
Lab Call FY18 (Reversible Fuel Cell): Bipolar Membrane Development to Enable Regenerative Fuel Cells

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Project Start Date: January 1, 2018
Project End Date: March 31, 2020

Overall Objectives

- Develop bipolar membranes (BPMs) utilizing a dual-fiber electrospun junction/interface for use in advanced and innovative reversible fuel cell concepts.
- Demonstrate the ability to fabricate and optimize BPMs made with perfluorosulfonic acid and National Renewable Energy Laboratory (NREL)-synthesized polymers used in anionic exchange membranes.
- Incorporate advanced BPMs in a membrane electrode assembly and evaluate their performance in both fuel cell and electrolysis mode in a unitized reversible fuel cell.

Fiscal Year (FY) 2019 Objectives

- Demonstrate area specific resistance $\leq 0.2 \Omega \text{ cm}^2$ for a BPM in fuel cell tests.
- Develop hardware that allows operation of a membrane electrode assembly in both fuel cell and electrolyzer modes without having to remove the membrane electrode assembly.
- Establish the capability to achieve $>500 \text{ mA/cm}^2$ in both fuel cell and electrolysis mode using a BPM reversible fuel cell approach.

Technical Barriers

While there are no codified technical barriers specific to reversible fuel cells, this project directly

addresses the Fuel Cell Technologies Office's interest in developing reversible fuel cells. The following excerpts are from the Fuel Cells section (*Technical Challenges*) of the Fuel Cell Technologies Office's Multi-Year Research, Development, and Demonstration Plan¹:

- *Reversible Fuel Cells*: Reversible fuel cells are of interest for energy storage applications and hold promise as an enabler for the implementation of intermittent renewable energy technologies. This technology allows for the storage of excess energy in the form of hydrogen during periods of low electricity demand that can then be used during times of peak demand. Reversible fuel cells are capable of operating in both power production (fuel cell) and energy storage (electrolysis) modes. **Advantages of reversible fuel cell technology include high round-trip efficiency (60–90%), decoupled power and energy capacity, long cycle life, low self-discharge rate, and reliable and stable performance. A key challenge to reversible fuel cells is maintaining electrode function and performance during repeated cycles between fuel cell and electrolysis modes.**
- “Cost and durability are barriers to the implementation of both reversible fuel cells and flow cells, but leveraging fuel cell R&D in the areas of membranes, electrocatalysts, electrode architectures, bipolar plates, and diffusion media for this technology would result in cost reduction and durability improvements.”

Technical Targets

This project is conducting studies of dual-fiber electrospun BPMs to improve their performance and durability when operated in reversible fuel cells. While there are no defined technical targets in the Multi-Year Research, Development, and Demonstration Plan, this project worked toward the following performance targets:

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

- Current density: 500 mA/cm² in both fuel cell and electrolyzer operation
- Durability: 8 hours of stable operation at 500 mA/cm²
- Area specific resistance: 200 mΩ cm².

FY 2019 Accomplishments

- Made BPMs entirely from electrospun fibers composed of 12 hours of anion exchange

ionomer spinning, 2 hours of co-electrospinning with both ionomer precursors, and another 12 hours of cation exchange ionomer spinning.

- Lowered the resistance of the interfacial layer by incorporating graphene oxide in the electrospinning ionomer precursors.
- Achieved 500 mA/cm² in both fuel cell and electrolyzer operation.

