Bipolar Membrane Development to Enable Regenerative Fuel Cells

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National Renewable Energy Laboratory
May 1, 2019

DOE Hydrogen and Fuel Cells Program
2019 Annual Merit Review and Peer Evaluation Meeting

fc182

Overview

Timeline and Budget

- Project start date: 01/01/18
- Project end date: 01/01/20
- Total project budget: $400k
  - Total DOE funds spent*: $200k

* As of 3/31/19

Barriers

- A – Cost
- B – Durability
- C – Performance

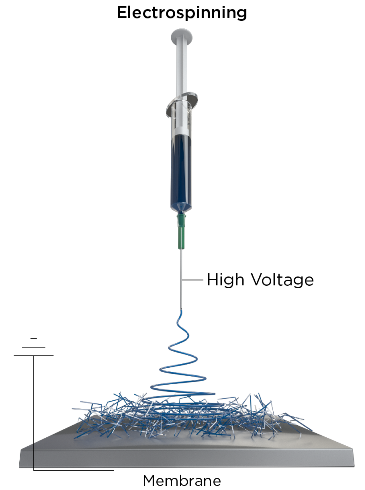
Partners

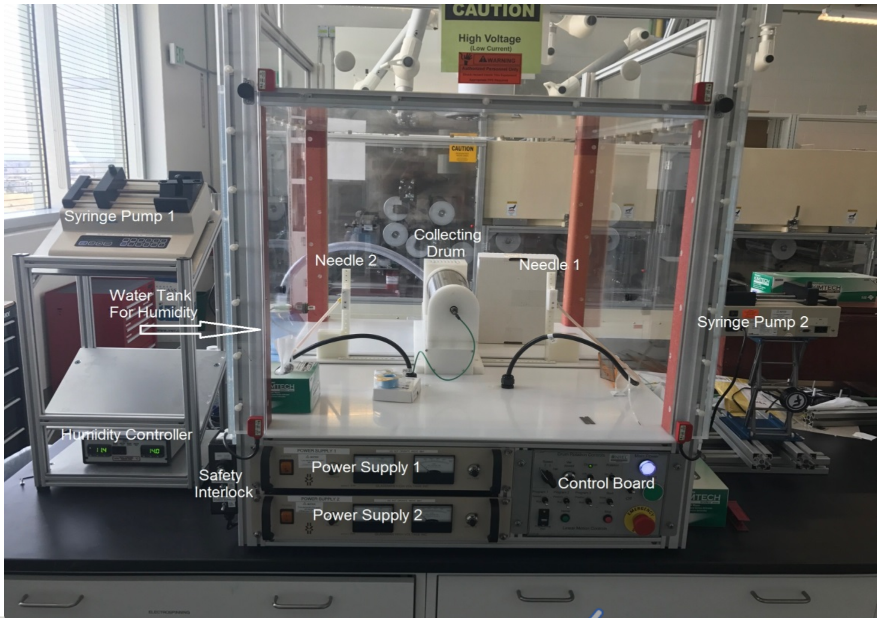
- Anion ionomer development program at NREL
- MEA fabrication group at NREL
- Fuel cell and electrolysis testing groups at NREL
- Colorado School of Mines – materials characterization

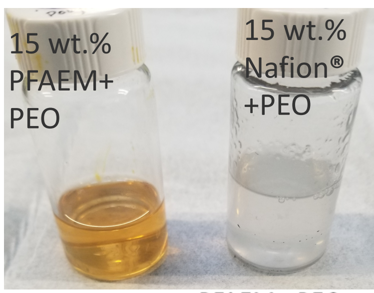
Relevance

- This project directly addresses DOE FCTO's interest in developing Reversible Fuel Cells (RFCs) – From MYRD&D, "**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.**"
- Objectives
  - Fabrication of a bipolar membrane (BPM) with a dual-fiber electrospun junction that can be employed in a stable, high-performance RFC membrane electrode assembly (MEA).
  - Our initial focus will be on fabricating and optimizing the BPM junction with available materials (leveraging NRELs ongoing anion exchange membrane (AEM) development), and obtaining a BPM device data in both fuel cell and electrolysis mode individually.
  - While electrode architecture/composition may have to be modified as the project progresses, the crux of this effort will be the optimization of the BPM junction interface.
  - The key technical aspects of the project are focused on fabricating/optimizing electrospun 3D junction for implementation into MEAs for fuel cell, electrolyzer, and RFC devices. Membrane characteristics such as composition, fiber diameter, and the incorporation of catalysts/particulates at the interfacial/junction will be tested first in either individual fuel cell or electrolyzer devices.
  - A BPM with an electrospun junction has never been integrated into a fuel cell or water electrolysis MEA, much less a unitized RFC. These studies represent a completely new field with significant promise to ameliorate some of the key challenges in RFC development, as well as provide significant gains to the BPM understanding.

