Bipolar Membrane Development to Enable Regenerative Fuel Cells

Co-PIs: Todd Deutsch, KC Neyerlin
Key contributors: Yingying Chen, Sadia Kabir, Ellis Klein
National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
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Project ID: fc182

Overview

Timeline and Budget

- Project start date: 01/01/18
- Project end date: 03/31/20
- Total project budget: $400k
  - Total DOE funds spent*: $400k

* As of 3/31/20

Barriers

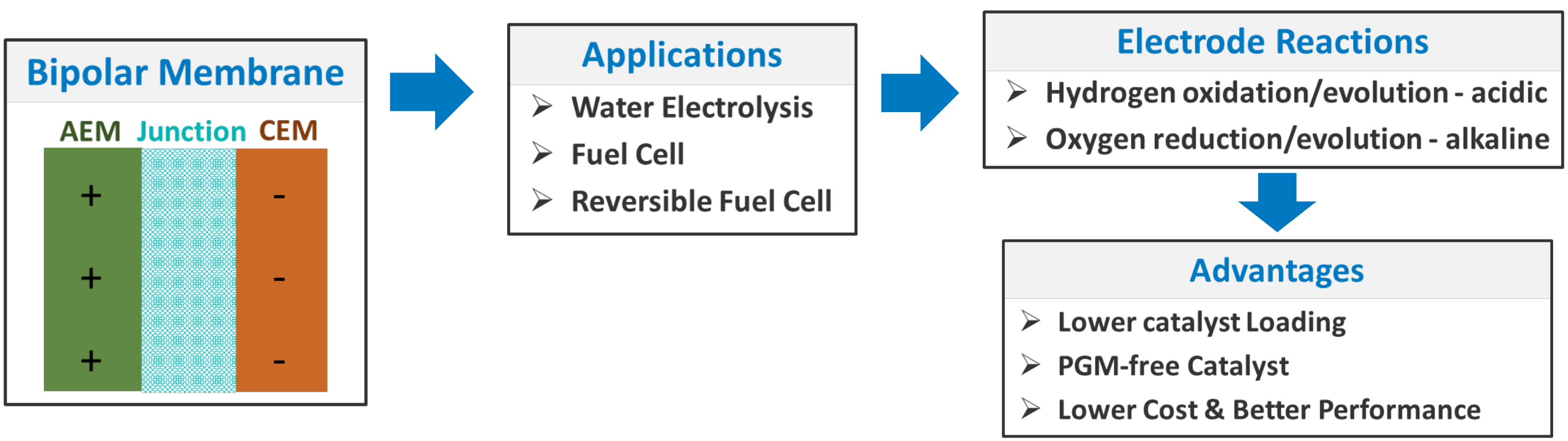
- A – Cost
- B – Durability
- C – Performance

Partners

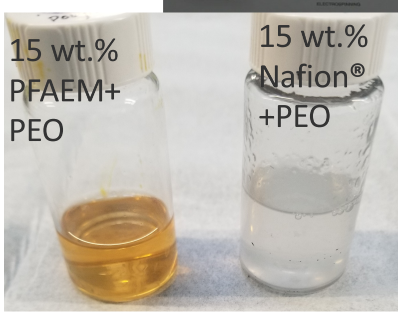
- Anion ionomer development program at NREL
- MEA fabrication group at NREL
- Fuel cell and electrolysis testing groups at NREL

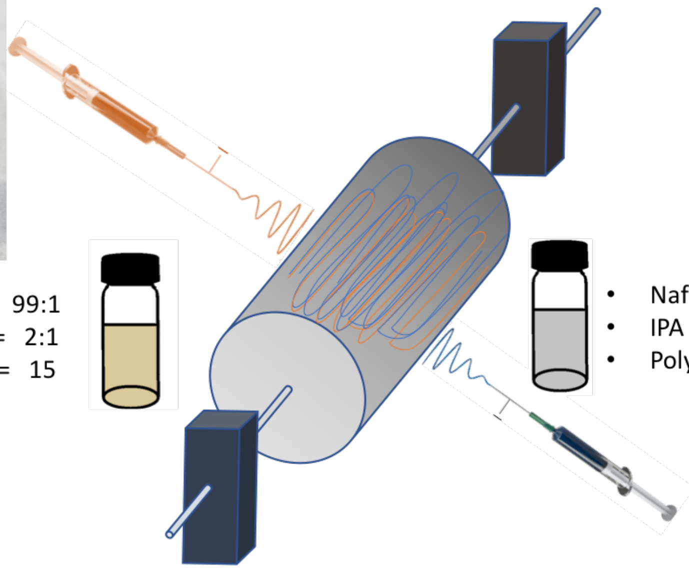
Relevance

- 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.**"
- 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.
- <u>**Objectives**</u>
  - 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).
  - 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.



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

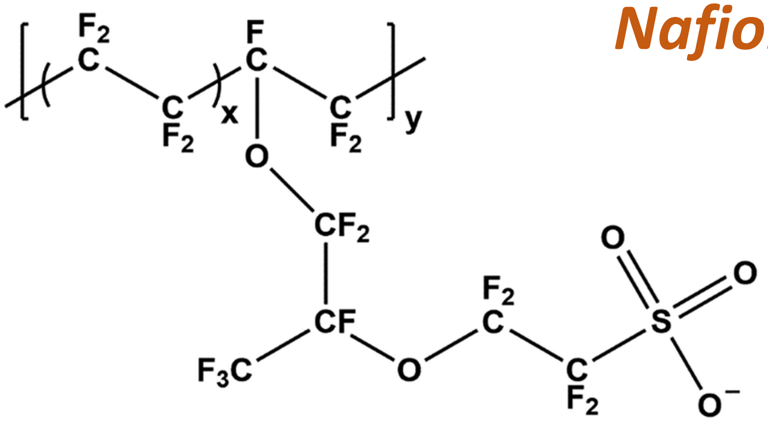
- Electrostatic voltage (4-50 kV) between a blunt tip needle and grounded substrate
- Charged polymer jet from a mixture of Nafion®/perfluorinated AEM (PFAEM) ionomer and/or catalyst in carrier polymer (e.g. PEO)
- Solvent (IPA and water) evaporates from fiber as it travels from tip to substrate, filament 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

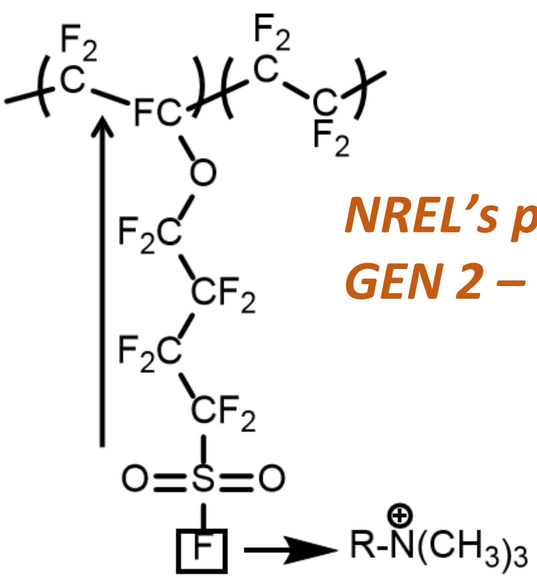
Approach – 2D BPM Fabrication

Materials

Nafion



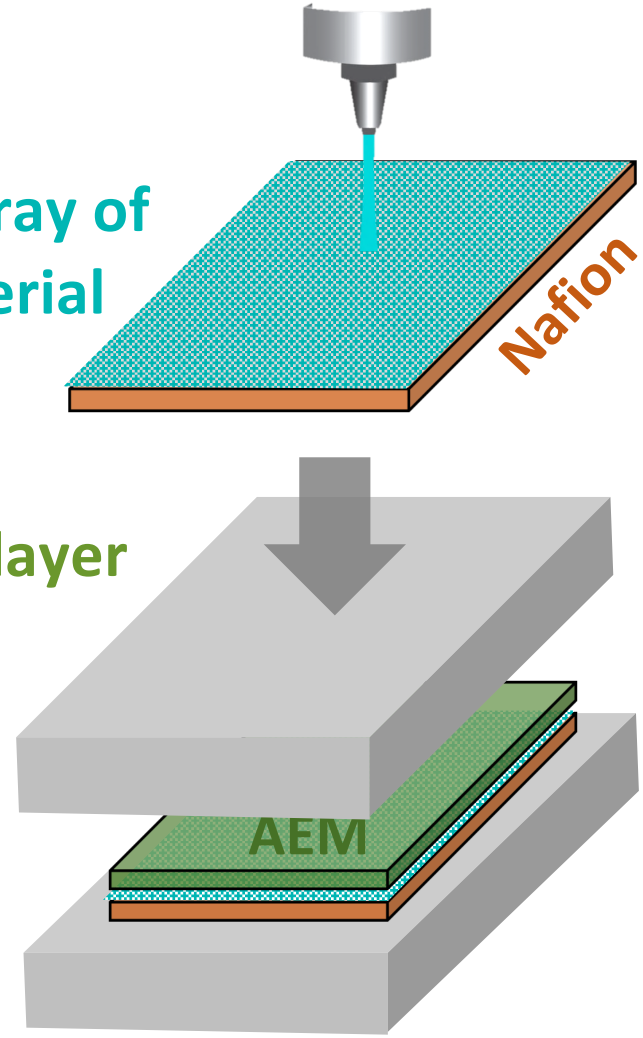
NREL's proprietary GEN 2 – PFAEM



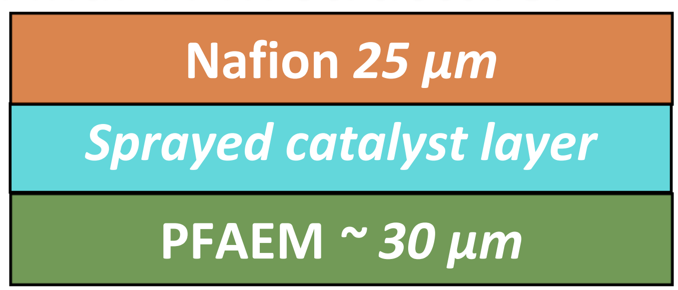
Step 1:
Ultrasonic spray of junction material on Nafion

