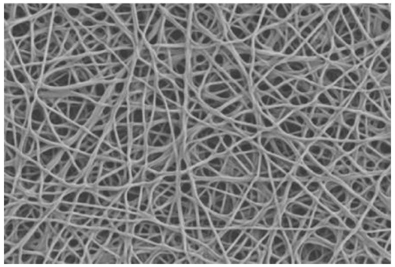
School of Engineering

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

PI: Ryszard Wycisk

Vanderbilt University



May 30, 2020

2020 DOE Hydrogen and Fuel Cells
Program Review Presentation

Project ID
FC310

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

School of Engineering

Overview

Timeline

- Project Start Date: 1/9/19
- Project End Date: 11/31/21 (extended)
- Percent Complete: 40%

Barriers

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

Budget

- Total Project Budget: $752,049
  - Total Recipient Share: $152,049
  - Total Federal Share: $600,000
  - Total DOE Funds Spent: $257,960 (as of 3/31/20)

Targets

- Cost < $20/m^2
- ASR at 80°C and water partial pressure from 25-45 kPa - 0.02 Ohm·cm^2
- Operating temperature up to 120^{o}C

Funded Partners

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

Prof. Morton Litt (Consultant) - Case Western Reserve University

Relevance

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

2020 DOE FCTO TARGETS:

- 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 $Ohm{\cdot}cm^2$
- ASR at 80°C and H_2O partial pressure 25-45 kPa - 0.02 $Ohm{\cdot}cm^2$
- Mechanical durability - 20,000 cycles
- Chemical durability > 500 hours
- Cost - $\$20/m^2$

TARGETS FOR THE CURRENT PROJECT YEAR:

- **Expected results**: Synthesized poly(phenylene sulfonic acid)s (cPPSA), identified working carrier and electrospinning conditions for well-formed fibers, prepared dual fiber cPPSA/PPSU membranes and performed basic ex-situ characterization (water uptake, conductivity and tensile strength).
- **Go/No-Go Decision point**: Demonstrate composite water-stable membrane with ASR of 0.03 $Ohm{\cdot}cm^2$ at 80°C and 40-90%RH, and tensile strength >20 MPa in water vapor equilibrated state at room temperature.

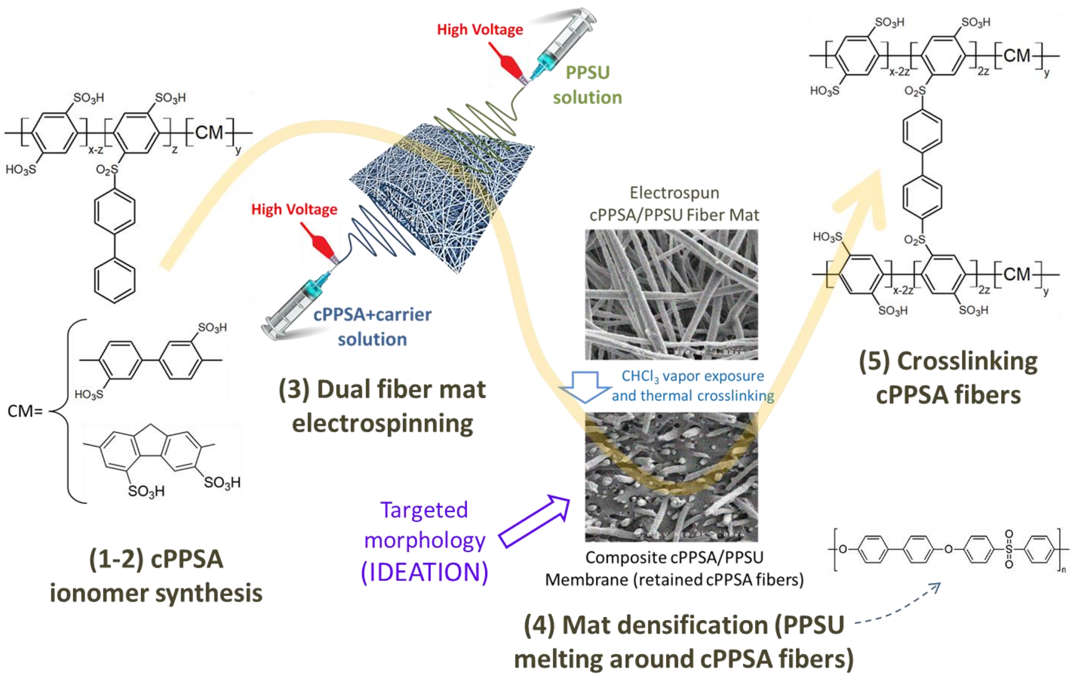
IMPACT:

