School of Engineering

Composite PEMs from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s

Ryszard Wycisk (P.I.)
Vanderbilt University

DOE project award # EE0008435

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DOE Hydrogen Program
2021 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID
FC310

Project Goal

Fabricate an electrospun composite all-hydrocarbon membrane and demonstrate its superior to PFSA membranes fuel cell performance.

- The membrane will exhibit excellent low RH proton conductivity and fuel cell durability, with fabrication cost competitive compared to that of PFSA membranes. It should also meet all 2020 FCTO MYRDD technical targets.

- Potential scale-up of the proposed composite membrane technology can significantly affect the automotive fuel cell industry by boosting the fuel cell power output and simplification of the cell hydration system, and can also have a positive environmental impact, by elimination of PFSA-based ionomers, which are known to release dangerous fluorides upon degradation.

Project Overview

Timeline

- Project Start Date: 1/9/19
- Project End Date: 11/31/21 (extended)
- Percent Complete: 70%

Barriers

- High cost of PFSA membranes
- Low proton conductivity at reduced humidity (water partial pressure)
- Performance drop above 80^oC

Budget

- Total Project Budget: $752,049
  - Total Recipient Share: $152,049
  - Total Federal Share: $600,000
  - Total Recipient Funds Spent*: $148,205
  - Total Federal Funds Spent*: $516,995

  (*as of 3/31/21)

Targets

- Cost < $20/m^2
- Operating temperature up to 120^oC
- Max H_2 and O_2 crossover ≤ 2 mA/cm^2
- ASR at 30°C and H_2O partial pressures up to 4 kPa - 0.3 Ohm·cm^2
- ASR at 80°C and H_2O partial pressure 25-45 kPa - 0.02 Ohm·cm^2
- Mechanical durability - 20,000 cycles, Chemical durability > 500 hours

Partners

Project Lead: Ryszard Wycisk (PI, Vanderbilt University)

Peter N. Pintauro (Co-PI, Vanderbilt University)

Mohammad Masem Hossain (Post-doctoral scholar, Vanderbilt University)

Zhihao Shang (Graduate student, Vanderbilt University)

Relevance/Potential Impact

RELEVANCE

*"The Office of Energy Efficiency and Renewable Energy is working to lower the cost and improve the durability of PEM fuel cells. Current R&D activities focus on **improving** electrocatalysts, **membranes** (both for ambient and high-temperature applications), and bipolar plate materials."*

From https://www.hydrogen.energy.gov/fuel_cells.html

This project's objective is to fabricate a **novel electrospun, non-PFSA fuel cell membrane** that can meet all 2020 FCTO MYRDD technical targets.

IMPACT

The project team will make available novel PEMs with characteristics competitive to PFSA PEMs (better low RH performance and higher operating temperature – which are very desired for application in automotive FCs).

Approach

- The overarching project's objective is to apply the highly conductive, rigid-rod poly(phenylenesulfonic acid) non-PFSA ionomers, developed in Prof. Litt's lab at CWRU, for the fabrication of **robust PEMs to be used in automotive FCs**. These ionomers are very brittle and soften at elevated RH and thus require some form of mechanical stabilization, which is developed by the present team.

- The proposed solution is **based on the use of electrospinning**, either through the dual fiber strategy or through pore filling.

- The two **major project tasks** are:

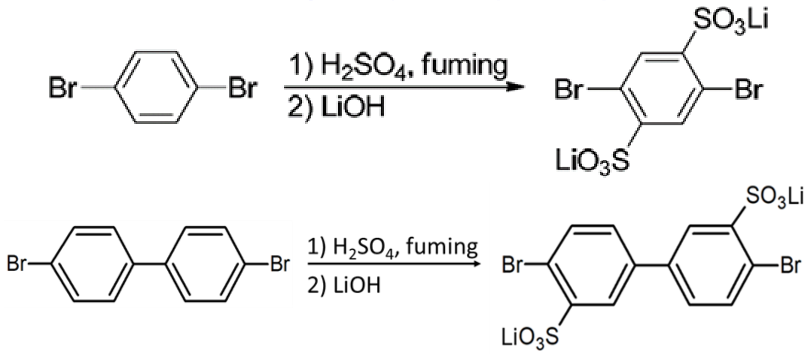
  (**1**) Reproducible **synthesis** of the ionomers with desired characteristics (molecular weight/film forming, conductivity, crosslinkability), and

  (**2**) **Integration** of the ionomer and the mechanical, chemically inert reinforcement into robust, thin membranes.

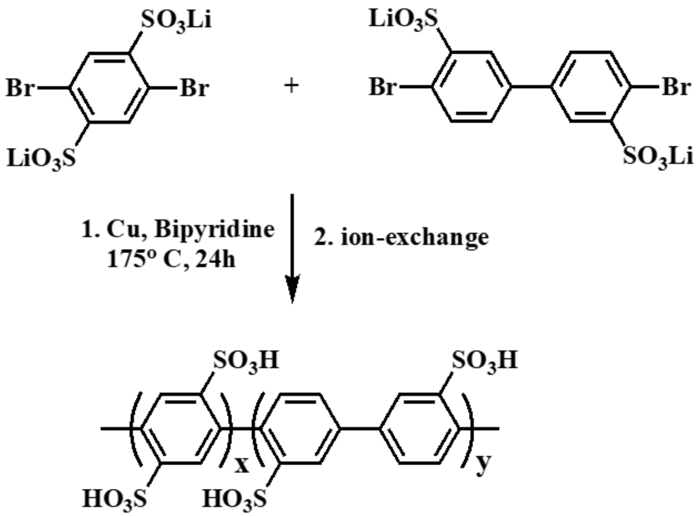
Approach

IONOMER SYNTHESIS

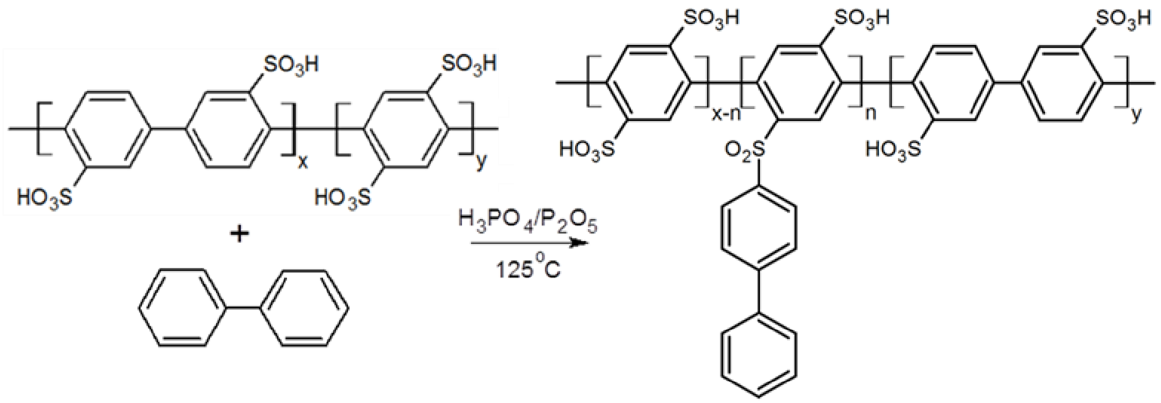
(**a**) Sulfonation of dibromophenylene (DBP) and dibromobiphenylene (DBBP)



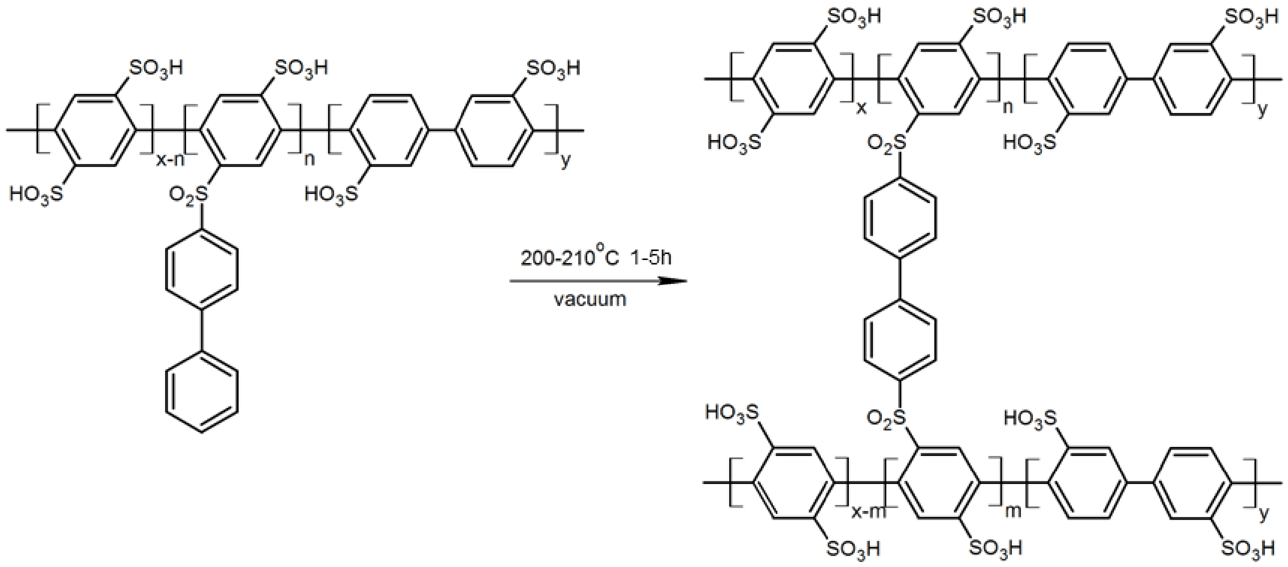
(**b**) Copolymerization (Ullmann coupling) of DBPDSA-Li and DBBPDSA-Li salts



