
High-Efficiency Reversible Alkaline Membrane Fuel Cells

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Subcontractors:

- University of Delaware, Newark, DE
- State University of New York at Buffalo (SUNY-Buffalo), Buffalo, NY
- National Renewable Energy Laboratory (NREL), Golden, CO

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Project End Date: December 31, 2020

Overall Objectives

- Explore alkaline membranes and ionomers that are stable under reversible alkaline membrane fuel cell (AMFC) operations.
- Synthesize bifunctional catalysts via enhanced active sites, surface area, and pore structure.
- Develop a membrane electrode assembly (MEA) fabrication process for bifunctional catalysts. This process will minimize transport loss thus maximizing the performance at high current density.
- Construct reversible AMFCs with the selected bifunctional catalysts and other components to evaluate their performance in fuel cell and electrolyzer operating mode.

Fiscal Year (FY) 2019 Objectives

- Develop novel oxidation-resistant alkaline exchange membrane (AEM) materials.

- Synthesize low-platinum group metal (PGM) and PGM-free bifunctional oxygen and hydrogen catalysts.
- Fabricate MEAs using novel AEM materials.
- Construct a test station for unitized reversible AEM fuel cell testing.
- Evaluate reversible AEM fuel cells for stability, performance, and round-trip efficiency (RTE).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Durability (catalysts, electrode layers)
- Cost (catalyst, MEAs)
- Performance (catalysts, electrodes, MEAs).

Technical Targets

This project aims to develop reversible AMFCs using novel membrane and catalyst materials. The individual components and/or the product fuel cells will achieve the following key targets at the end of the project:

- Demonstrate 30–50 μm self-supporting membranes with conductivity >100 mS/cm and tensile strength >50 MPa.
- Prepare 15 g of Co_3O_4 or NiCoO_4 bifunctional oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) catalyst
- Prepare 5 g of chevrel-phase NiMo_3S_4 hydrogen evolution reaction (HER) catalyst
- Achieve a reversible AMFC RTE of 50% at $1,000$ mA/cm² without the addition of salts or bases in the aqueous feed.

FY 2019 Accomplishments

- Produced more than 400 cm² of novel AEM material that shows an oxidation resistance 24x greater than commercial ionomers and

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- meets technical targets for conductivity and tensile strength.
- Developed metal oxide/nanocarbon bifunctional oxygen reduction/evolution catalysts
- Developed PGM-free bifunctional hydrogen evolution/oxidation catalysts.
- Achieved electrolyzer performance of 1.9 V at 2 A/cm² using pure water.
- Demonstrated a unitized reversible AMFC that achieved an RTE of 40% at 200 mA/cm².

INTRODUCTION

Reversible fuel cells have advantages over rechargeable batteries (Ni/MH or Li-ion) due to their high energy density, minimal self-discharge, and low cost. Reversible AMFCs are attractive due to their ability to work with PGM-free catalysts. The major factors that limit the application of reversible AMFCs are low performance of bifunctional oxygen catalysts, alkaline membrane stability, and water management, which lead to high cost and low RTE.

In previous Fuel Cell Technologies Office-funded research programs, Giner and collaborators developed a variety of high-performance metal oxide/nanocarbon bifunctional OER and ORR catalysts that have demonstrated remarkable reversibility and stability under harsh voltage cycling from 0.0 V to 1.9 V, providing a solid foundation for enabling reversible AMFCs. In this project, we are leveraging knowledge obtained from these previous programs to address the predominant alkaline membrane and ionomer challenges, thus realizing highly-efficient reversible AMFC operations.

APPROACH

This program builds upon knowledge obtained from previous research programs to develop highly-efficient reversible AMFCs. To achieve this goal, first we are pursuing an effective alkaline ionomer that will enable unitized reversible cells. Specifically, oxidation-resistant membranes are being utilized to make reversible MEAs without the addition of salts or base to the feed water. A family of poly(aryl piperidinium) (PAP) hydroxide exchange membranes has been developed by collaborators at the University of Delaware; in this program, a next generation of these radical-quenching polymers is being developed. These polymers are being integrated with novel bifunctional OER/ORR and HER/HOR catalysts developed by collaborators at SUNY-Buffalo and NREL to fabricate membrane electrode assemblies (MEAs). An MEA fabrication procedure is being developed, and interactions between the bifunctional catalysts and alkaline ionomer are being studied to improve water management to address flooding at high current density. Initial work in FY 2019 focused on single-cell electrolyzers and fuel cells, and in FY 2020 a reversible AMFC stack will be constructed to demonstrate high RTE.

