NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Bipolar Membrane Development to Enable Regenerative FCs

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National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

Project ID #: fc182

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline and Budget

- Project start date: 01/01/18
- FY18 planned DOE funding: $150k
- Total DOE funds received to date: $200k

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

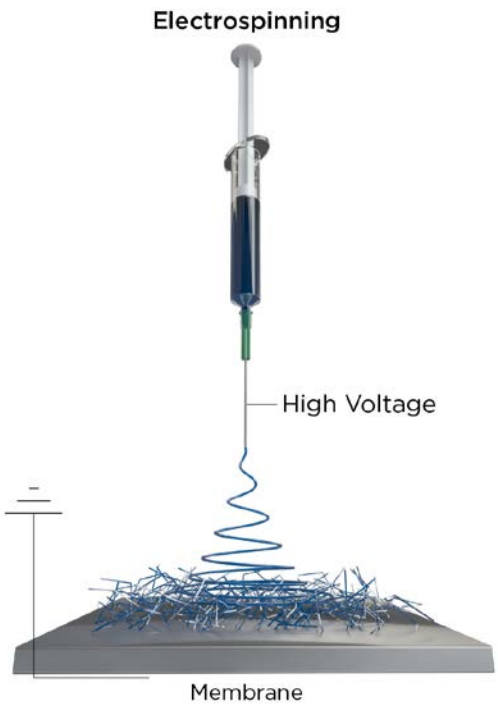
Relevance

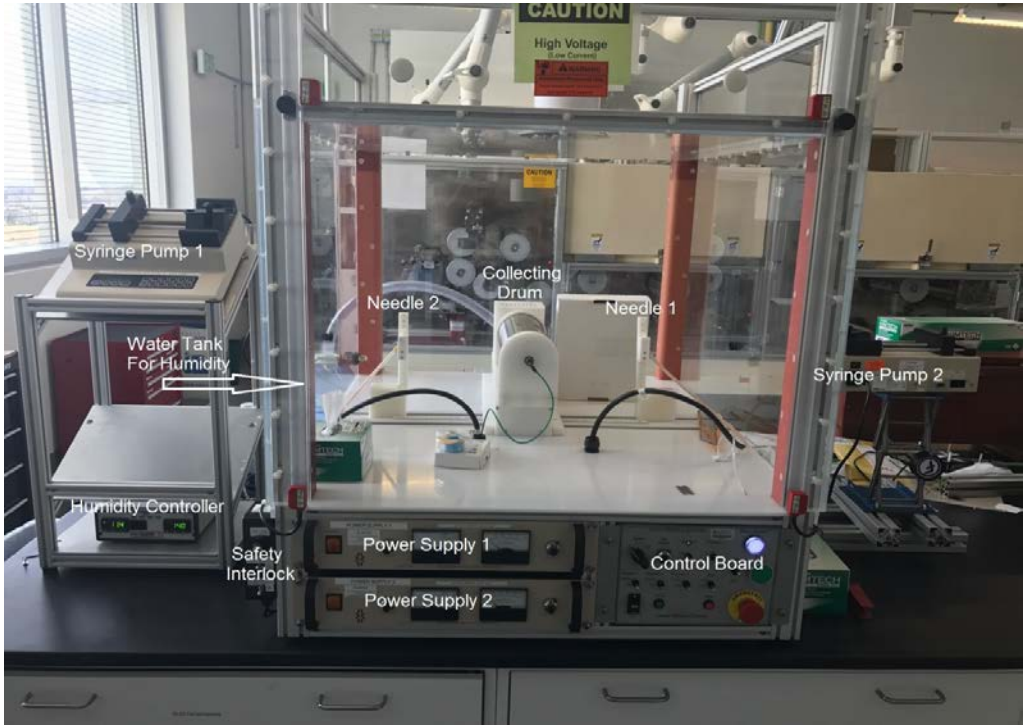
- This project is directly addresses DOE FCTO's interest in developing Reversible Fuel Cells
- The following section is from the FCTO's Multi-Year Research Development & Demonstration (MYRD&D) plan, Section 3.4.4 *Technical Challenges*
  - *"Reversible Fuel Cells:* Reversible fuel cells are of interest 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."
- There are no codified technical targets in the MYRD&D specific to reversible fuel cells

Relevance

- Objectives
  - 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 RFC MEA.
  - Our initial focus will be on fabricating and optimizing the electrospun junction in a BPM with available materials (leveraging ongoing AEM development), and obtaining BPM device data in both fuel cell and electrolysis mode individually.
  - While electrode architecture/composition may have to be optimized or 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 the described electrospun junction morphology for subsequent 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 would 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





