
FY17 SBIR II Release 1: Novel Hydrocarbon Ionomers for Durable Proton Exchange Membranes

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Overall Objectives

- Synthesize and characterize aromatic hydrocarbon proton-conducting membranes based on the novel concept of coordinated ion pairs as high-temperature polymer electrolyte membranes in fuel cells for transportation applications.
- Empirically establish structure-property relationships of synthesized materials that will afford optimal membrane properties through monomer selection and compositional manipulation.
- Measure proton conductivity and fuel cell performance of down-selected proton exchange membrane ionomers.

Fiscal Year (FY) 2019 Objectives

- Develop cost-effective poly(arylene benzonitrile) copolymers as proton-conducting membranes in fuel cells for transportation applications at 120°C.
- Demonstrate improved film-forming capabilities and mechanical properties.
- Determine membrane proton conductivity as a function of relative humidity and temperature

as compared to commercial perfluorosulfonic acid membranes.

- Demonstrate fabrication and performance of membrane electrode assemblies.
- Establish and optimize structure-property relationships for enhanced membrane and membrane electrode assembly performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (fuel cell membranes for transportation applications) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Maximum operating temperature of 120°C
- Durability: Mechanical and chemical stability
- Performance: Stable proton conductivity independent of relative humidity
- Membrane electrode assembly fabrication.

Technical Targets

This project is developmental research toward commercially viable membranes based on a new (2016) ion pair concept [1] of proton-conducting ionomers. The membrane properties and testing results shall be applied toward the design and fabrication of a proton-conducting ionomer that meets the following DOE targets for membranes for transportation applications:

- Maximum operating temperature: $\geq 120^{\circ}\text{C}$
- Durability: 20,000 cycles
- Cost: \$20/m².

FY 2019 Accomplishments

- Demonstrated scale up of polymer precursor to ~200-gram quantities.
- Demonstrated successful scale up of down-selected copolymers to 100-gram batches.

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

- Demonstrated scalability of surface treatment for glass substrates (24-in. x 24-in.), which allowed for fabrication of very thin membranes (14–30 μm).
- Explored the influence of ion pair formation conditions on phosphoric acid retention.
- Demonstrated exceptional proton conductivity for down-selected ion pair membranes.
- Demonstrated stable proton conductivity of membranes across a wide range of humidification.

INTRODUCTION

Fuel cells efficiently convert chemical energy to electrical energy and can operate on clean, domestically produced renewable fuels. Polymer electrolyte membrane fuel cells directly fueled by hydrogen are well-suited to applications, such as light- to medium-duty vehicles and backup power, that require fast startup times. The development of durable, cost-effective proton-conducting membranes for fuel cells is essential to a viable hydrogen-based energy economy. Internationally, researchers have focused efforts on various approaches to increase protonic conductivity, minimize electronic conductivity, limit fuel permeability, exhibit the requisite thermal and mechanical properties, and achieve long-term chemical stability. Perfluorosulfonic acid based membranes (sold by, e.g., Chemours, Dow) are expensive yet remain the leading employed commercially available membranes and account for a significant portion of cost in manufacturing fuel cell stacks. Technical shortcomings of perfluorinated membranes include limited operation temperature ($\leq 100^\circ\text{C}$), necessity of sufficiently high hydration for proton conductivity, low availability, and environmental hazards of their precursors. Fuel cells that operate at higher temperatures ($100^\circ\text{--}120^\circ\text{C}$) would enhance system efficiency, assist with water management, and possibly reduce precious metal catalyst loading levels in the membrane electrode assembly. Most current membrane technologies have a glass transition temperature in the range of 80°C to 120°C and suffer from thermoplastic deformation, creep, and pinholes when subjected to regular exposure above that range.

APPROACH

This project demonstrates development of a new class of hydrocarbon-based polymer electrolyte membranes as a viable alternative to expensive perfluorosulfonic acid membranes that are limited to less than 100°C operation. NanoSonic membranes are synthesized via industrial manufacturing procedures and incorporate a new functionalized comonomer precursor. The adaptation of current manufacturing processes could directly reflect a potential cost savings in manufacturing of the final functionalized copolymers at scale. The functionalized comonomer polymerization provides a reproducible route to tailored (compositional) copolymers. A low-temperature procedure has been developed to easily convert the functionalized copolymers into quaternary ammonium-ionomeric polymers. Controlled phosphoric acid imbibing results in ion pair formation with the quaternary ammonium groups and generates an intermediate-temperature class of proton-conducting membranes.