Synthesized and tested the target membrane polymer – highly conductive, crosslinkable poly(phenylene sulfonic acid)

Approach

Robust, low-cost composite all-hydrocarbon membrane will be fabricated via dual fiber co-electrospinning of a crosslinkable poly(phenylene sulfonic acid) (cPPSA) and poly(phenyl sulfone) (PPSU) mixture mat, followed by mat densification via solvent vapor induced softening of PPSU fibers and thermal crosslinking.

An alternative approach examined will be pore-filling of the electrospun reinforcing PPSU mat (single fiber electrospinning) with cPPSA ionomer and thermal crosslinking.



THREE STEP APPROACH:

(1) Synthesize, optimize and test crosslinkable, highly proton conductive poly(phenylene sulfonic acid) (cPPSA) ionomers (IEC > 5 mmol/g).

(2) Fabricate the membranes, employing single- or dual-fiber electrospinning and thermal crosslinking of the ionomer.

(3) Characterize and test fuel cell performance of the resultant membranes.

School of Engineering

Approach

The project builds on two earlier, DOE-funded studies demonstrating:

(1) **Exceptionally high proton conductivity**, even at very low RH, of cPPSA solution cast films (Litt's group), and

(2) **Excellent durability** of electrospun perfluorosulfonic acid (PFSA) ionomers/PPSU composite membranes, exceeding that of the pristine PFSA (Pintauro's group).

PROJECT MILESTONES AND DELIVERABLES

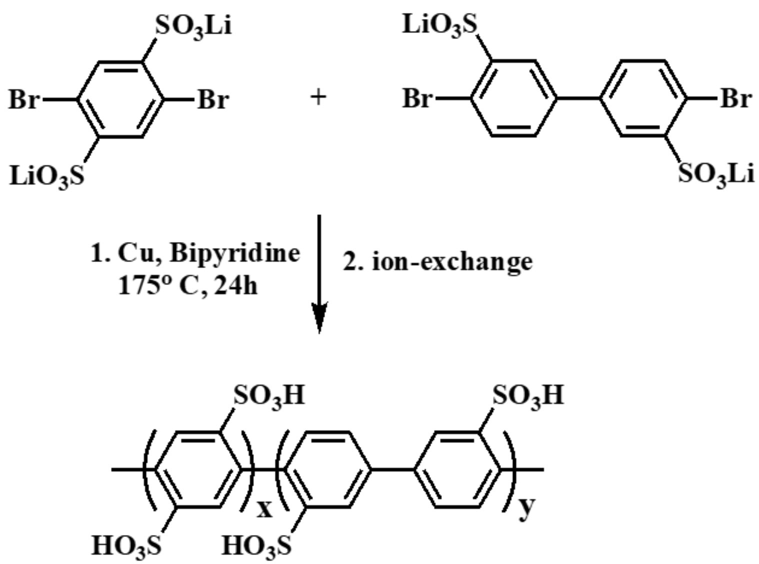
TASK NO	TASK NAME	GO/NO-GO	BUDGET PERIOD 1						BUDGET PERIOD 2					
			Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
1	Synthesis of lithium dibromodisulfonate monomers		M1											
2	Copolymerization of the lithium dibromodisulfonate monomers			M2										
3	Grafting biphenyl and crosslinking of BxPy and/or BxFy type cPPSA				M3									
4	Preliminary dual-fiber membrane fabrication	M4						M4						
5	Optimization of cPPSA composition								M5					
6	Optimization of electrospinning									M6				
7	Optimization of membrane composition											M7		
8	MEA fabrication and testing in H_2/Air fuel cell													M8