INTRODUCTION

Bipolar membranes have demonstrated potential in both discrete fuel cell and electrolyzer devices, but with significant limitations. In fuel cell mode with a 2-D junction between cationic and anionic membranes in a BPM membrane electrode assembly, peak power density is limited to only a few hundred mW/cm². Modeling suggests that a game-changing improvement to BPMs for fuel cell use would be implementation of an electrospun junction, where the interfacial surface area for reaction is significantly increased due to an interpenetrating polymer matrix creating a 3-D surface. No one has implemented a 3-D BPM in a membrane electrode assembly, which we expect to yield a significant performance gain. However, in electrolyzer development, others have demonstrated a BPM with a 3-D interpenetrating dual-fiber electrospun junction in a liquid electrolyte-filled H-cell where the onset of water splitting in Na₂SO₄ solution occurred 0.3 V earlier than with a commercial Fumasep membrane. Additionally, the electrospun-junction BPM outperformed the commercial membrane in cycling and durability tests. The interpenetrating network of anion exchange and proton exchange polymers was shown to yield a more robust interface during polarization reversal, a key enabling component of a reversible fuel cell, as well as prevent unwanted dry out over many cycles during high-current operation where water is dissociated at the BPM interface. This result, however, has not been demonstrated in an electrolysis membrane electrode assembly devoid of free ions. We hypothesize the advanced BPM structures developed in this project can overcome the limitations of previously tested BPMs for use in both fuel cell and electrolysis mode.

APPROACH

We will employ state-of-the-art cationic and anionic polymers to synthesize an electrospun BPM junction via dual-fiber electrospinning, where the two polymers are interwoven on the nanoscale. This principle has been demonstrated for several membrane applications, including BPM development, and can be leveraged to make the novel BPM membrane electrode assemblies.

The ultimate goal of this project is the fabrication of a BPM with a dual-fiber electrospun junction that can be employed in a stable, high-performance reversible fuel cell membrane electrode assembly. The crux of this effort will be the optimization of the BPM junction interface. Materials for the cation exchange ionomer consist of commercial Nafion perfluorosulfonic acid materials, while anion exchange ionomers will be fabricated from NREL-synthesized polymers, including perfluorinated and hydrocarbon ionomer formulations.

Membrane characteristics such as composition, fiber diameter, and the incorporation of catalysts/particulates at the interface/junction will be tested first in either individual fuel cell or electrolyzer devices. Operation of these novel membranes in membrane electrode assemblies will be demonstrated and optimized with typical electrodes for each device, which will isolate the unique advantages and challenges of the electrospun BPM morphology. It is likely that the final reversible fuel cell membrane electrode assembly will require catalyst and electrode architectures that differ significantly from those used in single-application devices. A BPM with an electrospun junction has never been integrated into a fuel cell or water electrolysis membrane electrode assembly, much less a unitized reversible fuel cell.

RESULTS

We fabricated several BPMs with varying recipes by tuning the ionomer used and altering the catalyst loading at the interface. We also varied the configuration, making catalyzed 3-D electrospun BPMs and catalyzed 2-D BPMs to compare with the performance of the commercially available Fumasep FBM. The performance of our optimized 2-D and 3-D bipolar membranes is clearly better than that of Fumasep FBM when tested under electrolysis conditions in a membrane electrode assembly (Figure 1). The advantage of having a 3-D interface can also be seen in Figure 1 where the greater area of catalyzed interfacial layer leads to lower cell voltages at the same current densities. We also observed better stability in the 3-D BPMs as determined by voltage differences between multiple scans between open circuit and high current conditions.