RESULTS

At the University of Delaware, the unsupported PAP-TP-85 AEM (shown in Figure 1a) has been shown to possess excellent oxidative stability, hydroxide conductivity, and tensile strength. The oxidative stability was investigated using potassium superoxide in DMSO/S₂O solution and measuring chemical degradation via nuclear magnetic resonance (NMR) characterization. Time-series ¹H NMR spectra were collected for the University of Delaware PAP-TP-85 material; no degradation was shown after 120 minutes, whereas the commercially available Tokuyama AS-4 ionomer showed degradation after only 5 minutes. This 24x increase in oxidative stability is very significant. The conductivity at 80°C was measured as 167 mS/cm (Figure 1b), which exceeds our technical target by 60%. Finally, a stress-strain curve (Figure 1c) shows a tensile strength of 62 MPa and a 115% elongation at break, both meeting our targets.

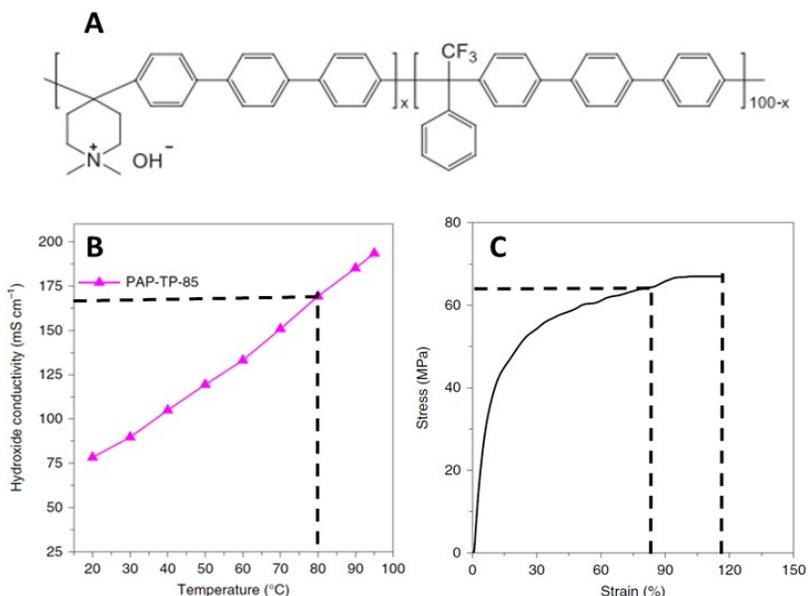


Figure 1. PAP-TP-85 membrane: (a) general structure of the PAP-TP-x polymer; (b) hydroxide conductivity measured vs. temperature; and (c) stress-strain characterization showing tensile strength and elongation at yield

Meanwhile, novel OER/ORR catalysts have been developed at SUNY-Buffalo building off previous collaborations between Giner and SUNY-Buffalo as discussed above. To improve upon the metal-oxide/nanocarbon catalysts already developed, the introduction of high-surface zeolitic imidazolate framework (ZIF)-67-derived carbon was investigated to increase the available surface area and therefore enhance activity. This process, shown in Figure 2a, led to substantial improvements in both ORR and OER activity compared to metal oxide baselines (Figure 2b). When a physical mixture of the individual Co-ZIF-8 and metal oxide catalysts was studied, no activity enhancement was observed, proving that the chemical interaction at the nanoscale as detailed in Figure 2a is crucial for activity improvement.

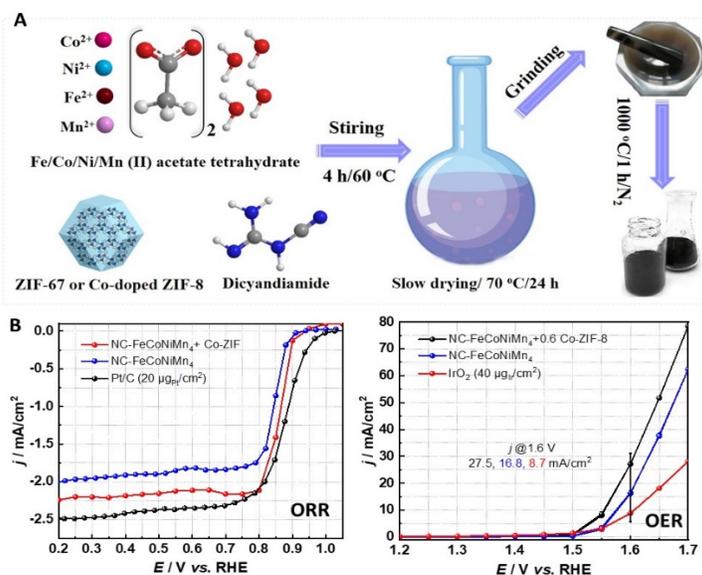


Figure 2. ORR/OER catalyst work at SUNY-Buffalo: (a) schematic showing the synthesis of graphene tube catalysts compositing with high-surface ZIF-67-derived carbon; and (b) ORR and OER activity on a rotating disk electrode for the composite catalysts compared with PGM baselines (900 RPM, 1.0 M NaOH, 25 °C)

Separately at NREL, low-PGM as well as PGM-free catalysts for bifunctional HER/HOR have been studied. Pt-Ni catalysts were prepared in a three-step process (platinum deposition and hydrogen annealing with a final acid leaching step) and are a viable option for improving performance at a lower platinum content.

