
Composite Polymer Electrolyte Membranes from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s

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Overall Objectives

The main objective of this project is to fabricate and demonstrate superior fuel cell performance of an electrospun composite all-hydrocarbon, non-perfluorosulfonic acid (non-PFSA) membrane. The membrane will be formed from an electrospun dual-fiber network of a crosslinkable poly(phenylene sulfonic acid) (cPPSA), a highly proton-conducting ionomer, and a robust poly(phenyl sulfone) (PPSU) for mechanical stabilization. The PPSU fibers will be selectively melted to obtain a thin composite with cPPSA conductive nanofibers embedded in dense PPSU matrix. The membrane will exhibit excellent low relative humidity (RH) proton conductivity and fuel cell durability, with fabrication cost strongly competitive compared to that of PFSA membranes, and will meet all 2020 Fuel Cell Technologies Office (FCTO) Multi-Year Research, Development, and Demonstration Plan (MYRDD) technical targets. The generation of useful correlations regarding the electrospun membrane composition/structure and its fuel cell performance will also be an important part of this work.

Specific objectives include:

- Fabricate a composite all-hydrocarbon, non-PFSA membrane formed from an electrospun dual-fiber network of a cPPSA, a highly

proton-conducting ionomer, and a robust PPSU for mechanical stabilization.

- Demonstrate that the membrane exhibits good low-RH proton conductivity and fuel cell durability, with fabrication cost strongly competitive compared to that of PFSA membranes.
- Demonstrate that the membrane meets all 2020 FCTO MYRDD technical targets.
- Establish working cooperation with a national lab to validate performance of the membrane in a fuel cell.
- Initiate consultations with a commercial manufacturing facility regarding potential scale-up of the proposed polymer electrolyte membrane (PEM) fabrication technology.

Fiscal Year (FY) 2019 Objectives

- Synthesize monomers, poly(phenylene sulfonic acid)s, and their grafts with biphenyl (cPPSA).
- Identify working carrier and electrospinning conditions for well-formed fibers and fabricate dual fiber cPPSA/PPSU membranes.
- Perform required ex situ characterizations (water uptake, conductivity, and tensile strength) and demonstrate composite water-stable membrane with an area specific resistance of 0.03 Ohm·cm² at 80°C and 40%–90% RH, and tensile strength >20 MPa in water vapor equilibrated state at room temperature (go/no-go milestone).

Technical Barriers

This project addresses the following technical barriers from the Early Stage, Innovative Fuel Cell Membrane R&D section of the FCTO MYRDD Plan¹:

- Low performance and durability of non-PFSA PEM membranes, including hydrocarbon membranes

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- High cost of PFSA membranes.

Technical Targets

This project is split into two one-year budget periods: BP 1 and BP 2. During BP 1 (2019), composite PEMs are to be fabricated, and in BP 2 (2020), testing and optimization of those PEMs will be performed so that the FCTO 2020 targets are met. Q4 of BP1 has just started and therefore only Q1–Q3 targets are addressed below:

- Q1: Monomers synthesized—total >120 g
- Q2: Copolymers synthesized—total >30 g
- Q3: Grafting successful—equivalent weight <250 g/mol.

INTRODUCTION

This work introduces a novel, low-cost composite cPPSA/PPSU (PEM that will meet all 2020 technical targets set forth by the FCTO MYRDD Plan, including low area specific resistance, low gas crossover, high mechanical strength, and high durability. This unique and commercially viable hydrocarbon PEM will be free of three major limitations of PFSA ionomers: (1) high cost, (2) ionomer dehydration and loss of conductivity at low RH, and (3) excessive lateral swelling and contraction on changing hydration condition, resulting in micro-crack formation and increased reactant crossover. Potential scale-up of the proposed composite membrane technology can significantly affect the automotive fuel cell landscape by eliminating the threat of dangerous releases of fluorine compounds to the environment and by boosting the fuel cell power output and simplifying the stack hydration system.

The proposed membrane will comprise an electrospun fiber network of a cPPSA as a proton-conducting component and PPSU as a mechanically stabilizing, uncharged polymer component.