(**c**) Grafting biphenyl (BP) linker via sulfone bridges



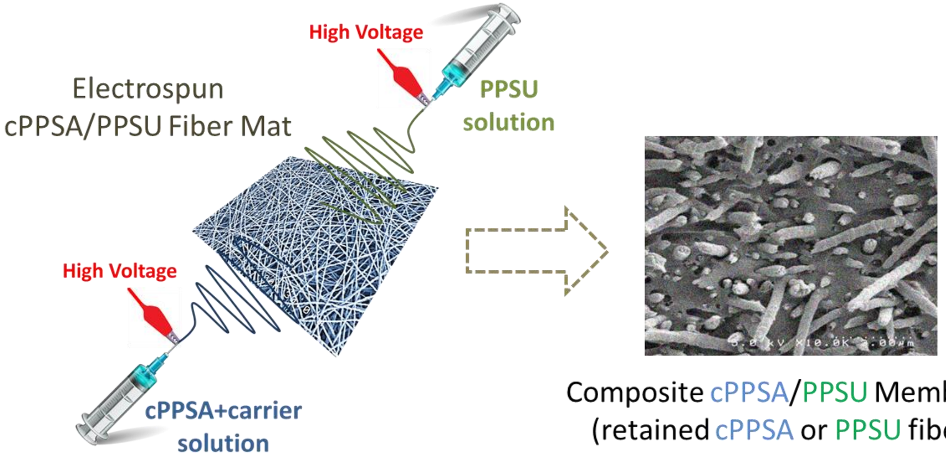
(**d**) Thermal crosslinking if the graft copolymer (cPPSA)



Approach

IONOMER-REINFORCEMENT INTEGRATION

Dual Fiber Electrospinning



Composite cPPSA/PPSU Membrane (retained cPPSA or PPSU fibers)

Co-Electrospinning

1 Spin dual fiber mat, a mixture of **cPPSA** and **PPSU** (reinforcement). Adjust the **PPSU** content to balance proton conductivity and mechanical strength.

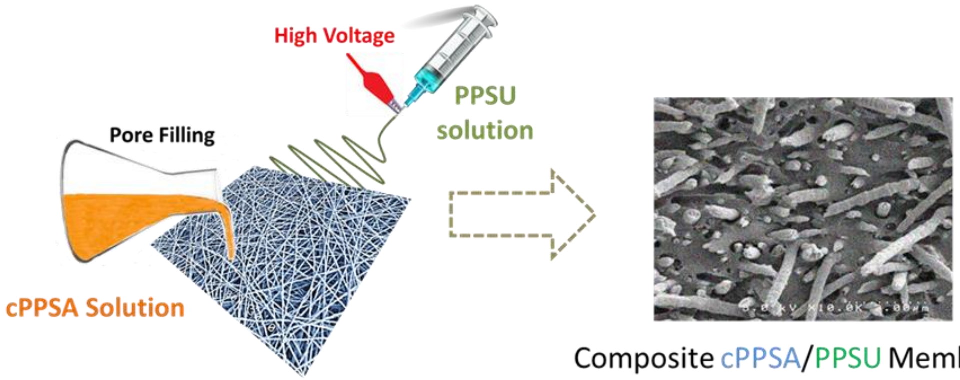
Densification

2 Expose the mat to proper solvent vapor, for fiber softening and then hotpress to obtain dense film.

Crosslinking

3 Heat the dense **cPPSA/PPSU** film at temperature around 200°C to crosslink **cPPSA**.

Pore Filling



Composite cPPSA/PPSU Membrane (retained PPSU fibers)

Scaffold Electrospinning

Spin **PPSU** or **PPSU/PBI** or **PBI** fiber mat. Press and expose to proper solvent vapor to generate interfiber welds and adjust porosity. 1

Pore Filling

Prepare **cPPSA** solution in alcohol mixture. Impregnate the scaffold with the solution. Heat to evaporate the solvent and close the pores with solidified **cPPSA**. 2

Crosslinking

Heat the dense **cPPSA/PPSU** film at temperature around 200°C to crosslink **cPPSA** in the pores. 3

Accomplishments and Progress for Current Reporting Period

Current Reporting Period (BP2) Tasks:

(i) Optimize the composite membrane
(ii) Fabricate MEAs, and
(iii) Perform fuel cell testing

Expected results: *Optimized cPPSA ionomer syntheses (BxPy). Optimized electrospinning conditions, mat densification and membrane composition, to meet the project goal. Fabricated and tested MEAs with selected membrane samples. Demonstrated fuel cell performance comparisons with Nafion 212 and 211 based MEAs.*

Decision point: *Demonstrate superior to Nafion 211 and 212 performance in fuel cell of an MEA with the electrospun or pore-filled composite membrane, including power output and durability (humidity cycling test). Demonstrate meeting the 2020 FCTO MYRDD performance targets.*

Accomplishments and Progress for Current Reporting Period

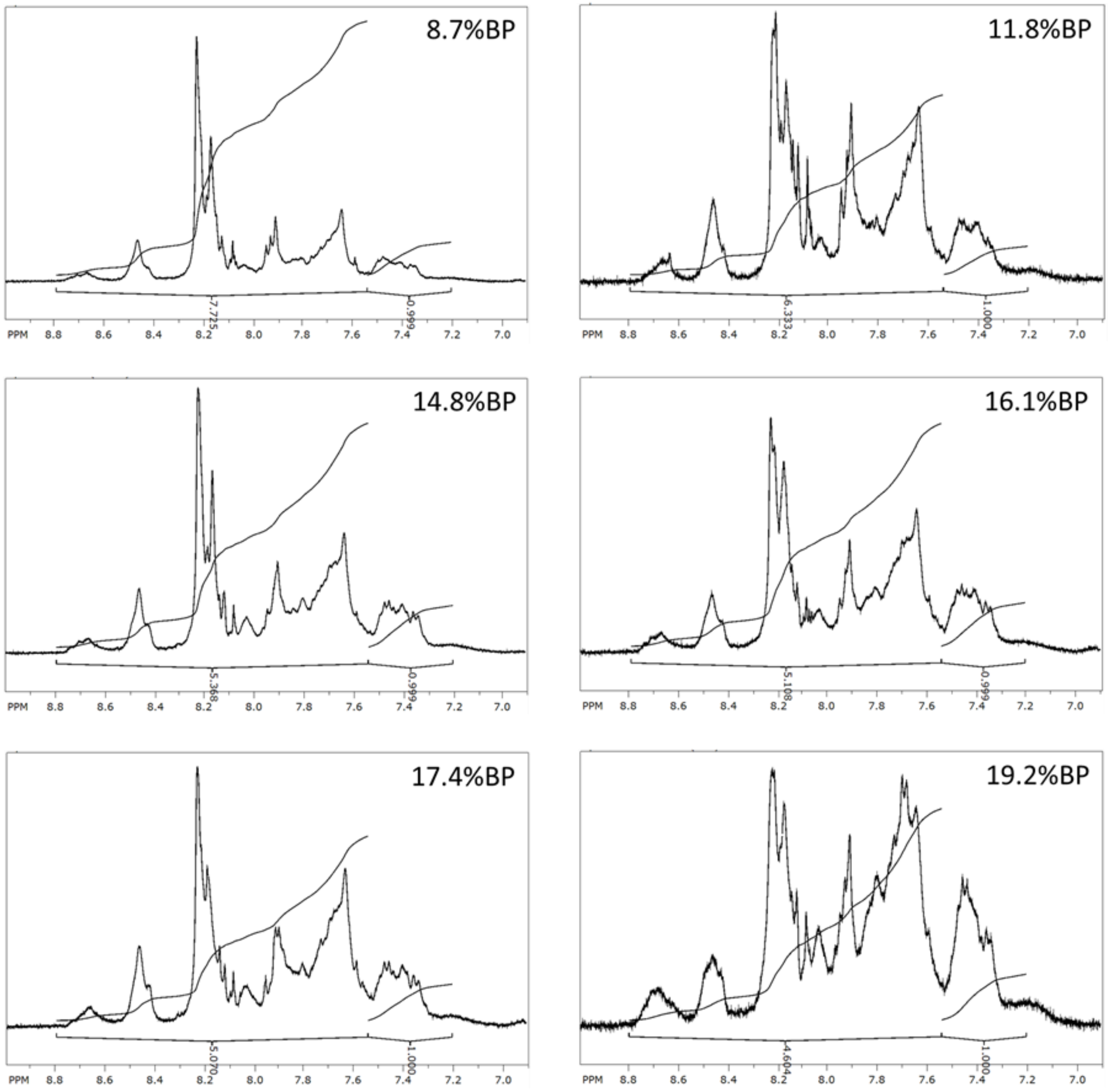
BP2 Milestone Summary Table						
Recipient Name:	Vanderbilt University (PI -Ryszard Wycisk)					
Project Title:	Composite PEMs from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s					
Task No	**Task or Subtask Title**	**Milestone Type**	**Milestone Number**	**Milestone Description (Go/No-Go Decision Criteria)**	**Milestone Verification (What, How, Who, Where)**	**Date (Months)**
5	Optimization of cPPSA composition	Milestone	5	Demonstrate crosslinkable disulfonic acid copolymer with through-plane conductivity > 0.1 S/cm at 80ºC and 40-90%RH	Supporting data available	21
6	Optimization of cPPSA electrospinning	Milestone	6	Report the optimal electrospinning conditions: less than 10% beads and droplets, fiber diameter variability < 50% by ImageJ.	SEM micrographs and supporting data available	24
7	Optimization of membrane composition	Milestone	7	Demonstrate water insoluble 15 µm thick PEM membrane with through-plane conductivity > 0.05 S/cm at 80ºC and 20-90%RH	Supporting data available	28
8	MEA fabrication and testing in H_2/Air fuel cell	Milestone	8	Demonstrate electrospun composite membrane meeting the projected characteristics (2020 FCTO targets)	Photographs and supporting data	35