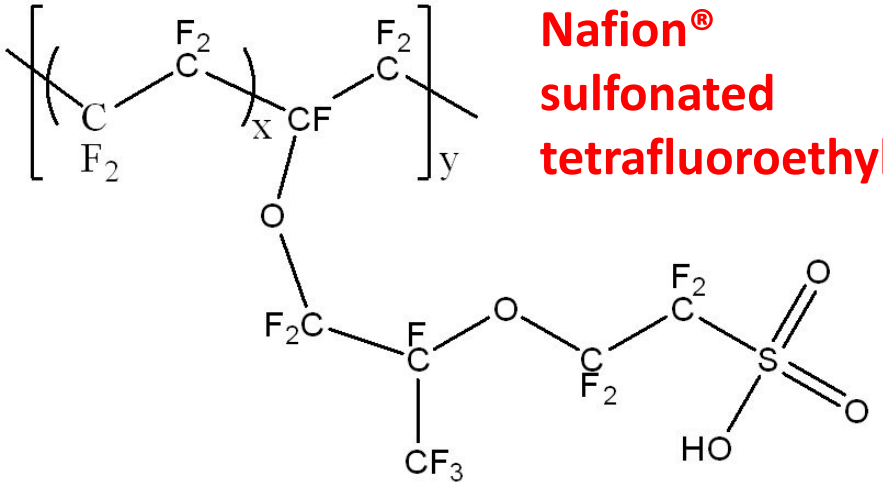
Electrospinning

- 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 CEM/AEM fibers**

Approach

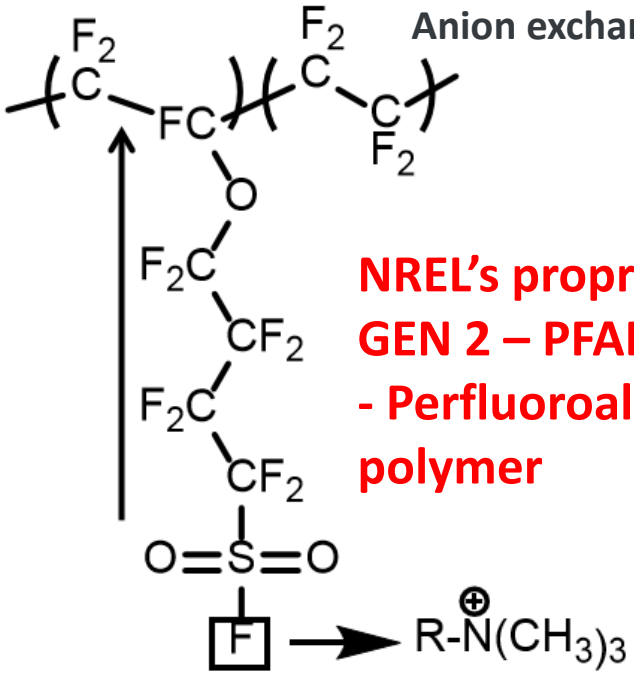
Chemistry

Cation exchange: H^+



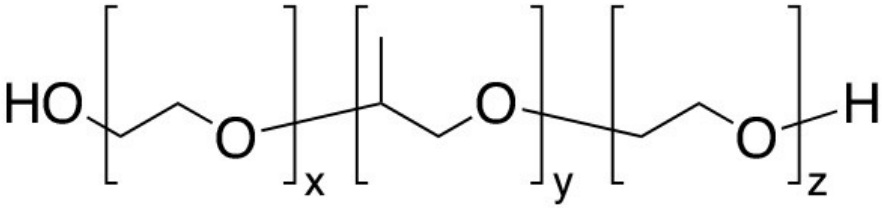
Nafion® sulfonated tetrafluoroethylene

Anion exchange: OH^-



NREL's proprietary GEN 2 – PFAEM - Perfluoroalkyl polymer

Carrier polymer

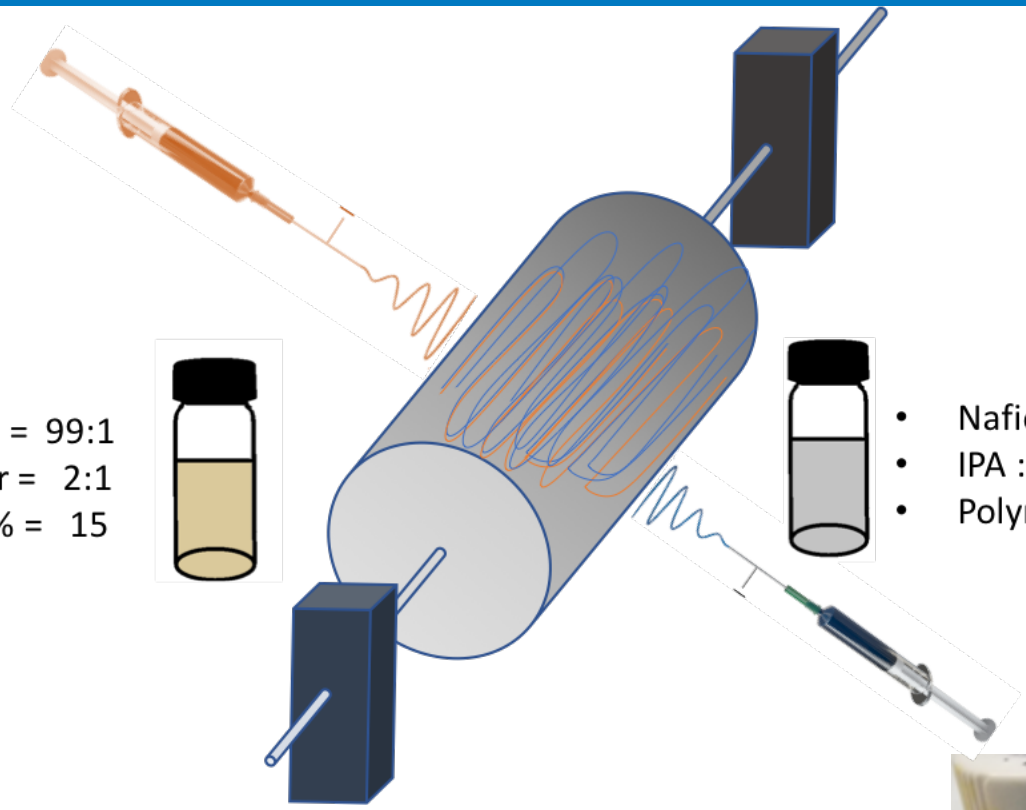


Polyethylene oxide (PEO)

- 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

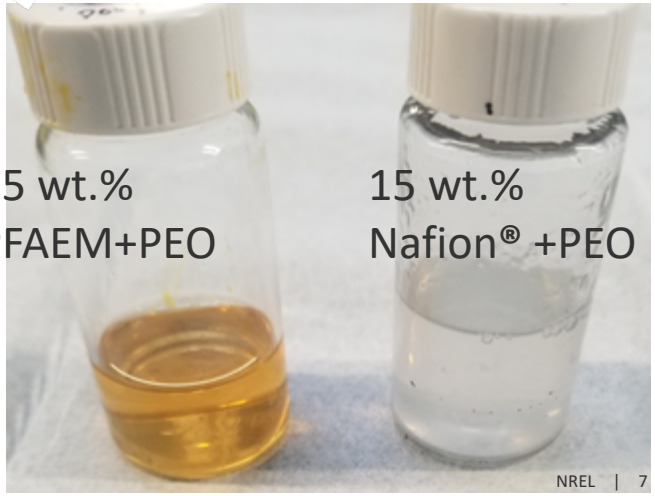
Approach



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

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

- Polymer dispersions electrospun concurrently on programmable, rotating, translating drum
- Substrate attached to drum
  - Glass, membrane, conductive carbon tape, TEM grid, etc.



Approach

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.	3/31/2018	Quarterly Progress Measure (Regular)	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 mWcm^2.	Demonstrate ASR ≤0.2 Ω cm^2 of BPM in fuel cell tests.	9/31/2018	Quarterly Progress Measure (Regular)	On-track