APPROACH

This project builds on two earlier DOE-funded studies demonstrating: (1) exceptionally high proton conductivity, even at very low RH (down to 20%RH), of cPPSA solution cast films, and (2) excellent durability of electrospun PFSA ionomers/PPSU composite membranes, exceeding that of the pristine PFSA. Unfortunately, the high proton conductivity of cPPSA films, especially at low RH, was offset by their significant brittleness, which made handling of those materials, including fabrication of membrane electrode assemblies, extremely difficult.

The unique blending of cPPSA and PPSU via electrospinning, proposed here (Figure 1), should alleviate the brittleness problem leading to a robust, low RH-conductive PEM that is a true competitor to PFSA membranes and suitable for commercial applications.

FY 2019 Accomplishments

- All the planned synthetic work has been successfully executed (over 120 g of monomers and over 30 g of copolymers were synthesized and characterized).
- An entirely new copolymer was also synthesized, which might be the best material for Year 2 experiments.
- Negotiations with potential industrial partners for scale-up (eSpin) and testing (Toyota) were initiated.

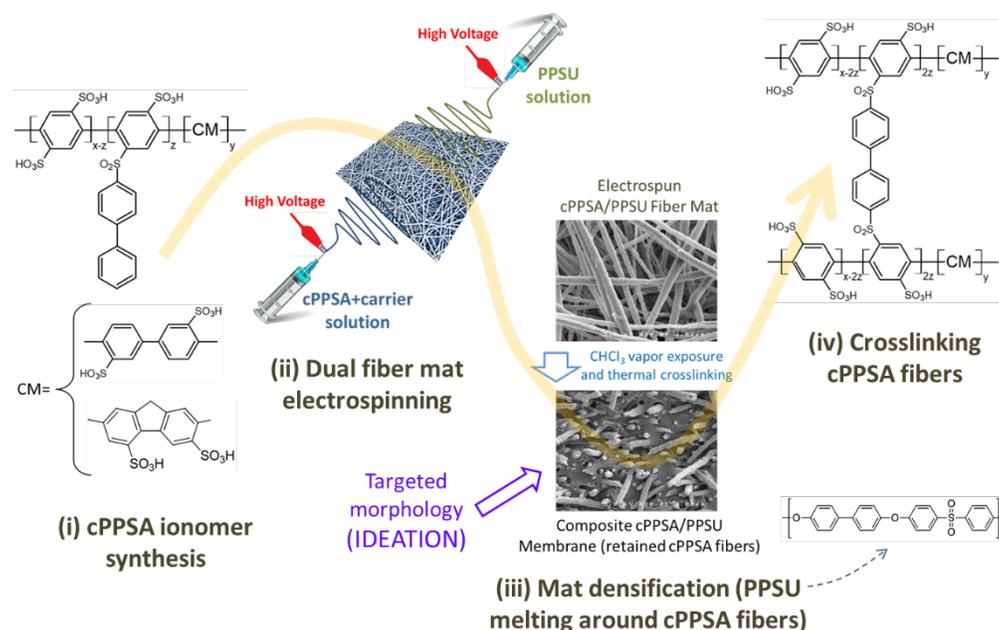


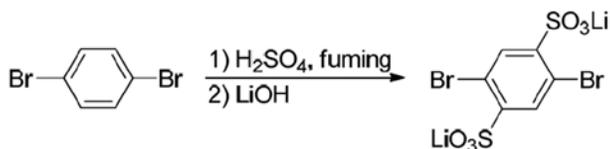
Figure 1. Fabrication scheme of the proposed composite PEMs from electrospun cPPSAs: (i) ionomer synthesis, (ii) electrospinning, (iii) mixed fiber mat densification, and (iv) thermal crosslinking of ionomer fibers.

RESULTS

During the reported period of performance (Q1–Q3 of BP 1) the following was accomplished.