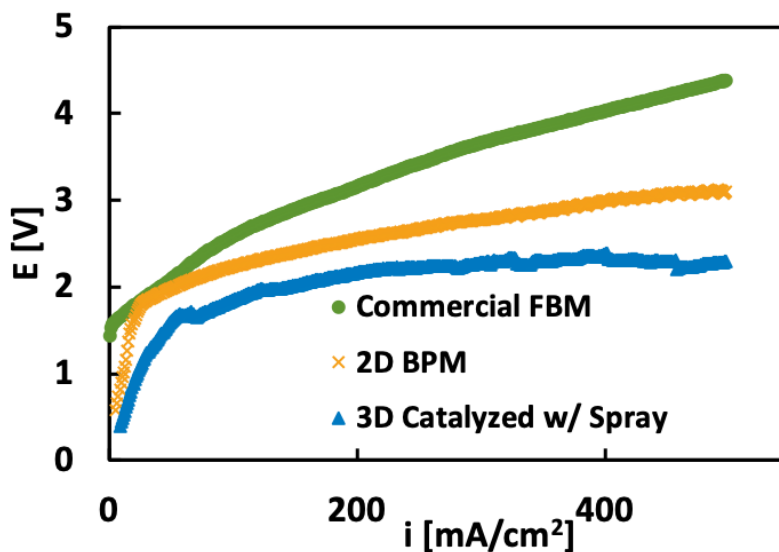


Figure 1. Performance of catalyzed 2-D BPM, catalyzed 3-D BPM, and the commercially available Fumasep FBM when tested in a membrane electrode assembly in electrolysis mode. The catalyzed 2-D BPM had better performance than the Fumasep FBM and the catalyzed 3-D BPM had better performance than both, highlighting the advantages of a 3-D interface

We encountered challenges performing in situ ion exchange of the anion exchange ionomer. The anionic ionomer has to be electrospun in the iodide form and must be exchanged to the hydroxide form for operation. Once in the hydroxide form, it is too mechanically unstable to be manipulated or electrospun. Running the 3-D BPMs in electrolysis mode allows the exchange to occur naturally from the hydroxide ions dissociated at the interfacial layer. However, when a BPM with the anion exchange ionomer in the iodide form is run in a fuel cell, the mobile ions accumulate at the interfacial layer and prevent the hydroxide ions from entering and fully exchanging the anionic ionomer, which leads to poor performance. One way around this is to ion exchange a 2-D film of the anion exchange ionomer and make a 2-D interface by applying catalyst to the interface, which allows testing in fuel cell mode. The configurations of BPMs that we tested in fuel cell and electrolysis mode appear in Figure 2. Graphene oxide is used for electrolysis mode testing because it is a better water dissociation catalyst. Carbon is used for fuel cell mode testing because it is better as a water recombination catalyst.

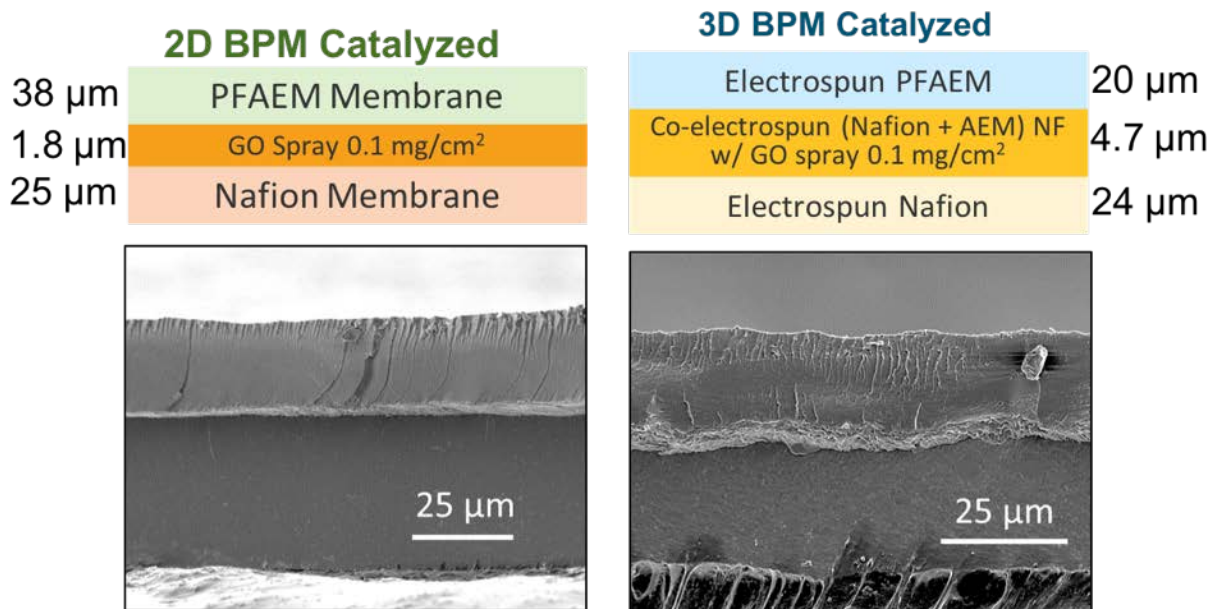


Figure 2. Configurations and scanning electron microscopy images of BPMs tested. The 2-D membrane tested in fuel cell mode has the same nominal thicknesses as above but has carbon catalyst at the interface. PFAEM – perfluoro anion exchange membrane; GO – graphene oxide; NF – nanofiber

