II.A.8 Low-Noble-Metal-Content Catalysts/Electrodes for Hydrogen Production by Water Electrolysis

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Subcontractor:
Brookhaven National Laboratory, Brookhaven, NY

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Overall Objectives

- Develop cathode catalyst materials for lower Pt concentration

- Investigate application on gas diffusion electrodes (GDEs) vs. membrane electrode assemblies (MEAs)

- Develop anode catalyst/support composition development and application methods

- Durability testing of ultra-low catalyst loaded electrodes

- Process scale up to demonstrate economic feasibility of the approach

Fiscal Year (FY) 2013 Objectives

- Optimize composition and microstructure of cathode catalysts on carbon-based substrates

- Demonstrate equivalent cathode performance to baseline with ultra-low catalyst loading

- Screen promising candidates for core-shell anode catalysts and non-carbon catalyst supports

- Demonstrate feasibility of reduced anode catalyst loadings

- Estimate the impact of noble metal reduction on the cost of hydrogen from water

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

Technical Targets

Technical targets are presented in Table 1.

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; LHV - lower heating value
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.

Ultra-Low Catalyst Loading

This project is developing methods to reduce the amount of platinum group metals (PGMs) used in the MEA, reducing the sensitivity to market fluctuations in precious metal costs. At today's precious metal prices, these advancements enable the following progress in capital cost of hydrogen:

- $0.04/kg reduction in stack capital cost

- Savings of ~$45,000 per MW

- Enables thinner membranes for lower total cost and higher efficiencies

FY 2013 Accomplishments

- Successfully synthesized and characterized catalysts for use on cathode GDEs

- Successfully fabricated catalyst coated GDEs for operational testing

- Durability target of 500 hours met and cell stack continues to operate

- Successfully synthesized and screened catalysts for oxygen evolution use.

- Surveyed anode support and gas diffusion layer (GDL) materials

- Conducted operational tests, demonstrating feasibility of the anode GDE approach

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INTRODUCTION

Proton OnSite has worked over the past several years to significantly reduce the cost of hydrogen production via proton exchange membrane (PEM) electrolysis. With progress made on the cost of the flow field/bipolar plate assembly, the MEA is currently the most expensive single component of the electrolysis cell. An important portion of MEA cost is related to the prices of PGMs, which are high and may rise with demand due to limited natural resources. Based on current noble metal prices, the catalyst represents half of the MEA cost. Recently, however, efforts have demonstrated that significant reductions in catalyst loading are feasible.

The high percentage of catalyst cost for electrolysis reflects the fact that MEA technology has lagged significantly behind fuel cells, for several reasons. First, the capital cost of electrolysis is already competitive in high purity industrial hydrogen applications for commercial viability, reducing the urgency of immediate change until the energy markets are more mature. Second, there has been resistance to the use of supported catalysts in electrolysis applications, because performance limitations have been noted on the cathode at fuel cell Pt loadings, and carbon supports are not stable on the anode side of the electrolysis cell. Finally, most manufacturing processes for electrolysis electrodes are still highly manual and require high loadings in order to achieve uniform catalyst distribution. This project leverages core shell catalyst structures developed for fuel cells by Brookhaven National Laboratory and application methods for improved utilization to reduce the catalyst loading by an order of magnitude or more.

APPROACH

In this project, catalyst structures developed by Brookhaven National Laboratory for fuel cells were investigated for use in electrolysis. These types of materials have achieved a large amount of attention due to their high mass activity, enabling ultra-low loading of PGMs for fuel cell MEAs. However, the conditions for electrolysis are more aggressive than in the fuel cell, and require modifications of the approach in order to translate technology from one device to the other. The Phase 1 Small Business Technology Transfer scope included advancement of initial feasibility studies on the cathode to define a durable and reproducible electrode configuration with equivalent performance to the production baseline. For the anode, the goal was to show feasibility for similar loading reductions, with more substantial development in Phase 2.

The approach to improving activity and reducing loading on the cathode (hydrogen production) side of the cell involves two steps; 1) increasing the catalyst specific surface area by synthesizing sized-controlled, core-shell nanocatalysts, and 2) achieving better utilization with a more effective GDE structure. Several GDL types and catalyst supports are being evaluated to determine the optimal interface for catalyst deposition while maintaining the required transport properties for electrolysis as well as the optimal formulation of catalyst, support, and ionomer for high utilization. Durability of the new electrode structures will be performed in commercial stack hardware. Scale up of the catalyst manufacturing process will then be performed and cost analysis documenting the savings through the new process will be provided to DOE.

