
Novel Non-Perfluorosulfonic Acid Proton Exchange Membrane for Fuel Cell Application

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Subcontractors:

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- University of Delaware, Newark, DE

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Overall Objectives

- Synthesize, optimize, and scale up highly proton conductive and durable non-perfluorosulfonic acid (non-PFSA) proton exchange membranes (PEMs).
- Demonstrate one or more reinforced composite membranes exceeding DOE technical targets: (1) low H₂ and O₂ crossover (<2 mA/cm²), (2) low area specific resistance (<0.05 Ohm cm² at 80°C and water partial pressures from 25 to 45 kPa), and (3) outstanding durability (<20% loss in open circuit voltage after 20,000 cycles of combined chemical/mechanical test protocol).
- Show fuel cell performance of 600 mA/cm² at 0.6 V with Pt loading below 0.1 mg/cm² and temperature >60°C.

- Demonstrate fuel cell durability equivalent to <10% voltage degradation over 2,000 h hold test at 600 mA/cm² and temperature >60°C.
- Conduct rigorous cost analysis to reflect final commercial cost of the membrane.

Fiscal Year (FY) 2019 Objectives

- Synthesize, optimize, and scale up non-PFSA PEMs.
- Evaluate the hydrolytic stability and proton conductivity of non-PFSA PEMs.
- Produce robust composite non-PFSA PEMs.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Durability
- Cost
- Performance.

Technical Targets

The DOE 2020 technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Synthesized, optimized, and scaled up Gen-1 and Gen-2 non-PFSA PEMs.
- Evaluated the membrane properties and proton conductivity of Gen-1 and Gen-2 PEMs.
- Demonstrated reinforced composite Gen-1 PEMs.

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

Table 1. Timeline and Target toward Meeting Technical Metrics

| ID | Technical Metric | Timeline and Target |
|----|--|--|
| 1 | In-plane proton conductivity (measured at 80 °C at 50%, 70%, and 95% RH conditions) | Q4: $\geq 15, 20, 60$ mS/cm at 50%, 70%, and 95% RH |
| 2 | Dimensional swelling ratio (in x-, y- directions in water at 25 °C in SO ₃ H form) | Q4: $\leq 15\%$ change |
| 3 | Mechanical strength (tensile strength and elongation at break [strain] measured at 25 °C and 50% RH in SO ₃ H form) | Q4: ≥ 25 MPa strength, $\geq 80\%$ strain |
| 4 | Mechanical durability under RH cycles (80 °C, dry/wet cycles between 0% RH and 90 °C dew point) | Q4: 5,000 cycles with ≤ 15 mA/cm ² H ₂ crossover |
| 5 | Chemical durability (90 °C, H ₂ /air, dry/wet cycles between 0% RH and 90 °C dew point) | Q4: 250 hours with ≤ 15 mA/cm ² H ₂ crossover or $\leq 20\%$ loss in open circuit voltage |
| 6 | Area specific resistance (determined via electrochemical impedance spectroscopy under H ₂ /N ₂ at 80 °C using 50%, 70%, and 95% RH) | Q4: ≤ 0.06 Ohm cm ² @ 80 °C and pH ₂ O from 25 to 45 kPa (~50%–100% RH) |
| 7 | Maximum operating temperature | Q4: 90 °C |

RH – relative humidity

INTRODUCTION

Our team plans to develop durable, high-performance, low-cost non-perfluorosulfonic acid (PFSA) proton exchange membranes (PEMs) made of reinforced composite membranes and demonstrate low membrane ionic resistance and good chemical and mechanical durability under both dry and wet cycles. Specific properties we want to achieve compared to the standard PFSA membrane Nafion 212 include but are not limited to: (1) better proton conductivity at various RH conditions, (2) lower material cost, (3) higher tensile strength, (4) lower area specific resistance (by reducing membrane thickness) and (5) greater durability under repetitive cycles of wet and dry environment with longer cycling life of PEM fuel cells.