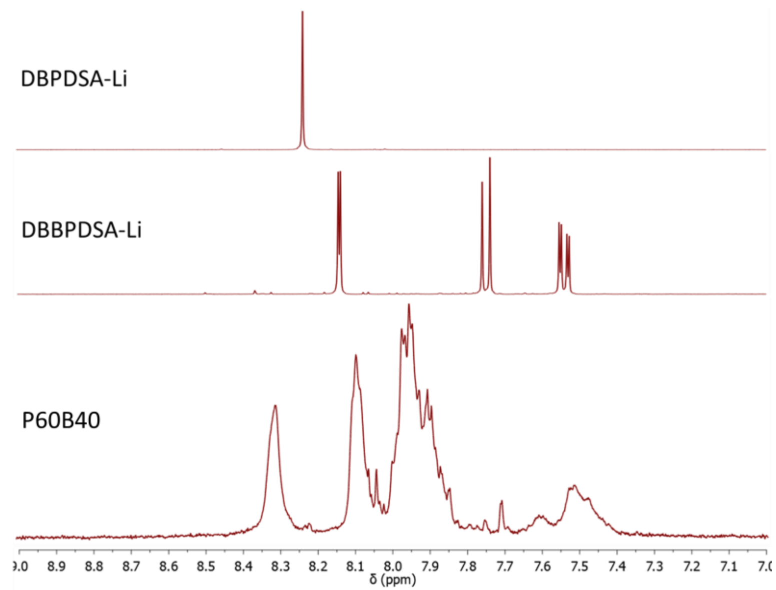
No-Cost Extension

Percent Complete	Progress Notes
90%	Monomers synthesized, 1H NMR spectra recorded, purities assessed but less than 99%
100%	Copolymers synthesized and purified. Composition confirmed via 1H NMR spectra.
100%	Grafting successful,1H NMR spectra and IEC available
90%	Work stopped due to COVID-19 pandemic. Activity to be resumed soon.
0%	Not started.
0%	Not started.
0%	Not started.
0%	Not started.

