Novel Membranes for Electrochemical Hydrogen Compression Enabling Increased Pressure Capability and Higher Pumping Efficiency

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Overall Objectives

This project is conducting fundamental studies of novel membranes for electrochemical hydrogen compression (EHC) application. Insights gained from these studies will be applied toward the synthesis of ionomers and fabrication of membranes that meet the following ultimate targets:

- Hydrogen stream: ≥1 kg/h
- Specific energy consumption: 1.4 kWh/kg
- Inlet pressure: 100 bar
- Outlet pressure: 875 bar.

Fiscal Year (FY) 2018 Objectives

- Synthesize biphenyl-quaternary ammonium (QA) ionomers enabling cell operation at higher temperature with better humidity tolerance and higher pressure.
- Prepare reinforced composite proton exchange membranes (PEMs) by impregnating QA-functionalized polymers into a mechanically robust matrix.
- Evaluate properties of polymer and composite membranes with reference to the technical milestones.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- Reliability and Costs of Hydrogen Compression.

Technical Targets

- Efficiency of 1.4 kWh/kg at an inlet pressure of 100 bar, outlet pressure of 875 bar, and flow rate of 1 kg/h.

FY 2018 Accomplishments

- Designed and synthesized four ionomers for EHC performance test.
- Discovered that polyethylene (PE)-reinforced membranes were more flexible with larger elongation at break and less Young's modulus compared to their free-standing counterparts.
- Studied the relationship between equilibrium proton conductivity and relative humidity (RH) for phosphoric acid (PA)-doped QA functionalized biphenyl-based polymer (BPN1)-trimethylamine (TMA), BPN1-piperidine (Pip) and BPN1-pyridine (Pyr) ion-pair ionomer membranes. The results showed that these membranes had moisture tolerance up to 90% RH without a significant conductivity drop.
- Studied the relationship between equilibrium proton conductivity and temperature. It is observed that high conductivity (>100 mS/cm)

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

can be achieved under relatively low RH (~50%) at elevated temperature (80°C).

- Identified that PA-doped BPN1 composite membranes have better water tolerance compared to commercially available Nafion XL.

INTRODUCTION

EHC has the potential for use in compressing hydrogen at refueling stations that serve hydrogen fuel cell vehicles. The pressure of compression required depends on the vehicle tank type and is currently either 350 or 700 bar. It is desirable for an EHC to have high proton conductivity (for high operating efficiency), large elongation at break (such that it can reliably withstand the pressure difference at both sides), and high durability (to reduce the maintenance required). Rensselaer Polytechnic Institute (RPI) is developing promising polymer candidates for EHC. For example, RPI created PA-doped BPN1 ion-pair ionomer membrane for EHC application with proton conductivity enabled by an excess of PA molecules surrounding the QA-dihydrogen phosphate ion pair [1]. Figure 1 shows the chemical structures of four proposed ionomers. The ion-pair interaction and PA-retention can be tuned by the QA groups with different basicity and size. Together, Xergy, a leading company in the field of electrochemical compression, and RPI are working together to create novel EHC membranes. The group has generated a performance map based on ionomer structures and membrane fabrication variables to down-select the ionomers based on expected long-term durability and enabling DOE targets. Using those polymer resins as active material, Xergy has manufactured both free-standing and reinforced composite membranes. The team has made progress in testing membranes for compressor performance.

