

II.B.3 High Performance Platinum Group Metal Free Membrane Electrode Assemblies through Control of Interfacial Processes

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Contract Number: DE-EE0006958

Subcontractors:

- Pennsylvania State University, College Park, PA
- University of New Mexico, Albuquerque, NM
- Northeastern University, Boston, MA

Project Start Date: May 1, 2015
Project End Date: April 30, 2017

Overall Objectives

- Evaluate non-platinum group metal (PGM) catalysts in gas diffusion electrodes (GDEs) in half cells.
- Evaluate most promising non-PGM GDEs in full-cell anion exchange membrane (AEM) water electrolysis configuration against PGM counter electrode.
- Further the fundamental understanding of non-PGM active sites and reaction mechanisms using synchrotron based in situ spectroscopy.
- Demonstrate translation from solution testing to solid electrolyte interface.
- Conduct assessment of ex situ and in situ stability comparisons to connect ex situ lab evaluation and in situ device results.
- Improve membrane and ionomer durability vs. current commercial options.
- Optimize water management through improved flow field and gas diffusion layer (GDL) design.
- Fabricate full-scale membranes and ionomer solution for electrolyzer testing.
- Identify most promising non-PGM GDEs for full-cell operation and test PGM-free membrane electrode assembly (MEA) for durability (continuous operation at 500 mA/cm² for up to 500 h).

Fiscal Year (FY) 2016 Objectives

- Evaluate most promising non-PGM GDEs in full-cell AEM water electrolysis configuration against PGM counter electrode.
- Further the fundamental understanding of non-PGM active sites and reaction mechanisms using synchrotron based in situ spectroscopy.
- Demonstrate translation from solution testing to solid electrolyte interface.
- Conduct assessment of ex situ and in situ stability comparisons to connect ex situ lab evaluation and in situ device results.

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

This project is working to establish a new cost curve for water electrolysis through elimination of the highest cost materials in the cell stack, such as PGMs and valve metals such as titanium. While electrolysis still has significant needs in manufacturing in order to reach 2020 targets and beyond, the end cost will be largely dependent on raw material costs. In the long-term, non-PGM catalysts for the hydrogen and oxygen evolution reactions (HER and OER) are needed. The current program aims at meeting the following targets:

- PGM content: none
- Cell voltage: <2 V
- Cell current: 500 mA/cm²
- Durability: 500 h of stable operation

FY 2016 Accomplishments

- Synthesized HER and OER catalysts with desired compositions (Ni-metal oxide materials) with similar physical properties (surface area, conductivity) to standard PGM catalysts.
- Achieved HER overvoltage of less than 200 mV at 20 mA/cm².
- Achieved OER performance of <1.55 V vs. RHE at 20 mA/cm².

- Operated an electrolysis cell with non-PGM metals at less than 2V at 500 mA/cm².
- Designed and built a membrane fixture for measuring water transport through membranes and gas diffusion layers with pressure.
- Developed a test system for operation in anode or cathode water feed mode.



INTRODUCTION

Completely carbon-neutral fuel cell vehicles will require a renewable source of hydrogen fuel, such as water electrolysis powered by wind or solar. The DOE cost goals for the production of renewable hydrogen are aggressively set to compete with existing fossil fuel-based infrastructure. Fuel cells and electrolyzers based on proton exchange membranes (PEMs) are well-known and continue to realize reductions in cost and improvements in performance. To meet DOE goals for renewable hydrogen production, and for growing energy markets, reductions in capital and operating costs are needed in order to justify electrolysis as a solution, particularly without incentives for zero carbon emissions.

To date, the only pathway with promise to achieve PGM-free electrode formulations in membrane-based electrolysis cells is utilization of AEMs. The basic local environment of the membrane allows a range of stable transition metals and metal oxides to be utilized at high potential for catalysis. AEMs also enable the use of much less expensive flow field materials other than the titanium often used in PEM systems. At the same time, the solid state electrolyte eliminates the need for corrosive liquid electrolytes such as concentrated potassium hydroxide and allows leveraging of high-performance MEA technology. Proton and team members Northeastern University and Penn State University have been exploring this technology since 2010 through an Advanced Research Projects Agency-Energy project in the Grid-Scale Rampable Intermittent Dispatchable Storage program and have made significant progress in understanding the limitations and potential of this AEM chemistry.

APPROACH

In the first year, project focus will be on catalyst synthesis and activity screening. HER catalysts will be based on Ni–Mo nanoparticles and other mixed oxides, while OER catalysts will focus on ternary catalysts based on Ni, Fe, Co, and Mo. A sacrificial support method (SSM) will be used to synthesize novel catalyst materials in high surface area format. Electrochemical characterization will be used to downselect materials with appropriate physical parameters for in cell testing. In parallel, polymers based on polyphenylene oxide will be synthesized for use in

ionomer solutions and membrane materials to look for higher membrane and ionomer stability than incumbent polymer materials. GDL materials and flow field designs will be optimized for AEM electrolysis performance and incorporated into the cell stack. Materials selection as well as application methods for coatings will be examined for controlling the hydrophobicity and hydrophilicity of the GDL materials.