Step 2:
Spread AEM layer
Squeeze out bubbles

Step 3:
Hot Pressing



Final BPM structure:

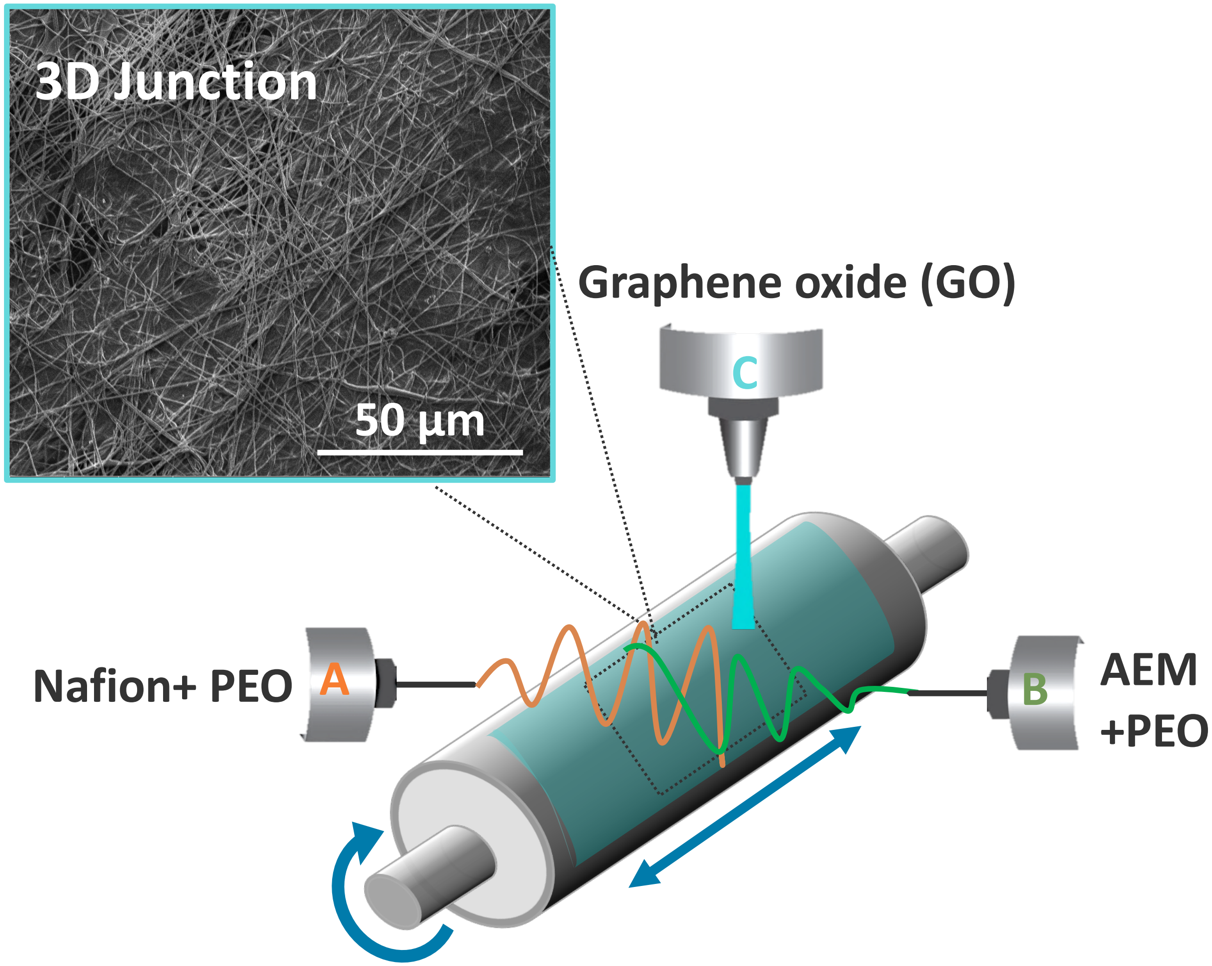


Approach – 3D BPM Fabrication

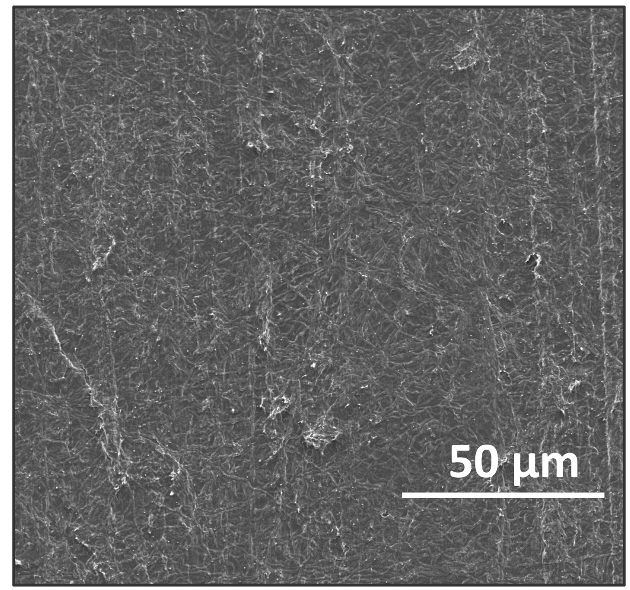
Step 1a: Electrospin Nafion nanofiber mat

Step 1b: Co-electrospin Nafion & AEM + GO spray

Step 1c: Electrospin AEM nanofiber mat

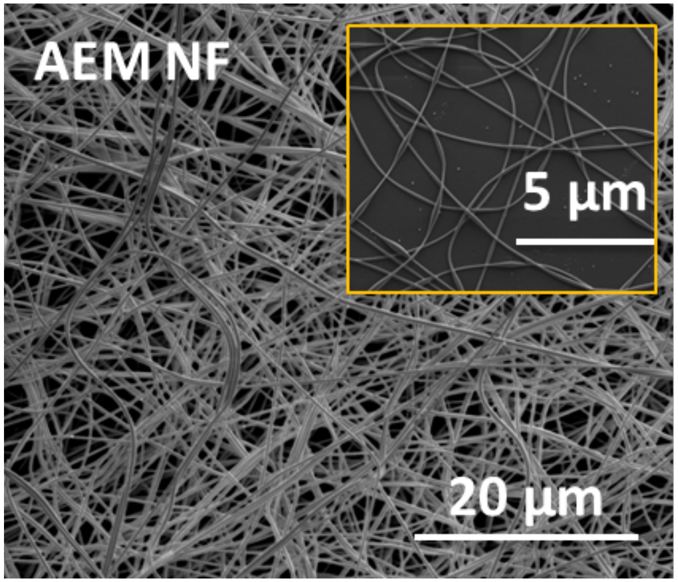


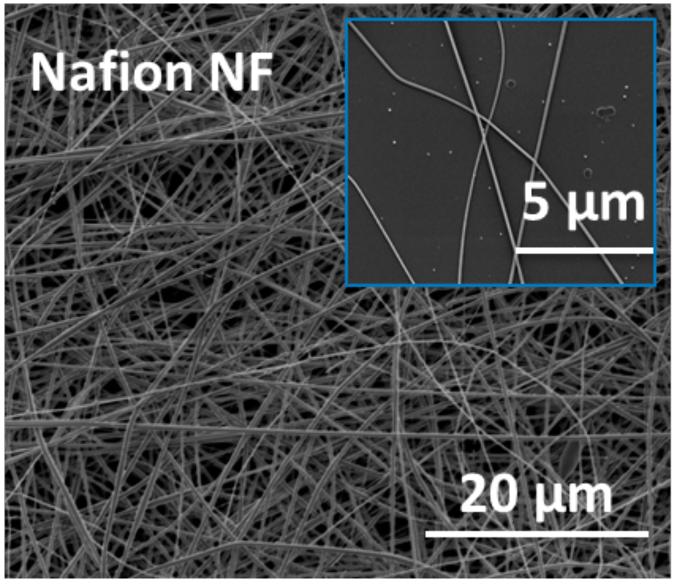
Step 2:
Nanofiber mat exposed to IPA vapor for 15 min each side; Hot pressed for 2 min