Accomplishments and Progress

1. PxBy copolymers have been successfully synthesized



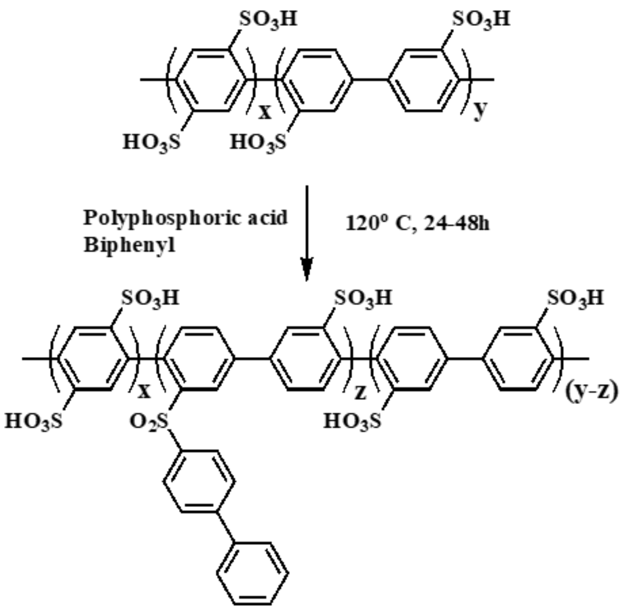


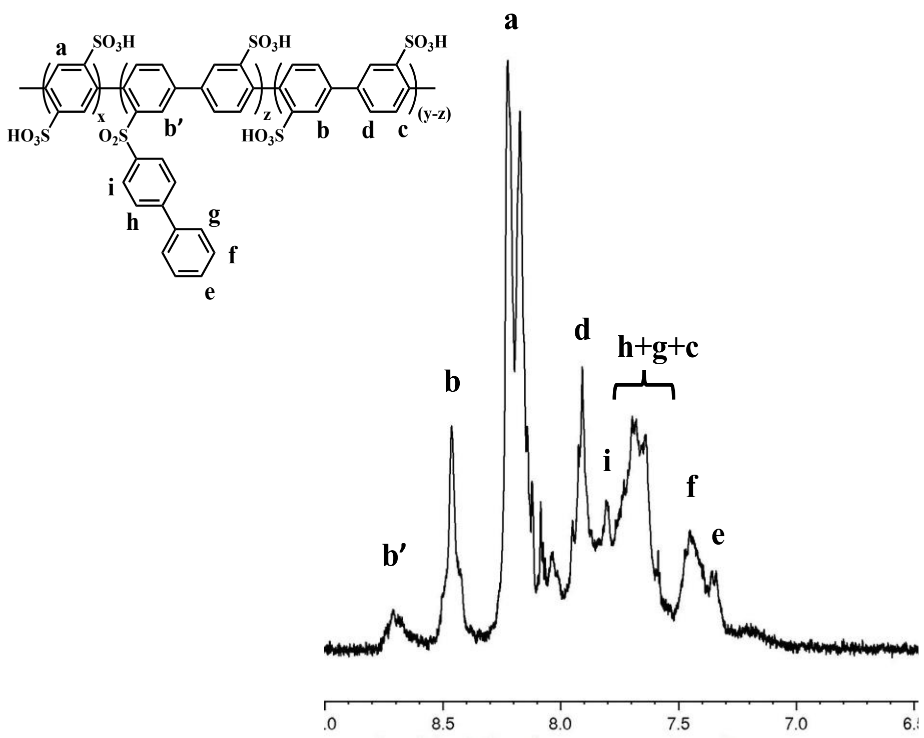
Run	Copolymer	DBPDSA:DBBPDSA	Yield (%)
1	P90B10	90:10	37
2	P85B15	85:15	52
3	P80B20	80:20	77
4	P75B25	75:25	97

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%.

Accomplishments and Progress

2. Grafting of biphenyl groups has been successfully accomplished

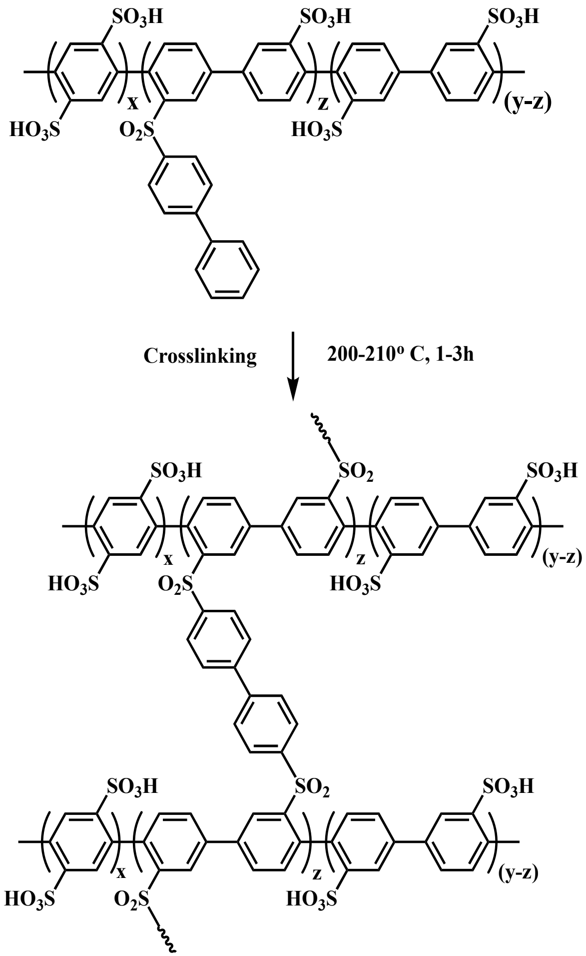




After careful in-situ generation of polyphosphoric acid and control of the reaction temperature it became possible to reproducibly graft 8-16% mole of biphenyl groups onto the PxBy backbone.