APPROACH

We propose to develop highly proton conductive and durable PEMs by tailoring micro-to-nano hierarchical ion channels within phase separated polymers. The unique design of the proposed polymer is that it consists of an all C–C bond backbone (i.e., no C_{sp2}–O bond) and a *locally* and *densely sulfonated* side chain. To achieve excellent proton conductivity and durability simultaneously, our team will use a material design concept in which the components responsible for ion conduction and mechanical stability are decoupled. Our approach is to engineer optimum conductive channels through phase separation between *tethered densely sulfonated side chains* and a *highly stable all-carbon backbone polymer*. Ion conductive channels will be engineered with optimal size and ion density so that protons are efficiently transported through the hydrophilic water channels with minimal unproductive water (unbound, free water). A reinforced composite membrane is critically important for this project to develop the next-

generation PEM. To achieve the DOE target, it is necessary to reduce the membrane thickness to less than 20 μm , thereby reducing ionic membrane resistance. Thinner membranes prepared from sulfonated polymers alone generally do not have sufficient mechanical strength due to unavoidable swelling when in contact with water. To produce thinner membranes (less than 20 μm), which can offer lower ionic resistance, we will impregnate the above synthesized polymer into a low-cost, chemically inert, mechanically stable matrix and produce thin reinforced composite membranes in this project.

RESULTS

Synthesis and Characterization of Non-PFSA PEMs

One of the main tasks of this project is to synthesize non-PFSA PEMs and evaluate their hydrolytic stability and proton conductivity. The synthesis of non-PFSA PEMs was carried out using high-molecular-weight ($M_w > 100,000$) aromatic precursor polymer, BPBr (Figure 1) developed by the Bae group at Rensselaer Polytechnic Institute (RPI). This aromatic precursor polymer does not have any heteroatoms in the backbone and side chain except for the precursor functional group $-\text{Br}$, which can be converted to a sulfonate group for PEM applications. At the beginning of Year 1, the research was focused on the functionalization of precursor polymers to synthesize proposed ionic polymer, BP-Ar3 (Figure 1). However, high ion exchange capacity (IEC) and good mechanical properties could not be simultaneously achieved from the proposed ionic polymer, so the structures of the ionic polymers were redesigned as shown in Figure 1. Unfortunately, some of these redesigned ionic polymers could not be synthesized and others either have the solubility issue or have low conductivities at lower relative humidity conditions. So, the RPI team came up with a new class of PEMs as shown in Figure 2.

