentation).
- This technology is in the early stages of development, but it appears to have potential for capital cost reduction in the area of bipolar plate and catalyst materials. The cell efficiencies will not be as high as PEM technology, however. Furthermore, stack capital cost contributes only ~10% to the total hydrogen production cost associated with PEM electrolysis. So capital stack cost savings will not make a major impact on hydrogen production cost by water electrolysis.
- Assuming the stated potential savings of $0.11/kg hydrogen with alkaline membrane electrolysis, the potential impact of this project is relatively small—at best 2% of the current hydrogen production cost of $5.00/kg.

Question 5: Proposed future work

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

- All of the proposed future work at IIT and Proton Onsite is good and important, especially the characterizing of the ionomer decomposition mechanisms and the corrosion study for titanium, stainless steel, and nickel porous micro-layers.
- The future work is well planned. It is important to perform some analysis with the Hydrogen Analysis model (H2A) to provide some guidance on how low this technology can push the hydrogen production cost relative to PEM. The planned operational testing of the complete stack/system should focus on durability, degradation, and efficiency.
- Proposed future work includes basic research tasks to be performed at IIT: membrane development and characterization, bipolar plate corrosion studies, and characterization of degradation mechanisms. Proton Onsite tasks include stack and system development. The future work plan is well reasoned.
- The proposed future work is adequate but would benefit from acceleration.

- The future work looks reasonable.
- It is too early to focus on stack development. The challenges associated with the cell components, such as the membrane, catalysts, and electrode, should have a higher priority. However, in view of the data in PD-102 that indicate electricity is the primary cost driver, the focus should be changed to a study to determine whether the efficiency of alkaline membrane electrolysis can be significantly higher than that of PEM electrolysis, and that the potential to meet DOE's targets exists with this technology.

Project strengths:

- The project takes a number of novel approaches to redefine what an electrolyzer can be. The team seems creative and effective at breaking down barriers.
- Excellent research was done by the individual partners in their respective fields of expertise.
- The principal investigator appears to be very knowledgeable with regard to water electrolysis science and technology. This highly innovative project is focused on the development of AEM for water electrolysis. These membranes are an alternative to PEM. They are conductors of OH-ions, rather than H+ ions. The potential advantages of this technology include the use of stainless steel bipolar plates instead of Ti and lower-cost catalysts.
- Leveraging the strong PEM-based skill set from the Proton OnSite team is a project strength.

Project weaknesses:

- The project does not provide contextual impact with respect to overall projected hydrogen cost. The stated potential of 80% material cost reduction over baseline of OER catalyst may be true, but it is a very tiny slice of the overall cost.
- Expected cell efficiencies will be lower than PEM efficiencies (but higher than alkaline electrolyzers). The potential capital cost savings associated with the use of stainless steel bipolar plates and lower-cost catalysts will not contribute significantly to the levelized cost of hydrogen production, which is dominated by feedstock (electricity) cost.
- From the results, the advantages over the classical advanced alkaline electrolysis are not seen, except the unneeded KOH.

Recommendations for additions/deletions to project scope:

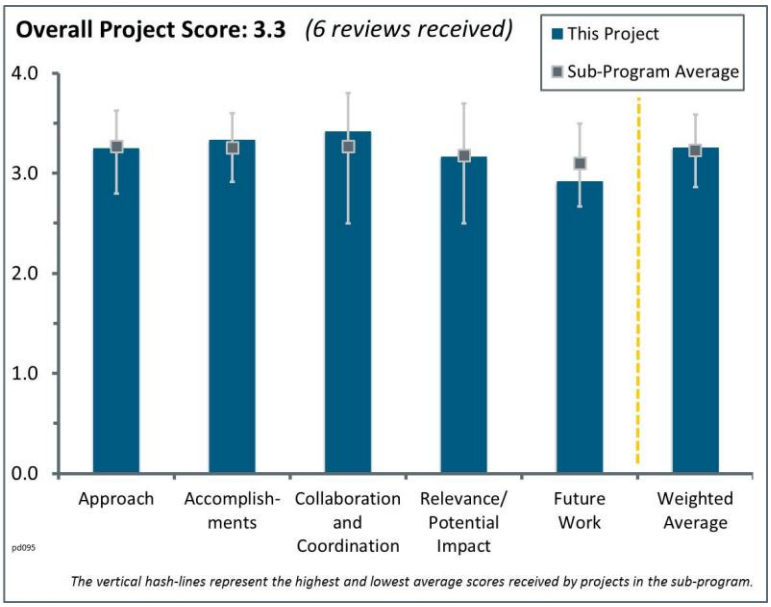
- The project should identify the potential niche applications for alkaline membrane electrolysis, and build relevance and economics accordingly.
- The project should focus more on fundamental research for membrane performance and durability issues before getting more involved in stack and system development.
- The project should do the following:
    1. Work with SNL Livermore on hydrogen embrittlement.
    2. Investigate working with JCAP on high-throughput catalyst screening.
    3. Perform an H2A analysis to investigate the hydrogen production cost from a commercial system.
    4. Perform durability testing on a completely integrated electrochemical package with the best catalyst and membrane that have been developed.
    5. Evaluate the cost/commercial implications of carbonated electrolyte or find a way to do without it.

Project # PD-095: Improving Cyanobacterial O_2-Tolerance Using CBS Hydrogenase for Hydrogen Production

Pin-Ching Maness; National Renewable Energy Laboratory

Brief Summary of Project:

The objective of this project is to develop a robust O_2-tolerant cyanobacterial system for light-driven hydrogen production from water while increasing system durability. This objective is divided into two tasks. Task 1 is to probe hydrogenase maturation machinery in the Casa Bonita Strain (CBS) of *Rubrivivax gelatinosus*, and Task 2 will express the more O_2-tolerant CBS hydrogenase in *Synechosystis*. The long-term goal is for cyanobacteria to be O_2-tolerant for eight hours (during daylight hours).



Question 1: Approach to performing the work

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

- The approach is well organized, using several researchers to systematically evaluate the CBS genome and the functions of several maturation genes in order to select the optimal genes to co-transform with O_2-tolerant hydrogenase into *Synechocystis* for increased hydrogen production activity in the presence of oxygen (O_2).
- This project is well focused on the oxygen accumulation barrier in a cyanobacterium and complements work by Dr. Maria Ghirardi with algae. The approach to probing the hydrogenase maturation machinery is commendable, as well as the promoter tuning strategy to improve hydrogenase activity in *Synechocystis*.
- There is a strong rationale and strategy for development of promoters for expression of CBS hydrogenase in *Synechocystis*.
- The approach is logical. The step taken to assess the lack of product for the tagged product was well thought out. The evaluation of the function of *hyp1* and *hyp2* followed. The knock-out evaluation has the potential to be challenging, but the investigator appears to have a clear approach to overcome the challenge.
- The project is focused on addressing the O_2 inhibition of the native *Synechocystis* hydrogenase. The project objectives are appropriate for understanding the ability of the CBS hydrogenase to overcome the limitations of the O_2-sensitive hydrogenase. Despite this, some of the experimental design glosses over critical experiments to add to the body of knowledge for the enzyme activity.
- The approach is clear and seems suitable to the objective as stated. But the objective itself is narrow, and it is not put into the broader context of producing hydrogen in a cost-effective manner. The problem tackled here is only one of the pieces needed to make hydrogen, but there is no information about the relative importance of this piece vs. the others (e.g., photosynthetic efficiency). It is perfectly fine to work on a piece of the whole in parallel, but context would be useful to assess whether the whole is worthwhile to begin with.

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

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

- There are multiple notable accomplishments, including the identification that *hyp1* genes cluster near the O_2-tolerant hydrogenase and have a similar induction profile to CBS hydrogenase whereas *hyp2* proteins cluster near the hydrogen uptake hydrogenase. Additionally, other maturation genes and their functions, in particular *slyD*, were identified in the CBS genome. Combinations of these genes and the O_2-tolerant CBS hydrogenase were successfully transferred into the host. But it is unclear why the tetramer was selected over the hexamer.
- Most milestones have been met. One delayed milestone is on track, as are the future milestones.
- With the exception of a one-quarter delay in Task 1's subtask to determine *hyp2*'s effect on hydrogenase activity, subtasks that have been accomplished appear to have been completed on schedule, and the remaining subtasks appear to be on track.
- The accomplishments on the various tasks appear to be satisfactory.
- Efforts were highly focused on strategies to insert and express CBS hydrogenase in *Synechocystis*. No actual hydrogenase activity or hydrogen production data to date were shown, although the task was scheduled to be completed by September 2014. There were two publications and three presentations resulting from the work during the reporting period.
- Qualitatively, it looks like good progress. But there are no data on hydrogen production, so it is not possible to judge whether the work led to progress. Based on duration of continuous hydrogen production (not the best or clearest metric for several reasons), the target is still far away.

Question 3: Collaboration and coordination with other institutions

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

- There are multiple collaborators with clearly identified roles, and their work is nicely integrated.
- There are strong academic collaborations.
- The project has partnerships with the J. Craig Venter Institute—Task 2, expression of CBS in *Synechocystis*—and the laboratories of Dr. Jin Chen (Michigan State University) and Dr. Jonas Korlach (Pacific Biosciences)—Task 1, probing CBS hydrogenase maturity machinery.
- The accomplishments were made through coordination with external partners.
- The collaboration on this project is sufficient.