RESULTS

For the cathode, improvements were made in the synthetic process for core shell catalysts, specifically on the PtRu system. Previous methods had produced a Ru-rich core and Pt-rich shell, but there were defects in the structure, causing partial alloying. In the Phase 1 project, atomic-level perfection was achieved in synthesizing core-shell electrocatalysts via green chemistry, using ethanol as the solvent and reductant without capping agents and templates. Figure 1 shows transmission electron microscopy data and schematics illustrating the improvement.

In addition, Brookhaven needed to develop a fast and sensitive technique for screening electrode configurations at the bench level, to conserve materials for larger scale testing to evaluate structures which had already shown promise at the screening level. A GDE hanging strip method was developed, in which the catalyst, support, and gas diffusion electrode material could be tested at a small but representative scale. In addition, this technique did not have the mass transport limitations of typical rotating disk electrode experiments. In general, the results translated well to full cells, except for any effects due to insufficient conductivity between the GDE and the membrane, which were not predicted in the acidic solution test.

Once the catalyst synthesis and catalyst-support systems were defined, samples were sent to Proton for screening at the 25 cm^2 level. Initial testing was performed in a non-proprietary test cell which Proton has used with several partners, in order to establish consistent and accessible benchmarks for electrolysis performance. Proton has developed techniques to test full and half MEAs and GDEs. This test cell is also simpler and faster to assemble than a
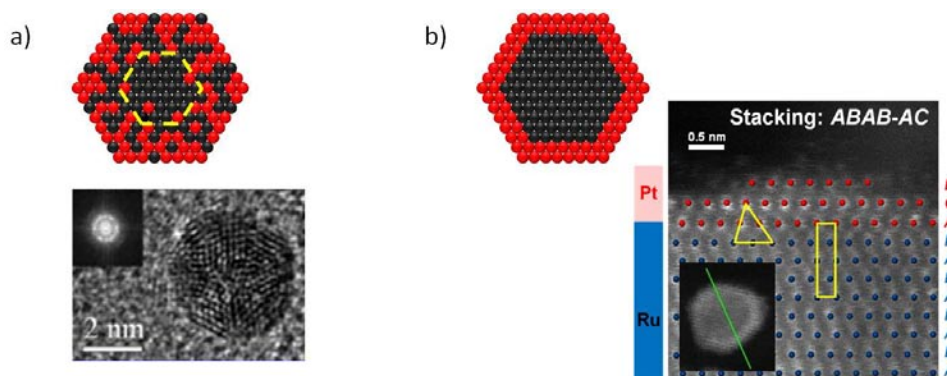
FIGURE 1. Structural Schematics and Transmission Electron Microscopy Data for Core Shell Catalysts: a) Defect-Induced Alloying; b) Atomically Perfect Core Shell
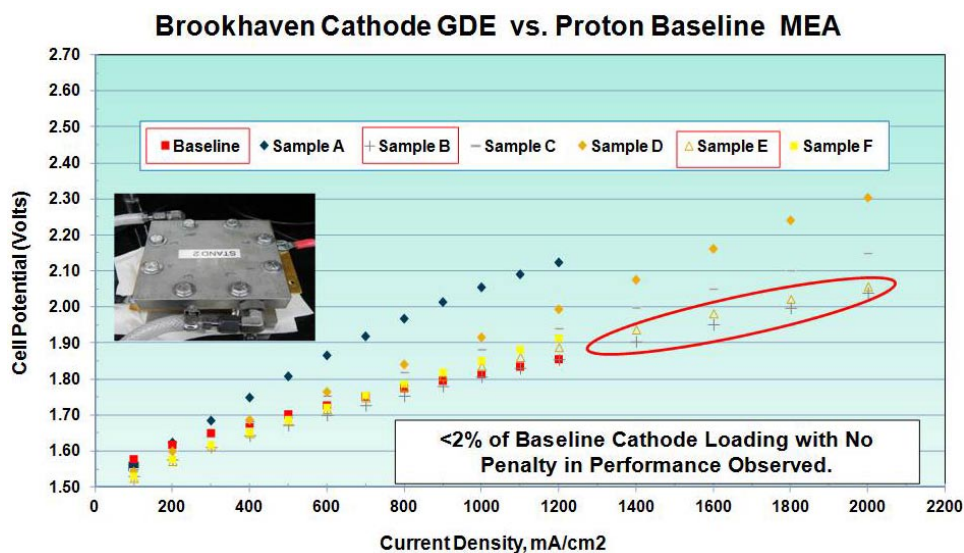

FIGURE 2. Cathode Performance Screening

full-scale commercial cell. While it cannot be operated at pressure and is not designed for long-term testing, it has been shown in other projects to yield very good predictions of performance. Several configurations were tested based on the Brookhaven cathode samples, with representative results shown in Figure 2. A Proton anode was used in all cases. The best performing samples were able to achieve equivalency to the Proton cathode, at 2% of the catalyst loading.