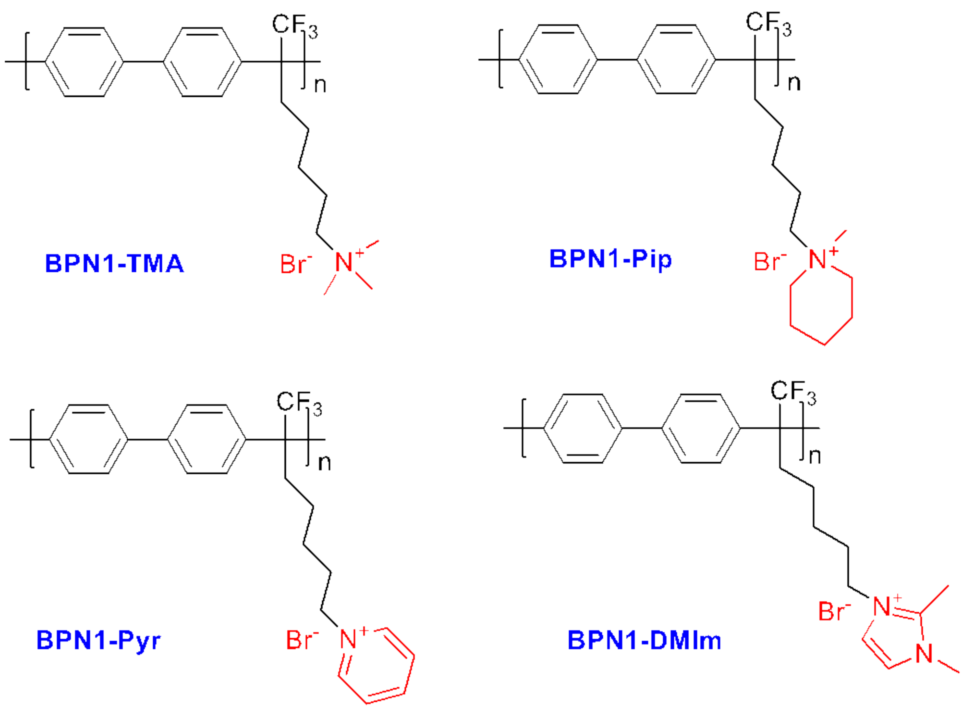

Figure 1. Chemical structures of ionomers with various quaternary ammonium groups

APPROACH

- Synthesize four ionomers (BPN1 series).
- Fabricate membrane: free-standing membranes and reinforced membranes.
- Characterize membrane (PA doping level by acid-base titration, equilibrium conductivity at different temperatures and RHs, and mechanical property by dynamic mechanical analysis).
- Test EHC at different temperatures and RHs.

- Generate performance maps as a function of membrane and operating condition variables.
- Down-select optimal ionomer(s).
- Test long-term durability of membranes made of optimal ionomer(s).
- Test EHC performance using optimal ionomer(s), and compare with DOE targets.

RESULTS

During FY 2018, RPI synthesized four ionomers by reacting BPBr-100 with TMA, Pip, Pyr, and 1,2-dimethylimidazole (DMIm). The chemical structures are shown in Figure 1. Xergy fabricated membranes from the RPI ionomers, including both free-standing and reinforced composite membranes. Hand-cast samples were prepared at sizes of approximately 15 x 15 cm (225 cm^2) or greater with thickness uniformity of ±10% (i.e., 20 ± 2 µm).

The mechanical properties of both free-standing and PE-reinforced membranes of BPN1-TMA and BPN1-Pip were evaluated. Since the membrane in EHC systems faces a significant pressure difference at inlet (low pressure) and outlet (high pressure) side, elongation at break is considered the most important mechanical property. Table 1 and Figure 2 indicate that PE-reinforced membranes have larger percentages for elongation at break and lower pressures for Young's modulus compared to their free-standing counterparts. The improved membrane flexibility is a result of the stretchability of the PE mesh. Therefore, further property studies for this project focused on the PE-reinforced membranes.

Table 1. Mechanical Properties for BPN1-TMA and BPN1-Pip at 30°C and 0% RH

Ionomer	Type	Elongation at Break (%)	Tensile Strength (MPa)	Young's Modulus (MPa)
BPN1-TMA	Free-standing	145	15.9	75.7
	PE-reinforced	269	13.0	11.7
BPN1-Pip	Free-standing	119	13.5	96.9
	PE-reinforced	331	17.6	11.7