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

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

- Development of a robust, O_2-tolerant CBS for solar-driven production of hydrogen from water represents a significant advance in photobacterial hydrogen production and progress towards Multi-Year Research, Development, and Demonstration Plan objectives. This project appears to be well focused upon identifying the genes involved with expression of an O_2-tolerant hydrogenase in *Synechocystis* and tuning expression levels to achieve adequate activity.
- There were no issues; the research is highly relevant to the DOE Hydrogen and Fuel Cells Program (the Program).
- If the right combination and levels of maturation genes and O_2-tolerant CBS hydrogenase are transferred into the *Synechocystis*, this could lead to hydrogen production that meets both cost and volume targets.
- The tasks outlined in the presentation have the potential to support Program objectives. However, there are concerns about the experimental design underpinning the tasks, which may make it difficult to meet milestones and prove process robustness.

- While the impact of this work is likely high, it was not possible to discern the high-level impact from the presentation. That is likely more a reflection of the presentation and less a reflection of the work.
- This is only a piece in producing hydrogen from water splitting by microorganisms. In isolation, it is hard to assess whether even complete success would help the final goal.

Question 5: Proposed future work

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

- The future work proposed includes the logical next steps. Much of the work has preliminary data that indicate success is likely.
- The project's proposed work is a logical continuation of current work.
- The future work seems appropriate for the narrow objective.
- While the proposed work has the potential to meet the project goals, there is concern that some of the experimental design is skipping crucial steps to better understand the nature of the CBS hydrogenase and its maturation pathway. For example, the CBS *slyD* homolog shares only 33% identity with the *E. coli* protein, and it is unclear from the presentation how much of the identity occurs within the catalytic domain/active site of the protein. A better understanding of the protein function of the CBS *slyD* is necessary before transforming it into *Synechocystis*. It is quite likely that the protein will not have the same activity and that this will be very difficult to troubleshoot without the fundamental knowledge of protein sequence, structure, and activity.
- More detail is requested on plans to "demonstrate in vitro and in vivo hydrogen production, the latter linking to the host photosynthetic pathway."

Project strengths:

- The principal investigator and team have a strong understanding of barriers to effective biological hydrogen production and have targeted a possible solution through engineering an O_2-tolerant hydrogenase into *Synechocystis*. The project milestones have been met or are on track to be met. Some project risks have been assessed and are being addressed. Previous weaknesses have been or are being addressed through current and future work.
- The organization of work is a key strength.
- The biology expertise is a strength.
- The project has a logical approach to address the stated objective. The investigator appears to have a clear vision for the project.
- A detailed description of progress was presented on the development and implementation of strategies to insert and express CBS hydrogenase into a non-hydrogen-producing strain of *Synechocystis*.

Project weaknesses:

- Some of the experimental design is questionable—more foundational knowledge about protein function should be determined before moving forward with some of the experiments proposed. The previously mentioned *slyD* experiment is one example. There are also concerns about the relative amount of focus on identifying and understanding the *hyp1* and *hpy2* deletion mutant—it is quite possible that this will not be as straightforward and should be emphasized more over transforming the proteins into *Synechocystis*. Some of the experimental rationale and results were not made clear. It was unclear how the evidence presented demonstrated that the affinity tag did not disrupt protein function. Relatedly, there are alternative methods for troubleshooting and problem solving that were not explored or explained.
- There may be other steps in the pathway that can limit hydrogen production even if the problem at hand is successfully solved.
- The big picture goals were not clearly stated. It would have been helpful for the reviewers to know what end applications are being targeted because this work does not appear to have just a basic science focus. The 2013 presentation had a large focus on the evaluation of promoters, but there seems to have been minimal progress in that area.

- At present, there are no results to demonstrate hydrogen production from the recombinant *Synechocystis* to determine whether the very detailed genetic engineering strategies will be successful.

Recommendations for additions/deletions to project scope:

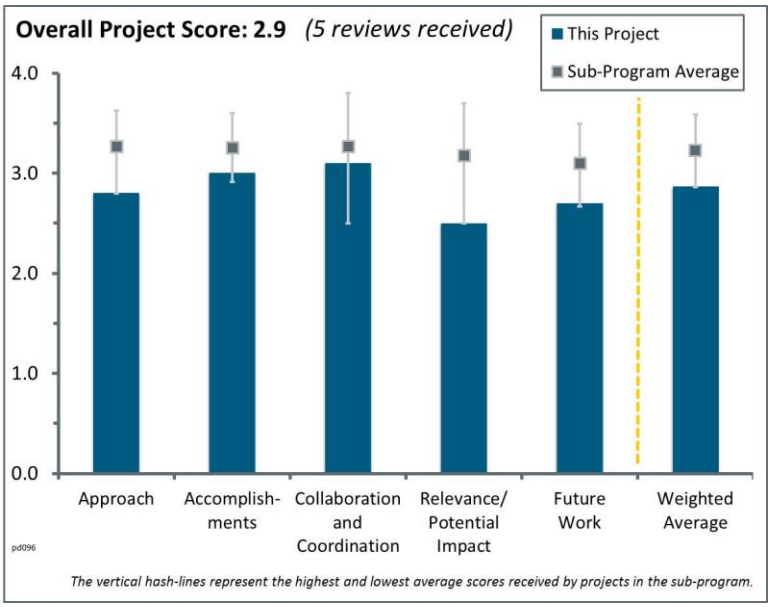
- It is recommended that some of the work be refocused to understanding protein function and activity in either the native organism (CBS) or *E. coli*, using deletion mutants where possible. Much of the work appears to be putting the cart before the horse by transforming the proteins into *Synechocystis* before having a good foundational understanding.
- A better definition of the entire pathway and overall potential for hydrogen should be added.

Project # PD-096: Electrolyzer Component Development for the Hybrid Sulfur Thermochemical Cycle

William Summers; Savannah River National Laboratory

Brief Summary of Project:

The overall objectives of this project are to develop improved technology for the hybrid sulfur (HyS) thermochemical process to permit low-cost, highly efficient hydrogen production from concentrated solar energy and to focus on the HyS SO_2-depolarized electrolyzer using polymer electrolyte membrane (PEM) technology. Fiscal year 2014 objectives are to identify and quantify performance of anode electrocatalysts and advanced PEMs; to address the challenges of faster reaction kinetics, high specific output, elimination of sulfur formation, and longer operating lifetime for the sulfur dioxide (SO_2) depolarized electrolyzer; and to demonstrate improved components through button-cell operation at increased temperature and pressure.



Question 1: Approach to performing the work

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

- The team had a good presentation. The approach is sound as it is critical that the electrolyzer in the HyS cycle operate at higher temperatures and at elevated pressures in order to meet the U.S. Department of Energy's (DOE's) cost targets. Demonstration of higher-temperature operation for the electrolyzer will show that it is possible to reduce cell voltage and decrease electric power consumption. However, other aspects of the work, e.g., high-temperature (HT) membrane development, must also be addressed.
- The approach to work in this project is good. Only one of the three barriers to performance was addressed specifically, although the particular task engaged was related to the other two barriers. The remaining barriers to cycle performance are nonetheless significant, and resolution of the barrier to efficient and cost-effective electrolyzer performance is not in and of itself sufficient to assure HyS performance. The funding level for the work was limited so that there were insufficient resources to undertake a broader set of tasks. Earlier assessment and laboratory efforts identified the electrolyzer as the critical barrier to improved performance, so the effort was appropriately focused on that topic, given resource constraints.
- The team is working on the right technical improvements for this process but is unclear on the basis for success. Particularly, it is unclear why a solar-based thermal process is better than other electrolytic pathways. Some advantages of this particular approach are highlighted (mostly lower potential compared to water electrolysis), but it is not clear how this translates into higher efficiency, lower cost, increased reliability, etc. Solar thermal heat is expensive to get and use. It is not clear what other advantages of this process are believed to compensate for that investment and how they do so quantitatively.
- Polybenimidazole (PBI) membranes are known to have durability issues. While they may have operated well in the short-term tests, it is unlikely they will in long-term tests (thousands of hours). A different material should have been used, and if not available, this could be an area of development. The theoretical potential was 0.16, and they are much higher than that (0.4 V). The voltage reduction goal seems moderate. It is good to see higher pressures being examined. An analysis using the Hydrogen Analysis model (H2A) should have been included in this work.

- The objective of this project is to develop and demonstrate improved component technology for the HyS thermochemical process. Along with the sulfur-iodine thermochemical process, the HyS process was originally developed by Westinghouse for coupling to nuclear energy for large-scale hydrogen production. As it is cast for this project, it could also potentially be coupled to concentrated solar energy for the HT heat input (the sulfur-iodine thermochemical process and HT steam electrolysis could also be coupled to concentrated solar for the required HT heat addition). The electrical requirement can be provided by the grid or photovoltaics. The HyS process includes an electrolysis step that operates at ~100°C in which sulfur dioxide and water react electrochemically to yield sulfuric acid and hydrogen in a SO_2-depolarized electrolyzer. The presence of SO_2 on the anode side reduces the open-cell voltage significantly to ~0.16 V. However, a significant activation overpotential must be overcome to drive the electrolysis cell with reasonable current densities such that practical cell voltage is ~0.6 V. A HT heat addition process in which SO_2 is regenerated by sulfuric acid decomposition is required to close the cycle. The electrolysis cells use PEMs, including PBI for HT (130°C) pressurized operation. Precious metal catalysts are required on the SO_2–sulfuric acid side of the cell. The work performed under this project addresses only issues associated with the electrolytic step of the overall process. The significant materials and reactor design challenges associated with the sulfuric acid decomposition step are not addressed.