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.	Establish capability to achieve >500 mA/cm^2 in both fuel cell and electrolysis mode using BPM RFC approach	12/31/2018	Annual Milestone (Regular)	On-track

Go/No-Go

Go/No-Go Description	Criteria	Date
BPM RFC performance	Establish capability to achieve >500 mA/cm^2 in both fuel cell and electrolysis mode using BPM RFC approach	12/31/2018

Accomplishments and Progress

- Synthesized several bipolar membranes (BPM) composed of interpenetrating Nafion®/Perfluoroalkyl polymer fibers
- Preliminary depositions were on glass substrates

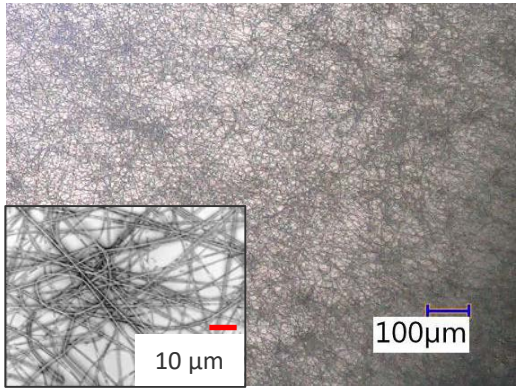
Bipolar Membrane 1 (Sk3a)	Bipolar Membrane 2 (Sk3b)	Bipolar Membrane 3 (Sk3b)
• Distance = 6 cm	• Distance = 6 cm	• Distance = 6 cm
• Duration = 20 min at 0.2 ml/hr	• Duration = 20 min at 0.2 ml/hr	• Duration = 20 min at 0.2 ml/hr
• **Humidity = 25%**	• **Humidity = 25%**	• **Humidity = 30%**
• **Potential = 10 kV**	• **Potential = 5 kV**	• **Potential = 10 kV**