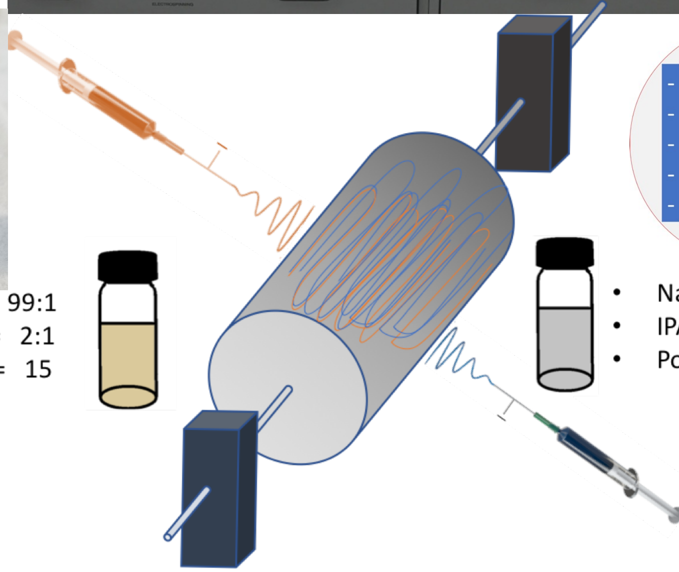
Approach

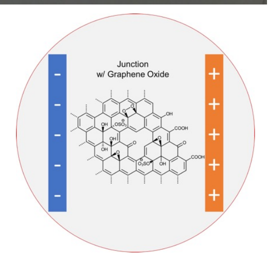






- PFAEM : PEO = 99:1
- IPA : DI water = 2:1
- Polymer wt.% = 15





- Nafion : PEO = 99:1
- IPA : DI water = 2:1
- Polymer wt.% = 15

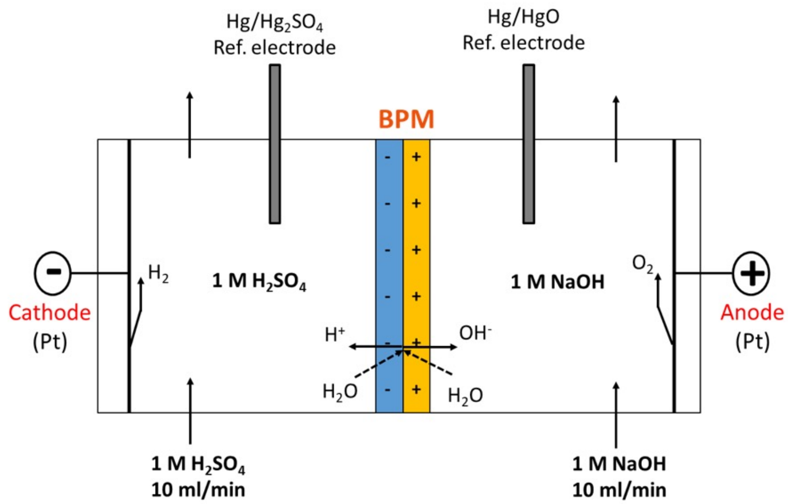
Electrospinning

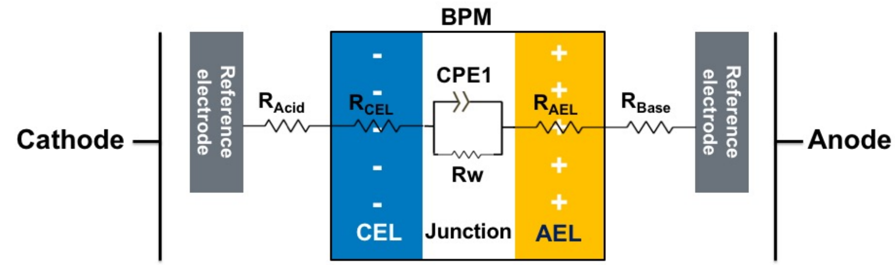
- Electrostatic voltage (4-50 kV) between a blunt tip needle and grounded substrate
- Charged polymer jet from a mixture of Nafion®/PFAEM ionomer and/or catalyst in carrier polymer (e.g. PEO)
- Solvent (IPA and water) evaporates from fiber as it travels from tip to substrate, filament also elongates during transit, narrowing diameter
  - Relative humidity in chamber is a critical experimental variable
- 300-500 nm diameter nanofiber threads
- Randomly aligned nanofibers collected as mat of uniform thickness and fiber volume fraction on a membrane
- **Unique aspect of our approach: Dual head electrospinning results in 3D interface of interpenetrating cation/anion membrane fibers**
- Polymer dispersions electrospun concurrently on programmable, rotating, translating drum
- Substrate attached to drum
  - Glass, membrane, conductive carbon tape, TEM grid, etc.
- **Water dissociation catalysts introduced to polymer dispersions**

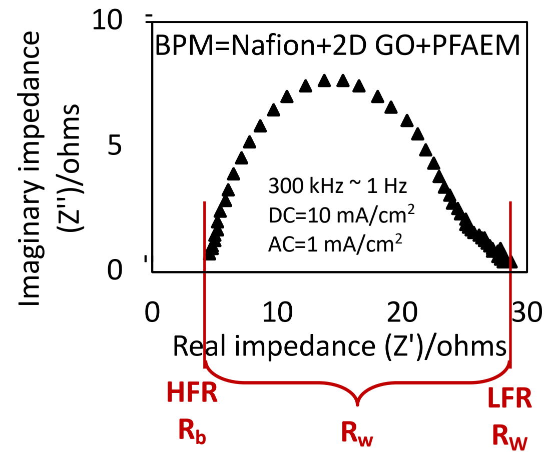
A high surface area 3D BPM interface should have improved properties over a planar, 2D BPM