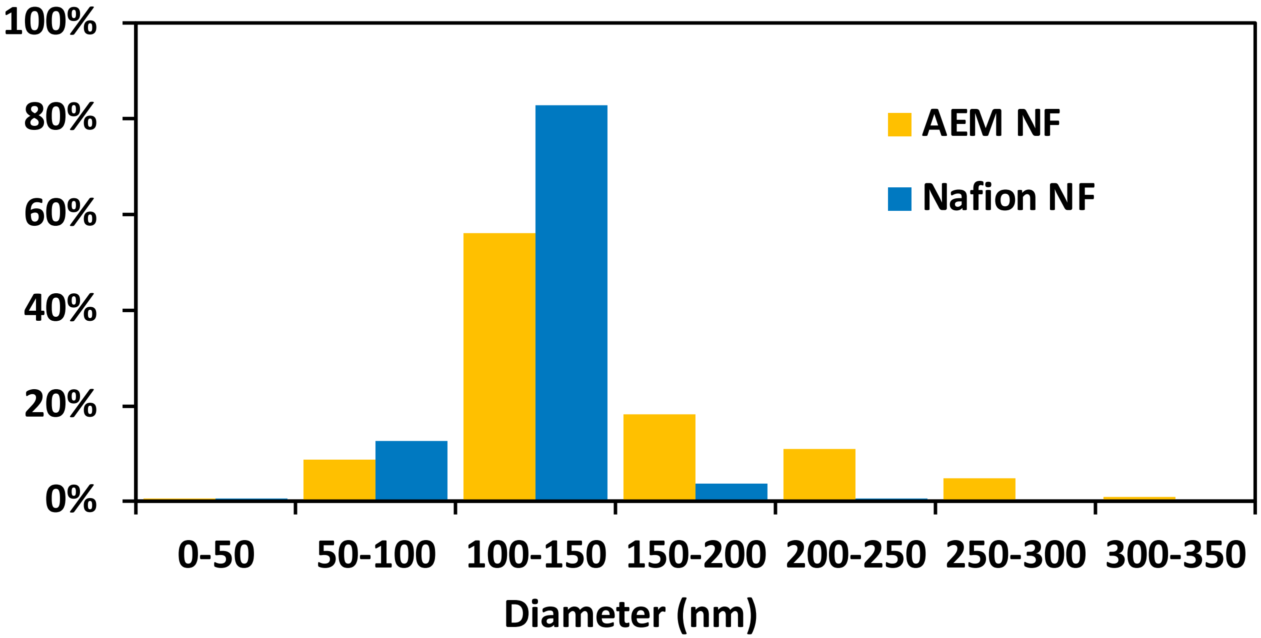


Nafion ~ *30 µm*
3D Junction ~ *3 µm*
PFAEM ~ *30 µm*

Approach – 3D BPM Fabrication







- **83%** of Nafion nanofibers (NF) and **56%** AEM NF diameters: **100 ~ 150 nm**
- AEM NF diameter ranges slightly broader due to occasionally beaded fibers

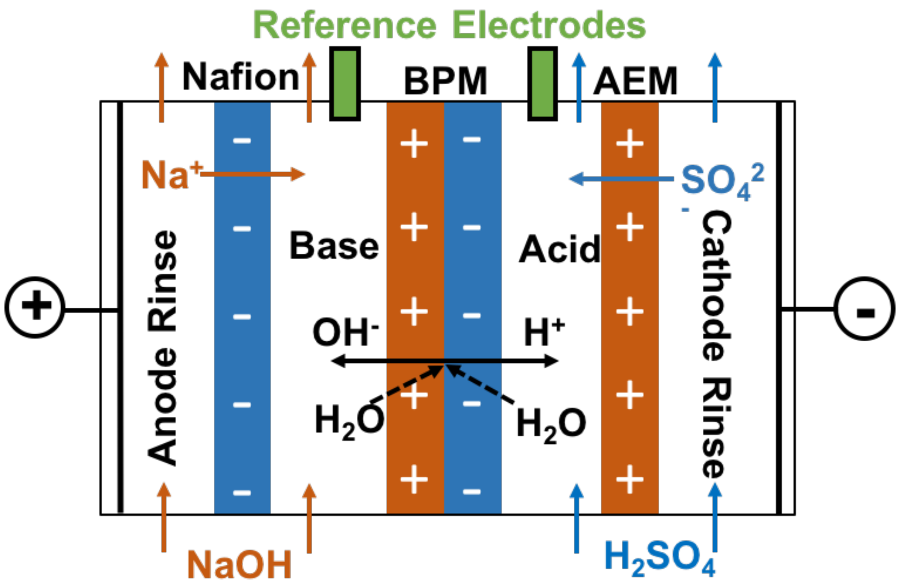
Approach

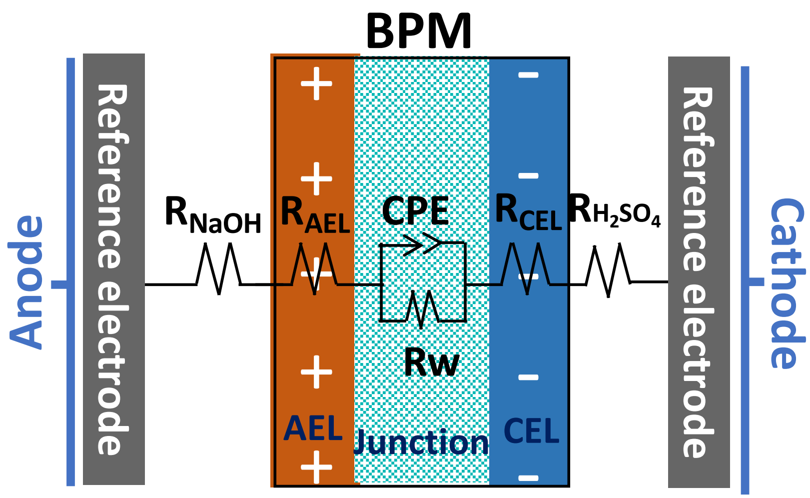
FY19/FY20 Milestones

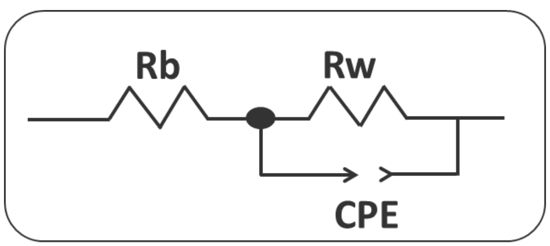
Milestone Name/Description	Criteria	End Date	Type	
Break down the ensemble BPM resistance into its discrete components and report the resistance contributions due to the PEM, AEM, and interfacial junction	Using AC impedance analysis, determine the individual component resistances.	6/30/2019	Quarterly Progress Measure (Regular)	Complete
RFC unitized cell hardware	Develop hardware that allows operation of an MEA in both fuel cell and electrolyzer mode without having to remove the MEA.	9/30/2019	Quarterly Progress Measure (Regular)	Complete
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.	12/31/2019	Quarterly Progress Measure (Regular)	Complete
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.	3/31/2020	Annual Milestone (Regular)	Partially met

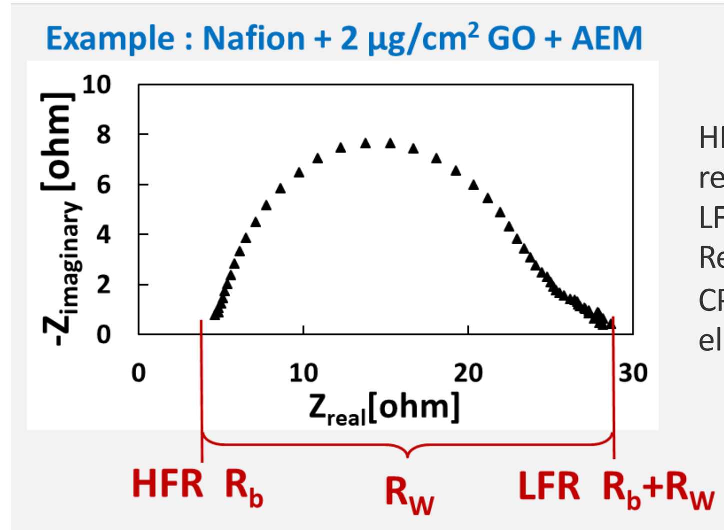
Accomplishments and Progress

Flow Cell Screening







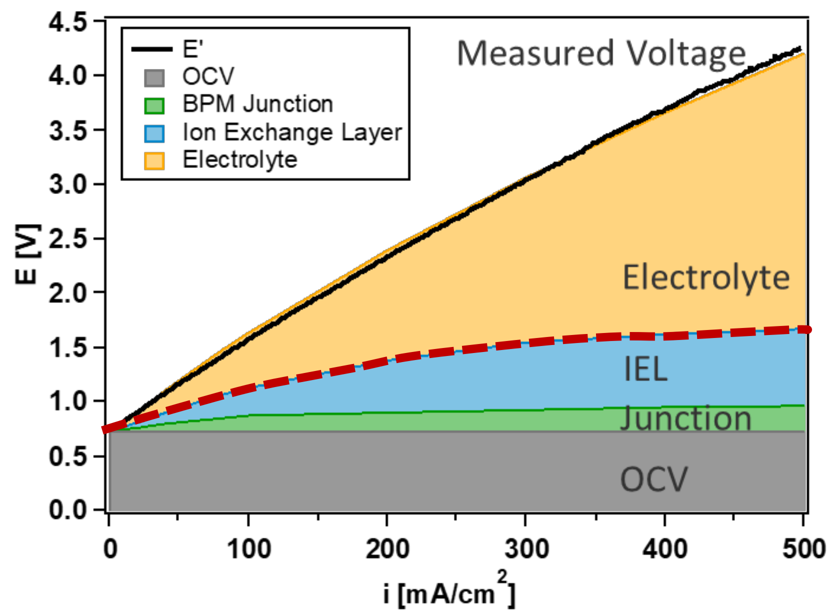


HFR: high-frequency resistance
LFR: low-frequency Resistance
CPE: constant phase element