RESULTS

NanoSonic has applied recent structure-property data to modify the composition of the functionalized copolymers toward design and fabrication of an optimum proton-conducting fuel cell membrane for transportation applications. NanoSonic has demonstrated and is actively evaluating these functionalized copolymers as scalable routes to quaternary ammonium materials via current commercial processes. The utilization of a pre-functionalized comonomer affords precise and reproducible control of the ion exchange capacity of the final membrane that is not possible through post-polymerization routes reported in literature. The down-selected polymer compositions have been scaled up to 100-gram synthesis batches and yielded high-molecular-weight copolymers.

The desirable high-molecular-weight copolymers are soluble in several common laboratory solvents. The monomer selection, structure, and molar composition influence many material properties, including solubility. Versatile solubility of the copolymers is favorable for future membrane fabrication and manufacturing options. Mechanically tough, very thin films (14–25 μm thickness) have been fabricated via solution casting on a proprietary surface treatment on glass substrates. The proprietary treatment has been demonstrated on 24-in. x

24-in. glass substrates and there is no concern that the treatment cannot be scaled to larger dimensions. These thin membranes are unsupported, which infers that the copolymer has achieved high molecular weight. Thinner proton-conducting membranes typically result in lower through-film resistance, which may improve system kinetics, reduce weight, and lower membrane cost.

Phosphoric acid-doped polybenzimidazoles (PA-PBI) are a specialty type of proton-conducting membrane. However, due to the extremely high loading (>600 wt %) of phosphoric acid within the membrane the mechanical properties are substantially compromised. In fact, the PA-PBI films are referred to as “gel membranes.” These gel membranes are primarily employed in high-temperature (>180°C) stationary power systems and are known to lose phosphoric acid even in the absence of water [2].

Significant research has been conducted to understand and develop the best conditions for formation of the ion pair membranes. Among the important factors are phosphoric acid concentration, phosphoric acid source (phosphoric acid or polyphosphoric acid), doping time, and temperature. NanoSonic’s proprietary ion pair formation of the thin membranes has resulted in exceptionally high proton conductivity. Figure 1 presents the proton conductivity versus relative humidity for several NanoSonic ion pair candidate membranes, as measured at Los Alamos National Laboratory (LANL). The sample stabilization times noted on top of the graph are the time the sample was allowed to equilibrate in the test cell prior to taking the measurement—not necessarily the required time to reach a “stable point.” Several of NanoSonic’s ion pair membranes display noteworthy proton conductivity, up to 100 mS/cm at 80°C, which is much higher than the Nafion 212 reference. As measured, the increasingly high proton conductivity for NanoSonic ion pair membranes continued to climb up to 70% relative humidity. These conductivity values and behavior across the relative humidity range is superior to the results published on PA-PBI and a Sandia National Laboratories/LANL polyphenylene-based ion pair membrane [2]. In fact, the conductivity of the PA-PBI membranes quickly decreases with increasing relative humidity (RH) above ~7.5% RH while the Sandia National Laboratories/LANL membrane conductivity begins to decrease at RH >40%.

