

II.A.4 Low-Cost Large-Scale PEM Electrolysis for Renewable Energy Storage

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Contract Number: DE-SC0001338

Subcontractors:

- 3M, Minneapolis, MN
- University of Wyoming, Laramie, WY

Project Start Date: June 19, 2010 (Phase 1)
Project End Date: August 18, 2013 (with Phase 2 continuation)

- Develop a concept design to scale the system to 50,000 kg/day H₂ production including:
 - Definition of the requirements for operation and maintenance
 - Updated H₂A analysis based on the actual 435 psi system cost and operation projected to 50,000 kg/day
 - Analysis of greenhouse gas and petroleum reductions that will occur with the successful implementation of the proposed technology

Fiscal Year (FY) 2013 Objectives

- Implement advanced catalyst application process for 50% reduction in catalyst loading
- Demonstrate equivalent oxygen evolution reaction (OER) activity in NSTF format to Proton baseline for 90% reduction in catalyst loading
- Manufacture NSTF or advanced catalyst process electrodes using alternate membrane and demonstrate 69% lower heating value (LHV) efficiency for 1,000 hours
- Complete environmental impact assessment based on renewable hydrogen vs. other technologies

Overall Objectives

- Demonstrate optimal membrane electrode assembly (MEA) efficiency through:
 - Refinement of catalyst composition for oxygen evolution reaction
 - Rapid screening of additional metal candidates through combinatorial methods to determine optimal anode catalyst composition
 - Fabrication of identified materials as both traditional and nano-structured thin-film (NSTF)-type electrodes
 - Integration of new catalyst materials with advanced thinner membranes
- Reduce catalyst loading through:
 - Formulation optimization of metal oxide based inks
 - Improved electrode application processes for uniform distribution
 - Application of NSTF structures
 - Demonstration in Proton's large active area format
- Demonstrate 1,000 hours system operation at >69% efficiency

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(F) Capital Cost

(G) System Efficiency and Electricity Cost

Technical Targets

Table 1 contains the technical targets for this project.

Advanced MEA manufacture

This project is designed to take the first step in implementing substantial reductions in precious-grade metal (PGM) content in the electrodes, while demonstrating feasibility for order of magnitude reductions. Feasibility has already been demonstrated on the cathode. In addition, higher activity catalysts and more efficient membranes will be examined for application in electrolysis. While there are

TABLE 1. Proton Energy Systems Progress Towards Meeting Technical Targets for Distributed Water Electrolysis Hydrogen Production

Characteristics	Units	2012 Target	2017 Target	Proton Status
Hydrogen Cost	\$/gge	<3.70	<3.00	3.46
Electrolyzer Capital Cost	\$/gge	0.70	0.30	0.64
Electrolyzer Energy Efficiency	% (LHV)	69	74	67

gge - gasoline gallon equivalent

Note: Estimates are based on H2A v2.1, for electrolysis only (compression-storage-delivery not included). Model assumes \$0.05/kWh.

Electrolyzer cost based on 1,500 kg/day capacity, 500 units/year; efficiency based on system projections, technology which could be implemented within five years, and demonstrated stack efficiency of 74% LHV efficiency.

no specific material metrics for electrolyzers as there are for fuel cells, the goals for this project are as follows:

- Membrane thickness <75 microns
- Total PGM loading <0.5 mg/cm²
- Stack efficiency >72%

FY 2013 Accomplishments

- Manufactured catalyst powders based on combinatorial synthesis predictions
- Validated general performance trends in full cell testing
- Evaluated ternary catalyst compositions for 500 hours and demonstrated presence of all elements in expected ratios
- Validated 50% reduction in loading for baseline catalyst formulation with no loss in full cell performance
- Developed improved quality control methods for inspection of new electrodes
- Demonstrated high activity NSTF electrodes for OER
- Demonstrated operation of improved membrane for 10,000 hours at 80°C
- Demonstrated >73% efficiency at stack level for advanced MEA



INTRODUCTION

This project addresses the DOE Hydrogen Program objective for distributed production of hydrogen from proton exchange membrane (PEM) water electrolysis. The DOE technical targets for hydrogen cost as well as electrolyzer efficiency and capital cost will be directly addressed through the advancement of key components and design parameters. For renewable applications such as grid energy storage, a continuum of options from distributed hydrogen

generation to centralized production at capacities on the order of 50,000 kg/day will be needed. The majority of the electrolysis efficiency losses arise from the oxygen evolution overpotential and the membrane ionic resistance. To reach a target system operating efficiency of 69%, new catalyst and membrane materials are needed. Especially for these large scales, it is necessary to minimize the use of precious metals. Much learning from fuel cell materials research can be applied to enable the required advancements. Design studies are also needed for PEM electrolysis at this scale to understand the capital costs, environmental impact, and operation and maintenance requirements.