We have just started working on the last task (Task #8)

Tasks reported in this presentation (Task #5 - #7)

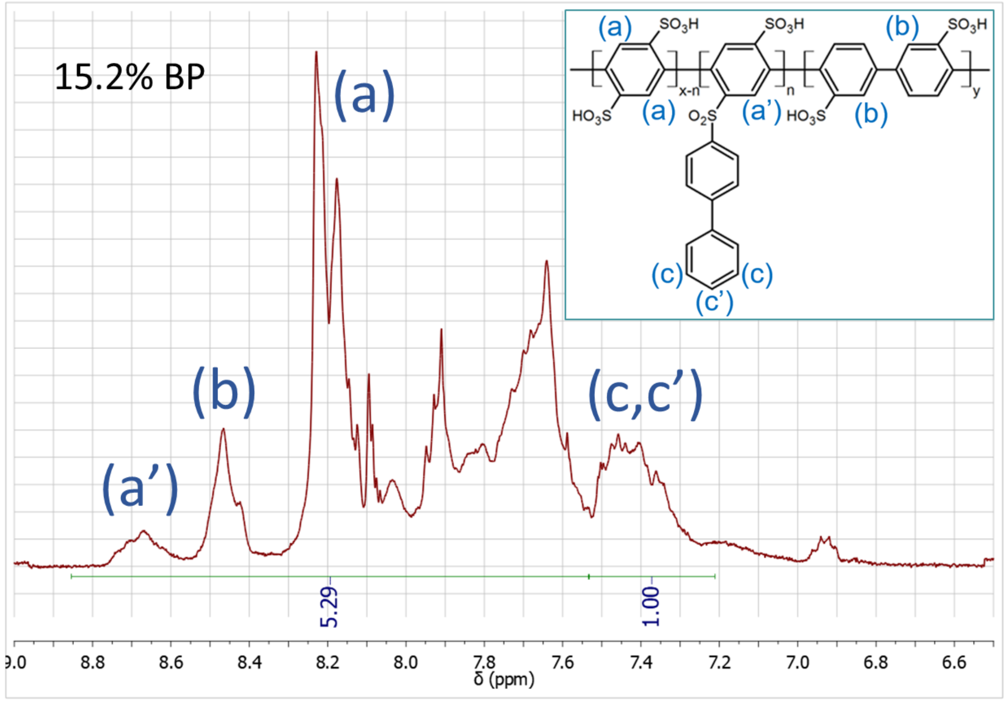
Accomplishments and Progress for Current Reporting Period

Task #5– Optimization of cPPSA Composition



Optimal backbone

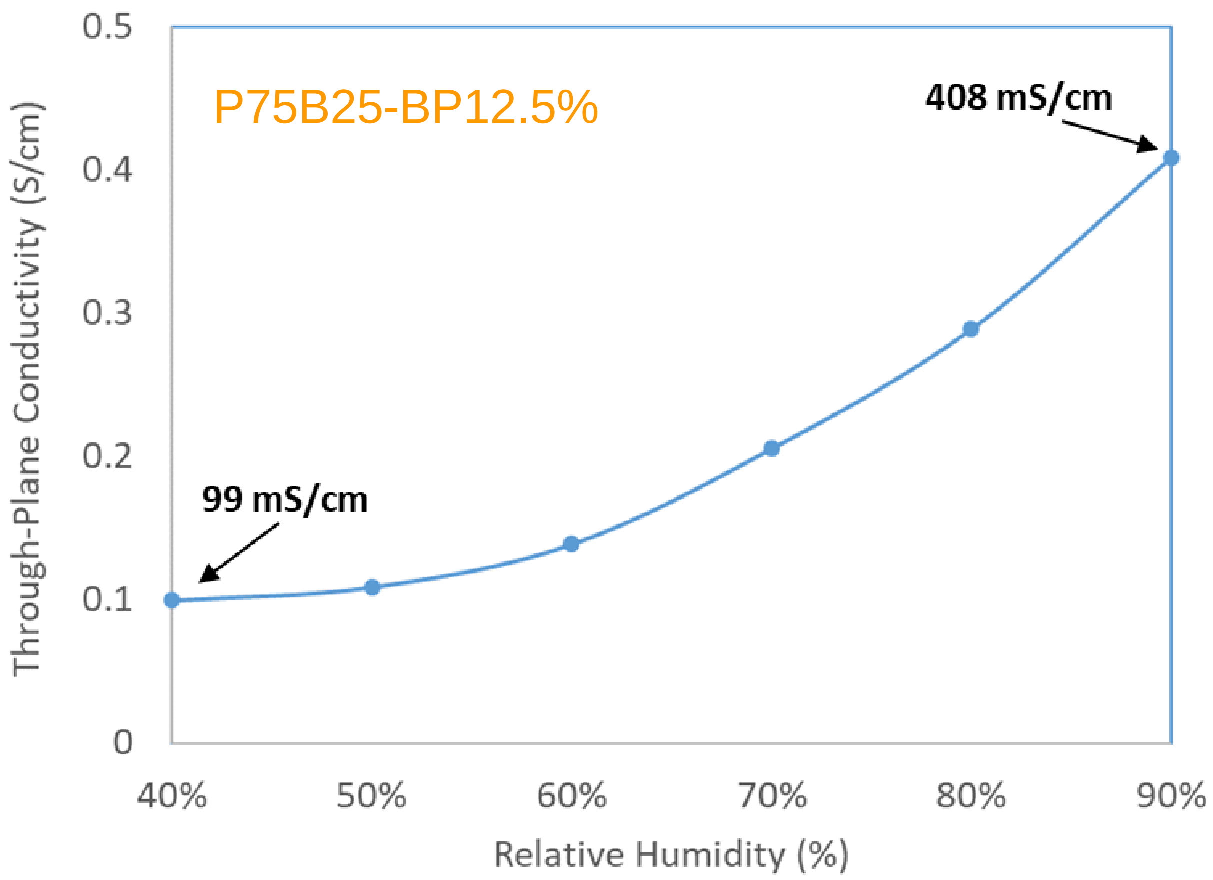
400 MHz ^{1}H NMR spectra of P75B25-g-BP copolymers with varying BP grafting degree (8.7%-19.2%) in CD_3OD



- For effective crosslinking of cPPSA the BP grafting degree should be in the 14%-16% range.
- Blending lower grafting degree batches with higher grafting degree batches also worked well.

Accomplishments and Progress for Current Reporting Period

Task #5– Optimization of cPPSA Composition



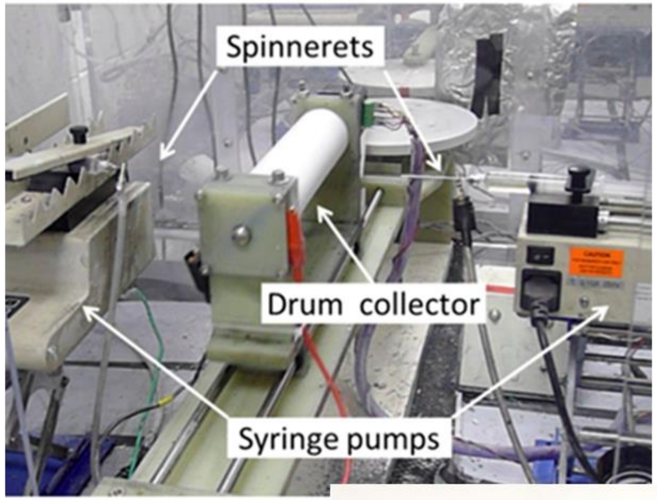
Through-plane conductivity measured with a cPPSA film cast from MeOH, annealed at 210°C for 3h, conditioned in 1MHCl for 20h at room temp, washed with DI water and air-dried.

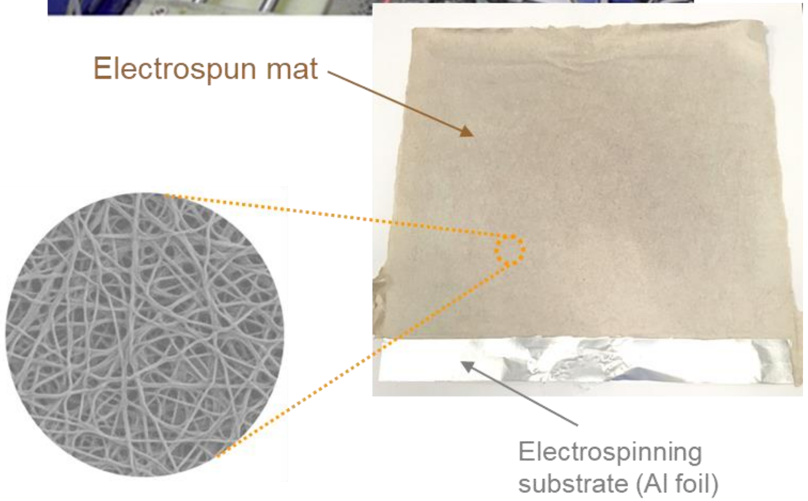
Milestone M5 - Demonstrate crosslinkable disulfonic acid copolymer with **through-plane conductivity > 0.1 S/cm at 80°C and 40-90 %RH**

Demonstrated cPPSA crosslinked film with through-plane conductivity ≥ 0.1 S/cm at 80°C and 40-90 %RH - **missed the condition of "> 0.1 at 40% RH"** ☺.