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.

- Accomplishments under the restricted funding were outstanding. Progress, however, was less impressive mostly because anticipated reduction in electrolysis power was only partially realized. Purported improvement through higher-temperature operation was demonstrated, although cell voltage required for 500 mA/cm^2 remained higher than 600 mV. The potential improvement from advanced catalysts is somewhat constrained because all improved catalysts are noble metals, so cost effectiveness might not be realized. The electrolyzer work focused entirely on sulfonated polybenzimidazole (s-PBI) membranes, and concerns regarding the long-term performance of this material in highly acidic electrolytes were expressed and not countered by the presentation.
- The project has made good progress in finding new catalysts with lower overpotential but did not quite reach the target of 100 mV reduction. It is unclear if this is enough for now until membrane electrode assembly (MEA) is fabricated and if further progress towards the target will come from other parts of the process or if further work on catalysts is critical. It is not clear if there are additional catalyst leads. The new PBI membrane looks very promising and seems critical to achieve targets. Questions were raised at the review about the stability of PBI and should be addressed. It is unclear what other leads there are should PBI not be suitable. The Pressurized Button Cell Test Facility (PBCTF) looks to be an important tool for this project, and good progress was made in building it. Researchers recognize that this process needs to be cost-effective, but no information or metrics were presented to judge.
- Improvements were achieved, meeting project goals. The higher current was good. It would have been nice to see how the improvements achieved would decrease hydrogen production costs. An updated H2A analysis would have been useful. The catalyst loading needs to be clearly stated. The major problem is that progress was made using a membrane that is likely not to be viable owing to likely limitations on its durability. PBI may work well for hundreds of hours, but not for the thousands of hours that will be required for this process to be viable. Phosphoric acid doped PBI has a history of problems during cycling on and off. It is likely that the version being used here will have the same issues.
- Good work has been made on screening potential anode catalysts. Good progress on completing fabrication of the pressurized button-cell has been made. The task of designing and fabricating a button-cell that operates at elevated temperatures and pressures is extremely difficult. Parts must be custom made and fabricated from corrosion-resistant materials for the very aggressive chemicals. Preparing a plan that meets all aspects for safe experimental work is time-consuming and is an essential task that is not fully appreciated by many. A promising membrane, s-PBI has been identified, but further development work is still required. The effort to complete this work by the end of 2014 appears gargantuan, and for this reason, the grade is a 3 because of the timeline.

- Technical accomplishments reported to date include development of improved electrocatalysts (Pt-Au alloys), screening of catalysts in acid solution, development of a pressurized button-cell test apparatus, and electrolyte membrane development at the University of South Carolina. The accomplishments were reasonable, considering the relatively low funding amount for this project ($300,000).

Question 3: Collaboration and coordination with other institutions

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

- Collaboration with the University of South Carolina is excellent, as membrane development work for this project has been ongoing and supported by internal funds.
- The project was led by the Savannah River National Laboratory (SRNL) with collaboration from the University of South Carolina. SRNL was responsible for the catalyst screening activities and cell testing. The university was involved with electrolyte membrane fabrication and characterization, including the development of advanced membranes, such as s-PBI.
- There was good collaboration with the University of South Carolina. The roles were clearly defined.
- This project has had a strong history of effective collaboration and coordination with other institutions and researchers. The current funding environment has affected this history so that, presently, the project includes a single partner. It is acknowledged that the choice of partner is consistent with use of s-PBI membranes, but it is not clear if the choice of membrane material is driven by the collaboration or whether there might be better membrane material options.
- The project team should look at opportunities for other potential collaborations to beef up the pipeline with additional catalyst and membrane leads.

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

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

- The HyS cycle is an all-fluid cycle relying on only two chemical reactions, thereby reducing cycle complexity. All-fluid cycles have material transport advantages over solid transport concepts. A two-step thermochemical cycle provides significant simplification advantages over multi-step cycles. The maximum temperature of this thermochemical process is lower than any other two-step thermochemical concept and provides materials of construction and capital cost advantages. These characteristics are relevant to the DOE Hydrogen and Fuel Cell Program (the Program) goals, and resolution of significant performance barriers could provide significant advances toward meeting the Program goals.
- The reviewer marked the relevance as satisfactory, but it is really not possible to judge potential to achieve the goal of cost-effective hydrogen production—needed information is not in the material presented.
- Much time and effort has been spent on the development of the HyS cycle. Considerable funds, most recently $5.2 million by the DOE Office of Nuclear Energy (NE) and an unknown inflation-adjusted amount by Westinghouse, have been expended, and yet cycle development is not complete. It is also expected that scale-up and completion of the current Task 3 (integration of the electrolyzer with the other steps) will be difficult and costly based on the experience at General Atomics for the S-I cycle. There is also concern that the bullet design for sulfuric acid decomposition is not practical from the perspective of industrial chemical engineering. Based on these issues, the chances for successful development of the cycle appear low. The project needs to determine how much funding is enough. Nevertheless, if the button-cell is successfully demonstrated at elevated temperature and pressure with the new membranes and catalysts and is durable for >100 hours, some degree of future work can be justified. H2A calculations indicate that DOE's cost target will be met if the electrolyzer's development is successful.
- The HyS cycle is interesting but was out selected by NE in favor of solid oxide electrolyzers. For this reason, it is not clear how much impact it can make. The process is interesting, but it is not clear that a low hydrogen price can be achieved because it combines solar and electrolysis. It would be interesting to compare the efficiency and economics of this process against a HT electrolyzer.

- This technology suffers from a number of serious challenges, including handling and circulation of highly corrosive sulfuric acid, large activation overpotentials, the requirement to use precious metal catalysts, membrane degradation, and special materials requirements for wetted components. While the potential exists for achievement of high overall hydrogen production efficiencies, the technical and cost (precious metal catalysts, special materials for handling hot sulfuric acid) challenges are formidable. The potential impact is therefore very long-term.

Question 5: Proposed future work

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

- The proposed future work follows logically from the tasks completed to date. Proposed tasks include button-cell testing for the baseline materials set, further membrane development, and testing of advanced MEAs.
- The plan is reasonable. PBCTF is a key tool for MEA testing. But it would be good to see more catalyst and membrane candidates in case current ones do not work out. Assume that PBCTF testing will address outstanding issues of S crossover with new membranes, PBI stability, and overall performance. The work presented has been focused on the electrolyzer, but the interface with the solar heat is also important and has not yet been considered in any detail. Given that, barring major issues with the new catalyst and membrane, the electrolyzer is approaching its target performance (see Chart 18). It may be time to start considering the solar interface.
- Degradation tests must be done. PBI is known to be unstable and difficult to handle. Most fuel cell companies that investigated using it have abandoned it.
- While the reviewer is sympathetic to the issues of materials and the need for custom parts encountered by the researchers, there is relatively little time to demonstrate the operation of the button-cell at elevated pressures and temperatures that will enable further funding.
- Proposed future work is essentially irrelevant in light of proposed future funding levels.

Project strengths:

- The HyS cycle is an all-fluid cycle relying on only two chemical reactions, thereby reducing cycle complexity. All fluid cycles have material transport advantages over solid transport concepts. A two-step thermochemical cycle provides significant simplification advantages over multi-step cycles. The maximum temperature of this thermochemical process is lower than any other two-step thermochemical concept and provides materials of construction and capital cost advantages.
- Clear targets for the electrolyzer are established. There is good progress towards targets with the new catalyst and membrane. Performance is not too far from the short-term target. Building PBCTF is a major step forward.
- Completion of the catalyst screening, test stand completion, and membrane development tasks are notable, considering the funding amount.

Project weaknesses:

- This is a hybrid thermochemical process requiring an electrochemical step that complicates the simplicity of a two-step cycle.
- There is a limited pipeline of catalysts and membrane candidates. It is unclear how electrolyzer targets connect to economics. There is not enough information provided or available. The interface with solar heat was not really investigated.
- The membrane the project has selected is known to be difficult to manufacture in high volumes and has degradation issues. The H2A analysis needs to be updated and the assumptions made transparent.
- The technological challenges associated with the HyS concept are very significant. Precious metals are required for catalysts. It is not clear if any non-precious-metal catalysts have been tried. PBI is difficult to manufacture in large quantities and has shown large degradation. Corrosion is a significant issue for all process components that come into contact with the sulfuric acid solution. A polymer lining must be used on steel parts while wetted metal parts must be fabricated from tantalum or zirconium.