(i) The required monomers were synthesized and purified:

1,4-dibromophenylene-2,5-disulfonic acid dilithium salt (DBPDSA-Li), 4,4'-dibromobiphenyl-3,3'-disulfonic acid dilithium salt (DBBPDSA-Li), and 2,7-dibromofluorene-3,5-disulfonic acid dilithium salt (DBFDSA-Li). Additionally, one more attractive monomer was synthesized as the potential replacement of DBFDSA-Li: 3,3'-disulfonated-4,4'-dichlorodiphenyl sulfone dilithium salt (CPSDSA-Li), based on the protocol developed by McGrath et al. [1]. All three monomers were synthesized by sulfonation of the selected dibromo-precursor with fuming sulfuric acid. An example sulfonation reaction scheme for the synthesis of DBPDSA-Li is shown below:



The sulfonations were carried out at 230°C for 24 h (DBPDSA-Li), at 125°C for 1 h (DBBPDSA-Li), at 24°C for 12 h plus 100°C for 1 h (DBFDSA-Li), or at 120°C for 6 h (DCPSDSA-Li). The reactions were terminated by pouring the mixtures on ice, filtration, and neutralization of the filtrate with NaOH. The monomers in Na-form were purified by salting out twice with NaCl, double recrystallization from deionized water, then ion exchange to H-form, titration with LiOH, and extensive drying. Typical yields, after some optimizations, were between 40% and 60%. ¹H nuclear magnetic resonance (NMR) spectra of the four monomers are shown in Figure 2.

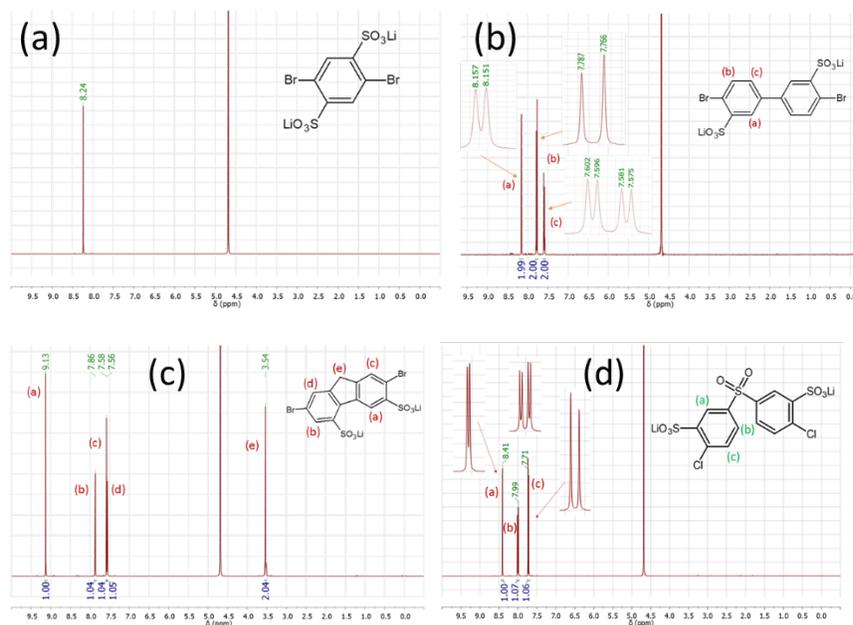


Figure 2. 400 MHz ^1H NMR (D_2O) spectra of the four monomers synthesized in Q1–Q2: (a) DBPDSA-Li, (b) DBBPDSA-Li, (c) DBFDSA-Li, and (d) DCPDSA-Li. The signal at 4.7 ppm comes from the residual protons of water present in D_2O and in the substrate.

(ii) The required sulfonic acid copolymers were synthesized and purified:

three batches of P_xB_y and three batches of P_xF_y , where $0.6 < x < 0.8$ for P_x (phenylnedisulfonic acid). Additionally, a homopolymer of DPSDSA and its copolymer with PDSA (P_xS_y) were also synthesized as an added effort. Copolymerizations were performed by Ullmann coupling at 160°C in *N*-methyl-2-pyrrolidone (NMP), employing activated copper powder/bipyridine as the catalyst, according to the protocols developed by Litt and coworkers (Figure 3) [2]. The ratio of the two comonomers in each copolymer type was adjusted to obtain the phenylene disulfonic acid content at 60–80 mol %. Purification of the copolymers was done by ultrafiltration using membranes with molecular weight cut-off of 5,000 Da.