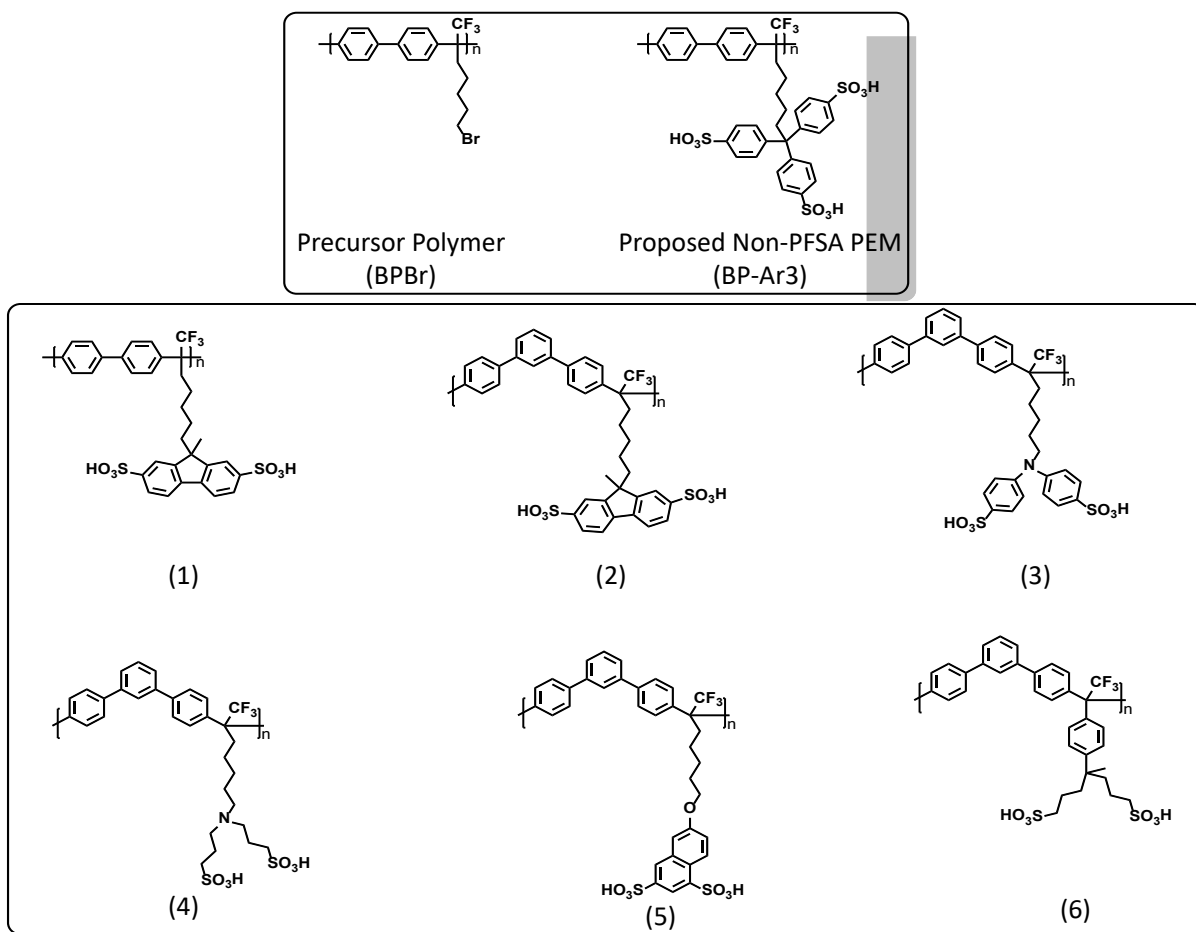


Figure 1. Structure of precursor polymer (BPBr), proposed non-PFSA PEM (BP-Ar3), and redesigned PEMs (1 through 6)