Recommendations for additions/deletions to project scope:

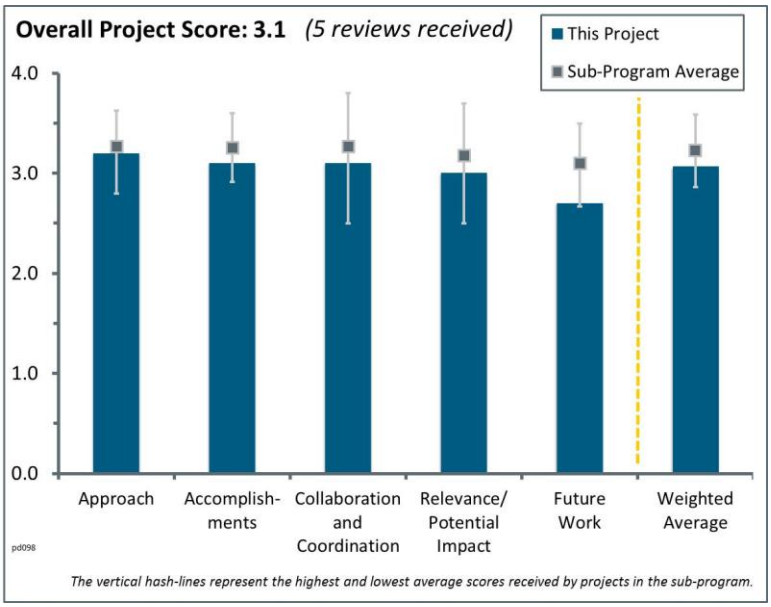
- In light of concerns expressed regarding viability of the choice of s-PBI membranes, the project should immediately resolve those concerns before undertaking any of the other tasks described under future work.
- A comparison between the best-case performance estimates and cost/kg for solar hydrogen production based on HyS vs. PEM water electrolysis powered by high-efficiency photovoltaics should be performed. For solar hydrogen production, the PEM/photovoltaic concept is a reasonable baseline because PEM electrolysis and photovoltaics are already commercially available.
- An H2A analysis needs to show how costs improve with their advancements. Development of other membranes should be considered.
- The project should: develop more catalyst and membrane leads, possibly through additional collaboration; begin studying/modeling an interface with solar heat; identify critical design issues and equipment needs; and develop an economic analysis to determine potential to achieve hydrogen cost targets.

Project # PD-098: Low-Noble-Metal-Content Catalysts/Electrodes for Hydrogen Production by Water Electrolysis

Katherine Ayers; Proton OnSite

Brief Summary of Project:

The overall goal is to reduce fuel cell stack capital costs for lower hydrogen production costs. This project leverages fuel cell advancements in electrolyzers to optimize anode catalyst utilization for >80% reduction in platinum-group metal (PGM) loading and to identify the optimum configuration for manufacturable, ultra-low loaded cathodes.



Question 1: Approach to performing the work

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

- This project is aimed at advancing polymer electrolyte membrane (PEM) electrolyzer technology with a focus on reducing PGM loadings while maintaining or improving electrode performance. Excellent cell performance (nearly equivalent to baseline) was demonstrated in the electrolysis mode in Phase I of this project with very low PGM loading on both electrodes. Phase II is focused on translating these advancements toward manufacturability and improving electrode durability. Low PGM loadings are achieved by synthesizing core-shell nanocatalysts, resulting in increased PGM-specific surface area and a significant reduction in required PGM loading. Ultrasonic spray (printer) coating of catalyst materials is being examined as a potential low-cost cell manufacturing technique.
- The concept of producing ultra-low Pt loading by synthesizing size-controlled core-shell nanocatalysts sounds interesting and has the theoretical potential of achieving the goal of 80% cost reduction in an oxygen-evolving reaction (OER) catalyst. This is a worthy approach if these materials are proven to be stable and can be easily be scaled up.
- The approach systematically works on cathode manufacturing, anode catalysts, and electrode and finally fuel cell development, finishing with cost analysis. The project takes advantage of technology developments at Brookhaven National Laboratory (BNL), which can lead to greatly reduced costs for catalysts.
- The approach was adequately explained. The milestone chart was useful at pinpointing the status of the progress on the project.
- The approach to reduce capital costs by reducing PGM loading and developing new manufacturing methods is aligned well with lowering the capital cost barrier. However, the catalyst represents only 6% of the total cost, as the principal investigator (PI) pointed out.

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

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

- The project has made good progress on reducing cathode loadings to under 0.1 mg/cm^2 and anode to less than 0.5 mg/cm^2 with performance close to baseline catalysts. Although the catalyst is not a major cost element in electrolysis systems, it is becoming more of the cost fractionally as the other pieces become less costly. Reduction of PGM catalyst content will help insulate manufacturers from PGM price shocks. The Ru core of the catalyst is ~20 times less costly per troy ounce than platinum. Stable performance over 500 hrs has been shown.

- The progress is reported on ultra-low PGM cathode synthesis with good (~50 mV higher than baseline for long-term tests; current density was not specified) initial and long-term stable performance (500 hrs).
- Good performance of a spray-deposited cathode gas diffusion electrode (GDE) was demonstrated. Ru-Ir nanocatalysts were deposited on TiO_2 supports, showing similar performance to unsupported catalysts.
- The progress was good. Proton OnSite has a great reputation for producing results. A higher grade could not be assigned because only the results were presented. There was little discussion of the work involved in obtaining each result and the limitations within each result. For example, little or no detail was provided for the following technical accomplishments: (1) synthesis of cathode catalysts and (2) demonstration of applying the catalyst with an ultrasonic nebulizer. BNL appeared to be responsible for developing the cathode catalyst that reduced Pt loading by 98%. Results from Proton OnSite showed Pt reductions of >80%. The method for applying the catalyst at BNL was manual, while Proton OnSite was tasked with developing a manufacturing method. An ultrasonic nebulizer was used and found to give satisfactory results. However, no details were provided on Proton OnSite's contributions. For example, it is not clear if a new synthesis method was developed by Proton OnSite. It is not clear what the challenges were in applying the catalyst on a larger scale. Some discussion was needed on how the work would achieve a higher efficiency for the overall process. The organization of the presentation was not conducive to understanding. It would have been helpful if the approach and accomplishment for each task were discussed together.
- It looks like the project team has achieved the goal of down-selecting the cathode material with 10% Pt loading and the same performance and testing for 500 hrs. However, on the milestone slide, the durability milestone is given as only 50% achieved. Progress on the anode side was not as strong.
- Progress seemed less than adequate for many of the upcoming task milestones for 2014.

Question 3: Collaboration and coordination with other institutions

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

- This project is an excellent example of leveraging technologies from the national laboratories in order to improve commercial energy projects and systems.
- This project was led by Proton OnSite in collaboration with BNL. BNL was responsible for synthesis and characterization of catalyst materials and electrode formulations. Proton OnSite led the cell testing and manufacturing efforts.
- Collaboration was demonstrated. Proximity of Proton OnSite and BNL was seen as an asset.
- It appears that progress might be enhanced with more intensive collaboration between the partners.
- Because the development of ultra-low-PSG materials is still considered to be at an early stage, more broader and rigorous collaboration could benefit this effort.

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

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

- This catalyst improvement effort is valuable to the delivery of this technology.
- This project has potential to reduce costs in electrolysis and, just as 3M's nanostructured thin film (NSTF) has been tested in electrolysis despite being developed for fuel cells, this project could have fuel cell applications.
- Breakthrough findings are unlikely. However, in light of the investment size to date on PEM-based electrolyzers, incremental improvements to lower the noble metals and cost are relevant.
- As the PI indicated in her talk, PGM catalysts represent only about 6% of the capital cost of the baseline stack. Therefore, the potential for cost reduction associated with low PGM loading is very limited. Some additional savings can potentially be realized through lower-cost manufacturing techniques, such as spray deposition of GDEs, which is also under investigation as part of this effort.

- The catalyst cost represents only 6% of the total cost. Further anode development and longer durability testing are required to fully assess any potential cost reductions. However, if the cost projections given in PD-102 are correct, the key driver for hydrogen production costs is electricity costs. Stack costs, especially for the future forecourt case, are a relatively small fraction of the total cost (see PD-102). Because Proton OnSite is an engineering company, the cost of the electric power needed should have been well known. Rate data are available on the website for Edison Electric Institute.

Question 5: Proposed future work

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

- Proposed future work includes scale-up of manufacturing methods, additional MEA testing for durability, optimization of anode and cathode materials, and cost analysis. This proposed work appears to move the project forward in a logical fashion.
- Focusing on cathode manufacturing and anode performance/durability early on, followed by cell testing and cost analysis, sound like the right path forward.
- The cost analysis step using the Hydrogen Analysis model (H2A) for this project is important. In fact, it is possible that the cost analysis should be started earlier in the project in order to estimate the impact of the project and also to give the project guidance on technological milestones. For instance, it could guide efficiency and durability targets. The rest of the future work is reasonable and well-organized.
- Proton OnSite has identified limitations and barriers well. However, the cost of the PGM is a small fraction of the total cost. And even a significant reduction in the amount of PGM will have a relatively small effect on the total cost of hydrogen production. Based on the data in PD-102, realigning this work on possible methods to improve efficiency, such as higher-temperature operation, is suggested.
- There was no clear description of the future work necessary to bring progress on milestones up to target.

Project strengths:

- The project has the potential for a step change in catalyst cost for PEM electrolyzers.
- Excellent performance of ultra-low loading catalysts has been demonstrated using core-shell nanocatalysts. Ultrasonic spray deposition of catalyst material on oxide support material may result in low-cost manufacturing techniques.
- The project team looks like it has a good understanding and progress in cathode screening and manufacturing.