Accomplishments and Progress

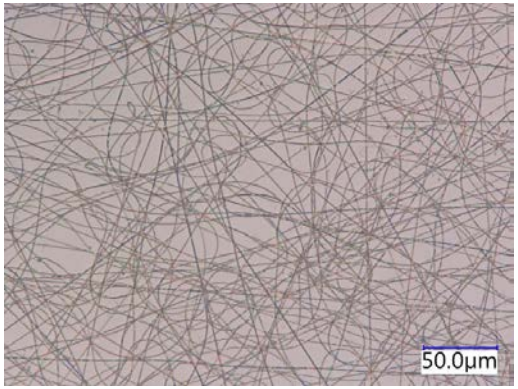
- Characterized electrospun films
  - Nafion® only, PFAEM only, three BPMs
  - Optical microscopy
    - Morphology
  - Scanning electron microscopy (SEM)
    - Morphology
  - Energy dispersive x-ray spectroscopy (EDS)
    - Elemental compositions
    - Estimate Nafion® /PFAEM fractions

Optical microscopy

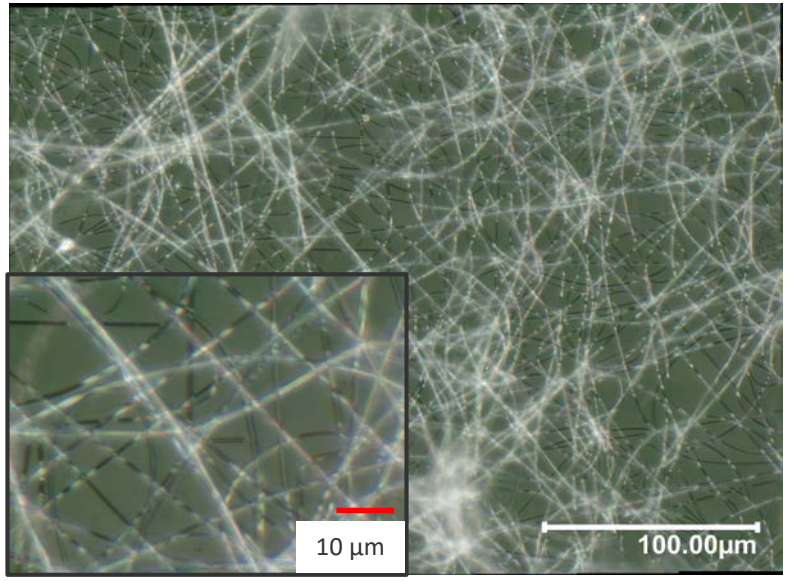
Nafion®



PFAEM



Sk2 PFAEM (10kV-20RH)

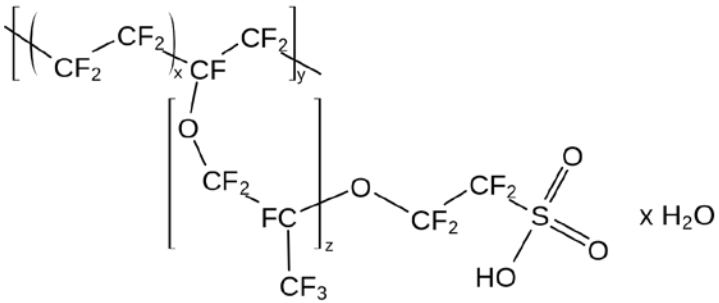


Accomplishments and Progress

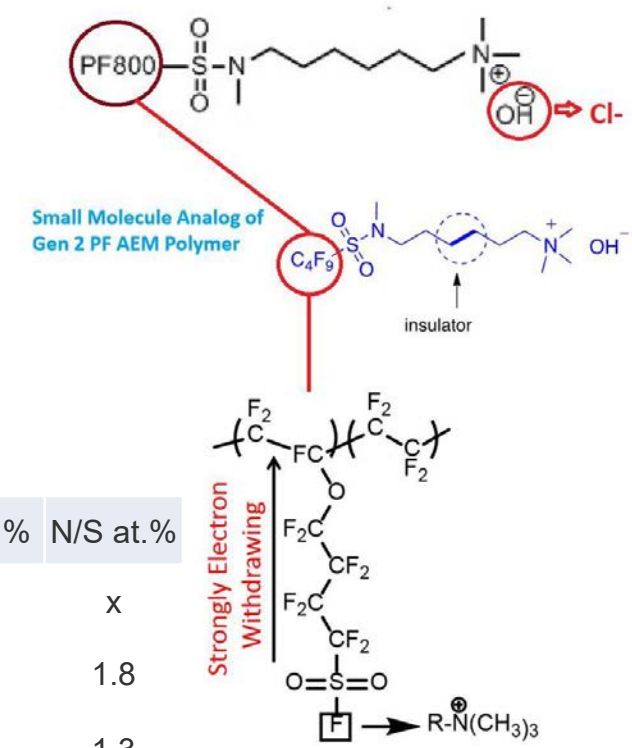
SEM and EDS on electrospun membranes at Colorado School of Mines