Accomplishments and Progress for Current Reporting Period

Task #6 – Optimization of cPPSA Electrospinning





Carrier	1MDa PEO	450kDa PAA
Solution concentration	30 wt.%	25 wt.%
Carrier content	5%	6%
Solvent composition	H_2O:IPA=1:1	H_2O:DMSO=3:1
Relative humidity	50%	40%
Voltage	10 kV	10 kV
Tip to drum distance	10 cm	9 cm
Flow rate	0.10 mL/h	0.25 mL/h

Mats from **PPSU**, **PBI**, **PPSU-PBI** blends and **cPPSA/PPSU** (dual fiber) were electrospun. Typically, their dimensions were 15 cm x 15 cm x 20-100 μm with estimated porosity of 80-90%.

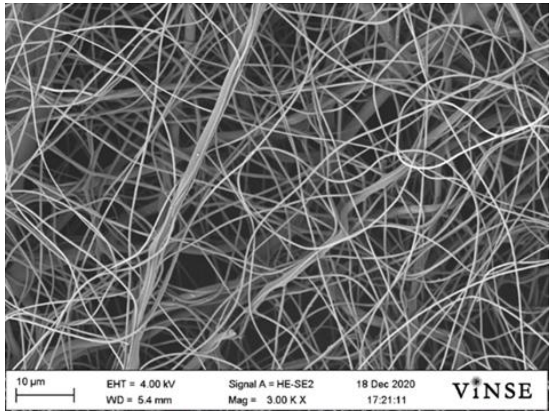
Milestone M6 - Report the optimal electrospinning conditions: **less than 10% beads and droplets**, fiber **diameter variability < 50%** by ImageJ.

Milestone M6 was fully met and conditions for uniform cPPSA fiber electrospinning were identified.

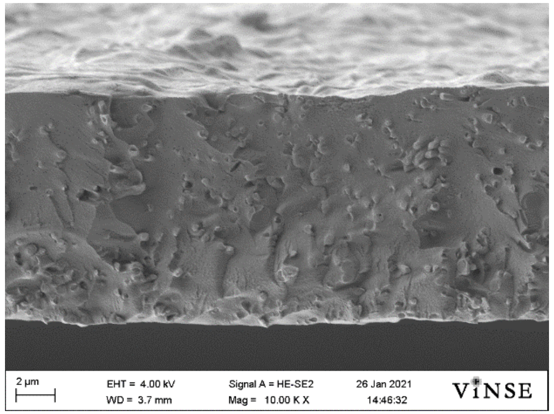
Accomplishments and Progress for Current Reporting Period

Task #7– Optimization of Membrane Composition

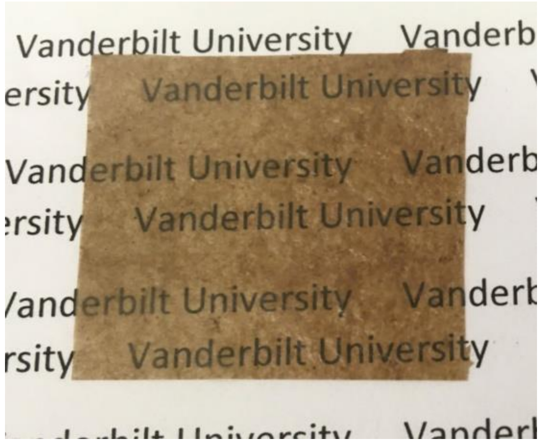
P75B25-BP15%-PBI(15%)



(a) Exposure to MeOH vapor
(b) Hydraulic press
(c) Heating at 205°C for 1h

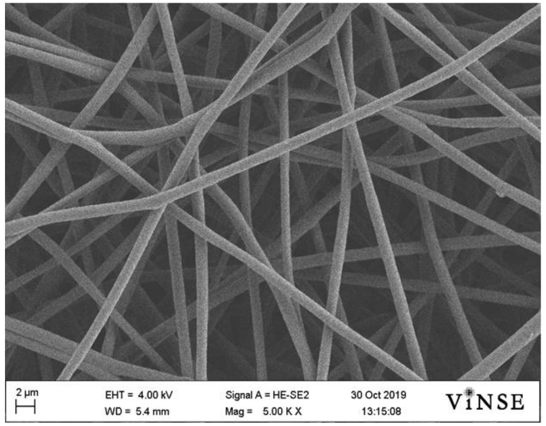


12 µm

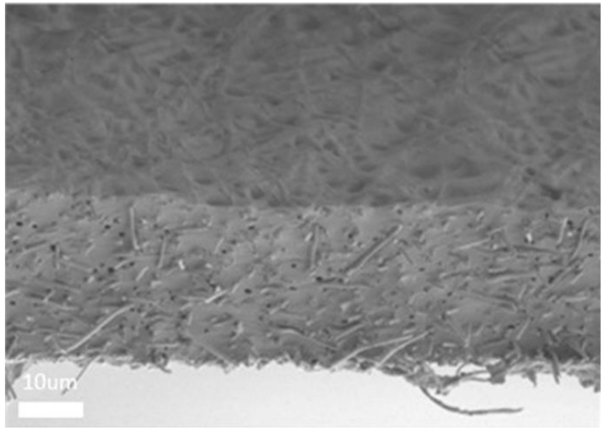


Electrospun dual fiber cPPSA/PBI mat and the composite membrane

P75B25-BP19%-PPSU(15.5%)



(a) 0.05% Poloxamer 407
(b) Sinking-in cPPSA cast film
(c) Heating at 210°C for 3h