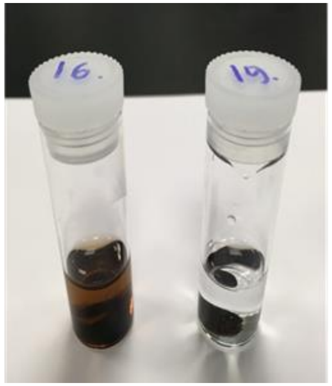
Accomplishments and Progress

3. Thermal crosslinking of the graft copolymer (cPPSA) was successfully demonstrated



Grafted ionomer	Grafting degree (%)	Temperature (°C)	Time (h)	Solubility in water
P75B25-g-BP-07%-210C-3h	7	210	3	YES
P75B25-g-BP-10%-210C-3h	10	200	3	YES
P75B25-g-BP-10%-210C-3h	10	210	3	PARTIAL
P75B25-g-BP-12%-210C-1h	12	210	1	PARTIAL
P75B25-g-BP-12%-210C-2h	12	210	2	NO
P75B25-g-BP-14%-205C-1h	14	205	1	NO
P75B25-g-BP-16%-205C-1h	16	205	1	NO

cPPSA **partially soluble** in hot water

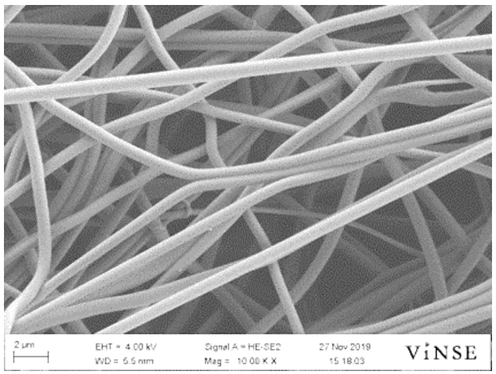


cPPSA **insoluble** in hot water

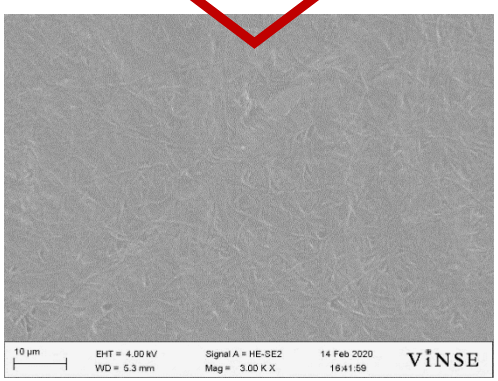
Accomplishments and Progress

4. Electrospinning and membrane formation was successful

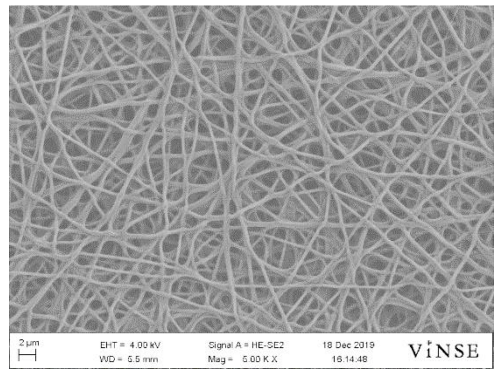
Dual-Fiber cPPSA/PBI Membrane



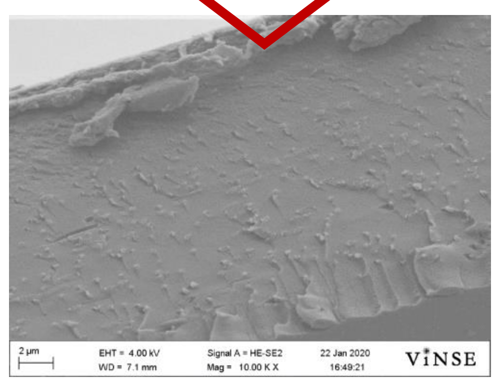
Densification through exposure to water/n-propanol vapor followed by hydraulic press and thermal crosslinking.