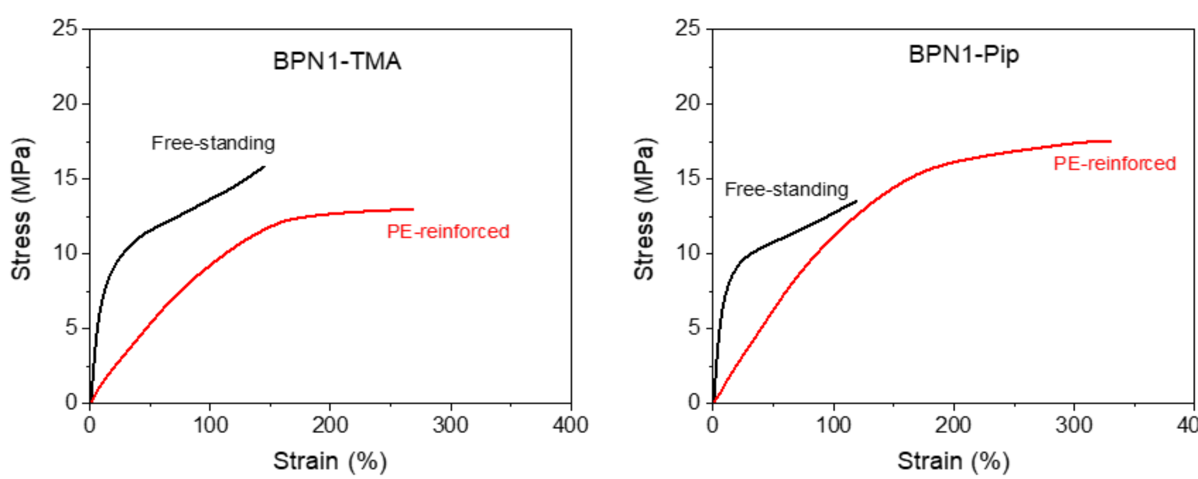

Figure 2. Stress-strain curve for (a) BPN1-TMA, and (b) BPN1-Pip at 30°C and 0% RH

Four BPN1-based reinforced membranes with different cation groups were prepared for EHC performance test. The four cation groups have different basicity and size, which affect the interaction with PA. The membrane was first immersed in a 1M NaOH aqueous solution for 12 hours followed by immersion in a PA aqueous solution (85 wt%) for 6 hours. Since proton conductivity is highly dependent on the PA content, the doping level (defined as the average number of PA molecules per cation group) was studied by acid-base titration. The results are summarized in Table 2. BPN1-TMA and BPN1-Pip exhibited similar doping levels due to the almost identical basicity of trimethylamine and piperidine. BPN1-Pyr, however, showed a lower doping level since pyridine is less basic. Thus, the pyridinium-dihydrogen phosphate ion-pair interaction is weaker than with the others.

Table 2. Doping Level of BPN1-TMA, BPN1-Pip and BPN1-Pyr

Ionomer	Doping Level
BPN1-TMA	8.3
BPN1-Pip	8.2
BPN1-Pyr	4.8

Acid-doped membranes typically show inadequate performance under humidified conditions [2]. To select the optimal ionomer for EHC performance testing, it is important to consider the extent of moisture tolerance as well as the equilibrium conductivity at different RHs and temperatures. We studied the equilibrium conductivity at 30°C (the common operating temperature for EHC) with RH ranging from 50% to 100%. The data were obtained after keeping the membrane at a fixed RH for at least 4 h before recording the conductivity value. As shown in Table 3, the equilibrium conductivity increases with as RH increases up to 90% but then drops significantly at 100% RH for all the three ionomers. The increasing conductivity is due to moisture facilitating proton transportation within the membrane. The conductivity, however, decreases under fully humidified conditions (at 100% RH) due to PA loss. To further confirm the tolerance of 90% RH, an extended test time of up to 14 h was applied, and no obvious conductivity drop was observed. Therefore, we conclude that PA-doped BPN1-TMA, BPN1-Pip, and BPN1-Pyr ionomers can be operated at up to 90% RH without significant PA leakage issues.