Project weaknesses:

- This project includes several fairly independent lines of research. The integration of these tasks is not completely obvious beyond the general topic of catalyst development and manufacturing. The potential for cost reduction associated with low PGM loading is limited.
- The project team should consider providing the potential impact of this effort with respect to the overall cost and DOE targets in order to provide the right perspective.
- The future efforts are lacking. Efforts could be better coordinated between partners. The formulation of Ru-Ir on specific Ti materials is an expensive starting point.

Recommendations for additions/deletions to project scope:

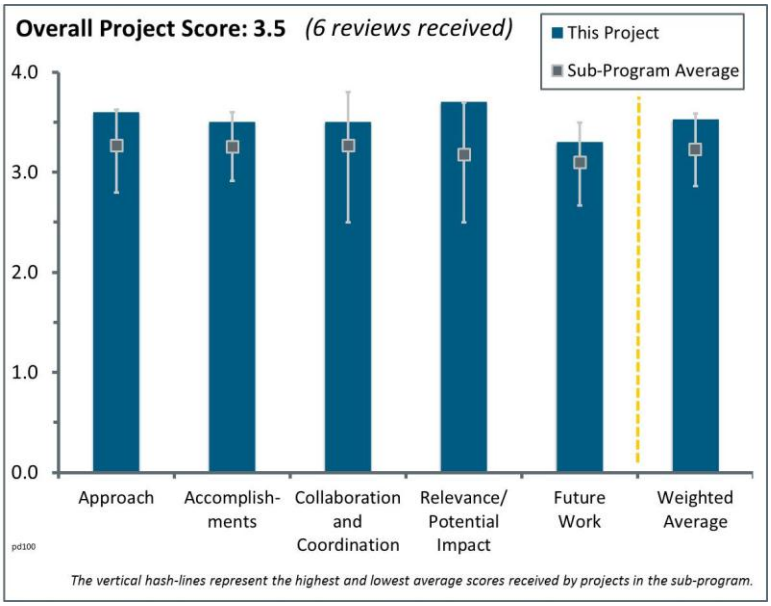
- The project should perform an initial H2A assessment of the potential benefits to help set technical targets. This will be more helpful than waiting until the end of the project, as is shown now in the project plan.

Project # PD-100: 700 bar Hydrogen Dispenser Hose Reliability Improvement

Kevin Harrison; National Renewable Energy Laboratory

Brief Summary of Project:

The objective of this project is to characterize and improve upon 700-bar refueling hose reliability under mature market conditions. The National Renewable Energy Laboratory (NREL) designed a test system that subjects refueling hose assemblies to pressure, temperature, mechanical, and time stresses. The high-cycling test reveals the compounding impacts of high-volume 700-bar fuel cell electric vehicle refueling that has yet to be experienced in today's low-volume market.



Question 1: Approach to performing the work

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

- The project design is very well thought out. The test protocol is appropriate to conduct accelerated testing of the refueling system. The only thing that is not clear is how the team is planning to reduce the cost of the hydrogen refueling hose assemblies. The knowledge of how materials perform during refueling will allow more companies to build the hoses, which will increase competition and reduce cost. However, there is no discussion of cost assessment in the presentation. It is unfortunate that the limited number of hoses available will limit the tests that can be performed (e.g., burst test at different conditions).
- The approach to performing the work is logical and addresses practical issues anticipated in the field. The project is well designed to account for potential barriers. The robotic system should allow for reproducible results. Test protocol and measurement techniques are adequately described, and milestones/deliverables are well defined. It may be helpful to include some real-life exposure conditions, such as sunlight, environmental contaminants, etc.
- This is extremely valuable work to assure safe retail conditions. This project should be accelerated, given the planned roll out of vehicles in 2015–2016.
- The objective is to characterize 700-bar hose reliability under mature market conditions. The approach is well defined and clear. The project is working with industry and Colorado School of Mines (CSM) on computer control with temperature and pressure cycling with leak monitoring work following SAE J2601. The project work scope appears to be well designed and thought out with industry partners to quantify the reliability of the dispensing hose.
- It appears to be a good approach, but there will be lessons learned when actual testing with hydrogen has been started, which may change the direction of the approach based on lessons learned. The reviewer rated it as "good" because it is early in the project process.

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 test protocols have been selected, and the equipment has been acquired. Furthermore, all the tests have been evaluated. Some of the tests have already started. The performance indicators that are being measured will help accelerate the introduction of safe and reliable 700-bar dispensing hoses. The test robot is pretty

impressive; conditions for the accelerated life testing seem to be in working order. The software works properly to direct the robot arm to connect and disconnect the hose.

- The work seems to have progressed well as per the plan. The installation and testing of the automation system has been completed. All of the test procedures have been established and characterized using hose material from one vendor. Additional hose materials need to be tested. There is no mention of any feedback and corresponding changes to the test plan as per the plan milestones and deliverables.
- An automated test fixture is in place, and the system is operational. Host failure was the baseline. Results indicate good bonding of exterior material with inner hose material. Expected results will show similar material degradation during host cycling. Scanning electron microscope (SEM) analysis will be used to show changes in material morphology.
- The progress is early development work. The project has not performed detailed tests to determine hose performance. The project succeeded in setting up the robot. The robot needs to include hysteresis to measure wear on the nozzle. Furthermore, the test setup should be benchmarked to existing installations at distribution centers across the United States.
- Hose pressure testing was done with air—it is not clear if this replicates the impact/effect of hydrogen at the same pressure. The project should consider repeating the test with hydrogen to find if differences in results occur. Nozzles will not last for 25,000-cycle testing; this should be considered as well, because it requires additional torqueing of hose and fittings (and potential damage). It will be interesting to see how fittings/crimps perform under climate extremes (hot and cold) and pressure cycling—the project should look into the fitting/crimps installation process and consider the impact of variations of crimp installation environments on operation in the field.

Question 3: Collaboration and coordination with other institutions

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

- At this point of the project, the right partners have been invited to participate. In the future, it would be good to invite additional host manufacturers to communicate the results of the testing and to boost confidence in the reliability of 700-bar dispensing systems to inspire domestic manufacturing.
- Host vendors are involved with testing at national laboratories. Future work/collaboration started with a small business and a university. NREL chemists are involved with determining the composition of the host material structure before and after testing.
- The project is working with CSM (SEM), SPIR STAR (hose manufacturing), Sandia National Laboratories, and NanoSonic (hose manufacturing). It would be good to see collaboration with station owners in California and distribution centers.
- Adequate collaboration partners are included. It may be helpful to include testing of a hose in-service in the field at an existing hydrogen fueling station.
- The project should explore collaboration and coordination with Yokohama Rubber in Japan—this company developed a 700-bar hose together with Iwatani Industrial Gases.

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

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

- Given that there is only one certified 700-bar hose manufacturer and that the manufacturer is involved and interested in the results of the project, this project has the potential to accelerate the introduction of refueling stations and boost additional hose manufacturing capability.
- The current industry's reliance on a single hose manufacturer (SPIR STAR) is not ideal, so testing the reliability of this product is a necessity.
- Accelerated testing of components in hydrogen service is important to the success of the overall Hydrogen and Fuel Cells Program. The hydrogen delivery hose is a critical component from a safety perspective, as it would be in contact with users. Demonstrating safe use of hydrogen is essential, and durability of components in hydrogen service is important for cost-effective hydrogen fuel.

- The scope of work will provide required critical information for the durability of dispenser hoses.
- There is a need to understand how leaks are analyzed. Sensors are calibrated to elevation. This work is vital to minimize the potential for an energy release in a retail location. Furthermore, extending the life of dispensing hoses will help reduce a major maintenance cost for the station owners.

Question 5: Proposed future work

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

- The future work plan is adequately summarized.
- The reviewer is looking forward to the initial results from testing using hydrogen.
- The team should also reach out to domestic hose manufacturers, as well as retail station owners, to get feedback on the testing protocol to discover what abnormal conditions need to be tested (e.g., breakaway events).
- The remaining scope of work includes full test-system integration and testing. An automated high-pressure, low-temperature cycling and post-material analysis after cycling should be done before going on to a testing program of other host manufacturers.
- The future work uses brand new materials from SPIR STAR (supplier). The project needs to improve compression equipment. It would be helpful to accelerate the effort.

Project strengths:

- The project is of high value to industry and is unique. Third-party testing is a project strength. Lessons learned from this project will improve knowledge available to manufacture reliable 70 MPa hydrogen fueling hoses.
- A project strength is that the host vendor is involved with testing at national laboratories. Future work/collaboration started with a small business and university. NREL chemists were involved with determining the composition of host material structure before and after testing.
- The technical capability, testing equipment, and laboratory space seem appropriate. The selected protocol is relevant to the performance indicators that need to be measured.
- Automation is a project strength, as is the extensive use of analytical techniques. Proper planning and appropriate collaboration are also strengths.
- Capturing an objective understanding of the equipment's performance under dynamic test conditions is a strength.

Project weaknesses:

- No project weaknesses were identified.
- No critical weaknesses were found.
- The involvement of additional stakeholders is a weakness.
- Limited comparison material is available; there is limited variation of movement to imitate the reality of hydrogen nozzle/hose assembly usage.
- There is no clear objective, and the project seems to be proceeding too slowly. It is recommended that the project adopt the intention to confirm double or triple life expectancy.