- Samples scraped on to conductive carbon tape
- 60-second EDS scans (5 keV) taken at 3 different regions for each mixed polymer with the corresponding elemental ratios of interest
- Some scans had regions with increased carbon tape contributions in the C ratios and are not ideal for showing meaningful comparisons

Sk1: Nafion®



Sk2: PFAEM



Averages	conditions	F/S at.%	F/N at.%	F/C* at.%	N/S at.%
Sk1: Nafion	6cm-10kV-20RH	63.4	x	4.1	x
Sk2: PFAM	6cm-10kV-20RH	35.6	20.0	3.4	1.8
Sk3a: Mixed	6cm-10kV-25RH	30.0	24.6	3.2	1.3

C* affected by carbon tape

EDS to evaluate Nafion®/PFAEM fractions in BPMs

Nafion®

- One S atom per repeating unit
- No N atoms

PFAEM

- One S atom per repeating unit
- Two N atoms per repeating unit
- N/S at. should be 2

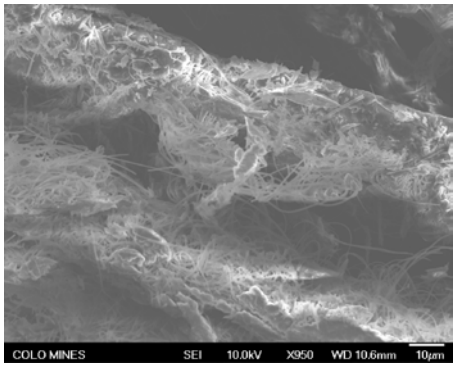
BPMs

- N/S should be a proxy for relative polymer ratios
- N/S of 1.3 for Sk3a is close to 1 which would indicate a 50%:50% mix

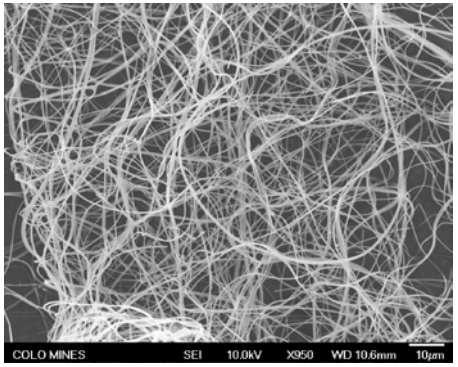
Accomplishments and Progress

SEM of fibers scraped on to conductive carbon tape

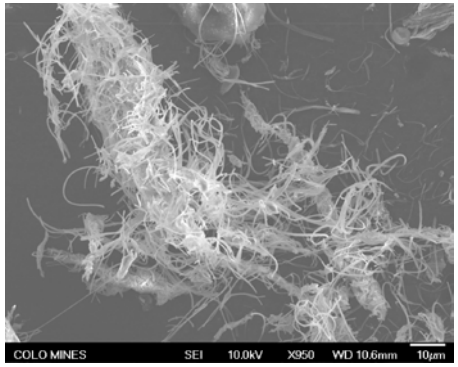
Sk1
Nafion® fibers on carbon tape



Sk2
PFAEM fibers on carbon tape



Sk3a
PFAEM + Nafion® fibers on carbon tape



Sk1 Nafion® (10kV-20RH) EDS Ratios

Area	C*/S at%	F/S at%	F/C* at%
1	21.1	71.7	3.4
2	10.5	53.3	5.1
3	17.7	65.2	3.7
Averages	16.4	63.4	4.1
Sample SD	5.4	9.4	0.9

C* affected by carbon tape

Sk2 PFAEM (10kV-20RH) EDS Ratios

Area	C*/S at%	F/S at%	F/N at%	F/C *at%	N/S at%
1	7.3	32.9	22.5	4.5	1.5
2	9.9	39.3	19.8	4.0	2.0
3	14.2	42.2	19.4	3.0	2.2
4	12.0	28.0	18.4	2.3	1.5
Averages	10.8	35.6	20.0	3.4	1.8
Sample SD	3.0	6.4	1.8	1.0	0.4

Sk3a PFAEM+ Nafion® (10kV-25RH) EDS Ratios

Area	C/S at%	F/S at%	F/N at%	F/C at%	N/S at%
1	8.2	25.2	27.0	3.1	0.9
2	6.8	26.8	26.2	3.9	1.0
3	14.1	37.9	20.6	2.7	1.8
Averages	9.7	30.0	24.6	3.2	1.3
Sample SD	3.9	6.9	3.5	0.6	0.5

EDS results vary significantly from different areas sampled within the same membrane