Based on these results, a final set of samples was created in Proton's commercial electrode format for durability testing. A three-cell stack in Proton's commercial GC format was built, using one baseline cell and two cells containing the Brookhaven-fabricated samples. All three cells operated at 2 A/cm^2 for 500 hours without measureable voltage decay, with the Brookhaven cells demonstrating performance within 0.03 V of the baseline cell.

For the anode, the GDE approach is somewhat more challenging, first because carbon-based support materials cannot be used in the formulation, and second because the porosity of the anode is designed for water flow, not gas flow. However, Proton provided GDL samples to Brookhaven for process trials, and GDE samples were successfully fabricated using unsupported core shell catalysts. While there is still room for optimization of catalyst composition and application method, the initial trials demonstrated near equivalent performance to the Proton baseline (Figure 3). These samples utilized 10-15% catalyst loading vs. Proton's internal baseline. The anode will be a focus area of the Phase 2 project.
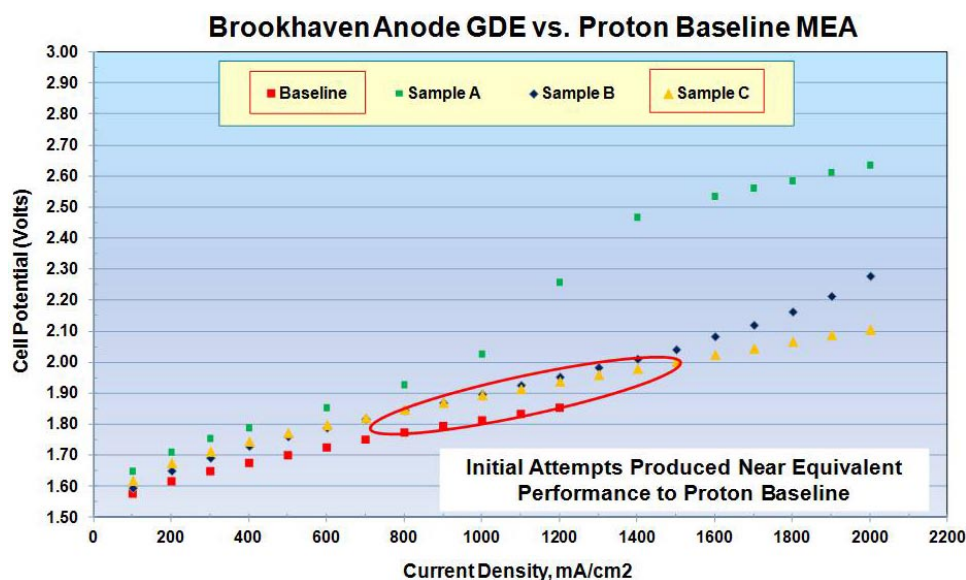
FIGURE 3. Anode Performance Screening

CONCLUSIONS AND FUTURE DIRECTIONS

- In the Phase 1 project, a screening protocol was developed to optimize the knowledge gained while maximizing efficiency and conserving materials. Results translated well from early bench tests to full cell testing.

- Catalyst syntheses were improved both in terms of removing structural defects as well as making the process more manufacturable and reducing environmental impact.

- Cathode samples demonstrated equivalent performance to baseline at 2% loading and anode samples were close to equivalence at approximately 10-15% loading. Cathode samples also passed the 500-hour durability test.

- The Phase 2 project will further develop the anode, leveraging work funded by DOE in non-carbon supports for fuel cells as well as new approaches. Catalyst composition, electrode formulation, and GDL type will be optimized.

- Technology transfer of the cathode formulations and manufacturing process development will continue for the cathode electrode.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Final Report, Phase 1 Small Business Technology Transfer.

2. "Bridging the Infrastructure Gap: Cost Effective Generation of Hydrogen from Water", Department Seminar, Colorado School of Mines, November 2012.

3. "Development of Megawatt Scale PEM Electrolysis: A Culmination of Cell Design and System Advancements", Spring ECS Meeting, Toronto, Canada, May 2013.

4. "Proton Exchange Membranes for H_2 Generation: A Tutorial on Research Needs and Challenges for PEM Electrolysis vs. Fuel Cells", Spring ECS Meeting, Toronto, Canada, May 2013.