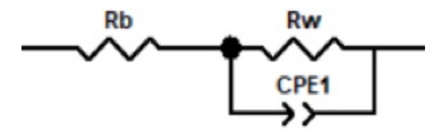
Accomplishments and Progress

Flow cell testing for preliminary BPM screening







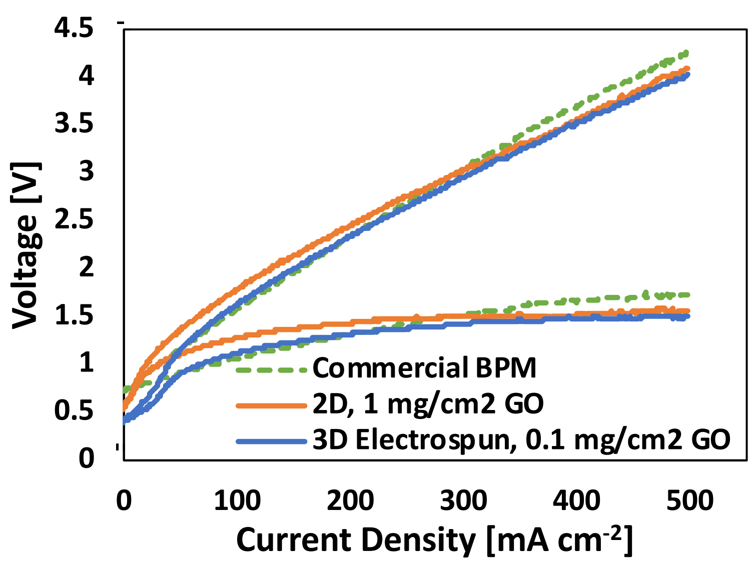


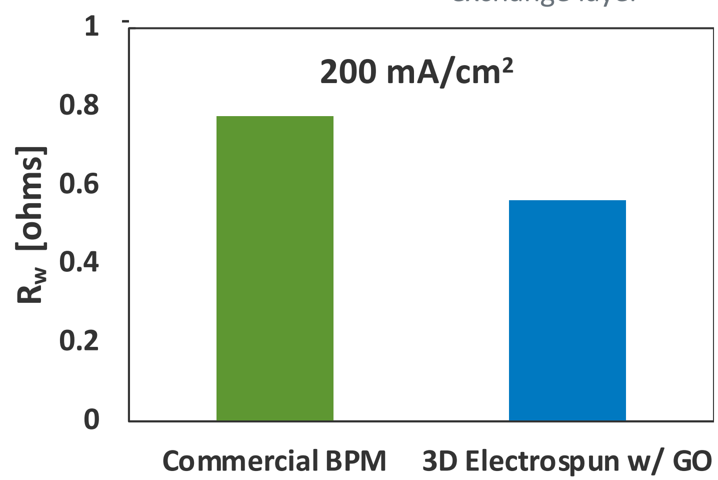
$R_b = R_{Acid} + R_{Base} + R_{CEL} + R_{AEL}$

R_w: Resistance of water dissociation reaction

CPE1: Electrical double layer (heterogeneity)