APPROACH

This project addresses crucial elements of Proton's technology roadmap, with a focus on improving MEA performance. The oxygen evolution catalyst and membrane are therefore the two key areas of focus. Critical issues include long-term stability of the membrane under electrolysis conditions, particularly as it relates to long term creep with a thinner membrane, and stability of the catalyst to dissolution. Continuation of the work completed in Phase 1 includes 1) refinement of the mixed metal oxide catalyst composition for increased activity while maintaining voltage stability, 2) initial reductions in catalyst loading of 50% or greater based on implementation of improved manufacturing processes at Proton, 3) integration of optimized catalyst compositions into nanostructured thin films to demonstrate an additional order of magnitude reduction in catalyst loading and development of high-speed manufacturing capability, 4) use of reinforced membranes in order to reduce membrane thickness and ionic resistance without decreasing durability, and 5) projection of these improvements to 50,000 kg/day production levels including cost modeling, impact on reduction of greenhouse gas emissions, and conceptual system design.

Catalyst compositions were made using two techniques. Promising compositions from Phase 1 were manufactured as nanopowders through fusion of soluble metal salt precursors with sodium nitrate at high temperatures. Nanopowders were screened through fabrication of bench-scale MEAs. New candidates were made through ink jet printing and sintering,

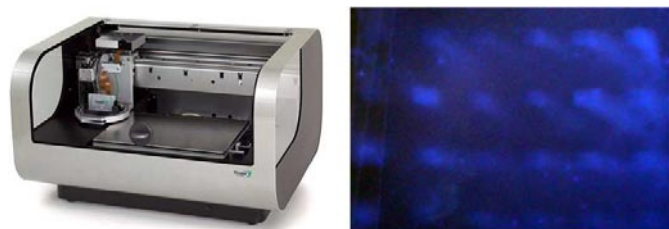


FIGURE 1. Combinatorial Electrode Fabrication Equipment and Measurement

and were screened through a fluorescence technique to determine the relative amount of oxygen evolution at a given overpotential. The approach is shown in Figure 1. The conceptual 50,000 kg/day system design was developed through sizing calculations of the major system components and consultation with relevant industries such as chlor-alkali to determine typical redundancy factors and margins. Items such as power conversion components, water treatment facilities, pressure vessels, and storage tanks were quoted through suppliers well versed in the relevant sizes. Cell stack costs were estimated based on a module similar to Proton's largest active area platform and known design improvements validated at a prototype level.

RESULTS

Combinatorial results from FY 2012 were used to select ternary catalysts for manufacture as nanopowders. Metals examined included Ir, Pt, Al, Ru, Sn, Rh, and Pd. Synthesis was successful using Proton's standard catalyst synthesis process and powders were successfully manufactured into acceptable MEAs. After 1,500 hours of operation, the oxygen electrodes were analyzed for composition. Percentages of the three metals were very consistent with the predicted formulation (Table 2).

For the near-term catalyst application process, the formulation and process variables optimization was completed, resulting in a 50% reduction in catalyst loading vs. the baseline process. This formulation provides some design margin based on the loading studies performed. This formulation also provided efficiency benefits vs. the baseline MEA, possibly due to reduced resistance across the layer. As part of this effort, a new quality control measurement scheme was developed. One of Proton's standard acceptance testing protocols is an electrical test, which gave non-meaningful data with the new process. Investigating the full impedance data, a more appropriate test point was determined and a production rig utilized to obtain more consistent data.

For the larger reductions in catalyst loading, several iterations were performed on the NSTF electrodes from 3M.

TABLE 2. SEM Analysis, Ternary Metal Oxide Catalyst, 1,500 Hours of Operation

	Metal 1 (at%)	Metal 2 (at%)	Metal 3 (at%)
Theoretical/ Design Point	51	23	26
Operated MEA, Point 1	56.25	20.00	23.75
Operated MEA, Point 2	47.58	21.61	30.86

Initially, the anode continued to show higher voltage than the baseline, apparently due to higher activation energy, while the cathode had been successfully demonstrated to match baseline performance. Polarization curves showed very linear behavior to high current densities, implying a lack of mass transfer limitations. Alternate loadings, catalyst compositions, surface treatments and coating variables were therefore tested over the course of these experiments to improve the anode activity. Based on this series of investigations, an electrode configuration meeting the performance targets was achieved, using less than 10% of the baseline catalyst loading (Figure 2).

Thinner, high mechanical strength membranes were also utilized to manufacture MEAs with the new manufacturing process as well as the NSTF configuration. Both types of electrodes yielded very good performance, with efficiencies above 72% at normal commercial operating current densities.

Finally, an environmental assessment was performed based on the plant design developed for 50,000 kg/day hydrogen. Hydrogen equivalency was calculated to other forms of energy such as gasoline, natural gas, and coal. Scenarios were examined based on transportation, building energy, and CO₂ emissions (Table 3). The analysis showed that for the transportation market, one 50,000 kg/day plant could cut CO₂ emissions by 100,000 metric tons per year, while building emissions could be cut by four times that for the same plant size.