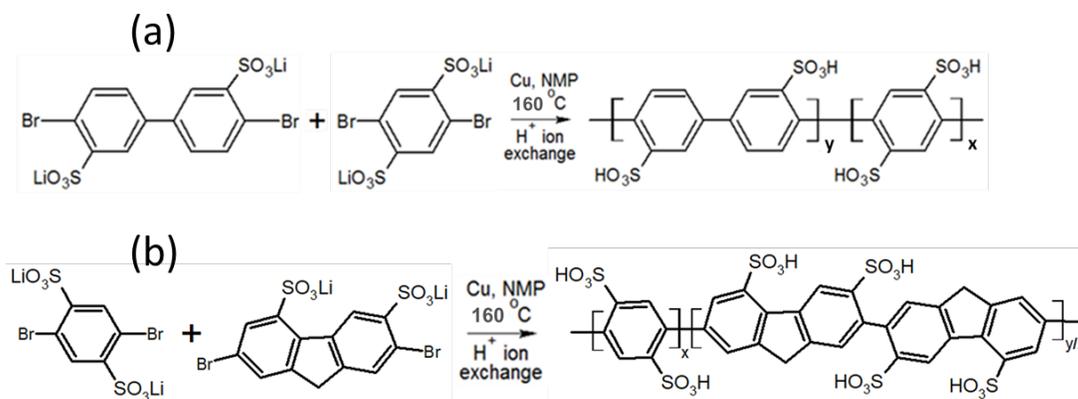


Figure 3. Synthesis scheme of the rigid rod: (a) poly(phenylnedisulfonic acid-co-biphenylnedisulfonic acid) copolymer (P_xB_y), and (b) poly(phenylnedisulfonic acid-co-fluorenylnedisulfonic acid) copolymer (P_xF_y).

Proton NMR spectra of examples of the two types of the copolymers, along with spectra of the respective monomers, are shown in Figure 4. The significant broadening of the resonance signals for the copolymers as compared to those of the monomers is indicative of the high molar mass and is an indirect way of confirming successful polymerization.

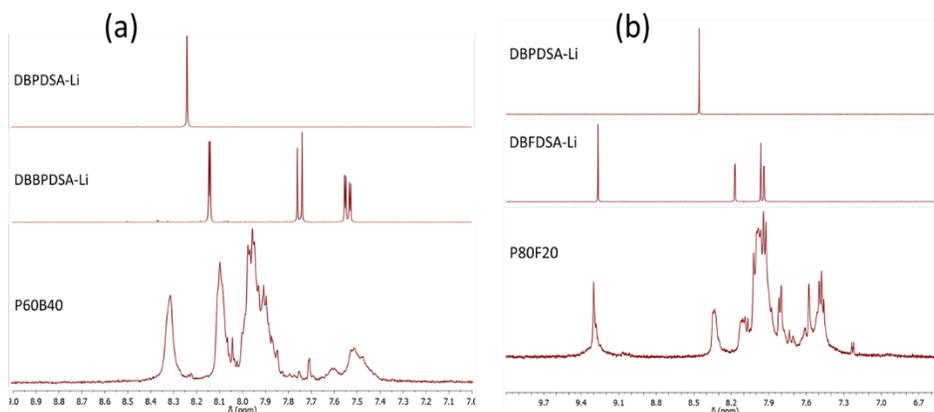


Figure 4. 400 MHz ¹H NMR (D₂O) spectra of (a) DBPDSA-Li and DBBPDSA-Li monomers, and the resultant copolymer (P72B28), and (b) DBPDSA-Li and DBFDSA-Li monomers, and the resultant copolymer (P80F20).