Table 3. Equilibrium Conductivity at 30°C under Various RH

Ionomer	Equilibrium Conductivity (mS/cm)					
	50% RH	60% RH	70% RH	80% RH	90% RH	100% RH
BPN1-TMA	49	65	77	126	136	63
BPN1-Pip	48	60	77	95	122	97
BPN1-Pyr	44	59	82	99	98	90

Conductivity usually increases under elevated temperatures because of the enhanced internal mobility of protons. Table 4 shows that the equilibrium conductivity of BPN1-TMA was higher at 80°C compared to that at 30°C under the same RH conditions. Additionally, it is worth noting that proton conductivity over 100 mS/cm can be reached even at 50% RH at 80°C. This finding provided us with an opportunity to explore EHC performance at high temperature and low RH conditions, which cannot be applied to the commercially available PEM Nafion, to improve the operating efficiency and ease the water management requirements.

Table 4. Equilibrium Conductivity of BPN1-TMA at 30°C and 80°C under Various RH

Temperature	Equilibrium Conductivity (mS/cm)								
	20% RH	30% RH	40% RH	50% RH	60% RH	70% RH	80% RH	90% RH	100% RH
30°C	N/A	N/A	N/A	49	65	77	126	136	63
80°C	62	78	96	114	139	171	175	190	155

EHC testing was carried out on both PE-reinforced BPN1 and Nafion XL. The initial polarization curve (Figure 3a) reveals that the BPN1-Pyr and BPN1-Pip composite membranes operate significantly better than the Nafion XL, initially presumed to be due to their better conductivity at lower moisture levels. However, it appears this is actually due to the fact that the cells had not been "broken in" yet. As the Nafion XL membrane becomes activated throughout the following tests (i.e., the membrane becomes more hydrated and the contact resistances in the cell are lessened by pressurizations), its performance increases to the order of the BPN1-Pyr and the BPN1-Pip. The polarization curve after the first (Figure 3b) and second pressurization (Figure 4a) shows consistent, nearly linear performance of the BPN1-Pyr and BPN1-Pip membranes. The Nafion XL membrane, however, shows a rapid deterioration at higher current densities. Since the protons require water molecules to be transported through the membrane, it is likely that the Nafion XL rapidly fails at higher current densities due to a lack of replenishment of water, whereas the BPN1-Pyr and BPN1-Pip membranes, which do not require as much water, do not exhibit this. In the long-term polarization curves (Figure 4b), the Nafion XL membrane shows higher total performance within the time-frame tested. However, if the slope of the curves is estimated by a fitting function, it shows that the rate at which the current is dropping per unit time for the Nafion XL membrane is greater than for the BPN1-Pyr and BPN1-Pip membranes. This suggests that, given a long enough time, the performance of the Nafion XL membrane will drop below that of both the BPN1-Pyr and BPN1-Pip membranes. This again could be due to the water requirements of the Nafion XL versus the BPN1-Pyr and BPN1-Pip.