Accomplishments and Progress

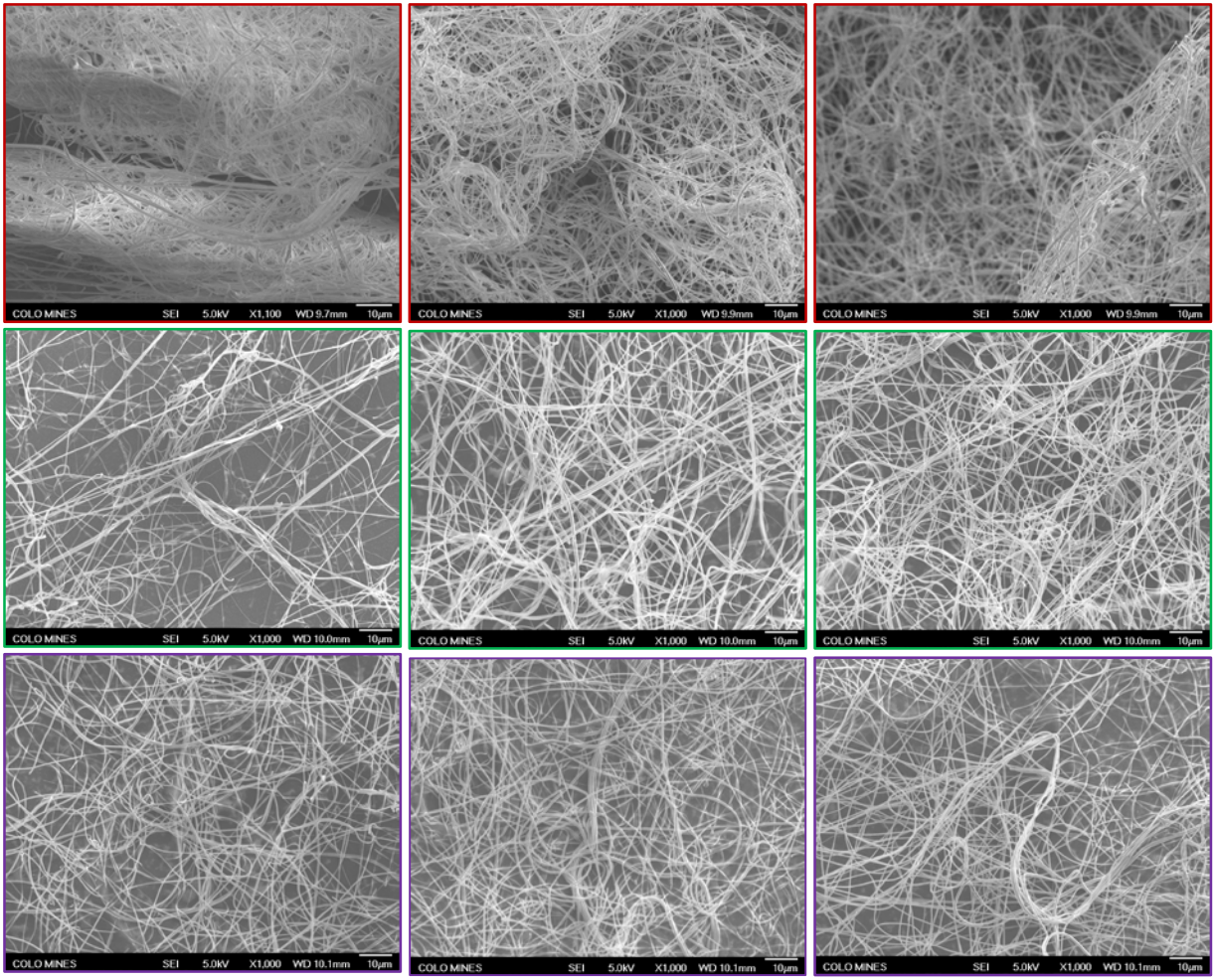
Ideally N/S =

- 2 for PFAEM
- 0 for Nafion®
- 1 for 1:1 mixture

N/S > 2 for Sk3b and Sk3c suggest EDS is not appropriate technique for evaluating polymer ratios

Unstained Mixed Fibers: SEM image at x1k magnification and corresponding EDS Ratios

Area 1 Area 2 Area 3



Sk3a PFAEM+ Nafion® (10kV-25RH)

Area	C/S at%	F/S at%	F/N at%	F/C at%	N/S at%
1	8.2	25.2	27.0	3.1	0.9
2	6.8	26.8	26.2	3.9	1.0
3	14.1	37.9	20.6	2.7	1.8
Averages	9.7	30.0	24.6	3.2	1.3
Sample SD	3.9	6.9	3.5	0.6	0.5

Sk3b PFAEM + Nafion® (10kV-30RH)