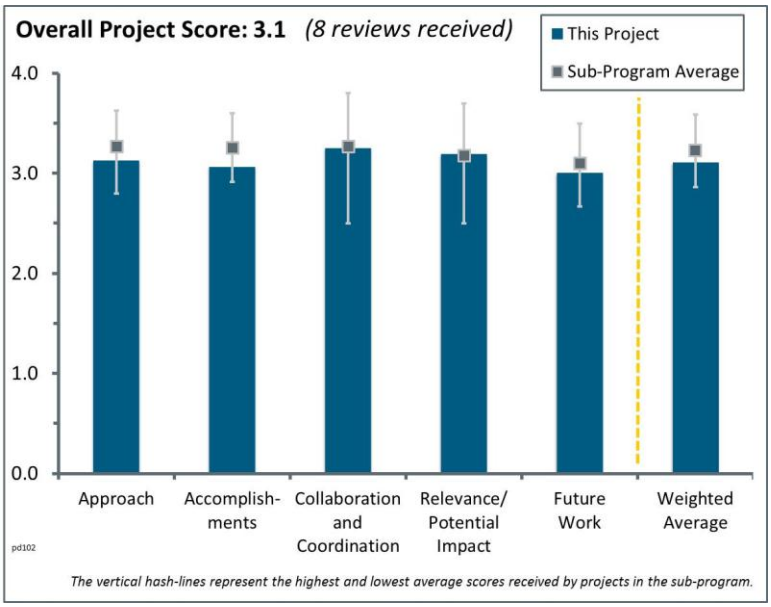
Recommendations for additions/deletions to project scope:

- The project team may want to mark the alignment of the hose with the nozzle to ensure consistent alignment and that there is no movement of the hose with the nozzle during the operation of twisting during the cycle test.
- The project should be expanded by adding additional hoses from different manufacturers.
- The testing and comparison of hoses in-service, which may be exposed to real-life conditions, is recommended.
- The project should bring in more data from field installations and operators.
- Domestic refueling hose manufacturers and/or station owners/designers should be brought in to provide input on additional mechanical stress conditions experienced by the hose during normal operations.

Project # PD-102: Hydrogen Pathways Analysis for Polymer Electrolyte Membrane Electrolysis

Brian James; Strategic Analysis, Inc.

Brief Summary of Project:



The objectives of this project are to analyze hydrogen production and delivery pathways to determine the most economical, environmentally benign, and societally feasible paths for the production and delivery of hydrogen fuel for fuel cell electric vehicles; identify key bottlenecks to the success of these pathways; assess technical progress, benefits and limitations, levelized hydrogen costs, and the potential to meet the U.S. Department of Energy (DOE) production and delivery goals; and apply the Hydrogen Analysis (H2A) Production Model as the primary analysis tool for the projection of levelized hydrogen costs and cost sensitivities. In 2013–2014, these project objectives were applied to develop a validation case based on hydrogen generation with standalone, grid-powered polymer electrolyte membrane (PEM) electrolyzers.

Question 1: Approach to performing the work

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

- The approach used by the researchers in obtaining relevant technical and economic data from existing electolyzer suppliers in order to populate the H2A model is an excellent approach toward the main goals of this project.
- This project is directed work with objectives and deliverables defined by the DOE Hydrogen and Fuel Cells Program (the Program). In that context, the approach is outstanding. The use of expert opinions and the integration of the study with industrial resource data and the ultimate consensus by industrial participants with findings are significant achievements. The logically predictable loss of economies of scale by feedstock cost domination should have relieved the project of the requirement to address central plant analysis. General preliminary analysis should have demonstrated this feature in lieu of investment in scaled-up technoeconomic assessments. Technology improvements could reduce feedstock domination, but until that is realized, economies of scale cannot be anticipated.
- The project is feasible and integrates with other efforts, namely H2A, U.S. DRIVE, and the MacroSystem Model. The project is well designed because it gathers the necessary industry data to update our understanding of the cost and performance of electrolyzers currently and in a future case scenario, adding to H2A a PEM electrolyzer case in addition to the existing alkaline electrolyzer cases. The project updates only the existing data in the H2A model but does not directly address how electrolyzer companies are planning to reduce capital cost, increase efficiency, or improve manufacturing. The additional case is necessary to complete the dataset in H2A, but given that the efficiency of the PEM electrolysis system is already known, extensive analysis is not needed.
- Strategic Analysis (SA) is taking a well-planned approach to assess costs of hydrogen from PEM electrolysis. The collaboration with the National Renewable Energy Laboratory (NREL) ensures that this work is consistent with previous technoeconomic analyses in H2A.
- The analysis approach is excellent, but the message could have been improved if the conclusions were properly benchmarked against the established DOE cost target. The main take-home message should have

been that hydrogen from PEM electrolyzers will never meet current DOE targets so long as the electricity price stays high. This obvious omission in the project summary created the unnecessary impression of ignoring the "elephant in the room." Granted, this may be more a problem for the overall DOE Program and not the project team.

- Looking at the 1,500 and 50,000 kg/day is good. But it would be interesting to see smaller cases that are nearer term—50-100 kg/day. In the smaller productions, the capital cost should be a larger portion of the hydrogen cost. The lower production amounts would be useful to better understand near-term production costs that California and other states may find useful. They could also be used to validate the model because there should be real-life data available. It is not clear what analysis was done to verify the accuracy of the data provided by the electrolyzer companies. The companies may be overly optimistic in where they are and what they can achieve. It is not clear why the capital cost spread was 20%. This seems arbitrary. This examined only PEM electrolysis. There are a lot of alkaline electrolyzers that could be included.
- Fiscal year 2013–2014 objectives were to develop a "validation case" for hydrogen production based on grid-powered PEM electrolysis. The approach used to meet these objectives was to solicit PEM system technical and cost information from four electrolyzer companies and apply the H2A cost analysis tool to estimate the levelized cost of hydrogen production based on this technology. Current and future cases were developed for the forecourt scale (1,500 kg/day) and the central scale (50,000 kg/day). The bulk of the presentation focused on presenting the details of the H2A results for the current and future cases at each scale.
- This project seems to lack an aspect of creativity from the analysis. It seems as though the project team met only the goals for the project and did nothing more, using a sterile interpretation of the results and very few conclusions or considerations. Implementing the model without asking the relevancy of the results seems not helpful to the Program's overall needs. It is not really apparent if this project is scoped appropriately.

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

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

- Progress/accomplishments for the presented work are outstanding. The defined work in the project is on track, and the milestone for presented work was met.
- The completion of PEM cases and the incorporation into H2A are significant accomplishments and will enable quick comparisons with existing production technologies. A breakdown of capital costs will be useful in guiding research.
- The project's accomplishments are clear and meaningful within the context of the hydrogen cost breakdown.
- Significant accomplishments on this project as shown by the completion of a validation case were completed for hydrogen production by PEM electrolysis using the H2A model. A very valuable accomplishment of this work is the detailed capital cost breakdown for the PEM electolyzer system along with the sensitivity analyses provided.
- The project clearly addressed the goals using the required tools and accomplished the specific tasks, but the team failed to provide conclusions and inferences on how the tool may be insufficient—particularly with respect to the current and near-term markets. The "bottlenecks" are near-term, and the team should have made a better attempt to infer those issues to better equip the Program with the guidance.
- The results that indicated large capital cost reductions are predicted between existing and current systems and between current and future systems. It is not clear whether there is a formal methodology for estimating these cost reductions. Obviously, economy of scale plays a role for the predicted reduction between existing and current systems, but it is not clear how this is quantified. Also, the basis for the predicted cost reduction in going from current systems to future systems is not clear. Again, it is not clear if a formal methodology has been applied. There is a potential conflict of interest for the companies to predict lower costs, so measures should be taken to ensure that there is a sound technical basis for the predicted current and future costs. Surprisingly, there were very few predicted cost reductions in going from the current case to the future case, at both scales. Overall production cost estimates were higher than previous estimates; this difference is attributed to a more detailed and realistic estimate of capital costs provided by

the companies. Contrary to what is stated in the presentation, the final report on "Central and Forecourt Polymer Electrolyte Membrane (PEM) Electrolysis" was not yet available on the DOE web site.

- To say that the detailed capital cost breakdown is unique is not true; Giner has provided as detailed breakdowns. The reported costs are very similar to that of the independent analysis done around 2009. The electrolyzer efficiency from the current case should have included the data that NREL has on electrolyzer performance. NREL has actual data of operating systems. The actual data should have been used to validate the efficiency stated by the electrolyzer companies. On the tornado chart, it is recommended to not use red and green because those who are color blind cannot tell the difference. Blue and red would be a better choice. The team should have compared their findings against the DOE targets. With electricity being the major cost, it is not obvious why operating the electrolyzer at a lower voltage to increase the efficiency was not considered. There was no justification for the 1.75 V selection other than what the companies prescribed. If the electrolyzer was operated more efficiently, this would increase the capital cost but may result in an overall reduction in hydrogen cost because less electricity would be needed.
- Data have been gathered, and analyses are under way. However, it is not evident how this work will meet all of the objectives stated in slide 3: "determine the most economical, environmentally benign, and societally feasible paths for the production and distribution of hydrogen fuel for fuel cell vehicles." The project does not address environmental or socio-economic issues. Regarding the second objective—identifying the key bottlenecks for the success of these pathways—these have not changed from the previous version of H2A. The bottlenecks are still the same; we just have better numbers now. That is the only difference. This project is not making a significant contribution to advancing progress toward DOE goals yet. Adding bio-fermentation and high-temperature steam electrolysis (HTSE) can provide interesting results, but both pathways are still too expensive. Also, it is a shame that the results of the "existing case" are not publicly available. These numbers can help with understanding the real status of the technology. The current case relies on an assumption of high volumes of production. This is not the principal investigator's (PI's) fault, so the score does not reflect this concern.