Additionally, three approaches have been investigated for synthesis of seven different PGM-free hydrogen catalysts. In the first approach, ZnCo-ZIF was prepared using zinc nitrate, cobalt nitrate, and 2-methyl imidazole in methanol. In the second approach, NiMoS₄ and NiCoMoS₄ were made by Kanatzidis' method using ammonium thiomolybdate, nickel nitrate, and cobalt nitrate salts in water. Catalysts were treated under H₂/Ar mixture to obtain annealed catalysts. NiCrMo/C was also prepared in a similar method by dissolving the metal nitrate or chloride salts in water and reducing the metals using sodium borohydride (NaBH₄). The solid product was obtained by filtration and was tested as is (denoted as NiMoCr-C nHT).

The third approach involved a hydrothermal/solvothermal method. NiMo₃S₄ was prepared using freshly synthesized Ni(OH)₂, hydrazine, and ammonium thiomolybdate in DMF at 200°C. A Teflon-lined autoclave chamber was used as reaction chamber. Finally, MoS₂/GO was made using two synthesis routes. MoS₂-GO was made by using sodium molybdate, L-cysteine, and graphene oxide in water in a Teflon autoclave at 180°C. Another type of MoS₂-GO (denoted as MoS₂-GO-hyd) was prepared using hydrazine, DMF, and ammonium thiomolybdate. All catalysts were tested for hydrogen evolution performance on the rotating disk electrode (see Figure 3) with the ZnCo-ZIF catalyst showing the most promising performance.

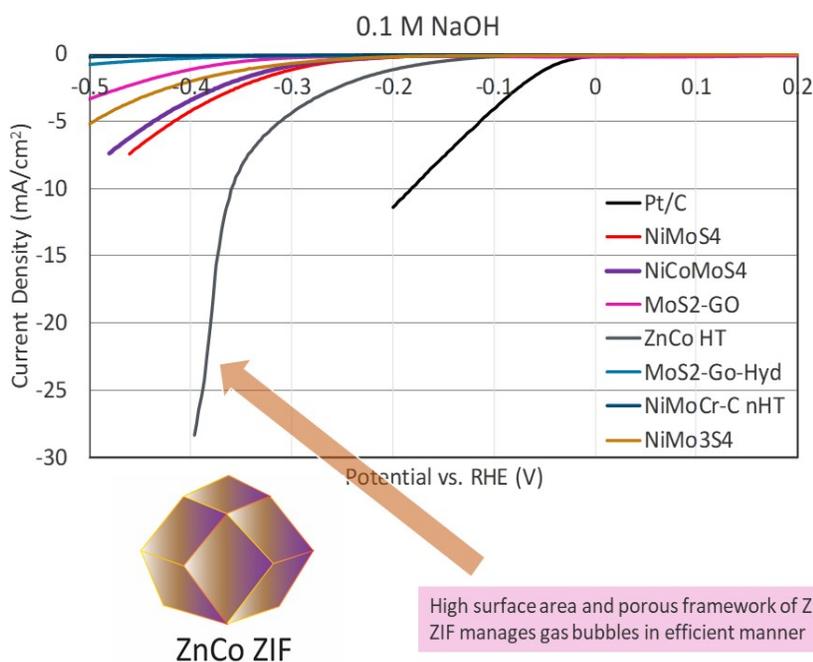


Figure 3. RDE activities of hydrogen evolution reaction catalysts (1,200 RPM, 0.1 M NaOH)

Finally, at Giner, an electrode fabrication procedure was developed for the University of Delaware AEM materials, and numerous MEAs were constructed and evaluated for electrolyzer performance. Using only pure deionized water as the feedstock, substantial performance improvements were achieved compared to previous work with commercial AEM materials (Figure 4a). Different anode (oxygen) catalysts were investigated, and further enhancements were seen by switching to RuO₂ in place of IrO₂ (Figure 4b). A potential of 1.9 V at 2 A/cm² was observed at 80°C with pure deionized water; this performance approaches that of traditional proton exchange membrane electrolyzers and presents a significant achievement for the alkaline membrane electrolysis community. A custom reversible fuel cell test station was designed and built at Giner, and initial reversible fuel cell performance was evaluated (Figure 4c). With IrO₂ as the oxygen catalyst and PtRu/C as the hydrogen catalyst, 46% RTE was achieved at 100 mA/cm² at 80°C with no added salt or hydroxide in the water stream (data not shown). An RTE of 38% was achieved at 200 mA/cm². Although there is much room

for improvement in the fuel cell performance, these initial results are very promising and indicate that we are well on our way toward achieving our technical targets.