CEL/AEL: Cation/Anion exchange layer



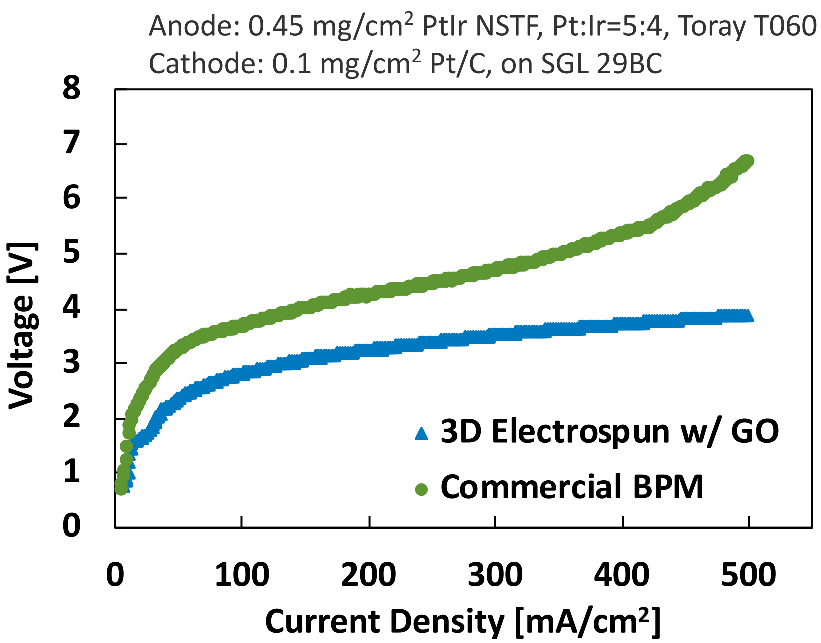


Graphene oxide at the BPM interface reduces R_W

Accomplishments and Progress

Electrolyzer MEA

Achieved 500 mA/cm²

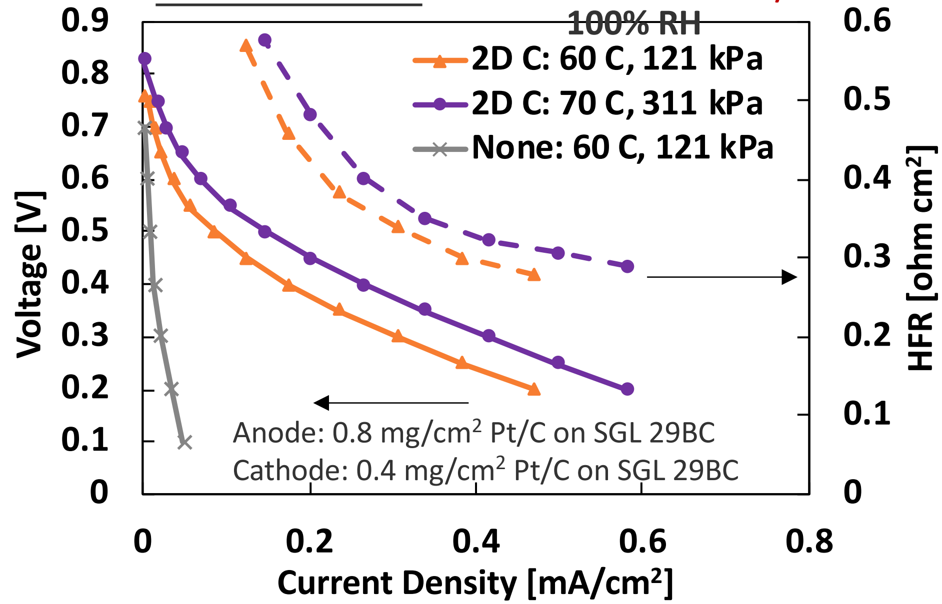


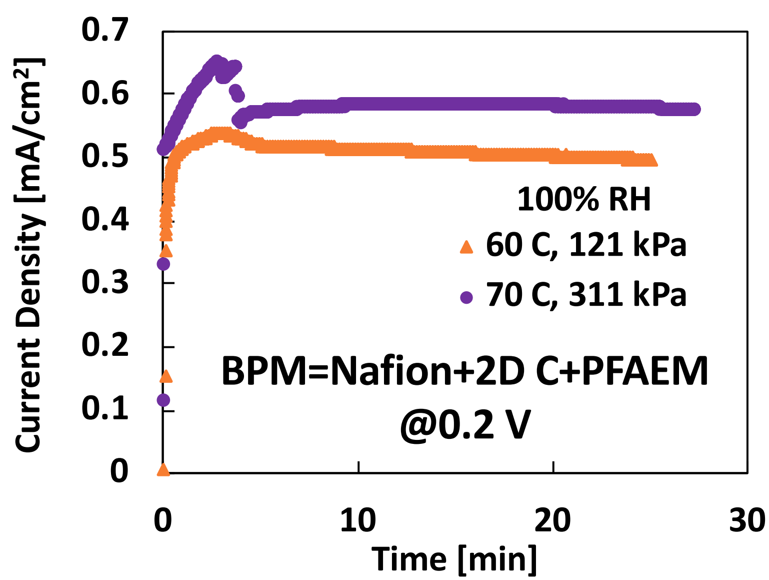
Current problems & Space to improve:

- RFC Hardware design & flow channel optimization
- GDE catalyst optimization
- Water transport management
- BPM junction optimization
- Avoiding salt ions in BPM fuel cell mode

Fuel Cell MEA

Achieved 500 mA/cm²





Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year

Collaboration and Coordination

- NREL's anion ionomer development program
  - Federal lab
  - Within DOE FCTO
  - Provide this project PFAEM polymer, we provide characterization results
- NREL's MEA fabrication, fuel cell and electrolysis characterization groups
  - Federal lab
  - Within DOE FCTO
  - Maintain equipment for MEA fabrication as well as fuel cell and electrolyzer test stands that enable performance evaluation of BPM devices
- 3M
  - Industry
  - Outside DOE FCTO
  - PtIr Catalyst
- Colorado School of Mines
  - University
  - Outside DOE FCTO
  - SEM and EDS characterization of electrospun membranes
- This project relies on a great working relationships that leverage materials and capabilities previously developed within NREL's fuel cell and electrolysis group to achieve its objectives

Remaining Challenges and Barriers

- Electrolysis
  - increase water dissociation catalyst loading at the BPM interface
  - upper limit to concentration ionomer precursors can handle and still electrospin
  - Ultrasonic spray head over electrospinning drum
- Fuel Cell
  - Need to remove Cl/I via ion exchange in BPM interface
- For RFC Operation
  - Optimize RFC hardware for liquid and gas flow – robustness is a current limitation
  - Optimize interface for reversible operation
  - Optimize electrode design for RFC (glean knowledge from other ongoing projects)
  - Test durability under reversible operation

Proposed Future Work

- Key Year 1 Go/No-Go decision: 3/31/19
  - Establish capability to achieve >500 mA/cm^2 in both fuel cell and electrolysis mode using BPM RFC approach
- For the remainder of FY19
  - Introduce ultrasonic spray head in electrospinning chamber to increase water dissociation catalyst loading at BPM interface
  - Optimize RFC hardware for liquid and gas flow MEA testing and optimization
  - Demonstrate stability and high fuel cell/electrolysis performance
- FY20
  - focus on developing and demonstrating a reversible fuel cell MEA in a unitized test stand that will allow cycling in both fuel cell and electrolysis modes, and study durability including issues of operating in both individual modes