$\mathbf{R_b} = R_{H_2SO_4} + R_{NaOH} + R_{CEL} + R_{AEL}$

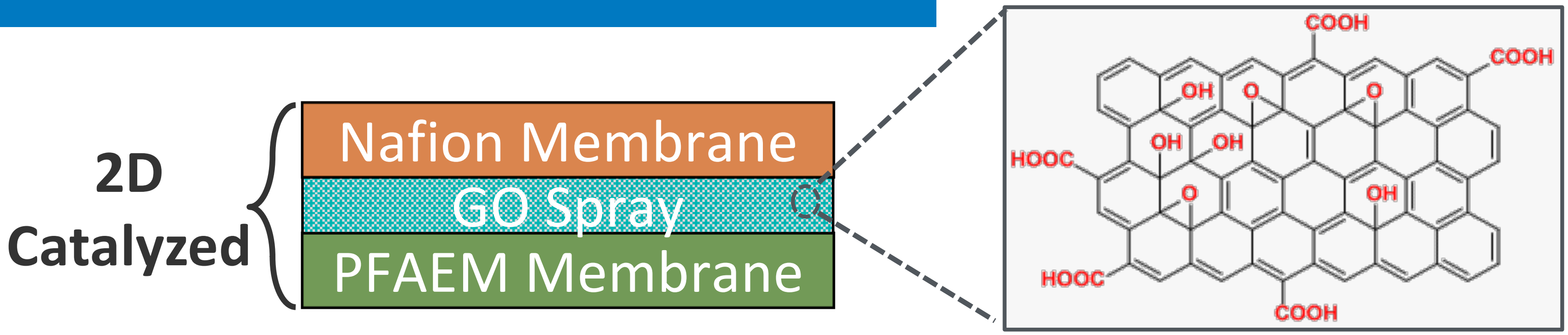
$\mathbf{R_W}$: Resistance of water dissociation reaction

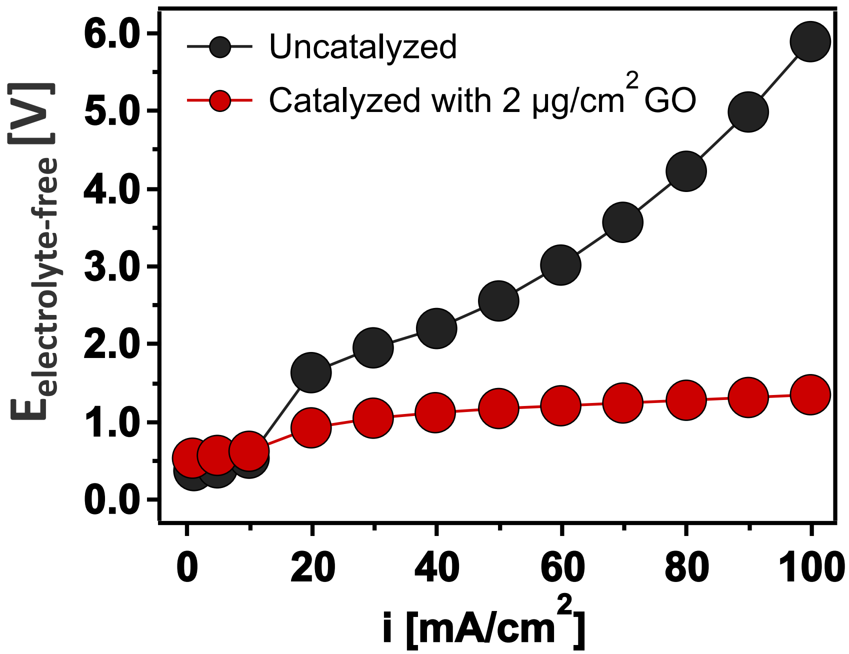
CPE: Electrical double layer (heterogeneity)

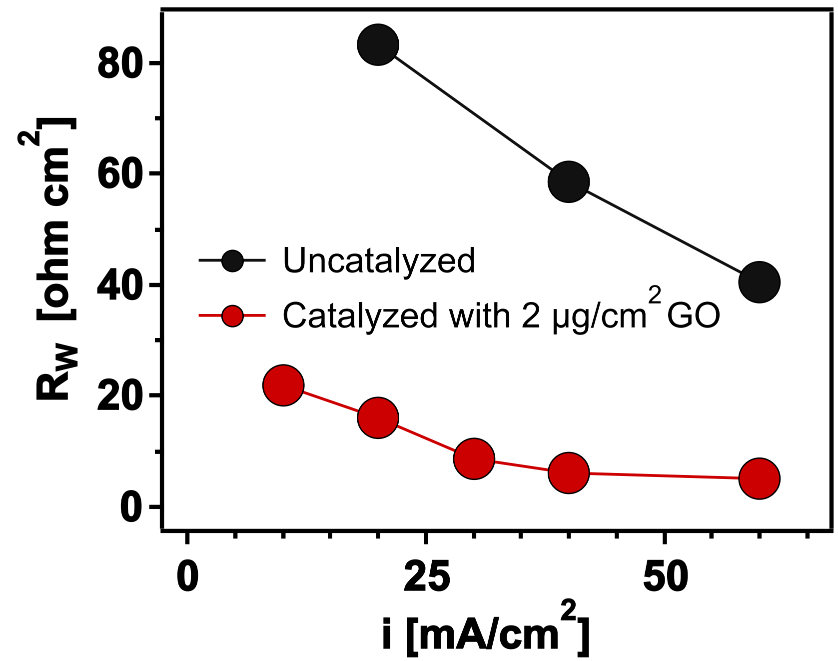


Accomplishments and Progress

Flow Cell Screening





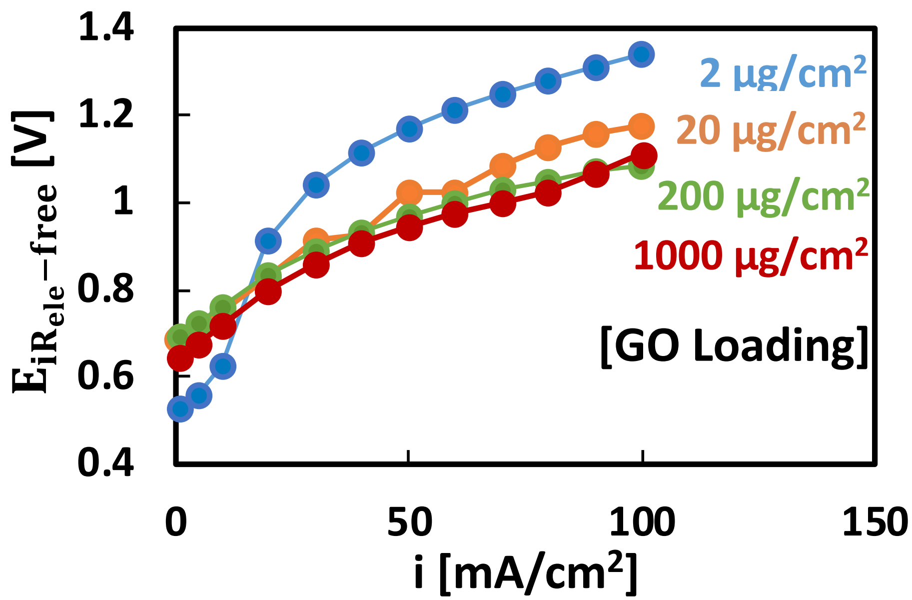


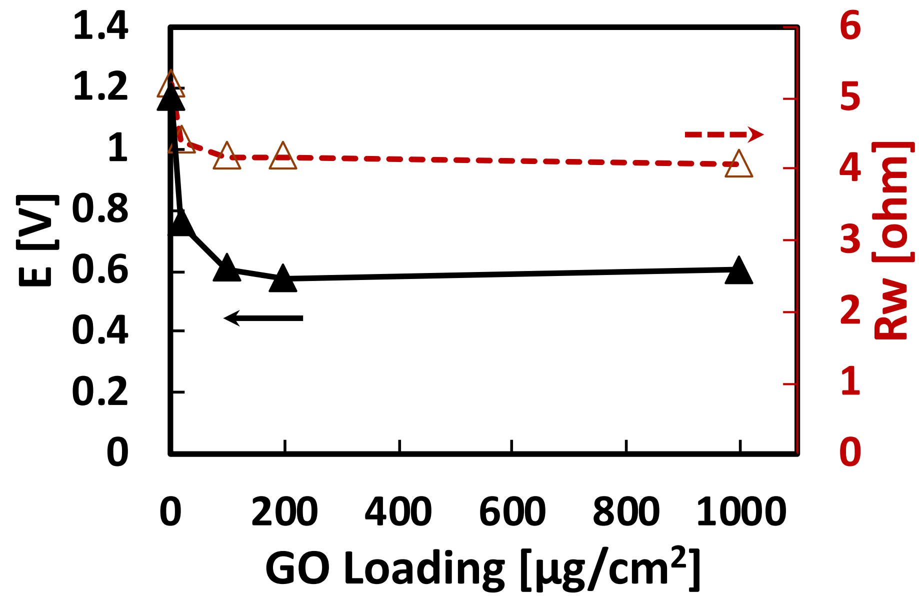
- Graphene oxide (GO) as water dissociation catalyst helps significantly lower the potential drop across BPM