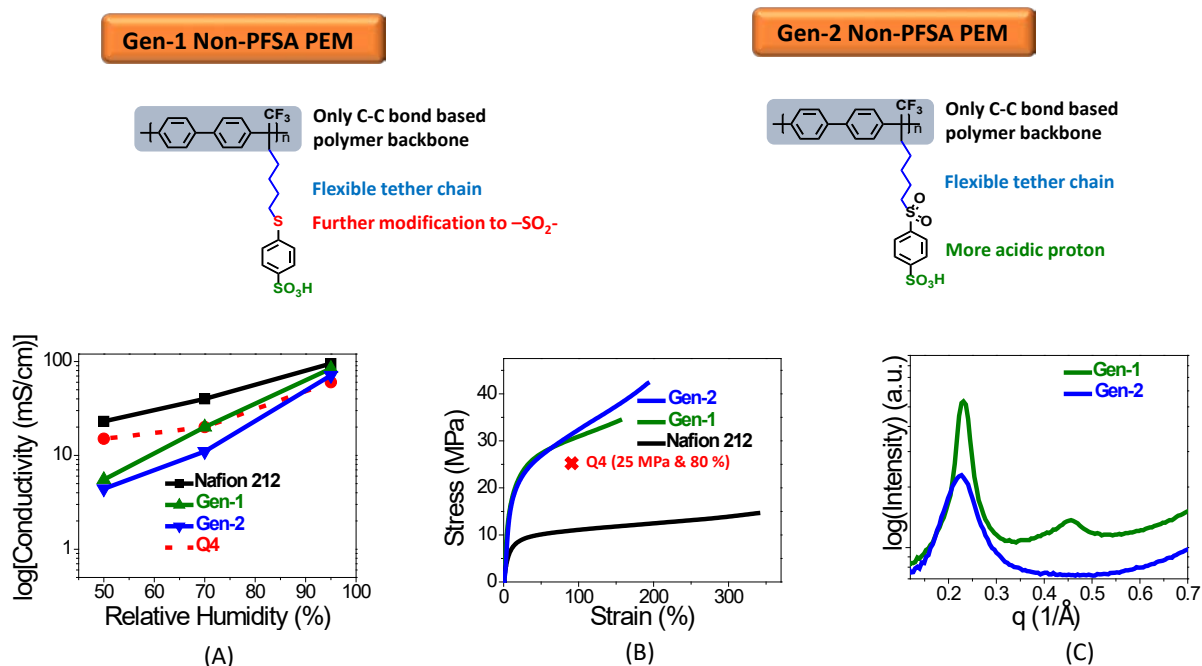


Figure 2. Upper row: structures of Gen-1 and Gen-2 PEMs. Lower row: (A) proton conductivities of Gen-1, Gen-2, and Nafion 212 at different RH measured at 80 °C, (B) stress-strain curves of Gen-1, Gen-2, and Nafion 212 measured at 50 °C and 50% RH, and (C) wide angle X-ray diffraction profiles of dry Gen-1 and Gen-2 PEMs in the H⁺ form.

Two generations (i.e., Gen-1 and Gen-2) of PEMs were successfully synthesized and scaled up. The proton conductivities and hydrolytic stability of these two non-PFSA PEMs were evaluated and the data is summarized in Table 2. Both of these PEMs have good dimensional stability and mechanical strength meeting the go/no-go targets. The dimensional stability and mechanical strength can be further enhanced by imbuing these ionomers into the porous polymer support to make reinforced composite membranes to meet the ultimate target. The proton conductivities of these PEMs were evaluated at 80 °C under different relative humidity conditions. As depicted in Figure 2A, the proton conductivities of Gen-1 are greater than that of Gen-2 PEM over a range of relative humidity, which can be attributed to the higher IEC of the Gen-1 PEM compared to Gen-2. The morphologies of these PEMs were evaluated using an X-ray scattering technique. Both PEMs showed intense wide-angle X-ray scattering and a clear ionomer peak in the dry state (Figure 2C). This demonstrated that the well-defined polymer structure and the ionic group tethered to the backbone by flexible chain facilitated the formation of ionic aggregates. The ionomer peaks of Gen-1 and Gen-2 PEMs correspond to characteristic interdomain distances of $d = 2.7$ and 2.8 nm, respectively. In the case of Gen-1, second order scattering was also observed indicating more ordered lamellar morphology, which may also account for higher conductivity of Gen-1 compared to Gen-2.

Table 2. Membrane Properties of Gen-1 and Gen-2 PEMs

| Polymer | IEC (mequi./g) | | Water Uptake (%) ^a | Swelling Ratio (% x-y) ^b | Stress/Strain (50 °C, 50% RH) ^c | Conductivities (mS/cm) ^d | | |
|----------------------|----------------|-----------|-------------------------------|--|--|-------------------------------------|--------|--------|
| | Theoretical | Titration | | | | 50% RH | 70% RH | 95% RH |
| Gen-1 | 2.03 | 1.92 | 25 | 7 | 27/121 | 5.5 | 20 | 84 |
| Gen-2 | 1.91 | 1.67 | 38 | 13 | 30/242 | 4.4 | 11 | 71 |
| Nafion 212 | - | - | - | 11 | 18/270 | 23 | 40 | 95 |
| Q4 (Go/No-Go) | - | - | - | <15 | ≥25 / ≥80 | 15 | 20 | 60 |
| Q8 (Ultimate Target) | - | - | - | <10 | ≥50 / ≥150 | 25 | 40 | 100 |

^{a, b, c} measured in –SO₃H form, ^dmeasured at 80°C, **meet Q4 targets**, **do not meet Q4 targets**

CONCLUSIONS AND UPCOMING ACTIVITIES

A new class of non-PFSA PEMs (Gen-1 and Gen-2, see Figure 2) has been successfully synthesized and scaled up. These PEMs showed decent membrane properties (see Table 2 and Figure 2) that meet most of the go/no-go targets that have been investigated so far. Further, the Gen-1 PEM has been successfully imbibed into the porous polymer support to make reinforced composite membrane of thickness <10 μm. The future work will be focused on investigating the properties of reinforced membrane, and a new PFSA PEM ionomer (Gen-3) that can meet the ultimate target will be designed and synthesized.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. 2019 Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Crystal City, VA, April 29–May 1, 2019.
2. 2019 US Fuel Cell Tech Team Meeting, USCAR office, Southfield, MI, September 18, 2019.