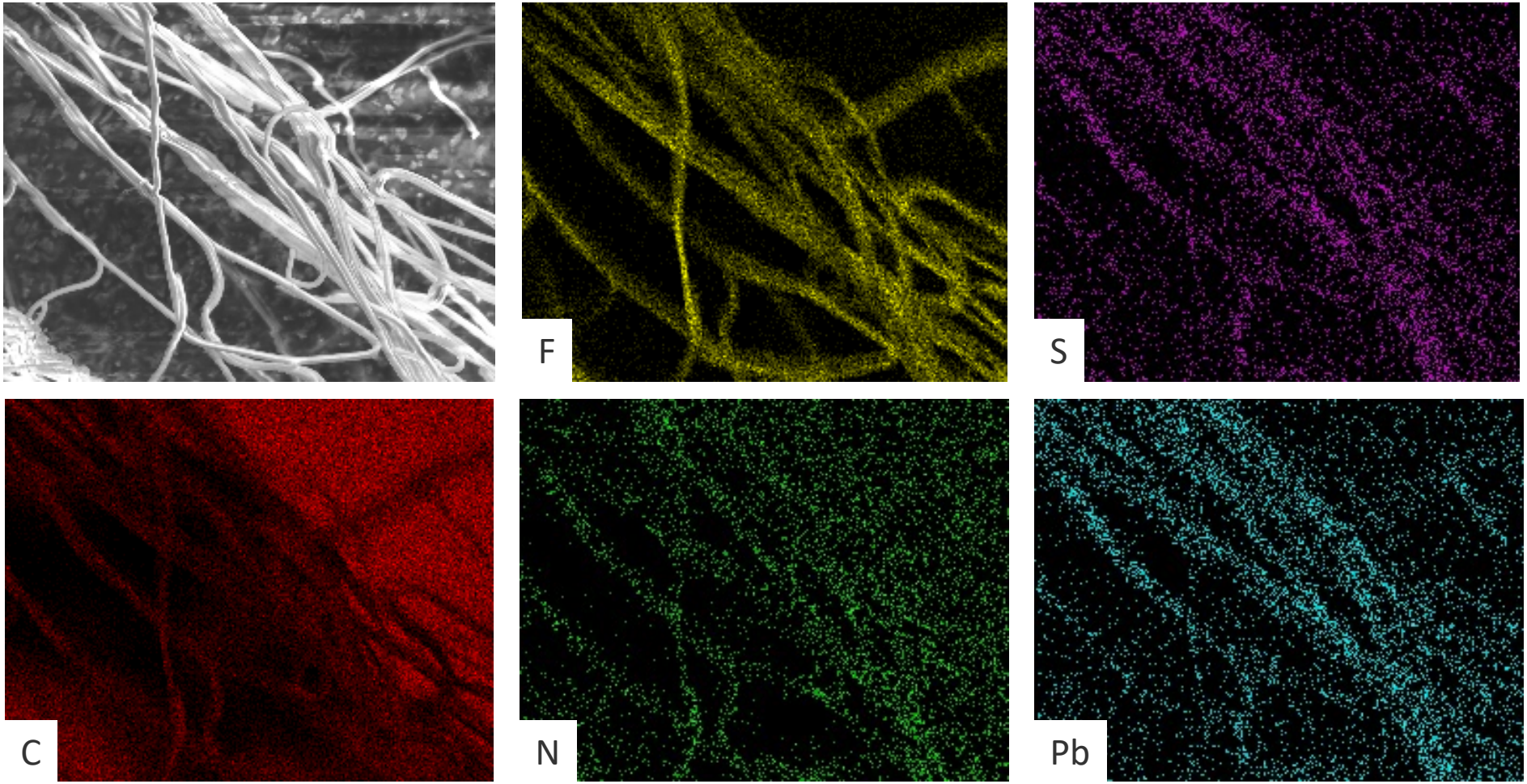
Area	C/S at%	F/S at%	F/N at%	F/C at%	N/S at%
1	71.8	60.1	10.3	0.8	5.8
2	45.9	68.7	15.7	1.5	4.4
3	38.5	67.5	18.6	1.8	3.6
Averages	52.1	65.5	14.9	1.4	4.6
Sample SD	17.5	4.6	4.2	0.5	1.1

Sk3c PFAEM + Nafion® (5kV-25RH)

Area	C/S at%	F/S at%	F/N at%	F/C at%	N/S at%
1	46.0	36.7	9.5	0.8	3.9
2	38.5	42.2	15.0	1.1	2.8
3	38.3	36.8	10.4	1.0	3.5
Averages	40.9	38.6	11.6	1.0	3.4
Sample SD	4.4	3.1	2.9	0.1	0.5

Accomplishments and Progress

Lead acetate stained mixed fiber Sk3a PFAEM + Nafion® (10kV-25RH) SEM/EDS maps at x2500 magnification
Samples on conductive carbon tape