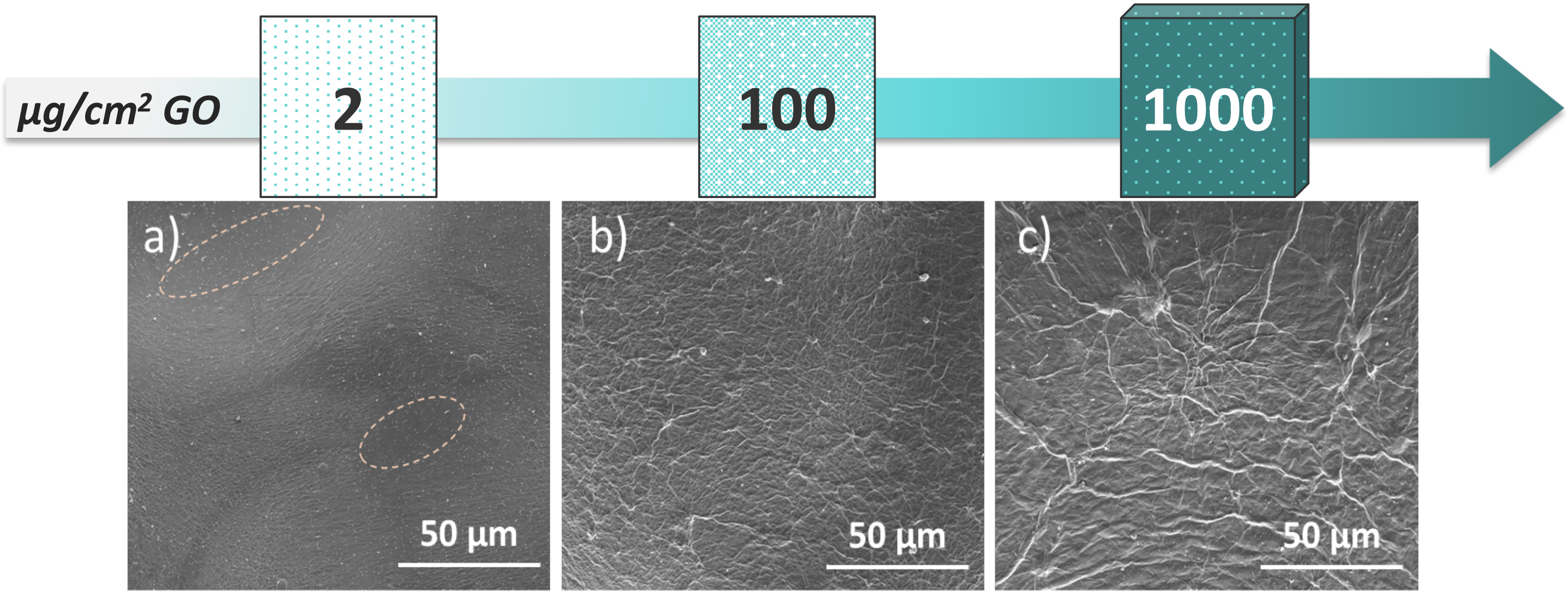
[1] Martínez, Rodrigo J., and James Farrell. "Water splitting activity of oxygen-containing groups in graphene oxide catalyst in bipolar membranes." *Computational and Theoretical Chemistry* 1164 (2019): 112556.
[2] McDonald, Michael B., and Michael S. Freund. "Graphene oxide as a water dissociation catalyst in the bipolar membrane interfacial layer." *ACS applied materials & interfaces* 6.16 (2014): 13790-13797.

Accomplishments and Progress

Flow Cell Screening



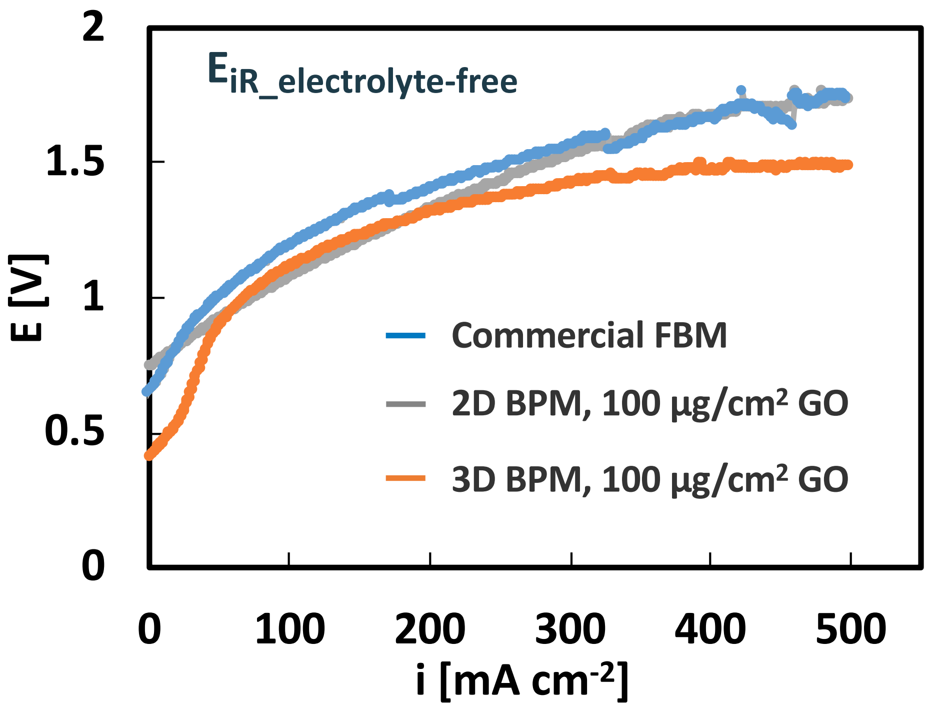


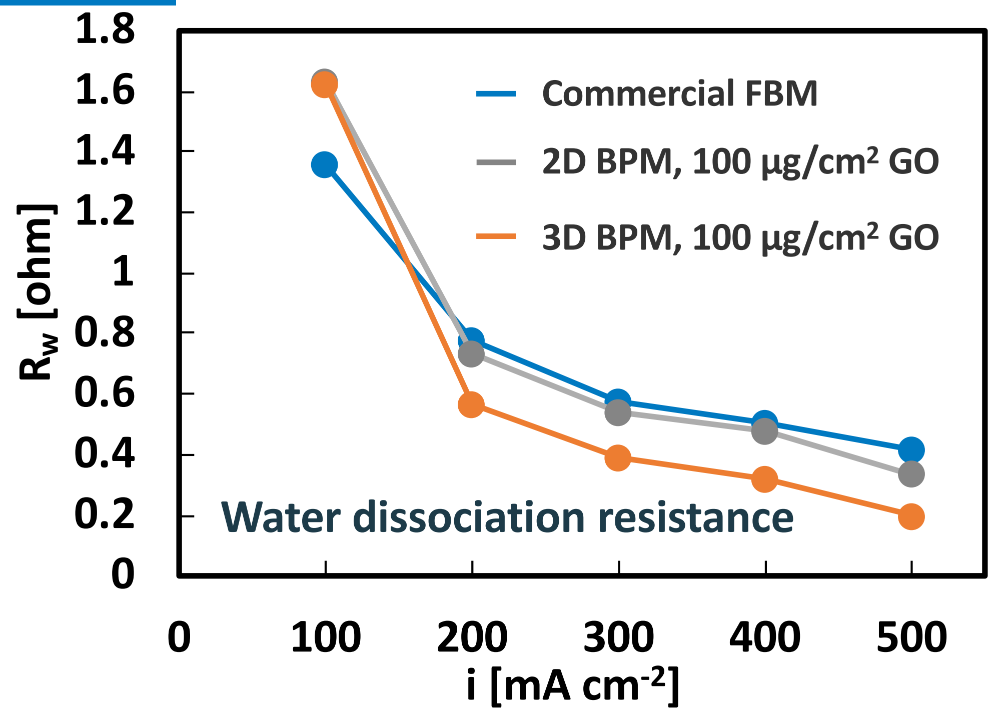


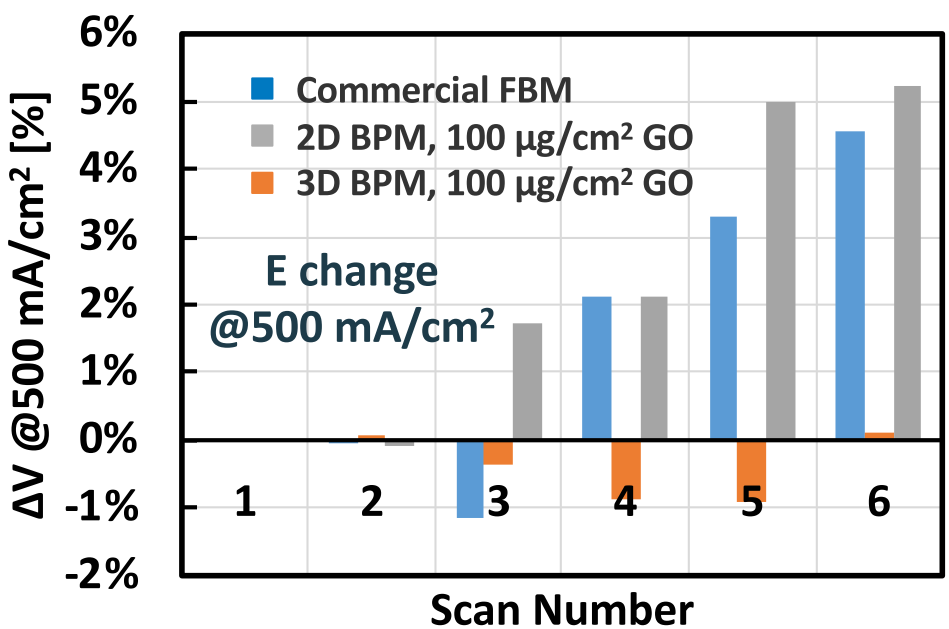
- ➢ Catalytic sites **increase**
- ➢ Junction conductance & Electric field & Water dissociation rate **decrease**