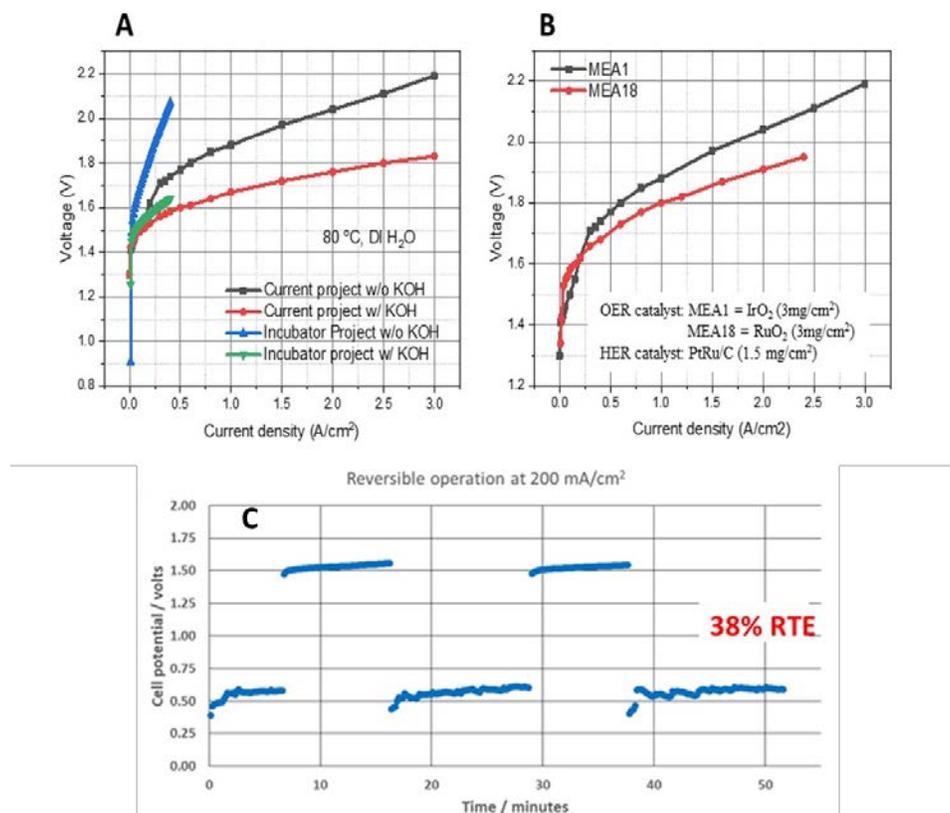


Figure 4. Performance of AEM electrolyzers and reversible AMFCs: (a) significant performance improvement of electrolyzer cells using University of Delaware AEM materials compared to commercial AEMs used in Giner's previous incubator project; (b) further performance improvement using lower-cost RuO₂ catalyst; and (c) reversible AMFC operation at 200 mA/cm².

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions

- A novel AEM material has been produced at the University of Delaware that shows significantly improved oxidation resistance compared to commercial ionomers.
- Unique metal oxide/nanocarbon composite bifunctional oxygen catalysts have been developed at SUNY-Buffalo by chemically integrating metallic organic frameworks; rotating disk electrode studies show substantial improvement over the baseline metal oxide catalysts.
- Seven PGM-free bifunctional hydrogen catalysts were synthesized and tested at NREL using three distinct synthetic routes; the ZnCo-ZIF catalyst in particular shows promising HER performance.
- A record-high electrolyzer MEA performance has been achieved at Giner using pure deionized water (without diluted KOH solution) and lower-cost RuO₂ catalyst on the anode.
- Initial unitized reversible AMFC studies at Giner achieved an RTE of 38% at 200 mA/cm².

Future Work

- Continue to improve individual MEA components (ionomer and catalysts) at the University of Delaware, SUNY-Buffalo, and NREL.

- Continue to improve the MEA fabrication process at Giner; investigate gas diffusion electrodes as a less labor-intensive route toward robust MEAs.
- Focus on reversible fuel cell performance and RTE at Giner.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. H. Xu, “Analyzing and Improving Performance of Anion Exchange Membrane Water Electrolysis,” presented in the 236th ECS meeting, Atlanta, GA, October 2019.
2. H. Xu, “Pathways Toward High-Performance Reversible Alkaline Membrane Fuel Cells,” presented in the 235th ECS meeting, Dallas, TX, May 2019.