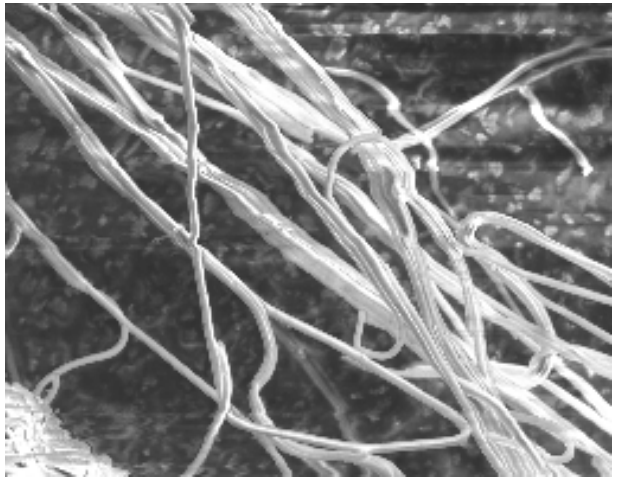


EDS mapping to track N in PFAEM and Pb^{2+} to track H^{+} in Nafion®

<u>Results are inconclusive</u>

Accomplishments and Progress

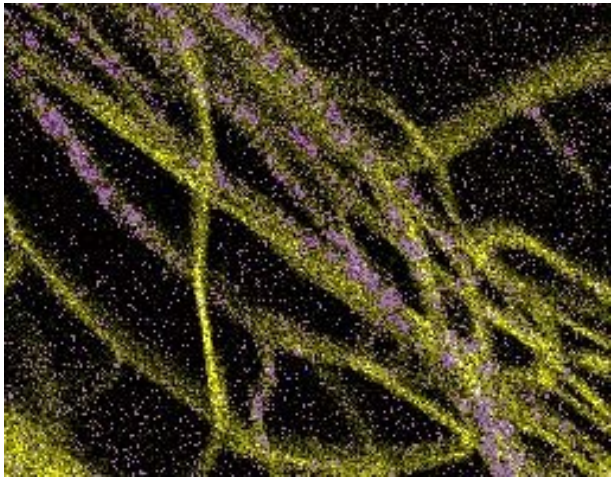
Lead stained mixed fiber Sk3a PFAEM + Nafion® (10kV-25RH) SEM/EDS maps at x2500 magnification



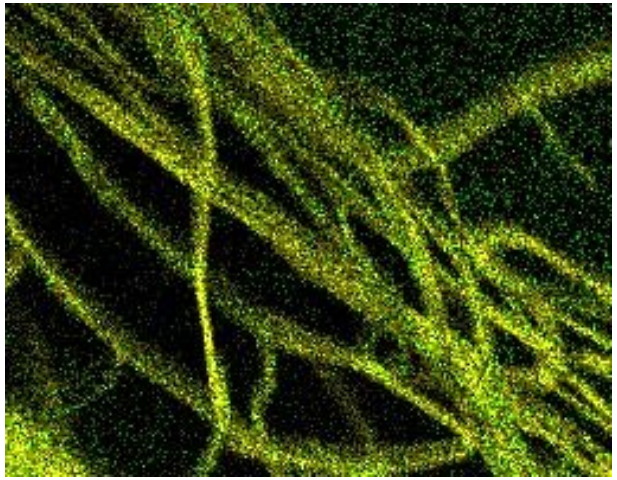
Samples on conductive carbon tape

**elemental overlays were obtained using image j software*

F-S map of mixed fiber



F-N map of mixed fiber



F-S-N map of mixed fiber

EDS mapping to track N in PFAEM and Pb^{2+} to track H^{+} in Nafion®

<u>Results are inconclusive</u>

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
- 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

- Identify appropriate technique for BPM optical/chemical characterization
  - Scanning transmission electron microscopy (STEM) coupled with EDS
  - Stain one fiber precursor solution
- MEA fabrication and testing
  - Turning spaghetti pile of nanofibers into functional MEA might pose challenges
- Introduction of water dissociation catalyst to reduce interfacial resistance

Proposed Future Work

- For the remainder of FY18
  - Continue electrospun junction synthesis tuning deposition parameters based on feedback from characterizations
  - Bipolar membrane characterization
  - MEA testing and optimization
  - Demonstrate stability and high fuel cell/electrolysis performance at high operating temperatures
- Key Year 1 Go/No-Go decision: 12/31/18
  - Establish capability to achieve >500 mA/cm^2 in both fuel cell and electrolysis mode using BPM RFC approach
- FY19
  - 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

Technology Transfer Activities

- Technology-to-market plans: develop technology to a sufficiently advanced level to introduce to market
- Plans for future funding: engaging academic and corporate sector entities to partner on upcoming FOAs
- Potential for generating IP while developing new membrane architectures

Summary

- This project is in its very early stages
- We are able to electrospin Nafion®, PFAEM, and membranes composed of a mixture of the two
- We characterized an initial set of membranes
- 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

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Technical Back-Up Slides