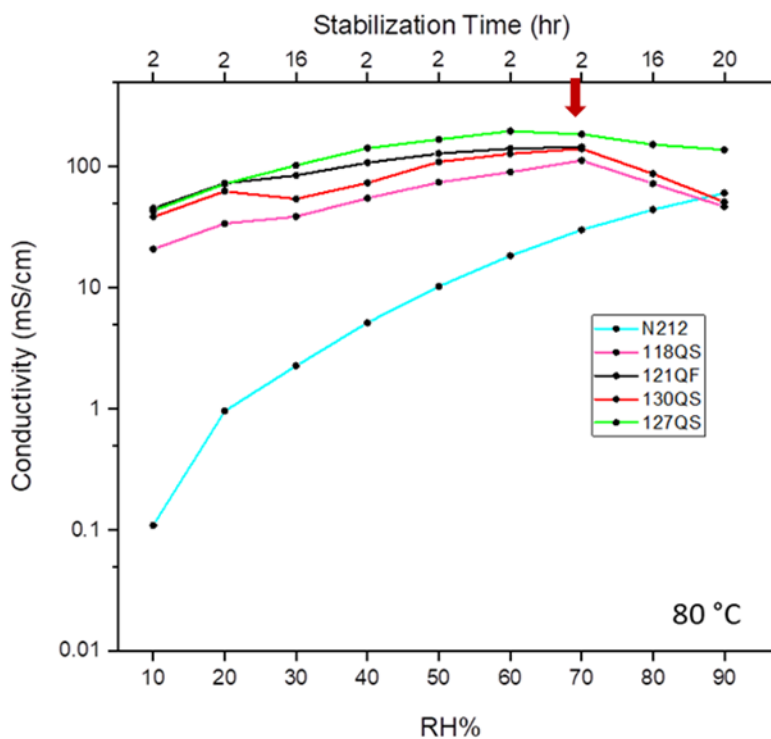


Figure 1. Equilibrium proton conductivity vs. relative humidity at 80 °C for select NanoSonic candidate ion pair membranes

Traditionally, ionomeric membranes require water (or humidification) for reasonable proton conductivity. Figure 2 presents the proton conductivity of several NanoSonic candidate ion pair membranes under zero

percent humidification. NanoSonic's copolymer ion pair membranes show noteworthy proton conductivity stability across the tested temperature range (80°–200°C). Sample 90QT is a quaternary ammonium membrane prepared via a popular chloromethylation route; the conductivity plot of this material is unlike that for NanoSonic's copolymer membranes. This difference in conductivity behavior is attributed to lower ion exchange capacity, the distribution of the ion pairs/clusters, and probable morphological differences. Proton-conducting membranes capable of operating at or above 120°C offer many benefits for fuel cell operations, including better tolerance to fuel impurities, improved electrode kinetics, and reduced requirements for heat and water management. Nafion membranes are not applicable under these conditions primarily due to dehydration and mechanical failure at 120°C (not shown).

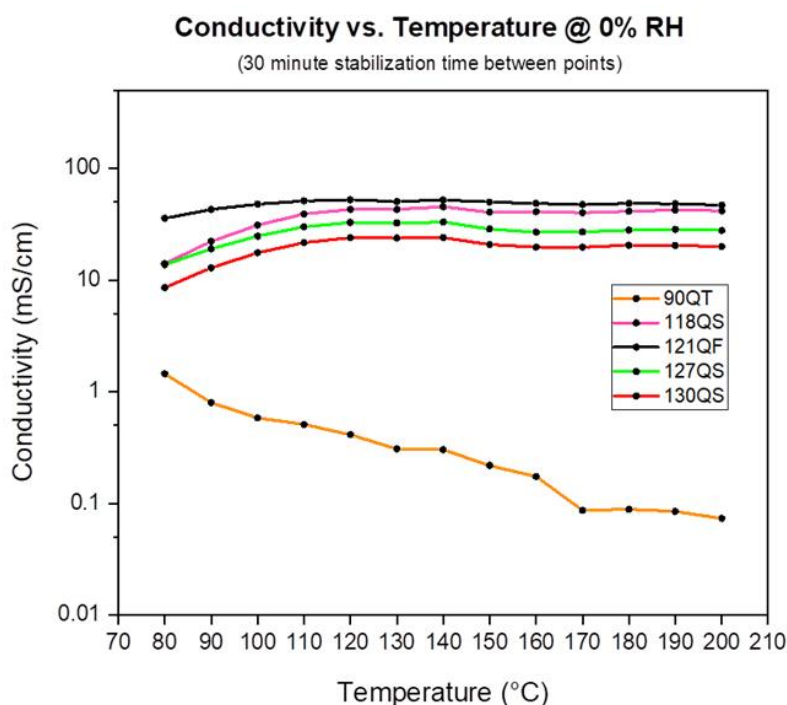


Figure 2. Influence of relative humidity on proton conductivity on NanoSonic ion pair membranes and Nafion (N212) control

The ion pair formation and phosphoric acid retention is important to the development of NanoSonic's copolymers and this membrane technology approach. As mentioned, NanoSonic has worked with LANL researchers to develop proprietary ion pair formation procedures for NanoSonic's down-selected copolymers. The parameters that are manipulated during ion pair formation are exposure time, temperature, and phosphoric acid concentration. The phosphoric acid retention (Figure 3) is calculated from the average of titration data for three samples removed at predetermined time intervals. The control samples (i.e., the reference = 100%) were titrated immediately following the phosphoric acid ion pair formation procedures. Presented are the results of exemplary samples that were placed in (a) a 90°C vacuum oven as a zero-RH environment or (b) a Blue M environmental chamber equilibrated at 90°C and 50% RH. Sodium hydroxide (0.01 N) is used as titrant with phenolphthalein as indicator.