CONCLUSIONS AND FUTURE DIRECTIONS

- Advanced catalyst formulations have demonstrated structural stability over several hundred hours of operation, with qualitative performance trends as predicted by the combinatorial screening.
- Process optimization has validated near term catalyst reductions of 50%.
- NSTF electrodes have demonstrated feasibility to reach less than 10% catalyst loading on multiple membrane types without loss of performance vs. baseline electrodes. Stack efficiencies of 72% or greater have been demonstrated at relevant stack operating current densities.
- An environmental analysis was conducted, demonstrating potential savings of 100,000 metric tons of CO₂ annually per 50,000 kg/day plant. The 50,000 kg/day plant concept is based on a modular design which is being leveraged in Proton's megawatt-scale system development effort.
- In the remainder of the project, scaled-up samples will be tested and the system efficiency measured based on electricity to hydrogen conversion.

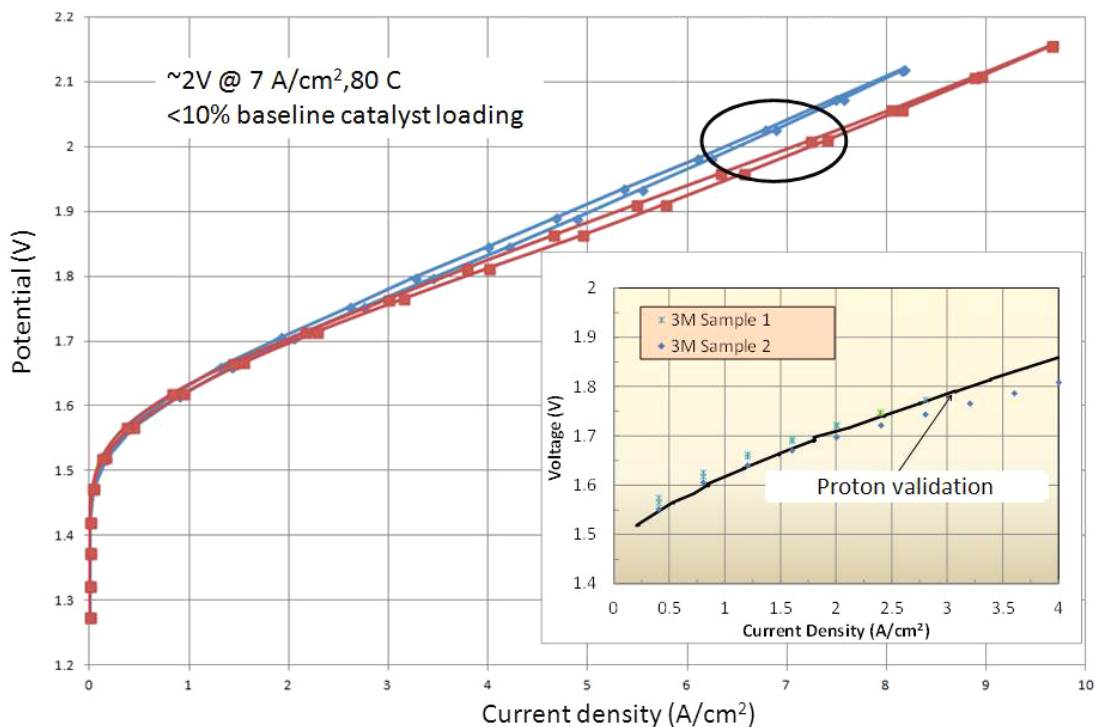


FIGURE 2. Progression of Performance for NSTF Electrodes for OER

TABLE 3. Reduction of CO₂ Emissions, 50,000 kg/day Renewable Hydrogen

	Greenhouse Gas Reductions (kg per 50,000 kg/day H ₂ plant)		
	CO ₂	Methane	Nitrous Oxide
Highway Vehicles	1.09E+08	3.86E+05	3.71E+06
Residential Buildings	4.06E+08		
Commercial Buildings	5.28E+08		

3. “Material Advancements for Cost Effective Hydrogen Energy Storage: Megawatt Electrolysis Development”, Spring ACS Meeting, Esther Takeuchi Award Symposium, New Orleans, April 2013.
4. “Development of Megawatt Scale PEM Electrolysis: A Culmination of Cell Design and System Advancements”, Spring ECS Meeting, Toronto, Canada, May 2013.
5. “Proton Exchange Membranes for H₂ Generation: A Tutorial on Research Needs and Challenges for PEM Electrolysis vs. Fuel Cells”, Spring ECS Meeting, Toronto, Canada, May 2013.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. “Bridging the Infrastructure Gap: Cost Effective Generation of Hydrogen from Water”, Department Seminar, Colorado School of Mines, November 2012.
2. “Combinatorial Search for Improved Metal Oxide Oxygen Evolution Electrocatalysts in Acidic Electrolytes”, Parkinson, B.; Seley, D.; Ayers, K.; ACS Combinatorial Science, Feb. 11 2013, 15(2), pp. 82-89.