II.B.3 Low-Noble-Metal-Content Catalysts/Electrodes for Hydrogen Production by Water Electrolysis

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Overall Objectives

- Translate catalyst synthesis to a manufacturable process at Proton
- Develop a robust technique for manufacturable electrodes
- Demonstrate feasibility for 80% cost reduction in the anode catalyst
- Downselect promising anode electrode configurations to achieve >100 hrs durability
- Achieve 500 hrs of operation in production hardware using cost-reduced electrodes
- Evaluate the cost benefits of new materials

Fiscal Year (FY) 2014 Objectives

- Demonstrate uniform and robust catalyst layer on anode gas diffusion layers (GDLs)
- Complete scale up synthesis of cathode catalysts to 10–100 g batch level
- Complete cell design analysis for cathode configuration
- Downselect optimal cathode material and process for reliable production
- Demonstrate improved activity and durability of selected anode gas diffusion electrode (GDE) samples in cell
- Provide initial cost assessment via H2A model
- Identify key issues for enhancing durability

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

Technical targets are presented in Table 1.

TABLE 1. Technical Targets for Distributed Forecourt Water Electrolysis Hydrogen Production [1]

Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost	$/kg	4.2	3.9	2.3
Electrolyzer System Capital Cost	$/kg $/kW	0.70 430	0.50 300	0.50 300
Stack Energy Efficiency	% (LHV) kWh/kg	74 45	76 44	77 43

LHV – lower heating value

Ultra-Low Catalyst Loading

This project is developing methods to reduce the amount of platinum group metals (PGMs) used in the membrane electrode assembly (MEA). Advancements made in this project will

- Reduce the capital cost of the system by requiring less precious materials while simultaneously reducing sensitivity to market fluctuations in precious metal cost
- Increase stack efficiency and lower total cost by establishing more uniform electrode layers, enabling thinner membranes.

FY 2014 Accomplishments

- Achieved technology transfer of the BNL core-shell synthesis technique with equivalent cathode performance at <1/10 commercial loading
- Showed feasibility for an alternative deposition technique which could result in more automated GDE manufacturing

- Showed >500 hrs durability with ultra-low-loaded Proton-made cathode
- TiOx-supported Ru-Ir catalysts were manufactured and characterized
- Uniform and stable anode GDEs were manufactured at lower loadings, and baseline performance was obtained with IrOx

INTRODUCTION

The economical use of hydrogen as a transportation and stationary power fuel remains a long-term Department of Energy objective. Energy storage applications in Europe such as wind capture and improved biogas conversion efficiency are also driving significant interest in hydrogen production from renewable sources. New and efficient catalytic processes for hydrogen generation are therefore needed to achieve production targets for hydrogen cost. In the Phase 1 project, Proton Energy Systems (d/b/a Proton OnSite), in collaboration with BNL, demonstrated feasibility for development of low-noble-metal-content catalysts/electrodes for proton exchange membrane electrolyzers, through design and synthesis of core-shell nanocatalysts. In Phase 2, continued development of the anode formulation is being performed for reproducible and stable electrode fabrication, while technology transfer and scale up from BNL to Proton is occurring for the cathode electrode fabrication. The Phase 2 project is strategically important because reduction of noble metal content is a significant opportunity for cost reduction to address large-scale opportunities for hydrogen-based energy storage and hydrogen fueling.

APPROACH

The Phase 2 project will continue maturation of the catalyst structures and electrode processing initiated in Phase 1, to develop a manufacturable electrode at relevant scale and ultra-low catalyst loadings. The overall technical approach will include development of the manufacturing process for the cathode electrode as well as cell stack validation for the alternative electrode configuration. For the anode, work will focus on continued optimization of catalyst application and GDL structure for reproducible and durable performance equal to or exceeding the current baseline. Additionally, catalyst composition will be refined for high activity and durability. The impact of these advancements will be quantified using the H2A model.

RESULTS

Core-shell nanoparticles were synthesized at Proton after on-site training at BNL and follow-up training at Proton. As a result, Proton has developed a detailed written protocol to guide the synthesis process. Consultation with BNL provided a number of specifications to judge the quality of the process (Table 2). Additional feedback from BNL was provided in terms of set up and refined in-process measurements, which were applied to trials #4 and #5, resulting in all targets being met.