In Year 2, results from the first year will be leveraged to optimize the GDE interface, including treatments for improved water management. Additional characterization methods will be used to study the structure–activity relationships of the non-PGM catalysts, to understand catalyst–ionomer interactions. The best performing catalysts based on the SSM approach will be scaled up to 10–25 g batches. On the membrane task, cation spacer polymers will be explored based on 5–10 times greater hydroxide stability vs. the side chain benzyl-linked cation materials. System architectures will be determined for optimum performance, and a test system will be built with capability for anode water feed, cathode water feed, or both. A water transport cell will also be fabricated to help understand flow characteristics as a function of membrane type, GDL, and operating conditions. Focus in cell testing will be on longer term durability testing, once initial performance targets have been met.

RESULTS

Initial catalyst synthesis was performed to demonstrate control over the process and composition. Mixed metal oxides were confirmed to have the desired composition and microstructure via scanning electron microscope and X-ray diffraction. In parallel, nickel oxide materials were synthesized via SSM to demonstrate the ability to reach the desired physical parameters such as surface area, conductivity, and onset potential in comparison to typical PGM catalysts for PEM electrodes. Surface areas of 20 m²/g and other metrics met targets as the synthesis was tuned (Table 1). The technique was then successfully translated to the mixed metal oxides. Rotating disk electrodes (RDEs) were then used to characterize catalyst activity. While our experience in the AEM environment is that good RDE results in strongly basic electrolyte do not always translate over to the ionomer-based environment, RDE can still act as a tool for screening out poor catalysts. Several candidates for

TABLE 1. Table of OER Catalyst Parameters for SSM vs. Baseline

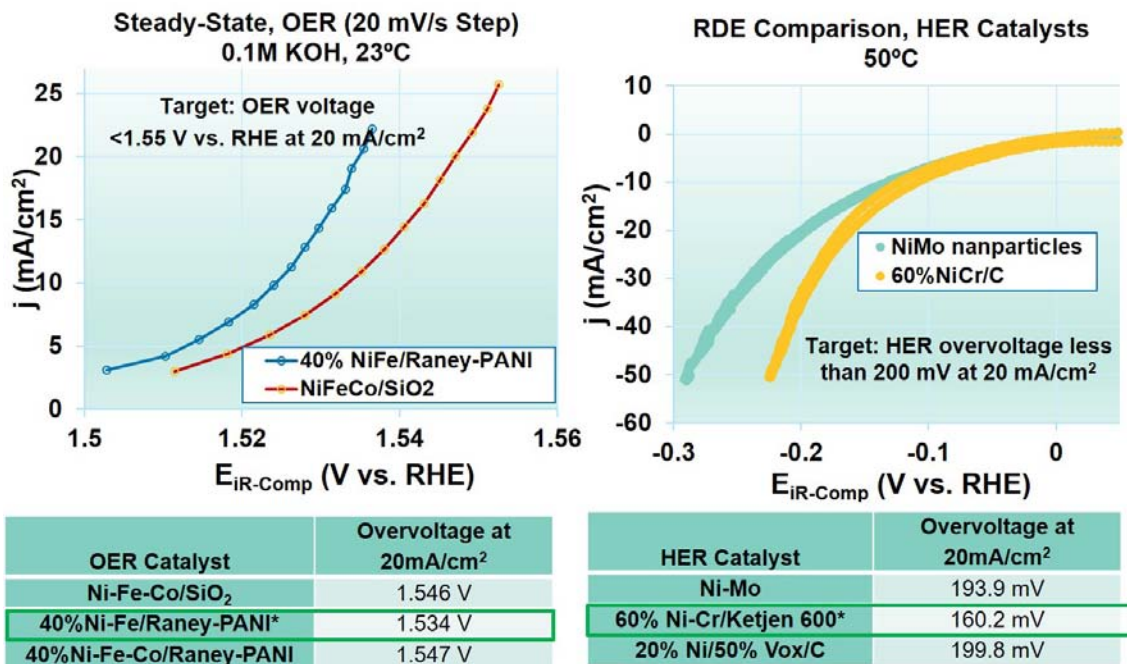
OER Catalyst	Conductivity [S/cm]	Onset Potential [V] vs RHE
NiO	0.00200	1.53
I-22 NiO SSM	0.00308	1.52
I-28 NiCoO ₃ SSM	0.389	1.54
NiMoCu-II	4.47	1.51
IrOx reference	0.0102	1.43

RHE – reversible hydrogen electrode

both OER and HER were tested which met the performance targets (Figure 1).