Accomplishments and Progress

Flow Cell Screening







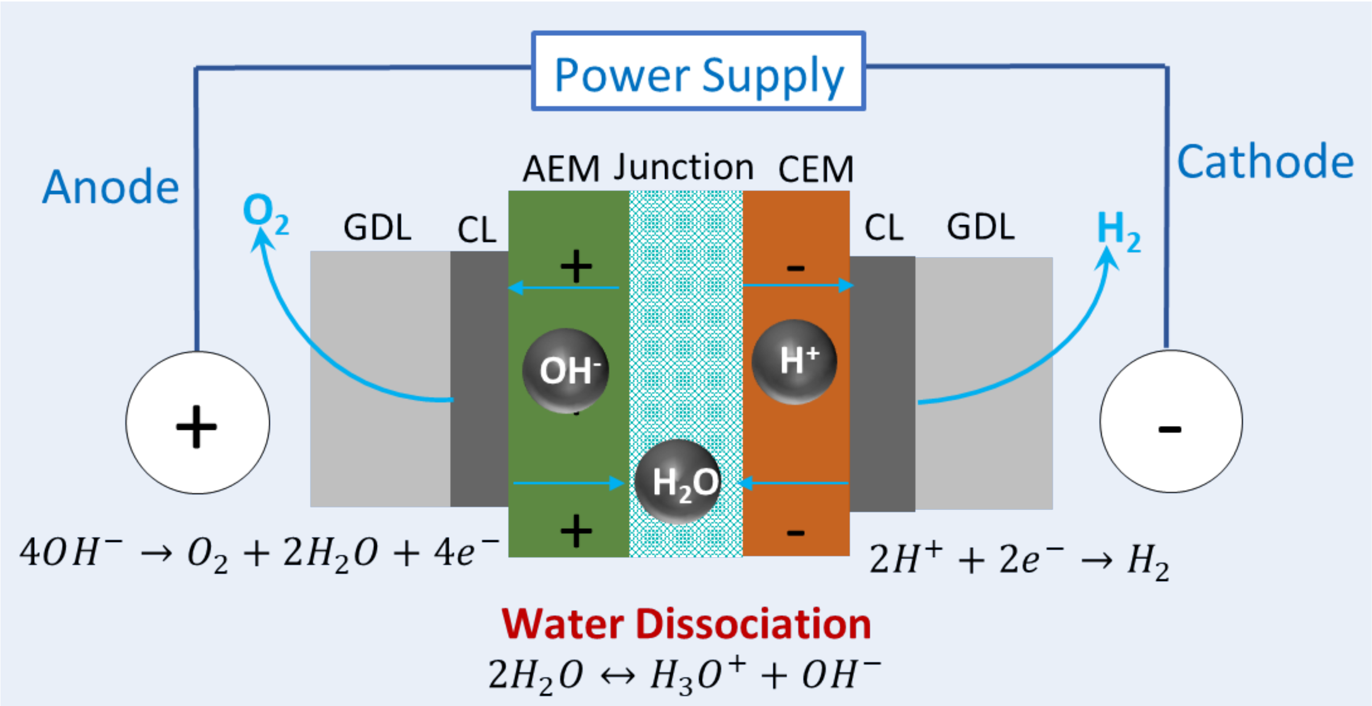
3D electrospun BPM

- **Lower voltage and lower water dissociation resistance** than commercial BPM, thanks to its 3D high surface area of catalyst
- **Best stability** under repeated high current scan
  - Strong adhesion from interpenetrating fibers in both 3D junction and the interface of ion exchange layer

Accomplishments and Progress

BPM MEA Electrolysis

- Anode GDE: 0.45 mg/cm^2 PtIr on 20% PTFE treated Toray carbon paper
  Cathode GDE: 0.4 mg/cm^2 Pt/HSC on Sigracet 29BC
- 1 M H_2SO_4 was fed to Nafion side and 1 M NaOH was fed to AEM side at 10 ml/min
- Room temperature, ~20 ^oC
- Galvanodynamic scan at 1 mA/cm^2*s



Accomplishments and Progress

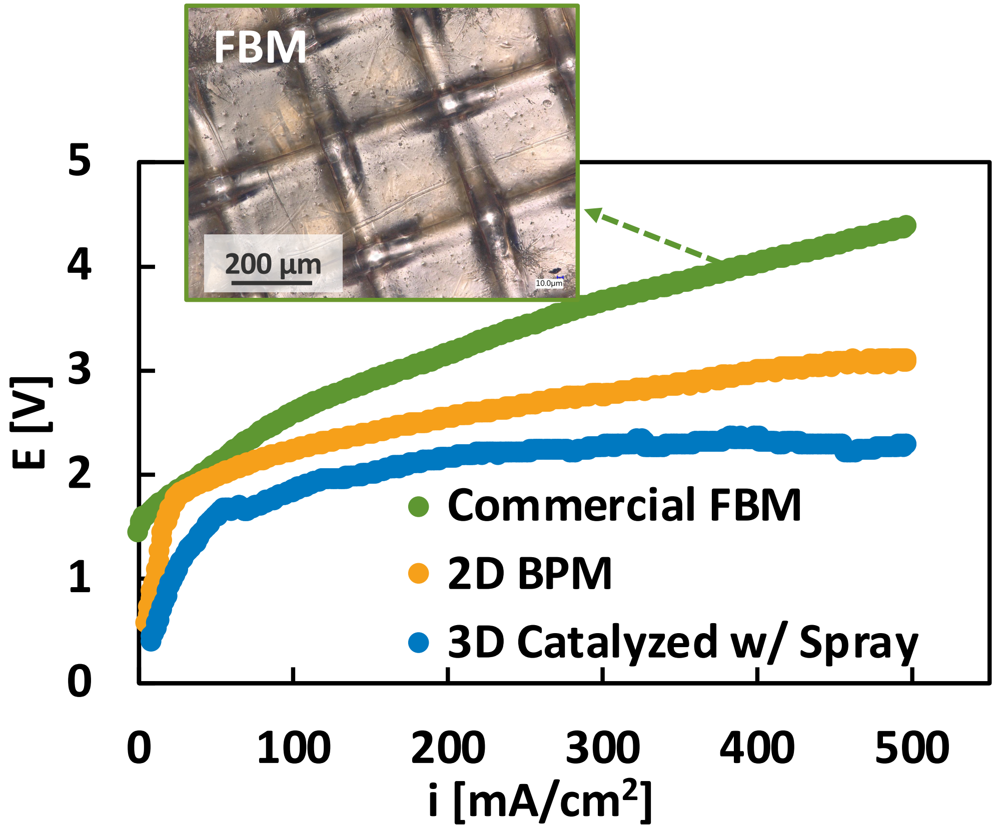
BPM MEA Electrolysis

2D Catalyzed
100 µg/cm²
GO

- Nafion Membrane
- GO Spray
- PFAEM Membrane

3D Catalyzed
w/ Spray
100 µg/cm²
GO

- Electrospun Nafion
- 3D Junction w/ GO
- Electrospun PFAEM



- **NREL fabricated** 3D Catalyzed w/ Spray BPM & 2D BPM **outperforms commercial BPM** in MEA electrolysis test
- **Commercial FBM is not designed for MEA** testing – uneven surface due to reinforcing fiber causes high contact resistance

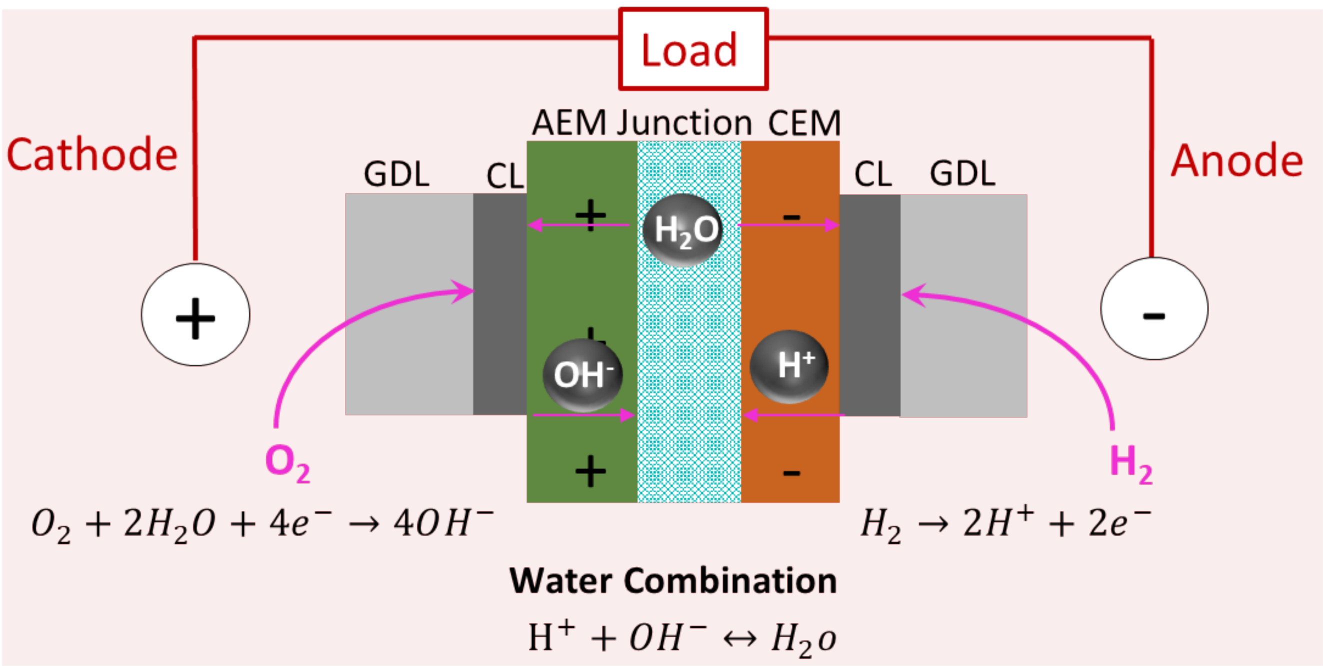
Accomplishments and Progress

BPM MEA Fuel Cell

- **AEM & Cathode GDE was ion-exchanged from I^-/Cl^- to OH^-**
- Cathode GDE: 0.8 mg/cm^2 Pt/HSC on 29BC
- Anode GDE: 0.4 mg/cm^2 Pt/HSC on 29BC
- H_2/O_2 for anode/cathode flow
- Temperature 60 °C
- Relative humidity ranged from 50% ~ 100%