Any proposed future work is subject to change based on funding levels

Summary

- Progress on this project has been delayed by staffing issues: a no-cost extension was requested and granted
- We are able to electrospin Nafion®, PFAEM, and membranes composed of a mixture of the two
- We are able to introduce graphene oxide to the ionomer precursor solutions that reduces the interfacial resistance
- While the morphology looks as expected, the tools we have used for compositional characterizations have, so far, not been able to unambiguously give qualitative or quantitative results on electrospun BPMs
- Additional spectroscopic characterization techniques are required to evaluate the chemical compositions of the BPMs

Thank You

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Publication Number

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

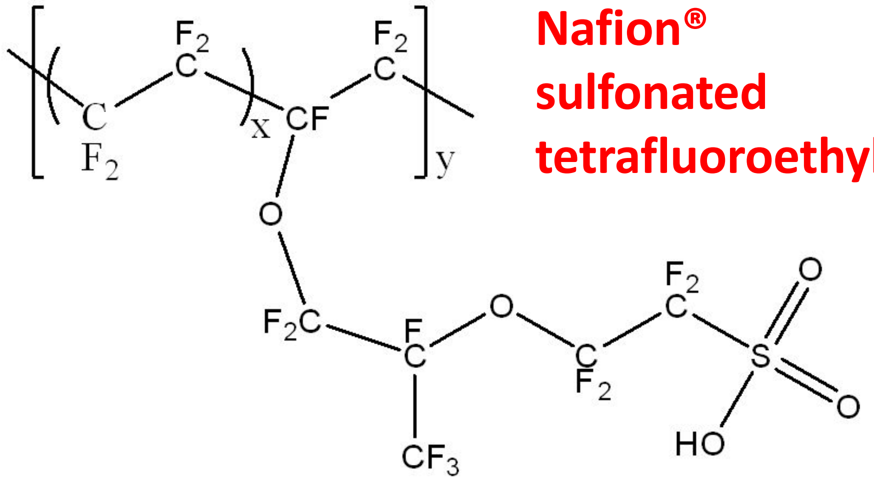
Technical Back-Up Slides

(Include this “divider” slide if you are including back-up technical slides [maximum of five]. These back-up technical slides will be available for your presentation and will be included in Web PDF files released to the public.)

Approach

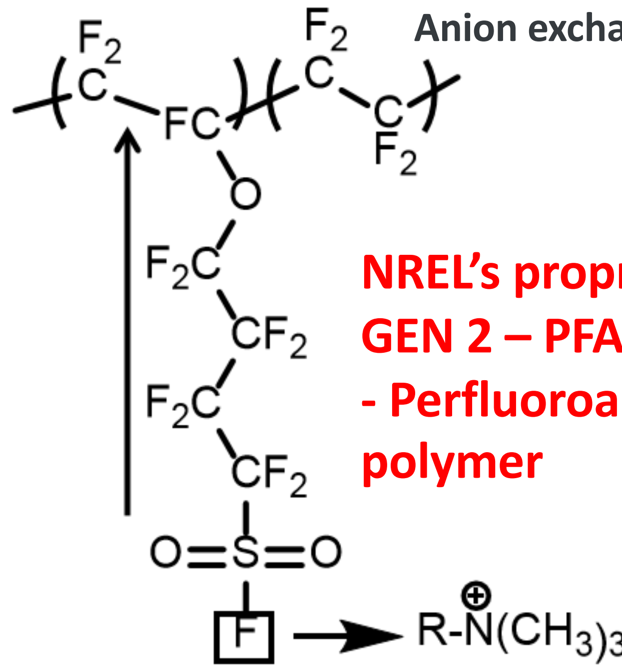
Chemistry

Cation exchange: H^+



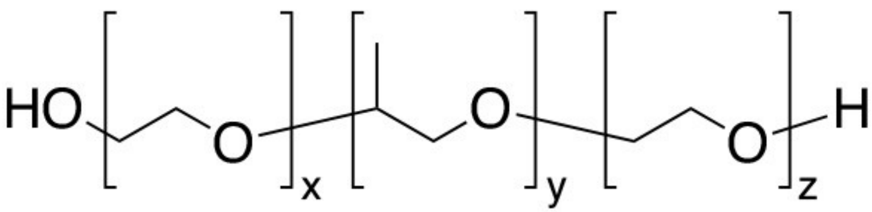
Nafion® sulfonated tetrafluoroethylene

Anion exchange: OH^-



NREL's proprietary GEN 2 – PFAEM - Perfluoroalkyl polymer

Carrier polymer



Polyethylene oxide (PEO)