Question 3: Collaboration and coordination with other institutions

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

- The existing collaboration on the analysis work with both NREL and Argonne National Laboratory (ANL) is of great value to this project. The collaboration with the electrolyzer companies was key to the achievements presented this year on this project.
- Collaboration and coordination is excellent with support from national laboratories and integrated contributions of data and opinions from industry. Coordination could perhaps be improved by making use of the extensive operational electrolyzer data collected by NREL over the course of its long-term electrolyzer testing project.
- Collaborators included NREL, ANL, and four electrolyzer companies. The laboratories were subcontractors on the project. The companies apparently participated voluntarily. The level of collaboration associated with this project was good. There was no university collaboration.
- The collaboration with the four unfunded PEM manufacturer companies provided a practical basis for performance and cost analysis, which probably is a strong point of this study.
- SA has done well in collecting data from PEM electrolyzer vendors and in collaborating with national laboratory workers to incorporate results into H2A.
- The review reports on compression, storage, and dispensing (CSD) costs without consulting CSD collaborators or without questioning the validity of the model to predict current state-of-the-art and near-term "bottlenecks." The team did a good job of working on the key area of electrolysis and clearly formed good collaborative relationships to provide trustworthy results.
- Collaborations seem appropriate. The team did not describe who they will be approaching to obtain help from with the two additional cases.
- Based upon the presentation, it was hard to tell what the roles of the partners (other than the electrolyzer companies) were. Though during the question and answer time, it was clear that NREL helped a lot because they answered several questions.

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

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

- The evolution of a vetted and community-accepted approach and associated tool chest to assess cost performance and its sensitivity to variations in technology component cost and performance is a significant accomplishment that will ultimately be of great value to the Program's need to establish priorities in its investments. This benefit will flow down to the project level, assisting researchers in project planning and investment priority. The apparent inability of the subject technology addressed in the presentation to meet long-term (future) DOE cost goals should help identify niche applications such as forecourt or grid stabilization in lieu of central production.
- This project is relevant and the findings are trustworthy. The project team did a good job.
- This project is definitely very relevant in identifying the key cost drivers for the levelized hydrogen cost for the production of hydrogen by water electrolysis.
- Technoeconomic analysis of PEM electrolysis is a critical component in justifying support. PEM electrolysis needs to have promise of a significant advantage over traditional electrolysis for research to be justified.
- Meaningful and timely cost projections are critical in advancing the goals of the Program. The results from this project make it clear what future priorities in PEM electrolyzer research and development should be, namely electricity usage rate and the breakdown of capital costs. But the impact is not as big because the capital cost remains a very small fraction of the overall cost, which is dominated by external factors in the cost of electricity.
- These types of studies provide useful baseline cost estimates for comparison of a wide range of alternative hydrogen production methods. This particular study should be reasonably accurate because PEM electrolysis is an existing commercially available technology. However, the exclusion of the "existing" cost case is a bit disappointing.
- It would be interesting to have an analysis of what DOE's investments have done to aid in electrolyzer improvements and the resultant hydrogen cost reductions or, in other words, to determine what impact the DOE's investments have made on costs over the years. Part of the reason for this work was to measure progress against DOE goals; however, this comparison was never presented. As mentioned before, DOE has invested substantial funds at NREL in testing electrolyzers, but it was not clear that any of the testing done at NREL was used in the analysis. At a minimum, it could have been used to validate the assumptions that the companies provided.
- This is just an update to H2A numbers so far. The results are not very different from the previous version and are not likely to make an impact in the electrolyzer industry. Furthermore, the project does not identify the most environmental or societally feasible paths.

Question 5: Proposed future work

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

- The proposed future work will complete the update to the H2A cases. Also, it would be beneficial to see the variability of the results in the waterfall charts as opposed to just the "most likely" case. Also, a horizontal line should be drawn to reflect the target cost on the chart.
- The proposed future work looks like a good path forward to this project's objectives, especially if the same methodology as for the PEM electrolysis case study is employed.
- The concepts going forward are good. CSD costs may already be addressed by other studies and not necessary, although this group of researchers could do well in that task.
- Two additional studies will be performed: bio-fermentation and HTSE. The HTSE case is of particular interest because the electrical requirement (which is the dominant cost for water electrolysis) for HTSE is reduced by about one-third compared to PEM electrolysis.
- Work on bio-fermentation and steam electrolysis are good additions but will be more difficult because these technologies are not close to commercialization. The PI should take care to ensure that current cases

are based on proven yields/efficiencies and not overly optimistic estimates of near-term improved technologies.
- Proposed future work is defined and directed by the Fuel Cell Technologies Office.
- It is hoped that biological hydrogen cases will not assume unrealistic accomplishments in terms of solar-to-hydrogen, efficiencies, and other assumptions that some of the previous studies in those areas have done. The researchers should talk with the Solid State Energy Conversion Alliance for the high-temperature electrolysis.
- The proposed future work in bio-fermentation and high-temperature solid oxide fuel cells appears to be independent from the current work. Therefore, there may not be much to build upon the current PEM cost analysis results, except perhaps the H2A methodology. If so, the project title should be modified to include the proposed future work.

Project strengths:

- This study provides useful, up-to-date baseline cost estimates for hydrogen production based on PEM electrolysis. Estimates for compression, storage, and delivery are also provided. The effort was a collaboration with industry and two national laboratories. This particular study should be reasonably accurate because PEM electrolysis is an existing commercially available technology.
- The capability to work with diverse communities representing universities, national laboratories, and industry is a significant strength in this project.
- The strength of the project is the partnership and collaboration component. Having actual performance and cost data from four PEM vendors gives valuable credibility to the analysis.
- The team was able to acquire the data and analyze them. The right collaborators were involved to produce the new version of the H2A electrolysis cases. Proposed work to add advanced hydrogen production cases to H2A will generate new and interesting information.
- The project had a great presentation. It covered the topics and summarized them succinctly, although it was a little busy on the slides with words, but it was a great job overall.
- The team members have engaged industry. They are breaking down the capital costs, which allows for the identification of where investments should be made.
- The project's good use of data from electrolyzer manufacturers was a strength.

Project weaknesses:

- The presentation never included assessment of the greenhouse gas implications of hydrogen production using U.S. grid mix or other electricity production schemes.
- The project completely ignored comparing their hydrogen cost results to established DOE targets, missing an opportunity to provide context of the real challenges. Had it stated the obvious, the project team could have rightly justified the case for PEM hydrogen for niche applications where there could potentially be a commercial success without meeting the current DOE cost targets. Again, this comment could be directed towards DOE headquarters.
- Higher-level analysis of the technoeconomic framework should precede implementation of the database-driven assessments to ensure efficient use of project resources.
- The team should have used actual data from NREL's electrolyzer work as available. With compression costs being so significant, a revisit on high-pressure electrolysis (above 1,000 psi) would be interesting. The team limited the scale to 1,500 kg/day, when the nearer term and most accurate numbers would be for smaller-scale systems. The team did not compare against DOE targets, or at least it was not reported in the presentation.
- The creativity and forecasting could have been better. Perhaps this was the result of DOE guidance regarding the presentation, or perhaps it was the approach of the PI; either way, it left the reviewer wanting a bit more insight. Also, CSD should have been deemphasized more clearly in the presentation because it was not entirely in the scope of the project.
- The basis for the predicted cost reduction in going from existing to current systems and from current to future systems should be described and justified. The exclusion of the existing cost case detracts from the overall usefulness of the study.

- The work done so far does not add much to the existing body of knowledge. The project does not develop the most "environmentally benign" and "societally feasible" technologies. The project does not compare environmental or social-economic impacts.