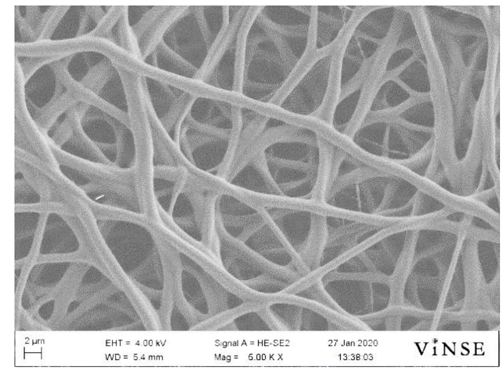
Pore-Filled cPPSA/PBI Membrane



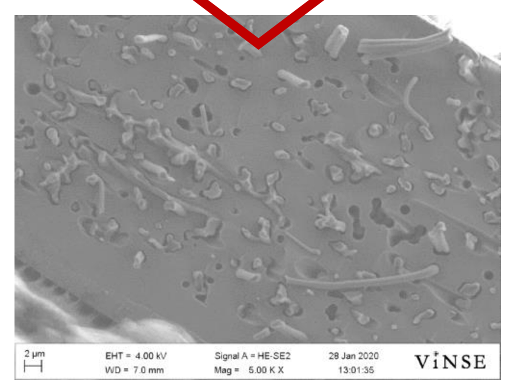
Partial fiber welding followed by pore filling with cPPSA solution and thermal crosslinking.



Pore-Filled cPPSA/PPSU Membrane



Partial fiber welding followed by pore filling with cPPSA solution and thermal crosslinking.