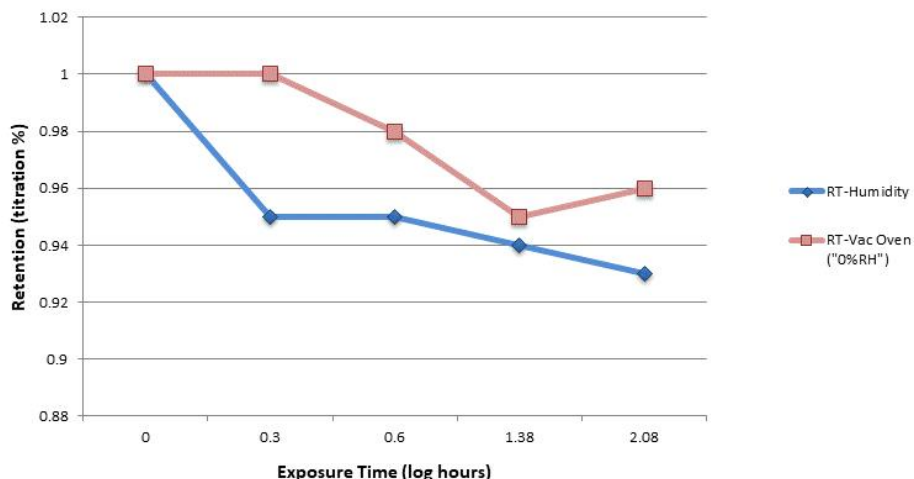


Figure 3. Phosphoric acid retention based on titration and test chamber vs. time (hours) and RH of NanoSonic’s ion pair membrane processed under room-temperature protocol

The controlled ion pair formation minimizes the excess “free” phosphoric acid within the membrane, thereby assuring a good association between the quaternary ammonium group and the imbibed phosphoric acid. The pink line in Figure 3 shows the retention of phosphoric acid in the membrane when exposed to 90°C and zero percent relative humidity (0% = under vacuum). After 120 hours (5 days) in the vacuum oven, the titrated samples retained ~95% of the phosphoric acid as the control (t = 0) sample. The samples appear to have reached equilibrium as samples titrated after 24 hours exposure showed the same retention percent. The blue line in Figure 3 shows the retention of phosphoric acid in the room-temperature doped ion pair membrane when exposed to 90°C and 50% RH. The membranes show a noteworthy 93% phosphoric acid retention after a 120-hour test period. This retention is near the same as the 0% RH, which correlates well with previously presented conductivity vs. RH data. These data demonstrate that a strong interaction exists between the NanoSonic copolymer (the quaternary ammonium group and polymer backbone) and phosphoric acid.

CONCLUSIONS AND ONGOING RESEARCH ACTIVITIES

Thin, proton-conducting copolymer membranes based on a novel ion pair concept have been developed. Controlled ion pair formation conditions result in mechanically stable membranes with exceptional proton conductivity. The ion pair membranes displayed proton conductivity independent to relative humidification and across a wide temperature range, exceeding the DOE target (120°C). The phosphoric acid retention based on titration experiments is very good. Development, fabrication, and testing of membrane electrode assemblies of the ion pair copolymer membranes is ongoing with promising preliminary success at our partners at LANL.

REFERENCES

1. K.S. Lee, J.S. Spendelow, Y.K. Choe, C. Fujimoto, and Y.S. Kim, “An Operationally Flexible Fuel Cell Based on Quaternary Ammonium-Biphosphate Ion Pairs,” *Nature Energy* 1, no. 9 (2016): 16120.
2. Albert S. Lee, Yoong-Kee Choe, Ivana Matanovic, and Yu Seung Kim, “The Energetics of Phosphoric Acid Interactions Suggests a New Acid Loss Mechanism,” *J. Mater. Chem. A* 7 (2019): 9867–9876.