We performed experiments and analyses to break down the ensemble BPM resistance into its discrete components and understand the resistance contributions due to the cation exchange membrane, anion exchange membrane, and interfacial junction. We performed these measurements for 2-D and 3-D BPMs (configurations in Figure 2) in electrolysis mode and 2-D BPMs in fuel cell mode. The Nafion (cation exchange ionomer) and anion exchange ionomer resistances were calculated from the known conductivity values [Nafion (H⁺): 70 mS/cm, perfluorinated anion exchange ionomer (OH⁻): 55 mS/cm] and thickness measurements. The anion exchange membrane resistance was calculated to be 69 mΩ cm² (2-D) and 55 mΩ cm² (3-D), while the cation exchange membrane resistance was 36 mΩ cm² (2-D) and 34 mΩ cm² (3-D). In electrolysis mode, the resistance of the interfacial junction with graphene oxide was found directly from impedance measurements. In fuel cell mode, the resistance of the interfacial junction with carbon was calculated by subtracting the resistance attributed to Nafion, the anion exchange membrane, and other electronic losses from the high-frequency resistance measured in fuel cell testing. The junction resistances found at various current densities appear in Figure 3 and show that we have not achieved our target interfacial resistance of 200 mΩ cm².

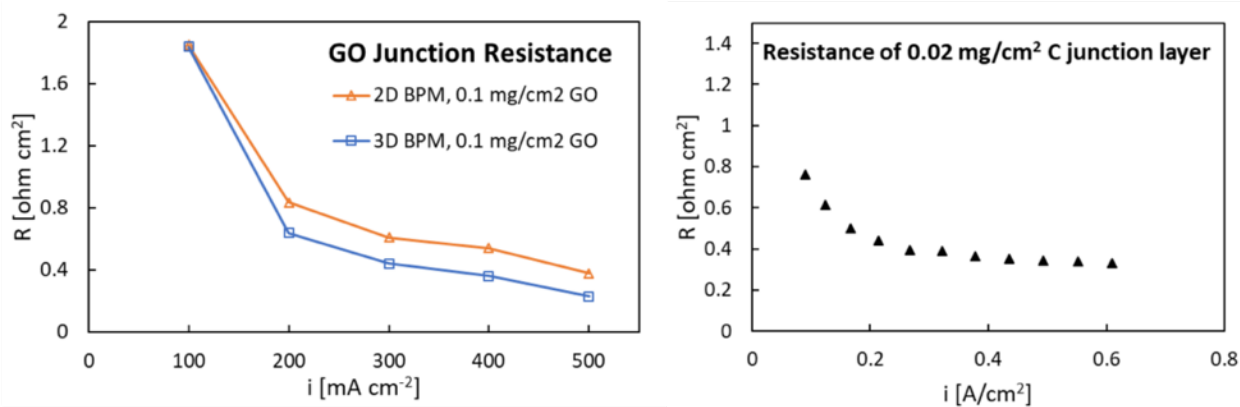


Figure 3. Junction resistance from electrolysis mode (left) and fuel cell mode (right)

CONCLUSIONS AND UPCOMING ACTIVITIES

Because the optimal catalyst composition and loading is different for fuel cell and electrolyzer mode, there might be an inherent limitation to reducing the interfacial resistance to $200 \text{ m}\Omega \text{ cm}^2$ or lower. We plan to evaluate durability of BPMs in fuel cell and electrolysis mode and push to achieve current densities up to 1 A/cm^2 in the final six months of this project.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Yingying Chen, “Bipolar Membrane Development for Fuel Cell and Electrolysis,” Talk presented at 235th Electrochemical Society (ECS) Meeting, Dallas, TX, May 30, 2019.