BNL's current method for manufacturing the cathode GDL involves hand application of the electrode ink to the surface. To replicate the previous results, Proton manufactured a GDE via hand application with nanocatalyst from trial 4 at 1/25th the PGM/cm^2 loading compared to baseline loadings in the MEA and GDE configurations. Polarization curves showed that the ultra-low-loaded cathode cell had equivalent performance to the baselines (Figure 1). It should be noted that the variance seen between the samples is typical of the variance seen in Proton's production-quality MEAs; however, a deeper investigation of slightly higher resistance in the new GDE material is underway. Proton allowed the 3-cell stack with the ultra-low-loaded Proton-made cathode to run for 917 hrs (Figure 2). No noticeable decay in performance was observed, and the voltage trended similarly to the baselines. This indicates that the core-shell structure is stable in the electrolysis environment.

While transfer of the BNL GDE manufacturing method to Proton shows substantial benefit as an implementation pathway (through elimination of over 90% of the catalyst material as well as some labor content), the end goal is to transition to a more automated, higher speed manufacturing

TABLE 2. Proton Synthesis Trials of Nanocatalysts Showing On-Target Specifications *(italics)* and Off-Target Specifications (grey)

Synthesis Trial	Color (green)	Soln. pH (5-7)	Weight (±5% of target)	Pt soln. pH (<1)	Final Weight (within ±5% of target)
1	*green*	10	200%	terminated	terminated
2	*green*	9	-20%	terminated	terminated
3	*green*	8	-20%	terminated	terminated
4	*green*	***5***	***2.0%***	***0.3***	***0.2%***
5	*green*	***5***	***-0.10%***	***0.4***	***3%***

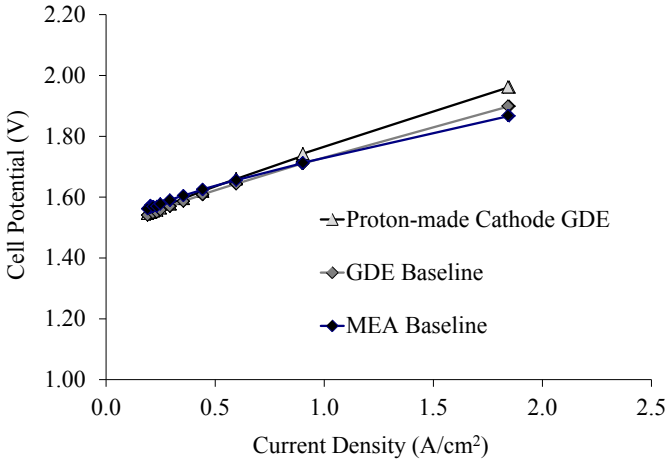

FIGURE 1. Cathode GDEs manufactured at Proton with Proton-made nanocatalyst demonstrated high performance nearly equivalent to baseline at 1/25th the precious metal loading.

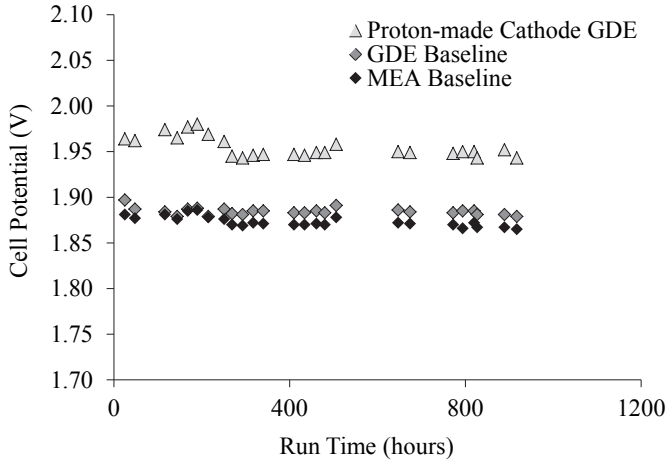

FIGURE 2. Ultra-low-loaded Proton-made cathode shows durability for 917 hrs.

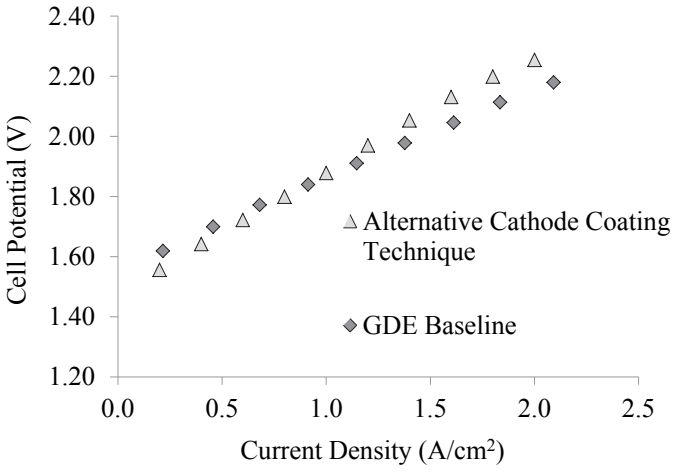

FIGURE 3. Performance of an alternatively manufactured cathode with Proton-made nanocatalyst at 1/100th the precious metal loading.