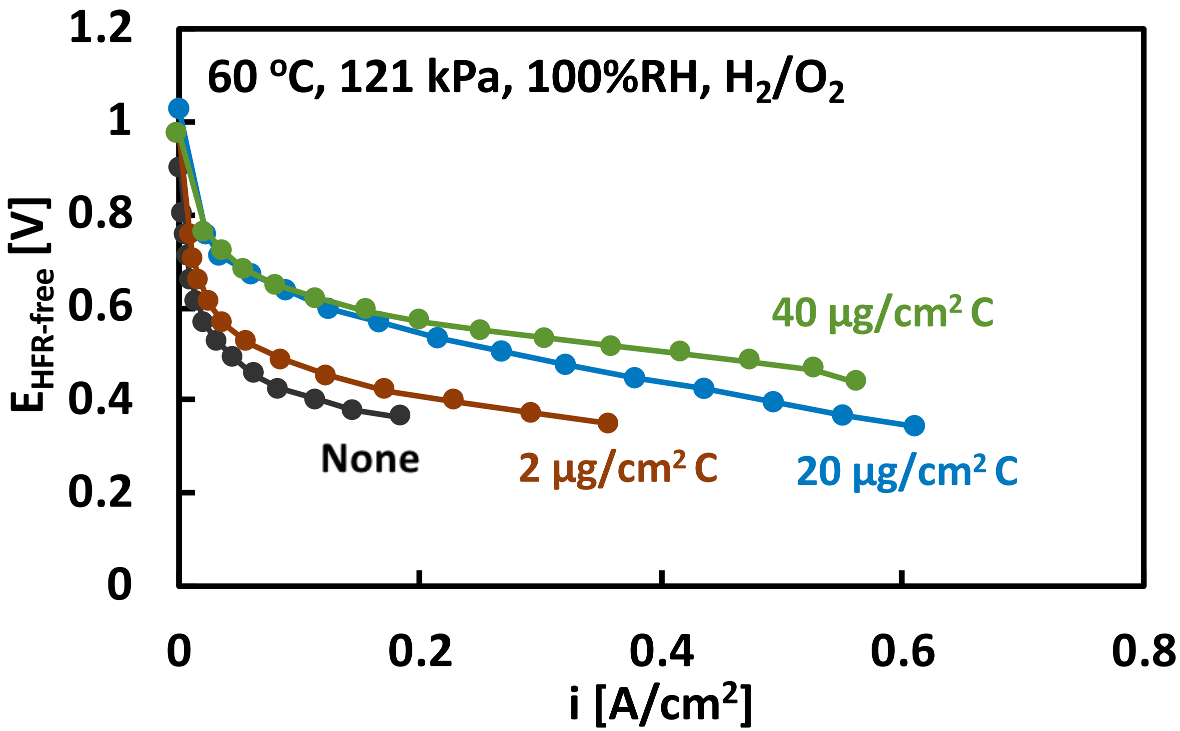
High Pt loadings used:

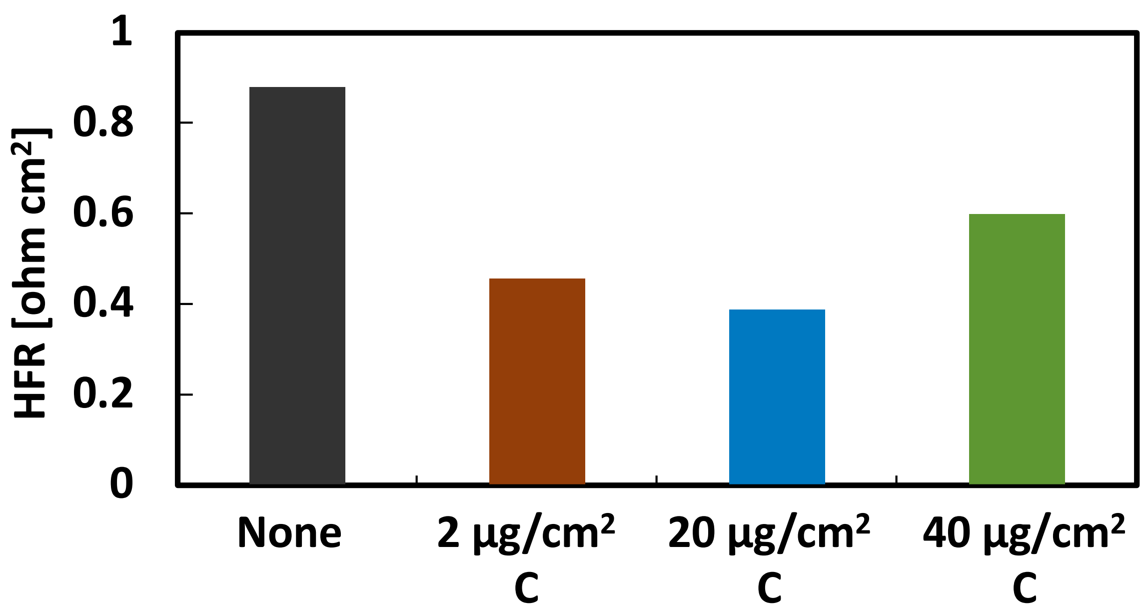
- *Minimize kinetic loss on electrodes*
- *Focus on BPM junction optimization for fuel cell performance*



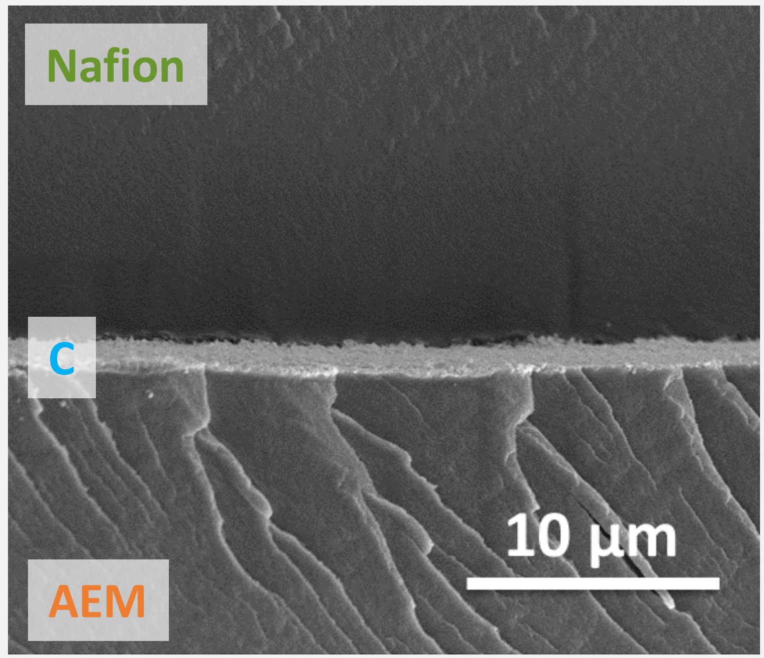
Accomplishments and Progress

BPM MEA Fuel Cell





BPM = Nafion + 20 µg/cm² C + AEM



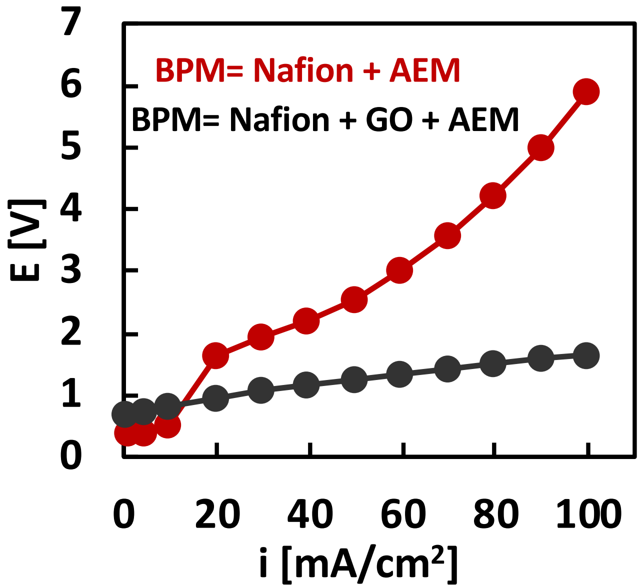
➢ **What does Vulcan carbon do?**

- Lower contact resistance
- Higher dielectric constant
- Water reservoir
- Mechanical strength

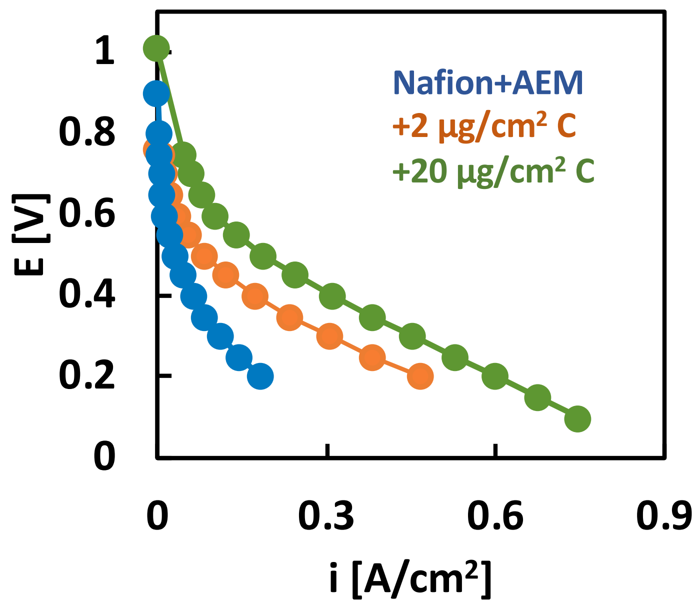
Accomplishments and Progress

BPM Junction Optimization for RFC

Graphene Oxide
(**Electrolysis** Performance)



Carbon
(**Fuel Cell** Performance)



Nafion
(Binding)