Recommendations for additions/deletions to project scope:

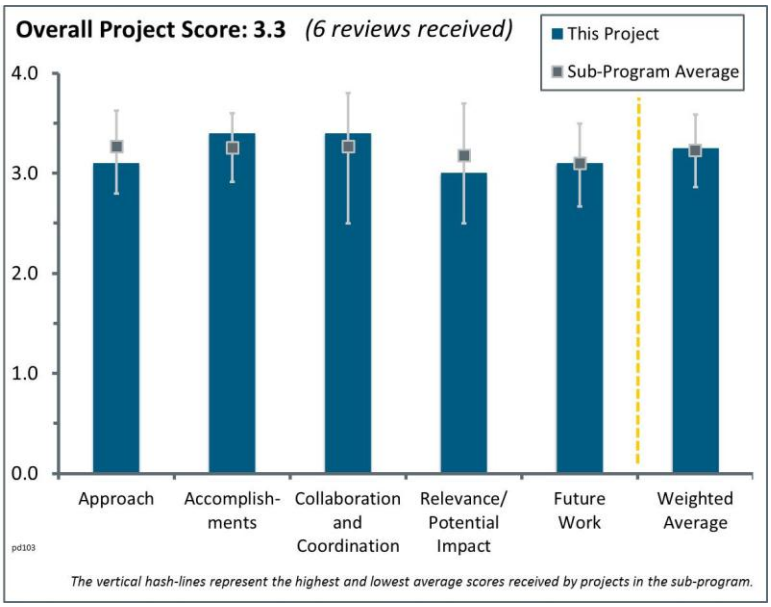
- The team should consider a better method for addressing the CSD aspect. Perhaps the recent independent panel review report—58564—would be a good reference. This was probably not available to this team at the time of the analysis.
- It is recommended that the team examine electrolyzer operating conditions to see if by changing the operating conditions, especially the voltage, the team could decrease the hydrogen cost. The DOE target is hydrogen costs. DOE provides a table of a way to achieve those costs, but if operating the electrolyzer differently from what is in the table results in lower hydrogen cost, the different operation would be preferred. The electrolyzer companies may not want to operate the electrolyzer at lower voltages because this would increase the capital cost and, therefore, decrease their sales. However, this would be important information for DOE to understand.
- The project should separate out the electricity use required for increased pressure in the future case.
- Project acceleration including studies of new long-term research projects would be valuable in getting early assistance in identifying research investment priorities at the project level.
- Changing the objectives of the project to reflect the accomplishments is recommended. The electrolyzer cases of the H2A model should be updated with data from manufacturers. The project should make sure that the team involves the right stakeholders to develop the next two scenarios.

Project # PD-103: High-Performance, Long-Lifetime Catalysts for Proton Exchange Membrane Electrolysis

Hui Xu; Giner, Inc.

Brief Summary of Project:

The objectives of this project are to develop advanced, low platinum group metal (PGM) loading catalysts for high-efficiency and long-lifetime polymer electrolyte membrane (PEM) water electrolysis, including improved mass and specific activity, and to evaluate the impact of newly developed catalysts on the PEM electrolyzer efficiency and cost through materials and system cost analysis.



Question 1: Approach to performing the work

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

- The development of advanced, low-loading catalysts for PEM water electrolysis is a promising approach to develop lower-cost electrolyzers and to increase the stack efficiency. This project is taking an excellent approach in developing electrocatalysts and integrating them into PEM water electrolysis.
- The researchers did a good job screening the catalysts. They have plans for some durability tests.
- The work addresses electrolyzer cost and efficiency. The project is focused on developing low-PGM loading oxygen-evolving reaction (OER) catalysts with improved activity, which will contribute to improving efficiency and reducing electrolyzer capital cost. The National Renewable Energy Laboratory's (NREL's) work focusing on Ir nanowires takes advantage of advances made in the Extended Thin Film Electrocatalyst Structures (ETFECS) program to develop low-Pt oxygen reduction reaction catalysts and has potential for similar gains in activity as seen for the Pt and Pt alloy nanowires from having extended surfaces and non-PGM cores. There is potential for large improvements in performance with supported catalysts (similar to those seen in PEM fuel cells going from Pt black to Pt/C) if stable conductive supports can be found. 3M's nanostructured thin film (NSTF) approach has potential to provide stable materials with high activities.
- The current approach has done an adequate job of scoping the NREL and 3M catalyst formulations.
- A better screening method is needed, possibly one designed on performance, fabrication costs, and durability. The approach to identifying high-performance, long-lifetime catalysts for PEM electrolysis consisted of developing and studying three types of current state-of-the-art Ir catalysts, i.e., (1) Ir on supports (titania nanowires and particles), (2) NSTF, and (3) Ir nanotubes. The project is well designed but ambitious because of the amount of development work required. The researchers did not expect positive results for the three types of samples. This is a good thing and a bad thing because parameters were not defined to limit the scope of work after the initial screening process.

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.

- Significant progress was made during the past year. However, the different types of catalysts should be compared on the same basis. It appears that the state of development varied considerably; whether this was due to more difficult fabrication methods or more highly developed starting materials, such as for the

NSTF, was not discussed. Possible limitations were not mentioned. For example, one of the other speakers indicated that NSTF had durability issues. Fabrication difficulties and costs were not addressed. If skill was involved in the selection of potential materials, the accomplishments are excellent to outstanding. If luck was involved, then the accomplishments are good to excellent.

- Significant progress has been made in all fields of work. The high cell performance with low anode catalyst loading is especially impressive. The newly developed catalysts from NREL and Giner look very promising, but here in situ electrolyzer tests must show if the catalysts are comparable to the NSTF catalysts from 3M.
- The project has shown significant advances over Ir black and Giner's standard anode catalysts at lower Ir loadings. Initial support work has demonstrated improved Ir activity on W-doped TiO_2, with similar stability to Ir black (double the activity at 1.8 V). NREL Ir/metal nanowires have shown improved specific activity and mass activity compared to Ir black. Stability still needs to be improved. NSTF Ir-coated whiskers show high activity and good performance in membrane electrode assemblies (MEAs) at $1/16^{th}$ the standard Giner PGM loading. NSTF structure showed minimal transport losses at current densities up to $5.7 A/cm^2$. Initial tests suggest Ir NSTF has good durability, surpassing milestone durability.
- The progress made by partner 3M is notable. Overall project status is adequate but now needs to accelerate.
- The researchers have tested many different catalysts. It is not clear that the complicated catalyst synthesis can be done economically. The 3M catalyst performance was very good. Durability at 100 hrs is a good start. It will be interesting to see longer tests. They should try to better understand the catalyst and support interactions to better understand why their supported catalyst performs so much better. The speaker said it was improved dispersion. It seems that the doped Ti support is participating in the reaction in some way. They did a lot of rotating disk electrode (RDE) testing and not as much testing in real systems. RDE testing is good for screening, but testing in the electrolyzer is the real test of a catalyst's performance.

Question 3: Collaboration and coordination with other institutions

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

- Collaborations between Giner, NREL, and 3M appear to be working excellently.
- Excellent collaboration was evidenced in the presentation, and there was clear delineation of the work. However, it would have been appropriate to acknowledge the contributions of the collaborators on the pages of the presentation.
- The role and activities of the different team members was clearly communicated. There is good collaboration among the team members.
- Collaboration seems to be working effectively. Giner has been able to integrate 3M NSTF MEAs with its flow field and obtain good performance.
- It is difficult to gauge the level of interaction. The 3M technology description did not seem to demonstrate enough interaction.

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

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

- The major cost for electrolysis-based hydrogen production is electricity cost, so catalyst development to increase efficiency is very important. It is good to leverage the work done by the fuel cell team on catalyst development for electrolyzers. Decreasing the amount of PGM catalyst can decrease the costs, but the complex synthesis may offset some of the lower costs. Also, the reality is catalyst costs are relatively minor. What is really needed is a more active catalyst.
- Reducing PGM content to $1/16^{th}$ current loading will have a substantial impact on electrolyzer costs and reduce the cost of hydrogen from electrolysis. There do not appear to be any efficiency improvements in the MEA tests on Ir NSTF, so electricity costs will not be affected. RDE shows the promise of lower onset potential for Ir supported in W-doped TiO_2.

- The project is targeting the main challenges of the hydrogen production targets for electrolysis: reduction of the high amounts of expensive anodic PGM catalysts currently needed and reduction of electrolyzer capital cost by reducing the PGM loading and decreasing the hydrogen production costs by increasing the system efficiency (reducing anode overpotential).
- This project has the potential to address the goal of reducing Pt loading significantly, thereby lowering costs. However, as was pointed out during the presentations, the catalyst cost is about 6%. The reduction in Pt loading will have a relatively small effect on reducing the cost of hydrogen production. Unless DOE changes the cost target for hydrogen production or electricity costs are significantly reduced, this project has little relevance.
- This project reads on the goals of the Vehicle Technologies Office.

Question 5: Proposed future work

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

- The proposed future work addresses relevant questions. Economic analysis will be important.
- There are well-defined, challenging milestones.
- The researchers should include the impact of long-term cycling to better understand the durability. This should be in addition to the 1,000 hr test.
- A down selection should be made as soon as possible. Electrodes have to be designed, fabricated, and tested. The cell performance is critical, and durability must be investigated.
- Although there was discussion of the future work, it was not clear why there must be continued comparison among all of the partner formulations. It seems with 3M offering superior performance, the others should be put aside, and all efforts should be aimed at maximizing the 3M formulation. This will require intensive cooperation among all partners.

Project strengths:

- Excellent research was done by the individual partners.
- The project has a good team with appropriate experience and expertise in catalysts that can be leveraged to optimize electrolyzer OER catalysts. There are good initial results.
- The researchers are leveraging catalyst development from the fuel cell work. 3M and Giner are a strong team.
- A formulation with improved performance has been identified.

Project weaknesses:

- There are no significant weaknesses. The project has a strong focus on anode catalyst development.
- There was a lack of focus on the best performing catalyst. Working with Ir puts the project at a cost disadvantage.
- The researchers need to better understand the catalyst support interaction. Longer-term testing is needed, as well as cycle testing. The cycle testing is particularly important because the electrolyzer will be turned on and off repeatedly. They need to focus more on increasing the catalyst activity.

Recommendations for additions/deletions to project scope:

- The RDE measurement should also be extended to NSTF catalysts if possible. TiO_2-supported Ir catalysts with a higher Ir-loading (>60 wt.%) should be tested.