- Water-soluble, high MW, synthetic polymer
- Basic unit: $(-CH_2-CH_2O-)_n$
- When dissolved in water:
  - Hydrophilic interactions through O; hydrophobic interactions through CH_2CH_2

- Sulfonic acid (SO_3^-) groups on Nafion® conduct H^+ cations and block anions
- Alkyl (N^+) groups on PFAEM conduct OH^- anions and block cations
- PEO added to enable electrospinning of Nafion® and PFAEM

Approach

FY18 Milestones

Milestone Name/Description	Criteria	End Date	Type	
Electrospun Junction Synthesis/ Investigate spinning of PEM and AEMs through dual head spinning.	Fabricate a BMP junction that has fibers of AEM penetrating into the PEM and PEM fibers penetrating into the AEM.			Completed
MEA testing / Experiments will examine static and dynamic operation, and include advanced cell diagnostics, including impedance, kinetics, cycling voltammetry (including CO stripping) and limiting-current measurements to help elucidate specific performance loss mechanisms.	Using 3 different electrospun BPMs in MEAs, use polarization curves to begin elucidation of performance loss in both fuel cell and electrolyzer mode.	6/30/2018	Quarterly Progress Measure (Regular)	On-track
Reduced interfacial resistance for bipolar membranes/ Using both electrospun junctions and additives, we will reduce the high frequency resistance (at zero imaginary as measured by AC impedance) to less than or equal to 200 mΩcm^2.	Demonstrate ASR ≤0.2 Ω cm^2 of BPM in fuel cell tests.	9/31/2018	Quarterly Progress Measure (Regular)	No-cost extension Delayed until 3/31/19
MEA testing and further optimization / Experiments will examine static and dynamic operation, and include advanced cell diagnostics, including impedance, kinetics, cycling voltammetry (including CO stripping) and limiting-current measurements to help elucidate specific performance loss mechanisms while targeting attainable routes to > 500 mA/cm^2 in both fuel cell and electrolysis mode using BPM RFC approach.			Annual Milestone (Regular)	Delayed until 3/31/19

Go/No-Go

Go/No-Go Description	Criteria	Date	
BPM RFC performance			Delayed until 3/31/19

Approach

FY19 Milestones

Milestone Name/Description	Criteria	End Date	Type	
Develop method for characterizing individual ionomer fibers in electrospun bipolar membrane interface.	Identify a synthesis procedure or selective staining method that permits the AEM and CEM nanofibers to be distinguished from each other under microscopic observation.	3/31/2019	Quarterly Progress Measure (Regular)	On-track
Reduce the high-frequency resistance (at zero imaginary as measured by AC impedance) to less than or equal to 100 mW/cm^2 by using both electrospun junctions and additives.	Demonstrate ASR $\leq$0.1 Ω cm^2 of BPM in electrolysis tests.	6/30/2019	Quarterly Progress Measure (Regular)	On-track
Evaluate the stability and performance in fuel cell and electrolysis mode at elevated temperature.	Determine the degradation profile of BPM MEAs while operating continuously for 8 hours in fuel cell and electrolysis mode at 80°C.	9/31/2019	Quarterly Progress Measure (Regular)	On-track
Demonstrate >1A/cm^2 in both fuel cell and electrolysis mode using BPM RFC.	Measure current densities >1 A/cm^2 in both fuel cell and electrolysis mode with a BPM MEA.	12/31/2019	Annual Milestone (Regular)	On-track

Go/No-Go

Go/No-Go Description	Criteria	Date
Demonstrate >1A/cm^2 in both fuel cell and electrolysis mode using BPM RFC.	Measure current densities >1 A/cm^2 in both fuel cell and electrolysis mode with a BPM MEA.	12/31/2019