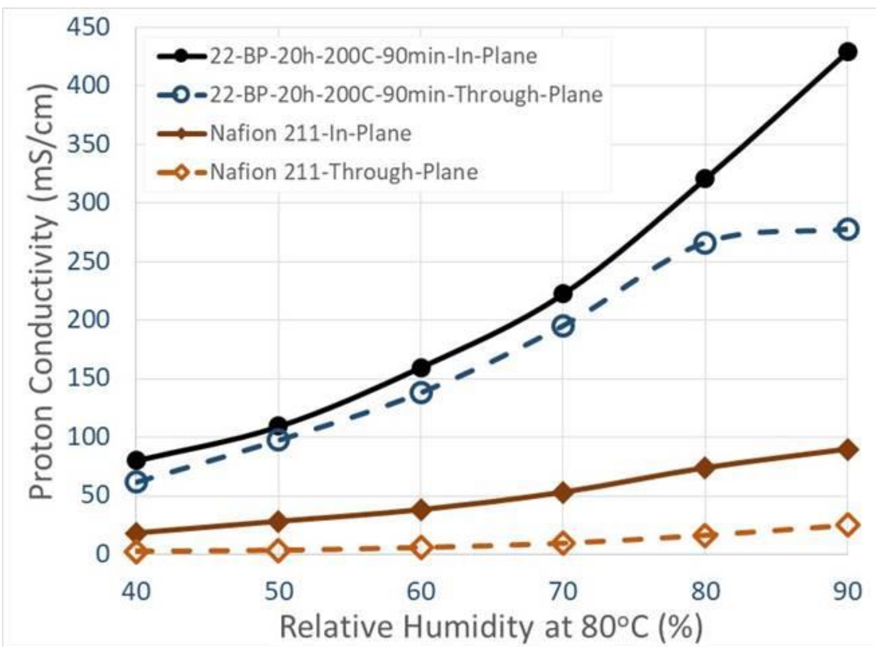


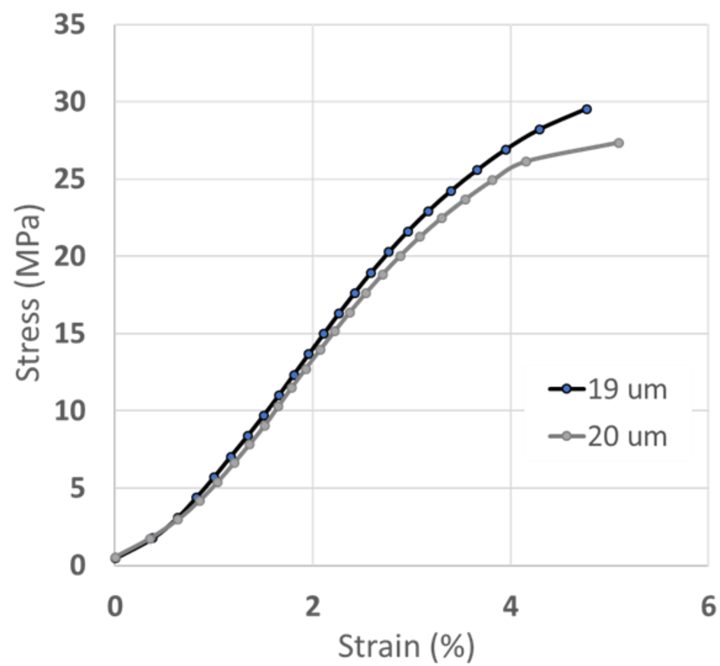
Accomplishments and Progress

5. Tensile strength better than the target and ASR slightly lower than expected (at 40% RH limit and 80°C).

- The selected cPPSA/PPSU composite membrane had excellent conductivity - 5-10 times greater than that of Nafion 211, in the 40-90% RH range at 80°C. But its ASR of was greater than the 0.03 Ohm·cm value of Go/No-Go milestone. A 20 µm thick membrane had ASR 0.04 Ohm·cm at 40% RH and 80°C, which was close to the required target.

- Tensile strength (27-29 MPa) exceeded the Go/No-Go milestone of 20 MPa.





Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

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 9.

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 an important part of budget period 2 efforts.

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 & Coordination

- Prof. Morton Litt (Case Western Reserve University) serves as a consultant for all the polyphenylene ionomer synthesis tasks.
- Prof. Peter N. Pintauro (Vanderbilt University) serves as a Co-PI and is helping in all the fiber electrospinning tasks.

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

- Compatibility of the polyphenylene ionomer and the reinforcing polymer: *The originally selected reinforcement (PPSU) shows moderate adhesion to the polyphenylene ionomer. It was found out the PPSU/PBI blend show improved compatibility with the ionomer. These systems will be investigated in Budget Period 2.*

- Poor mechanical characteristics of the polyphenylene ionomer: *Balancing conductivity and mechanical strength of the composite membranes is a serious challenge. Increasing the reinforcing polymer content leads to a loss of conductivity. Meeting both, the ASR and tensile strength targets will require extensive optimization.*

Proposed Future Work

This project has been extended and will now end on November 14, 2021. During the Budget Period 2 the following tasks will be performed:

(i) Optimization of the poly(phenylene sulfonic acid) composition (especially biphenyl grafting degree) and its electrospinning conditions.

(ii) Fabrication of pore-filled membranes using electrospun fiber mats from PPSU/PBI blends and selected poly(phenylene sulfonic acid) ionomer.

(iii) Fabrication of dual-fiber membranes from co-electrospun poly(phenylene sulfonic acid) and PPSU/PBI fibers. In addition to dual-fiber electrospinning, electrospinning of PPSU/PBI fibers and concurrent electrospraying of the poly(phenylene sulfonic acid) will also be investigated.

(iv) Ex-situ characterization of the membranes (conductivity, water uptake, tensile strength, radical stability).

(v) MEA fabrication and testing with the selected membranes.

As mentioned earlier, the team will be actively looking for industrial partners that can assist in membrane testing.

Proposed Future Work

Budget Period 2 tasks and milestones.

Milestone Summary Table						
Recipient Name:						
Project Title:	Composite PEMs from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s					
Task No				Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification (What, How, Who, Where)	
5		Milestone	5	Demonstrate crosslinkable disulfonic acid copolymer with through-plane conductivity > 0.1 S/cm at 80ºC and 40-90 %RH	Supporting data available	
6		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	
7		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	
8						

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

Technology Transfer Activities

- The proposed membrane can be used in a number of electrochemical and pressure driven separation processes. Suitable alternative applications will be actively sought after during the project lifetime.

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

- The team has initiated talks with eSpin Technologies, Inc. (Chattanooga, TN), a commercial manufacturing facility, regarding potential scale-up of the proposed PEM fabrication technology.

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 will be fabricated via dual fiber co-electrospinning of a crosslinkable poly(phenylene sulfonic acid) and poly(phenyl sulfone) (PPSU) mixture mat, followed by mat densification via solvent vapor induced softening of PPSU fibers, and thermal crosslinking.

Accomplishments: The target ionomer was synthesized and characterized, dual fiber and single fiber mats were electrospun, pore-filled membranes were successfully fabricated but the dual-fiber membranes require more work. The Go-No/Go milestone demonstration was estimated as 90% complete. The work was stopped for two months due to COVID-19 pandemic, and is currently being resumed.