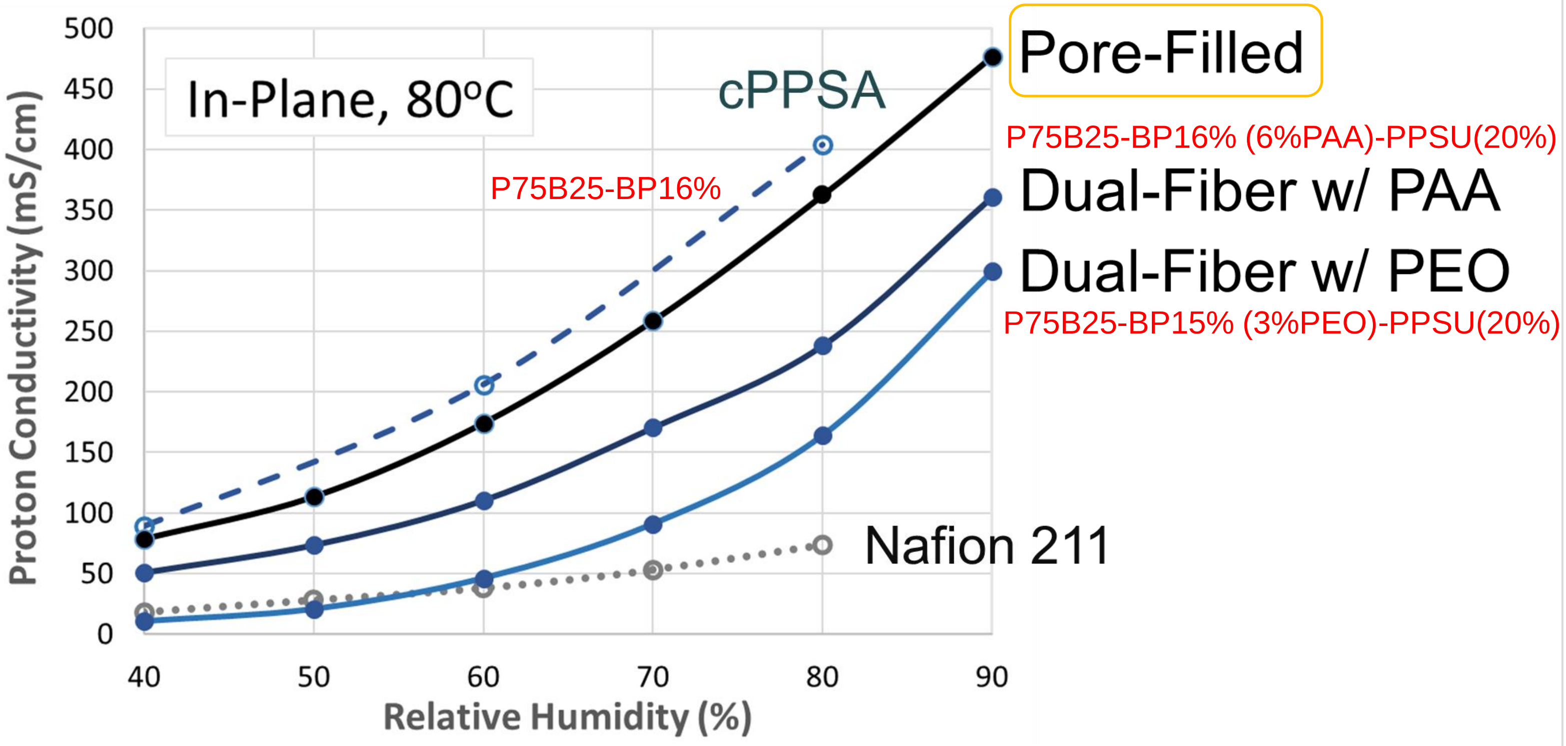


25 µm

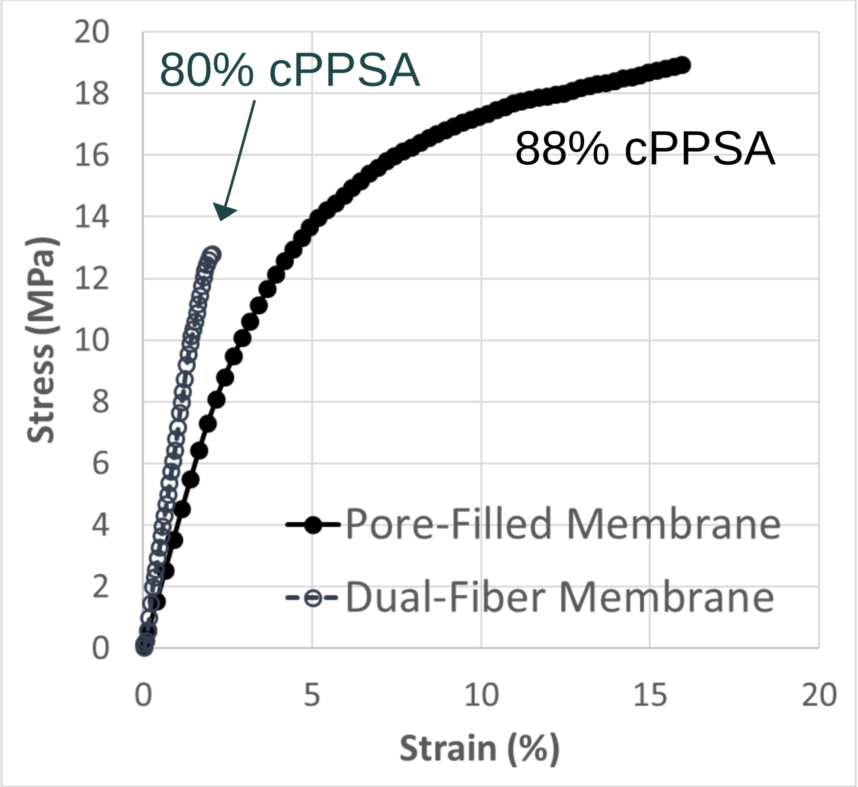
Electrospun PPSU mat and a composite pore-filled cPPSA/PPSU membrane

Accomplishments and Progress for Current Reporting Period

Task #7– Optimization of Membrane Composition



RT, 50%RH

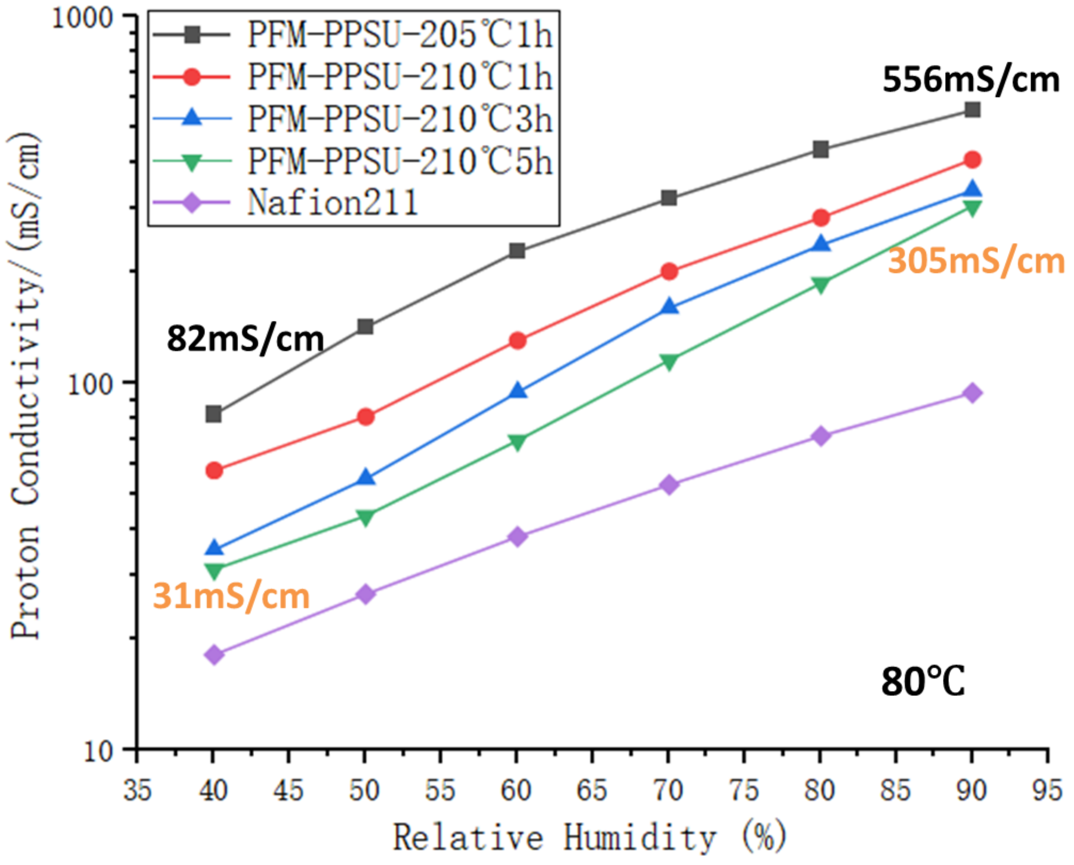


The pore-filled membranes outperformed the dual-fiber membranes in terms of both, proton conductivity and tensile strength.

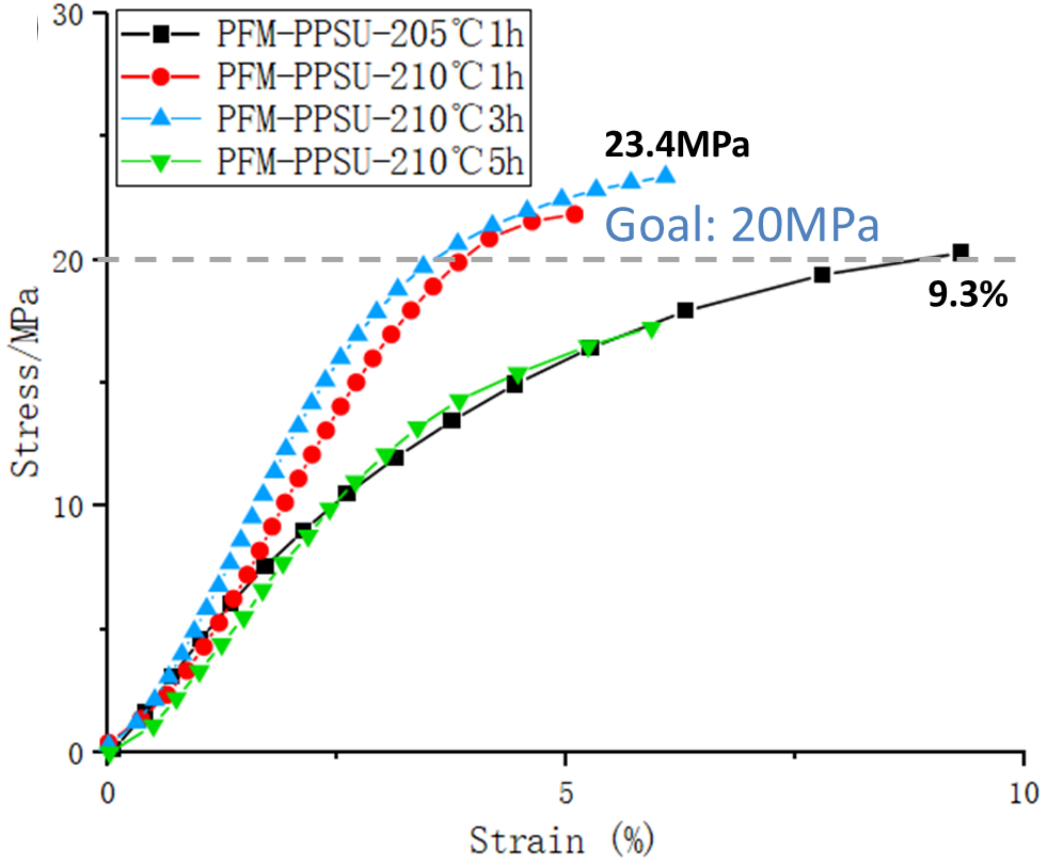
Accomplishments and Progress for Current Reporting Period

Task #7– Optimization of Membrane Composition

P75B25-BP15%-PPSU(15%)



P75B25-BP15%-PPSU(15%)