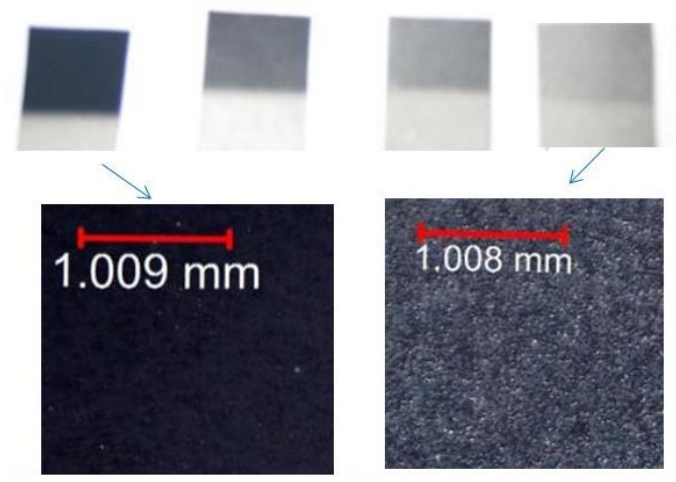

FIGURE 4. Photos and optical images of catalyst-coated anode GDLs with ~1, 1/2, 1/4, and 1/10 of the loading compared to baseline anodes show uniform distribution.

process. Therefore, Proton and BNL engaged suppliers of alternative catalyst coating machines capable of high-throughput automated processing. A sample GDE at 1/100th the PGM loading compared to baseline was manufactured. The coated GDE was operated in Proton's 25-cm^2 bench-scale hardware to assess performance at 50ºC (Figure 3). At 1.8 A/cm^2, the coated GDE was only ~85 mV higher, showing roughly equivalent performance to the baseline and proof-of-concept for the alternative manufacturing technique.

For anode development, BNL synthesized and characterized Ru-Ir core-shell nanocatalysts on TiO_2 supports. X-ray diffraction was used to confirm the nanocatalyst synthesis. Performance was similar to unsupported catalysts, and the results indicated that the interaction with the anode GDL may be important. Initially, BNL reported weak adhesion with the anode catalysts on the GDL when testing in solution, as well as difficulty in obtaining uniform, reproducible samples. BNL has overcome these issues by using a printing method as well as post-processing to make a uniform and stable catalyst coating on the anode GDL. Figure 4 shows photos and optical images of catalyst-coated anode GDLs. In Proton's current process, even distribution of catalyst is difficult without using higher loadings. The electrodes manufactured by BNL show uniformity at 1/10th the loading, representing a significant achievement. Baseline performance was measured in solution via an electrochemical cell using standalone GDE strips.

CONCLUSIONS AND FUTURE DIRECTIONS

- The procedure for synthesis of nanocatalysts and GDEs has been transferred from BNL. Proton has scaled the nanocatalyst synthesis process from 1 g to a relevant production capacity of 10 g and is currently testing the material in cells.
- Proton-made cathodes demonstrated >900 hrs durability in production-quality hardware while achieving the milestone performance of <2.0 V at 1.8 A/cm^2. Proton will also work to identify an optimum cathode and anode GDL materials to increase the efficiency and maintain durability.
- The scale up of the GDE manufacturing process is feasible using a more automated coating technique. Proton will continue to explore this process as a viable manufacturing alternative.
- TiOx-supported nanocatalysts were manufactured and characterized. BNL is developing an anode nanocatalyst with improved durability with two parallel approaches.
- Uniform and stable anode GDEs were manufactured, and baseline performance was obtained. BNL will develop ways to enhance the catalyst-GDL interaction as well as study the impact of the GDLs on the oxygen evolution performance.
- The H2A model and Proton's electrochemical interface model will be used to refine the impact of design changes developed in this Phase 2 project on the $/kg of H_2.

REFERENCES

1. The Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, 2012. http://energy.gov/eere/fuelcells/fuel-cell-technologies-office-multi-year-research-development-and-demonstration-plan