To prevent dissolution of the highly sulfonated copolymers in water, crosslinking of their chains will be accomplished with biphenyl spacer/linker. The process involves two steps: grafting of the linker onto the copolymer (P_xBy, P_xFy, or P_xSy), and then linking the grafts via thermal activation with another chain through sulfone bridges.

(iii) The required grafting of biphenyl (BP) on the PBy and PxFy copolymers was successfully performed.

Grafting of P_xSy is currently carried out. A modified Graybill's [3] protocol developed by the present team was employed, where the copolymer was dissolved in o-phosphoric acid at room temperature prior to the addition of polyphosphoric acid and P₂O₅. The grafting degree was controlled by varying the reaction time at 120°C. A range of grafts was obtained with degree of grafting 1%–20% (per mer, equal to 0.5%–10% per sulfonic group) and with equivalent weight between 120 and 130 g/mol, meeting Milestone 3: equivalent weight <250 g/mol. As an example, P83B17 grafted with BP at two levels, 2% and 5% with respect to moles of sulfonic groups, is shown in Figure 5.

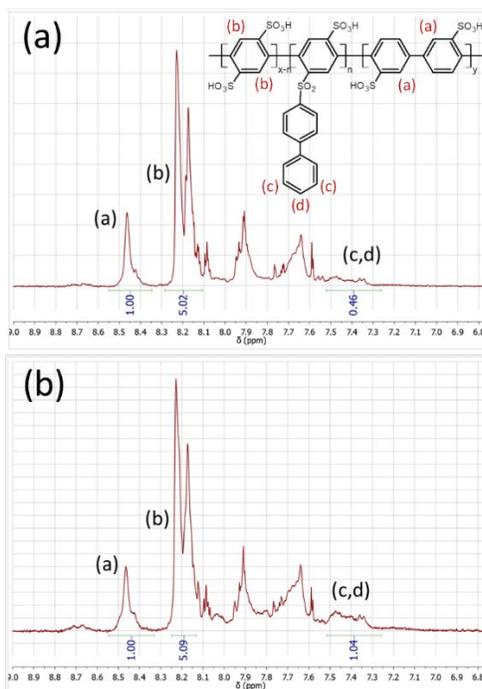


Figure 5. 400 MHz ¹H NMR (D₂O) spectra of P83B17 grafted with (a) 2% BP (per sulfonic acid group) and (b) 5% BP.

CONCLUSIONS AND UPCOMING ACTIVITIES

The project activities are progressing as planned after an initial minor delay caused by the late arrival of the postdoctoral scholar. Now, at the end of Q3, it can be stated that all the necessary synthetic work needed for successful execution of Q4 tasks has been completed. Moreover, in addition to the originally proposed monomers, dichlorophenylenesulfone disulfonic acid dilithium salt (DCPSDSA-Li) was also synthesized, homopolymerized, and copolymerized with dibromobenzenedisulfonic acid dilithium salt (PxSy). The PxSy copolymer has never been synthesized before and the team is very excited to explore its application in the composite PEM fabrication.

Q4 activity will encompass two tasks: (i) preliminary electrospinning of the BP-grafted copolymers followed by (ii) dual fiber membrane fabrication (Gen1). The team will be required to meet the go/no-go milestone by demonstrating composite water-stable membrane with area specific resistance of $0.03 \text{ Ohm}\cdot\text{cm}^2$ at 80°C and 40%–90% RH, and tensile strength $>20 \text{ MPa}$ in water vapor equilibrated state at room temperature.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. R. Wycisk, “Composite PEMs from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s,” Presentation FC310, DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluating Meeting, Crystal City, VA, April 29, 2019.
2. R. Wycisk, “Composite PEMs from Electrospun Crosslinkable Poly(Phenylene Sulfonic Acid)s,” US DRIVE Fuel Cell Technical Team Meeting, Detroit, MI, September 18, 2019.

REFERENCES

1. McGrath et al., *J. Appl. Polym. Sci.* 100, no. 6 (2006): 4595.
2. Litt et al., *Macromolecules* 46 (2013): 422.
3. B.M. Graybill, *J. Org. Chem.* 32, no. 9 (1967): 2931.