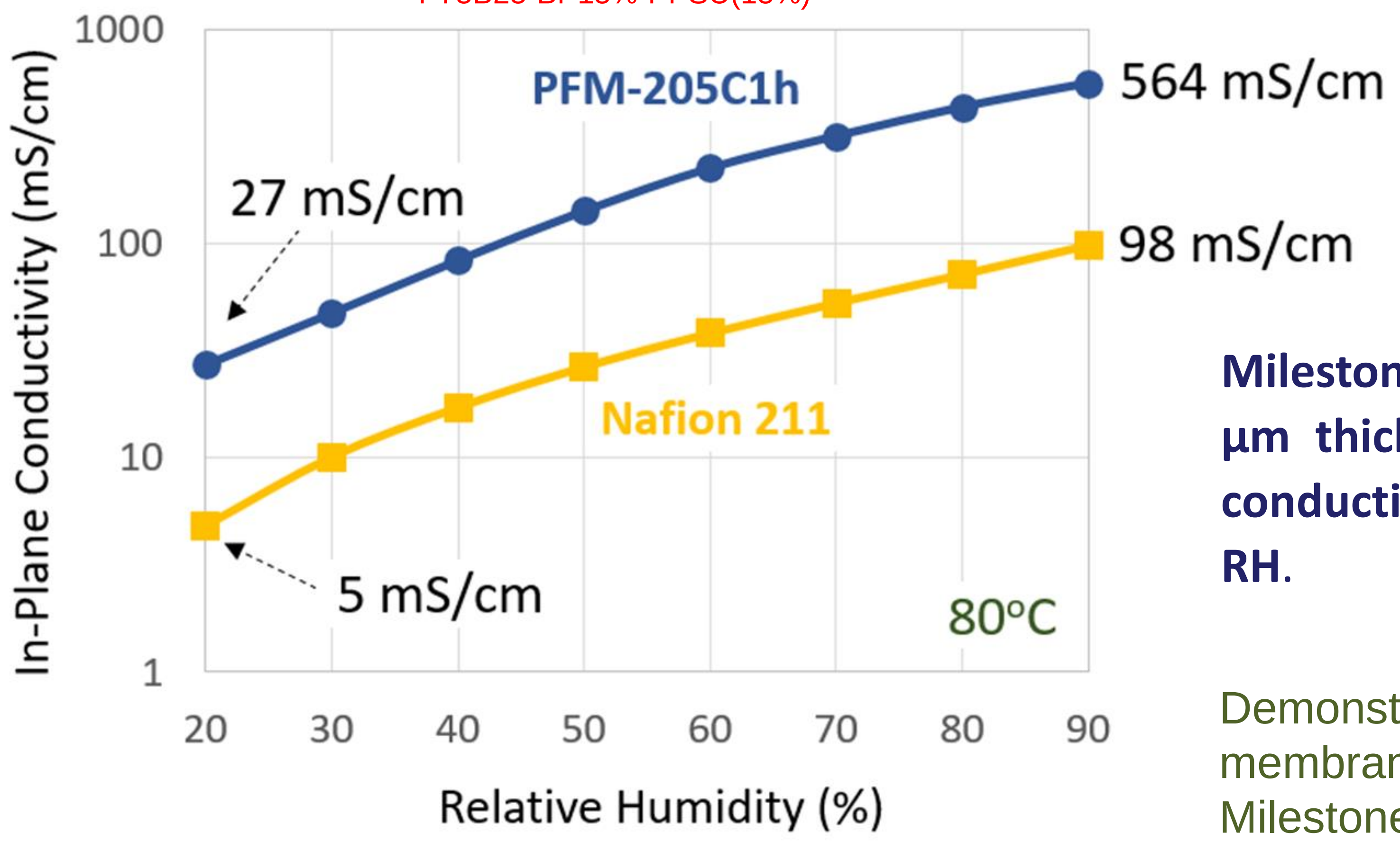


Annealing (cPPSA crosslinking) time and temperature had a significant effect on proton conductivity and tensile strength of the composite pore-filled cPPSA-PPSU membranes.

Accomplishments and Progress for Current Reporting Period

Task #7– Optimization of Membrane Composition

P75B25-BP15%-PPSU(15%)



Milestone M7 - Demonstrate water insoluble **15 µm thick PEM** membrane with through-plane **conductivity > 0.05 S/cm at 80°C and 20-90% RH**.

Demonstrated cPPSA-PPSU pore filled membrane with 0.03 S/cm at 20% RH. M7 Milestone low RH conductivity limit met at 31%. However the membrane was 25 µm thick, instead of 15 µm, and the test was done in-plane and not through-plane.

Responses to Previous (2019) Year Reviewers' Comments

(The project was not reviewed in 2020)

It will be interesting to see cross-sectional views of the overall structure once membranes are produced.

Some examples of cross-sectional views are shown on Slide 10.

One concern with this technology is the viability of the chemistry, from a chemical resistance and durability standpoint, inside fuel cells and electrolyzers. Durability should be investigated.

Yes, chemical resistance and durability testing will be tested in the following quarters.

The project seems too empirical and relies on the need to address several key issues, such as carrier polymers, solutions, heat treatment, etc., by formulation processes.

This project is mostly empirical. However, the budget period 2 optimization work will be augmented by semi-empirical modelling efforts.

In situ (or application-oriented) testing must be done. Perhaps the PI needs industrial partners that can assist with this effort. That should be added as part of the scope of work.

The team will be actively looking for industrial partners that can assist in membrane testing.

Collaboration and Coordination

- **Prof. Morton Litt** (Emeritus - Case Western Reserve University) served throughout 2019 as a consultant for all the polyphenylene ionomer synthesis tasks.
- **Prof. Peter N. Pintauro** (Vanderbilt University) is a Co-PI. The project is realized in his lab and he advises the graduate student doing most of the membrane fabrication and testing work.
- **Dr. Md Masem Hossain** (Post-doctoral scholar, Vanderbilt University) is doing all the syntheses.
- **Mr. Zhihao Shang** (Graduate student, Vanderbilt University) is making and testing the membrane.

This project was originally designed to be realized within one institution (Vanderbilt University). Dr. Rangachary Mukundan (LANL) expressed interest in testing the resultant membranes.

Once the membrane optimization is concluded the team will look for a possible closer cooperation with an industrial partner/laboratory.

Remaining Challenges and Barriers

- Thermal crosslinking of the poly(phenylenesulfonic acid) ionomers: *The reported crosslinking temperature is very close to the ionomer degradation point. Optimization of the ionomer composition, temperature and duration of the crosslinking process is still being carried out to overcome the challenge.*

- Poor mechanical characteristics of the polyphenylene ionomer: *Balancing conductivity and mechanical strength of the composite membranes is one of the tough challenges. Increasing the reinforcing polymer content leads to a loss of conductivity. It appears that meeting both, the ASR and tensile strength targets would require moving away from the dual fiber system and focusing on the pore filled cPPSA/PPSU (or PPSU-PBI) membranes.*

- Issues with reproducible copolymerization and biphenyl grafting: *Progressive improvements are being made but variability of the grafting degree from batch to batch is still a problem. Blending of various batches may partially solve the problem.*

Proposed Future Work

FC Testing

The major work ahead is **fabrication of membrane-electrode assemblies (MEAs) and their testing in H_2/Air fuel cell**, including application of various accelerated stress testing (AST) protocols.

The team will also look for a possible cooperation on this task with an industrial partner/laboratory.

Summary

Objective: Fabricate a novel electrospun, non-PFSA fuel cell membrane that can meet all 2020 FCTO MYRDD technical targets.

Relevance: The project could lead to a non-PFSA (environmentally friendly and inexpensive) membrane with excellent mechanical, chemical, and thermal stability, and low fuel crossover, enabling increase in the operating temperature and humidity ranges of fuel cells.

Approach: The composite all-hydrocarbon membrane are fabricated from a crosslinkable poly(phenylene sulfonic acid) (cPPSA) and poly(phenyl sulfone) (PPSU) mixtures. Two strategies are investigated: **(1)** Dual fiber, concurrent cPPSA and PPSU electrospinning, followed by mat densification, and **(2)** Pore-filling of electrospun PPSU fiber mats with cPPSA. Thermal crosslinking of cPPSA prevents its leaching out from PPSU scaffolds.

Accomplishments: The target ionomers were synthesized and characterized, dual fiber and single fiber mats were electrospun, pore-filled and dual-fiber membranes were fabricated and tested. The Go-No/Go milestone demonstration was estimated as 99% complete. The work was stopped for two months due to COVID-19 pandemic, and is currently moving forward. Some issues with polymer synthesis and membrane fabrication still need to be resolved.

The project was no-cost extended until November 2011.

Technical Backup and Additional Information

Technology Transfer Activities

- The proposed membrane can be used in a number of electrochemical and pressure driven separation processes. Once suitable samples are available they will be sent to potential users for testing.

- Upon achieving the desired membrane characteristics, the PI will team up with an industrial partner to submit an application for SBIR or STTR funding.

- Co-PI (PNP) is negotiating potential business engagements with several companies interested in electrospun membranes and electrodes.

Progress Toward DOE Targets and Milestones

Milestone Summary Table								
Recipient Name:	Vanderbilt University (PI -Ryszard Wycisk)							
Project Title:	Composite PEMs from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s							
Task No	**Task or Subtask Title**	**Milestone Type**	**Milestone Number**	**Milestone Description (Go/No-Go Decision Criteria)**	**Milestone Verification (What, How, Who, Where)**	**Date (Months)**	**Completion (%)**	**Progress notes**
1	Synthesis of lithium dibromodisulfonate monomers	Milestone	1	Demonstrate 60 g of DBBDSA, 50g of DBBPDSA and 10 g of DBFDSA, and confirm their purity >99% with ^{1}H NMR spectra.	NMR spectra available	9	90	Monomers synthesized, 1H NMR spectra recorded, purities assessed but less than 99%
2	Copolymerization of lithium dibromodisulfonate monomers	Milestone	2	Demonstrate at least three batches of different composition, for the both copolymer types, each batch weighing not less than 5g. Confirm copolymer composition with ^{1}H NMR spectra (0.6>x>0.8 for Px).	NMR spectra available	9	100	Copolymers synthesized and purified. Composition confirmed via 1H NMR spectra
3	Grafting biphenyl onto PxBy and PxFy and crosslinking of the resultant cPPSAs	Milestone	3	Demonstrate successful grafting of BP (by ^{1}H NMR) on at least one copolymer and demonstrate its EW > 250 g/mol.	NMR spectra and IEC data available	9	100	Grafting successful,1H NMR spectra and IEC available
4	Preliminary dual-fiber membrane fabrication	Go/No-Go Decision Point	4	Demonstrate composite water-stable membrane with ASR of 0.03 Ohm·cm^2 at 80^{o}C and 40-90%RH, and tensile strength >20 MPa in water vapor equilibrated state at room temperature.	Supporting data available	17	100	Work delayed due to COVID-19 pandemic. Dual fiber membranes fabricated – **Go/No-Go Milestone met partially.**
5	Optimization of cPPSA composition	Milestone	5	Demonstrate crosslinkable disulfonic acid copolymer with through-plane conductivity > 0.1 S/cm at 80oC and 40-90%RH	Supporting data available	21	99	cPPSA (solution cast film) demonstrated with through-plane conductivity 0.1 S/cm at 40% RH and 0.4 S/cm at 90% RH and 80oC.
6	Optimization of cPPSA electrospinning	Milestone	6	Report the optimal electrospinning conditions: less than 10% beads and droplets, fiber diameter variability <50% by ImageJ.	SEM micrographs and supporting data available	24	100	Electrospinning conditions optimized.
7	Optimization of membrane composition	Milestone	7	Demonstrate water insoluble 15 µm thick PEM membrane with through-plane conductivity > 0.05 S/cm at 80^{o}C and 20-90%RH	Supporting data available	28	60	M7 Milestone met at RH >30%. At 20%RH achieved 0.03 S/cm vs. required >0.05 S/cm.
8	MEA fabrication and testing in H_2/Air fuel cell	Milestone	8	Demonstrate electrospun composite membrane meeting the projected characteristics (2020 FCTO targets)	Photographs and supporting data	35	1	Just started.