The best performing catalysts were then integrated into full cells and tested individually against PGM counter electrodes. Once stable short-term performance was achieved that was close to the full cell targets, a fully non-PGM cell

was built and tested. The combined performance met the initial targets (Figure 2). This cell hardware is intended for screening and therefore is not qualified for unattended operation, but the stability of the cell over the first several hours was very encouraging.



PANI – polyaniline

FIGURE 1. RDE data and overpotentials for OER and HER catalysts meeting targets

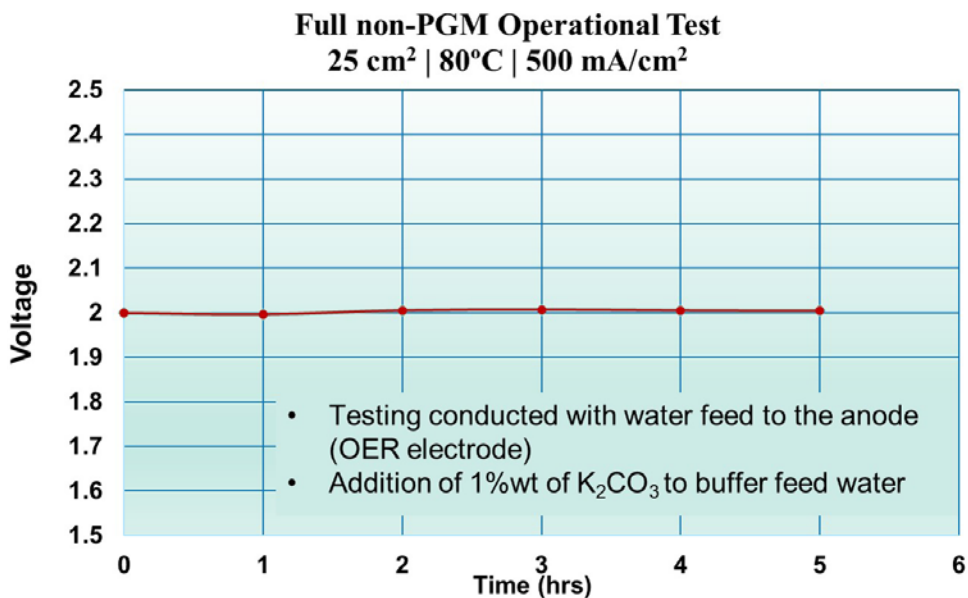


FIGURE 2. Fully non-PGM AEM electrolysis cell performance

In parallel to the catalyst work, membranes were synthesized with spacers between the polymer backbone and the ion exchange sites in order to minimize electron withdrawing effects in the main chain and add hydroxide stability. Ionomers were fabricated into inks and deposited on the membrane samples. Initial electrodes were highly unstable, with poor mechanical integrity. Step by step exposure of the membranes to components of the ink revealed that the membrane surface was melting in contact with the solvents, and was unstable. New samples have incorporated cross-linking to further stabilize the backbone, and improved stability has been achieved over short term tests.

Finally, design and assembly work has been initiated on the dual water feed test stand and water transport fixture. Components for the water transport fixture are being procured, and the test stand has passed initial design reviews and has been assembled. Currently, the system is undergoing final safety checks in preparation for operation (Figure 3).

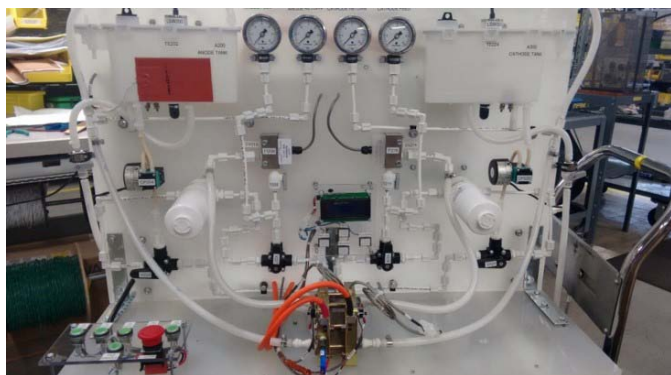


FIGURE 3. Proton test stand for dual water feed operation

CONCLUSIONS AND FUTURE DIRECTIONS

The Year 1 quarterly milestone was achieved, as demonstrated in discrete operation of the HER and OER electrodes in a liquid cell and in a full solid polymer membrane operational test. The full operational test not only represents the first full non-PGM MEA operated in AEM water electrolysis, but also demonstrated performance that was stable enough to operate for several hours at the overall program current density targets of 500 mA/cm^2 . Next steps include further optimization with the high surface area catalyst synthesis methods, and work on longer durability membranes, as well as testing in dual operational modes (anode or cathode water feed).

FY 2016 PUBLICATIONS/PRESENTATIONS

Presentations:

1. Fuel Cell Seminar, November 2015, "R&D Advances in AEM Electrolysis."
2. Power Sources Conference (Poster), June 2016, "Research Advances in Anion Exchange Membrane Electrolysis to Enable Low-Cost Hydrogen Energy Storage."