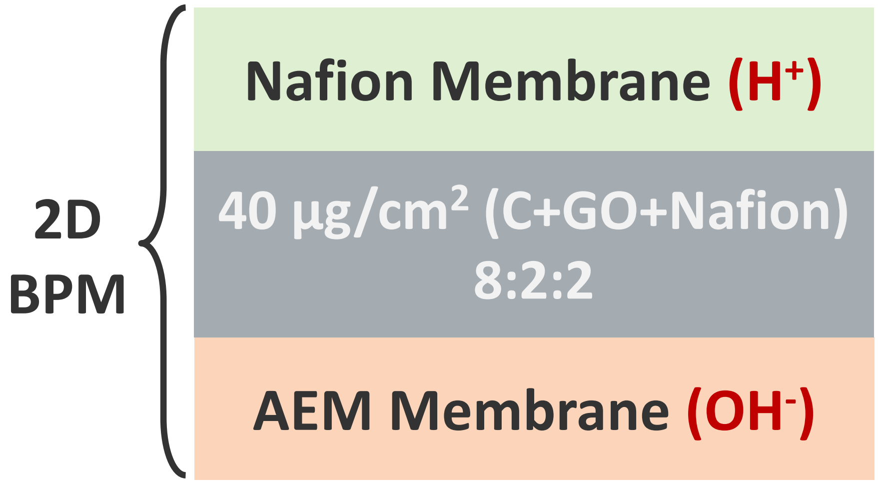
- With ionomer in junction as binder when C/GO >20 µg/cm²
- Achieve mechanical strength in junction

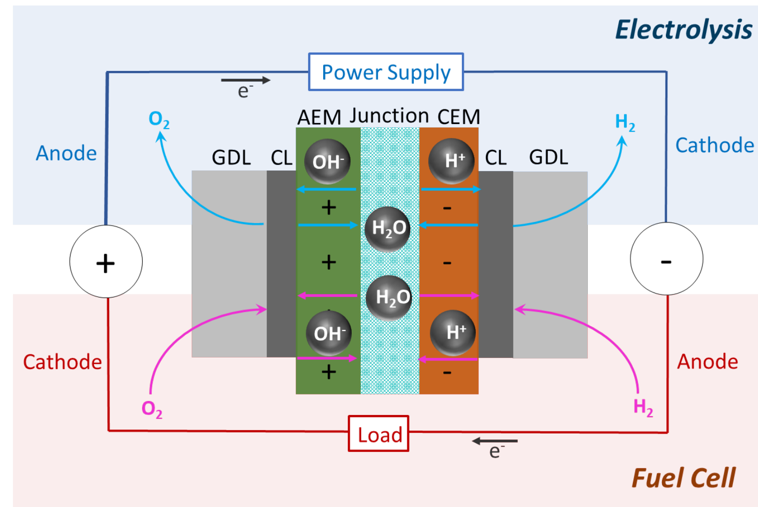
Optimize the recipe for BPM junction to achieve BPM reversible fuel cell operation:

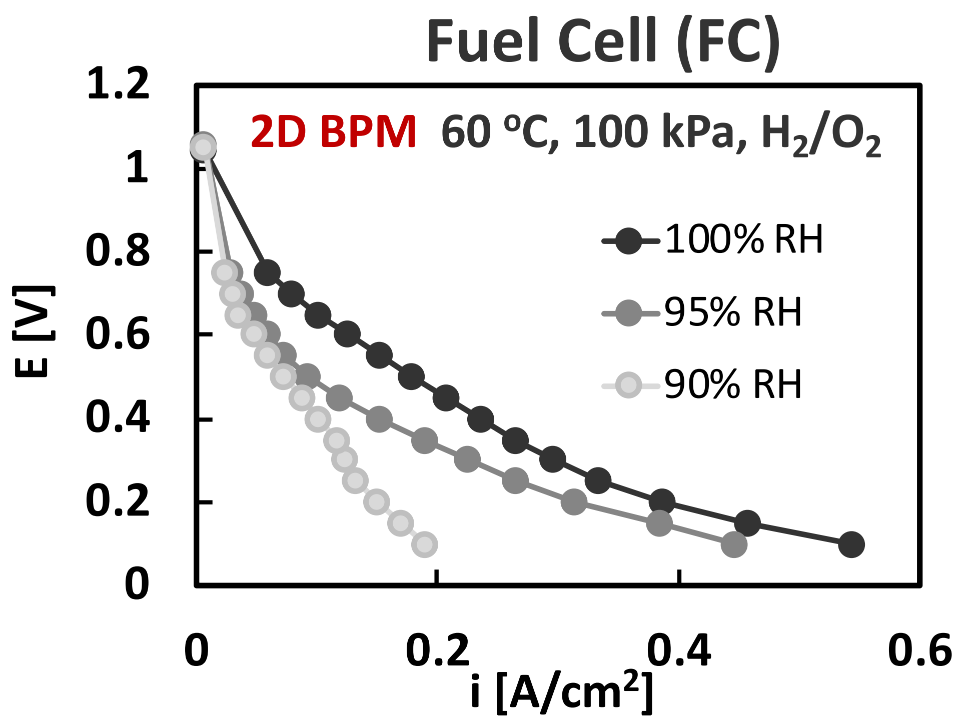
Carbon + GO + Nafion

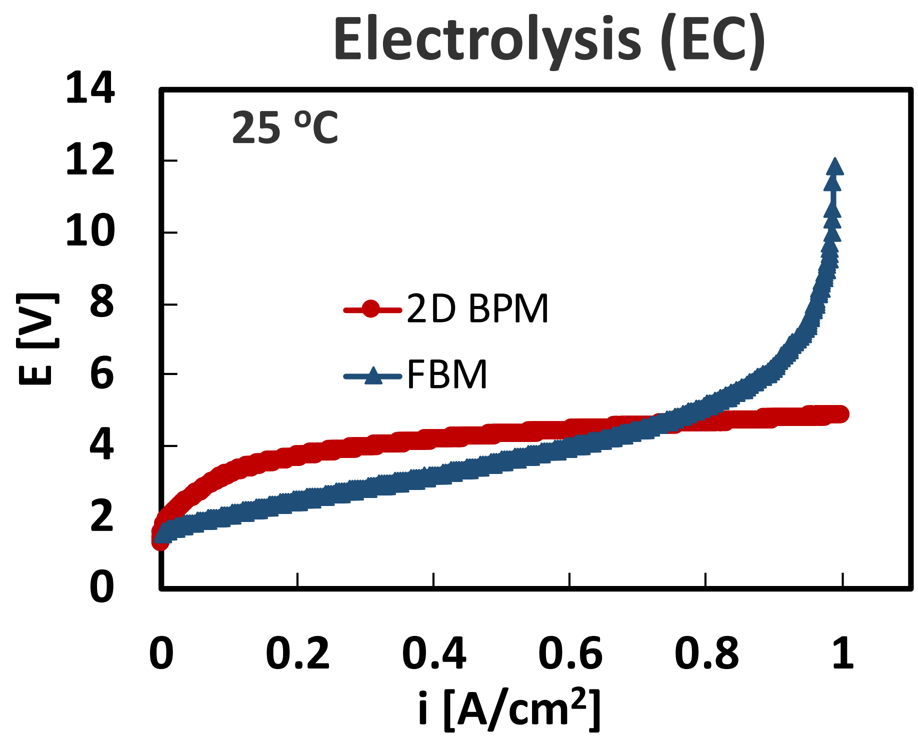
Accomplishments and Progress

Same BPM in FC and EC









Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- Modeling would help with the fundamental understanding of BPM performance and its optimization.
  - The relatively small budget does not permit inclusion of experiment, characterization, and modeling components of this study. We have incorporated finite element modeling of 3D electrospun BPM junctions in another HFTO-supported BPM project on CO_2 reduction.
- The project team needs to measure the round-trip efficiency and cycle life of the most optimized 3D BPMs.
  - From the data presented on slide 18, the round-trip efficiency is 21% at 100 mA/cm^2 and drops to 12% at 200 mA/cm^2. The difficulty of finding a common catalyst optimized for both water dissociation and recombination as well as the challenge of removing halide from the electrospun AEM fibers results in a mismatch between the best performing fuel cell and electrolyzer BPMs.

Remaining Challenges

Remaining Challenges:

- The gas diffusion electrode is not optimized for reversible fuel cell operation
  - MPL works for fuel cell, but causes the membrane to dry out in electrolyzer mode
  - Carbon paper is prone to corrosion in electrolyzer mode

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
- 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

Proposed Future Work

- Optimize the 3D junction (C+GO+N) in electrospun BPM for RFC
- Exchange the AEM layer in electrospun BPM from I^- to OH^- by in-situ conditioning in electrolyzer
- Test durability and performance under reversible operation in repeated cycles

End of project milestone: 3/31/20

- Demonstrate >1 A/cm^2 in both fuel cell and electrolysis mode using BPM RFC approach
  - Achieved 1 A/cm^2 in electrolysis mode but only 550 mA/cm^2 in fuel cell mode.

This project ended 3/31/20

Technology Transfer Activities

- We are responding to FOAs that use BPMs for other applications, such as CO_2 electrolyzers and electrodialysis.
- We are in discussions with companies with a potential for funding 3D electrospun BPMs for water and energy applications

Summary

- We are able to make electrospun BPMs with 3D junction showing high performance and high durability in electrolysis mode
- We were not able to condition BPMs (exchanging to H^+/OH^- ionic form) due to the fast corrosion of carbon paper in electrolysis mode. This prevented us from testing the commercial BPM or electrospun BPM in fuel cell mode.
- A 2D BPM with carbon in the junction was optimized for fuel cell operation.
- We are able to achieve 550 mA/cm^2 in fuel cell mode and 1000 mA/cm^2 in electrolysis mode with the same 2D BPM
- Future work
  - Optimizing the 3D junction of electrospun BPM for RFC
  - Optimizing the electrode and hardware for continuous RFC operation

Thank You

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NREL/PR-5900--76878

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