Current activity

Progress Toward DOE Targets and Milestones

MYRD&D Plan

Technical Targets: Membranes for Transportation Applications

Characteristic	Units	2020 Targets		Current status of the project
Maximum oxygen crossover[a]	mA / cm^2	2		Not available yet
Maximum hydrogen crossover[a]	mA / cm^2	2		Not available yet
Area specific proton resistance at:				
Maximum operating temperature and water partial pressures from 40–80 kPa	ohm cm^2	0.02		Not available yet
80°C and water partial pressures from 25–45 kPa	ohm cm^2	0.02	√	0.02 with 20 μm pore-filled membrane
30°C and water partial pressures up to 4 kPa	ohm cm^2	0.03		Not available yet
-20°C	ohm cm^2	0.2		Not available yet
Maximum operating temperature	°C	120	√	120°C (estimated)
Minimum electrical resistance	ohm cm^2	1,000		Not available yet
Cost[d]	$ / m^2	20		Not available yet
Durability[f]				
Mechanical	Cycles until >15 mA/cm^2 H_2 crossover[g]	20,000		Not available yet
Chemical	Hours until >15 mA/cm^2 crossover or >20% loss in OCV	>500		Not available yet
Combined chemical/mechanical	Cycles until >15 mA/cm^2 crossover or >20% loss in OCV	20,000		Not available yet

AST experiments will begin next quarter

Publications and Presentations

- R. Wycisk, Md. M. Hossain, Z. Shang, P.N. Pintauro and M. Litt, Composite Polymer Electrolyte Membranes from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s, U.S. DRIVE - Hydrogen Fuel Cell Tech Team Meeting, Detroit, MI, September 18, 2019.

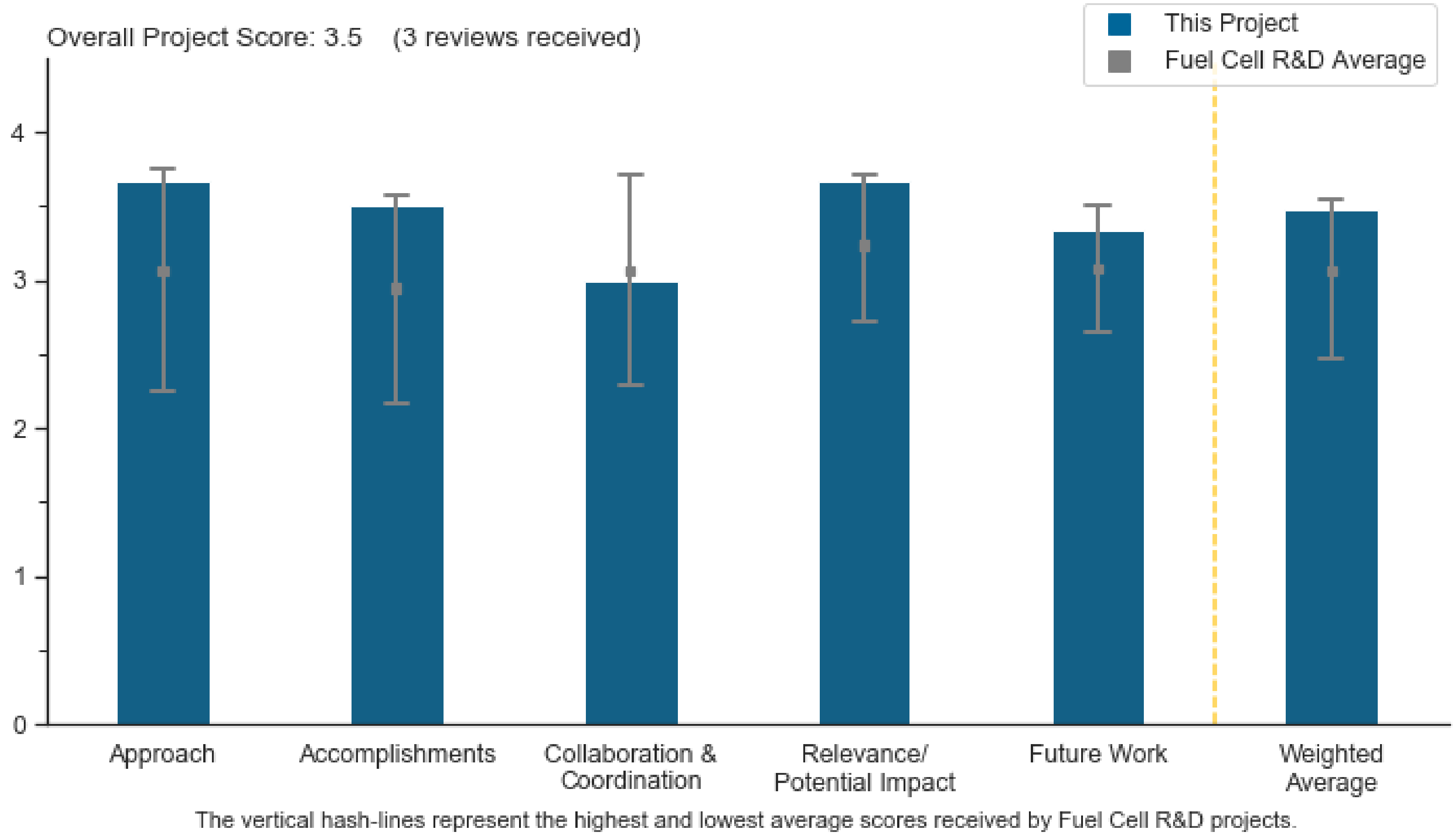
- R. Wycisk, Md. M. Hossain, Z. Shang, P.N. Pintauro and M. Litt, Composite Polymer Electrolyte Membranes from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s, Fuel Cell Tech Team Meeting, Webex, June 8, 2020.

- R. Wycisk, Md. M. Hossain, Z. Shang, and P. N. Pintauro, Pore-Filled PEMs from Poly(Phenylene Sulfonic Acid)s and Electrospun Poly(Phenylene Sulfone) Fiber Mats, (I01C-2244), PRiME 2020, October 4-9, 2020 (virtual conference presentation).

- Md. M. Hossain, Z. Shang, R. Wycisk, and P.N. Pintauro, Pore-Filled PEMs from Poly(Phenylene Sulfonic Acid)s and Electrospun Poly(Phenylene Sulfone) Fiber Mats, ECS Trans. 98, 367 (2020).

- R. Wycisk, Md. M. Hossain, Z. Shang and P.N. Pintauro, Proton Exchange Membranes for Low Relative Humidity Fuel Cell Operation Based on Poly(Phenylene Sulfonic Acid), Session 423B - hosted on the iPosterSessions platform at the 2020 Virtual AIChE Annual Meeting, November 16-20, 2020 (virtual conference presentation).