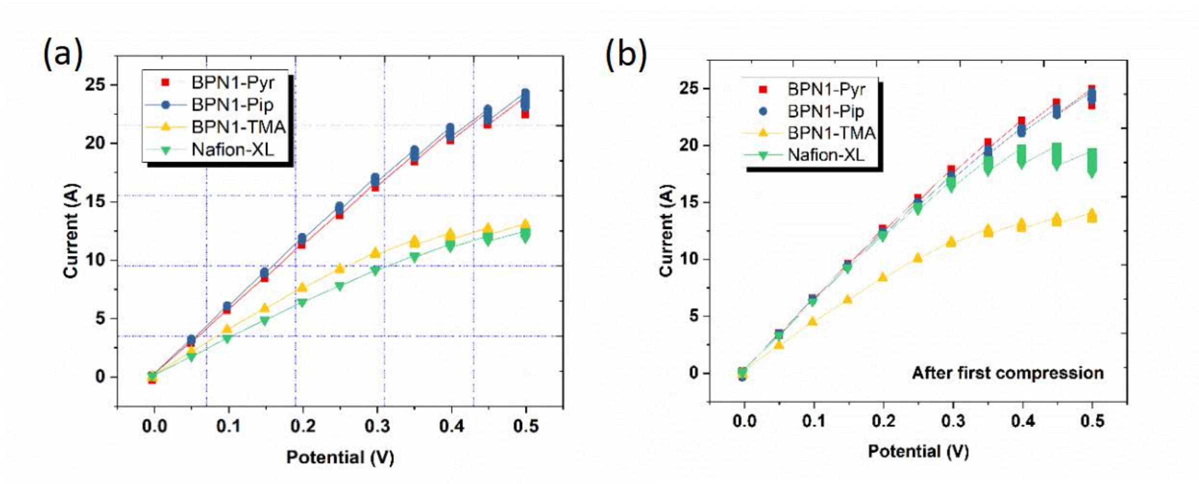

Figure 3. ECC testing results: (a) initial results; (b) after first compression

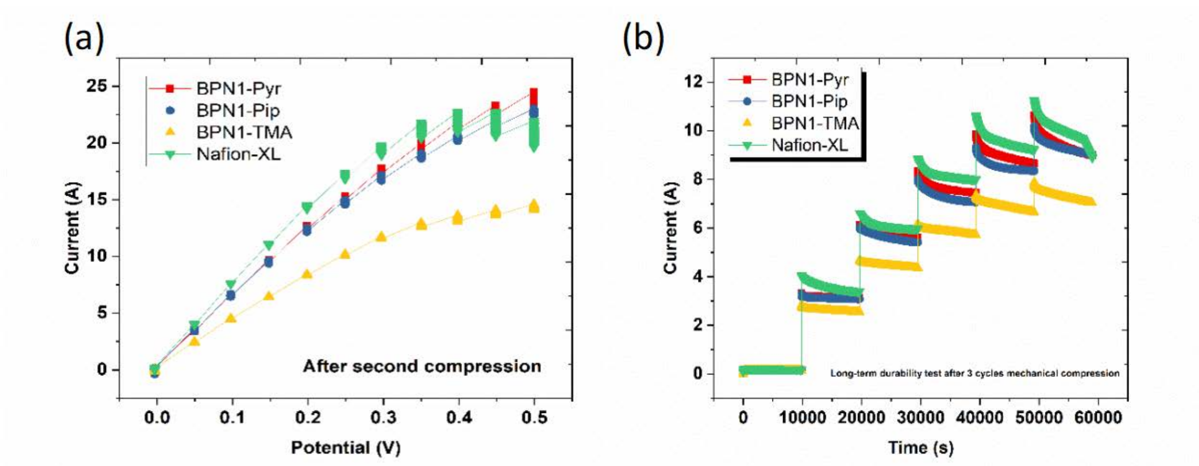

Figure 4. ECC testing results: (a) after second compression; (b) long-term durability test

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions

- Four ionomers (BPN1-TMA, BPN1-Pip, BPN1-Pyr, and BPN1-DMIm) were synthesized and characterized.
- The PE-reinforced membrane outperformed the free-standing membrane in terms of elongation at break.
- The PA-doped ion-pair ionomer membrane exhibited moisture tolerance up to 90% RH.
- The elevated temperature can help achieve high conductivity at lower RH range.
- PE-reinforced BPN1 outperforms Nafion XL at high current densities in EHC due to better water management.

Upcoming Activities

The project teams have made major progress over the last months. There are still tasks to be completed before the electrochemical compressors can match DOE's target performance. These include, but are not limited to, the following items:

- Down-selecting the best candidate polymer and evaluating its long-term stability
- Preparing reinforced membranes with down-selected polymer
- Testing EHC performance and long-term stability, iterating key variables including ionomer structure, temperature, and RH
- Continuing to validate compressor performance at different temperatures
- Continuing data collection, analysis, and reporting on performance data to meet DOE targets.

REFERENCES

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2. K.-S. Lee, J.S. Spendelow, Y.-K. Choe, C. Fujimoto, and Y.S. Kim. *Nat. Energy* 1 (2016): 16120.