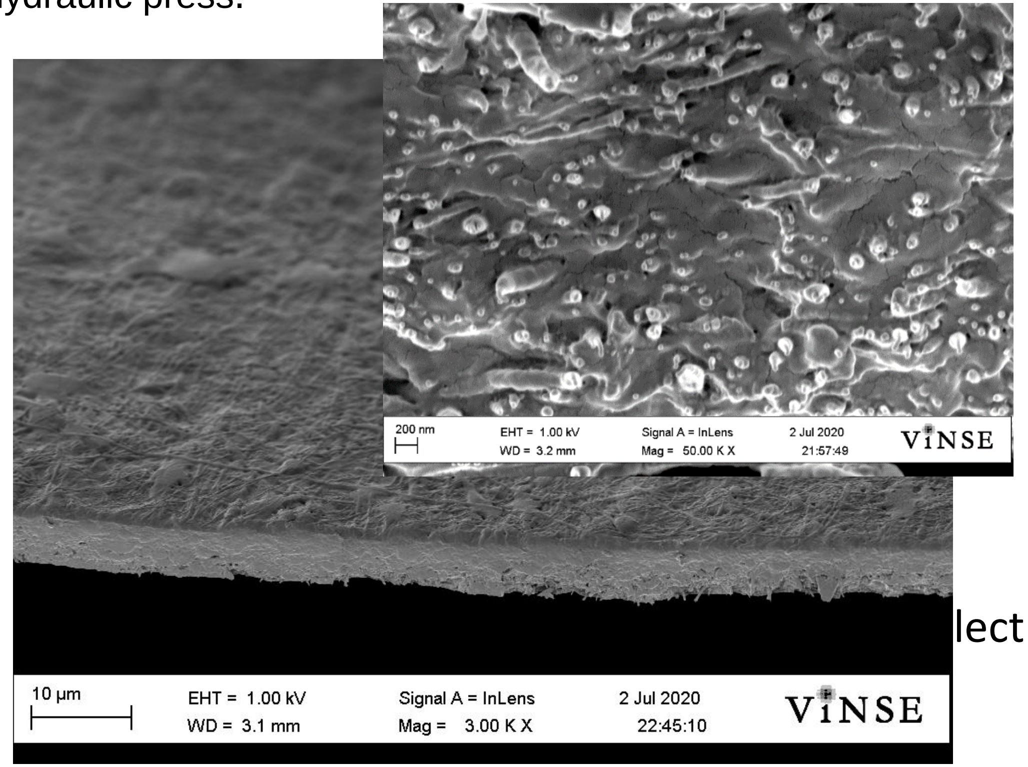
2019 AMR – Project Scoring



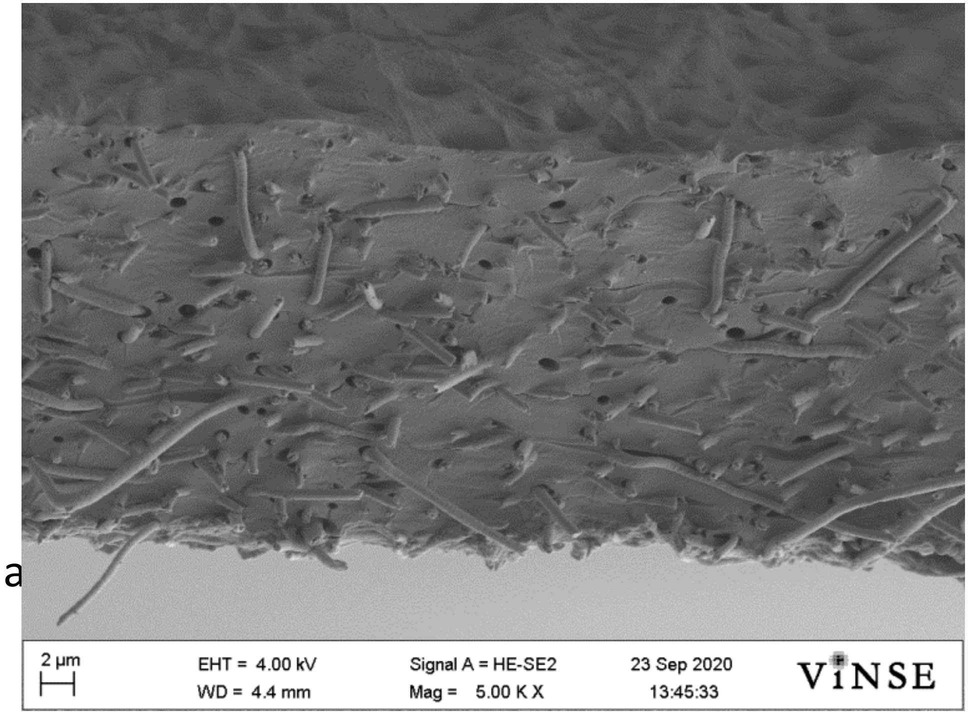
Cross-Sections of DF and PF cPPSA/PPSU Membranes

A dual-fiber membrane made by exposing the electrospun cPPSA/PPSU mat to alcohol vapors and then compacting in a hydraulic press.

Pore-filled membrane made by embedding cPPSA into electrospun PPSU scaffold followed by compaction on a hydraulic press.



lectrospun dua



SEM image (cross-section) of cPPSA/PPSU **dual-fiber membrane**.

P75B25-BP16%-PPSU(30%)

SEM image (cross-section) of cPPSA/PPSU **pore-filled membrane**.

P75B25-BP19%-PPSU(15.5%)

Critical Assumptions and Issues

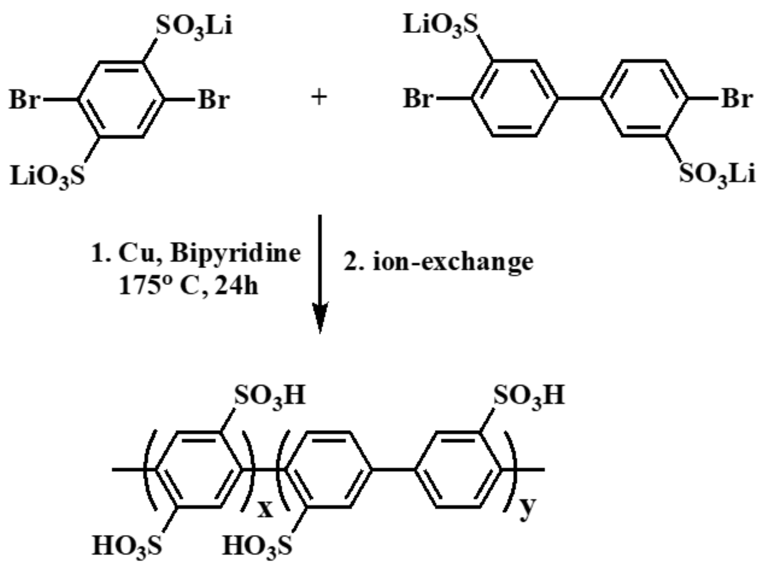
- **Issue**: Oxidative stability in fuel cell environment may be insufficient to meet the 2020 FCTO MYRDD technical targets.

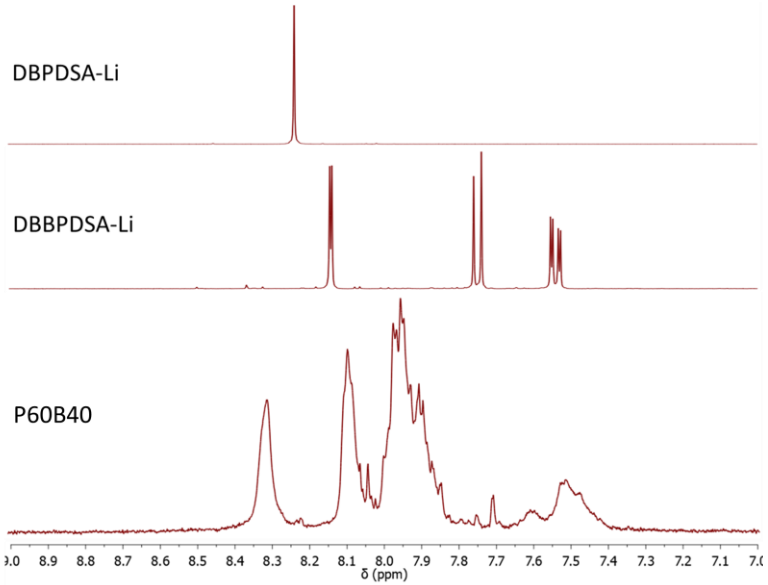
  Approach: We will investigate addition of fast radical scavengers to the cPPSA before electrospinning or embedding.

- **Issue**: For proper fuel cell performance, cPPSA binder will need to be employed as the electrode binder, which would require heating to 200-210^{o}C for its stabilization.

  Approach: We may consider, using uncrosslinked membrane for MEA fabrication followed by concurrent thermal treatment of both the membrane and the electrodes.

PxBy copolymers – Solubility vs. Yield

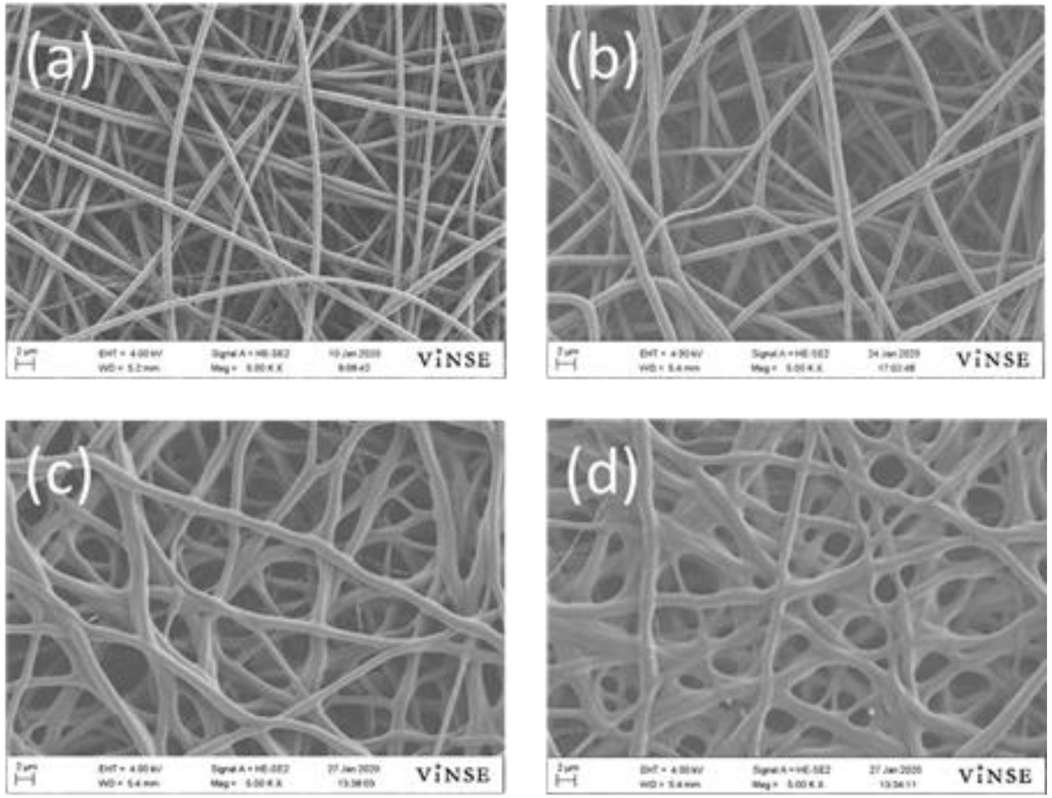




Run	Copolymer	DBPDSA:DBBPDSA	Yield (%)
1	P90B10	90:10	37
2	P85B15	85:15	52
3	P80B20	80:20	77
4	P75B25	75:25	97

When the content of DBBPDSA-Li in the reaction mixture was approaching 25 mol%, the solubility of PxBy-Li copolymer increased and the reaction yield was nearly 100%.

PPSU Fibers Welding by Solvent Vapor Exposure



SEM images of **PPSU** mats: (a) raw-unwelded, (b) under-welded, (c) properly welded, and (d) over-welded. Magnification 5,000x