
FY17 SBIR II Release 1: Novel Hydrocarbon Ionomers for Durable Polymer Electrolyte Membranes

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Overall Objectives

- Synthesize and characterize aromatic hydrocarbon proton-conducting membranes based on 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) 2018 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.

- Measure 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 of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- Maximum Operating Temperature of 120°C
- Low Cost, Non-Perfluorinated Membranes
- Durability: Mechanical and Chemical Stability
- Performance: Stable Proton Conductivity independent of Relative Humidity.

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 meet the follow DOE membrane for transportation application targets:

- Maximum operating temperature: 120°C
- Area specific proton resistance: 0.02 Ω cm² at 120°C with 40 kPa water partial pressure, and 0.03 Ω cm² at 30°C with 4 kPa water partial pressure
- Durability: 20,000 cycles
- Cost: \$20/m².

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

FY 2018 Accomplishments

- Synthesized a new polymer precursor to allow the synthesis of new functionalized copolymers with tunable ion exchange capacities.
- Demonstrated tailorability of thermooxidative stability of membranes via polymer design.
- Developed a scalable surface treatment for glass substrates that allows for fabrication of very thin membranes (15–30 μm) using simple polymer solutions.
- Demonstrated superior membrane mechanical and dimensional stabilities.
- Demonstrated stable proton conductivity of membranes across a wide range of humidification.
- Successfully fabricated membrane electrode assemblies using NanoSonic’s new functionalized ion-pair copolymers at Los Alamos National Laboratory.
- Demonstrated operation of NanoSonic ion-pair membranes at 120°C and higher (DOE target for 2020).
- Initiated fuel cell test stand durability evaluation of NanoSonic’s down-selected membranes at Los Alamos National Laboratory.

INTRODUCTION

Fuel cells have many attractive features as a sustainable power source, such as high-efficiency energy conversion from a variety of fuels, near-zero greenhouse gas emissions, quiet operation, low air pollution, low maintenance, and scalability based on energy needs (i.e., hand-held/portable devices, vehicular propulsion, stationary power). A critical component necessary to a viable hydrogen-based energy economy is the development of durable, cost-effective proton conducting membranes for fuel cells. 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. Expensive perfluorinated polymers containing sulfonic acid-type ionomers (e.g., Nafion) remain the leading commercially available membranes. Noted shortcomings of these expensive perfluorinated membranes include limited operation temperature ($\leq 100^\circ\text{C}$), necessity of sufficiently (high) hydration for proton conductivity, and low availability. 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 creep and pinhole formation when subjected to temperatures above that range.

APPROACH

This project demonstrates a new class of hydrocarbon-based polymer ion-pair electrolyte membranes as a viable alternative to expensive perfluorosulfonic acid membranes which 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 should directly affect a cost savings in manufacturing the functional 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. Phosphoric acid imbibing occurs quickly (<4 hours) to successfully produce ion-pair membranes.

RESULTS

NanoSonic has continued efforts to further understand important structure-property relationships towards design and fabrication of an optimum fuel cell ionomeric membrane through syntheses and characterization of copolymers. NanoSonic has demonstrated a series of new candidate functionalized copolymers as scalable routes to quaternary ammonium materials via current commercial processes. Currently, perfluorinated sulfonic acid membranes account for a significant cost in the implementation and manufacturing of fuel cell stacks. Therefore, beyond developing a new membrane, reducing the thickness of the membrane should influence the relative cost of the membrane. Beyond the immediate cost impact, there are several kinetic and systematic advantages to utilizing a thinner membrane, including higher through-film proton conductivity, reduced weight, and improved water diffusion, while maintaining the membrane's important function as an effective fuel barrier. Interest in proton conducting membranes on the order of sub- $25\text{-}\mu\text{m}$ thickness has been expressed by potential automotive customers.

NanoSonic has developed a new surface treatment for glass substrates used to solution-cast membranes. This aqueous treatment modifies the surface chemistry of the glass to produce a very hydrophilic surface; treated-glass substrates show improved wettability as compared to the cleaned substrates. Pinhole-free membranes as thin as $15\ \mu\text{m}$ have been produced from 5 wt% to 10 wt% polymer solutions. This is significant, as most proton exchange membranes reported in literature and commercially available are much thicker than this or require some structural support (e.g., mesh, nonwoven backing).

Unsurpassed dimensional stability has been observed for the ion-pair membranes. Alternative hydrocarbon-based membranes with pendant sulfonic acid groups display very large swelling (volumetric) and dimensional changes (300% to 800% reported) as a function of ion exchange capacity. These large dimensional changes

add stress to the membranes and the membrane electrode assembly, effectively limiting their application. The low swelling behavior observed in the ion-pair membranes is nearly negligible with regard to membrane stress. Figure 1 shows dimensional stability of ion-pair membranes. Inferences can be made to the exceptional mechanical durability of the ion-pair membranes. The candidate membranes have successfully demonstrated multiple (20+) wet-dry cycling without signs of mechanical degradation. The superior dimensional stability is attributed to a combination of tailored polymer (compositional) design, targeted copolymer functionalization, and ion-pair doping procedure.



Figure 1. Dimensional stability (low volumetric change) of NanoSonic membranes in dry and wet (hydrated) state

The vast majority of ionomeric membranes require water for reasonable proton conductivity. Also, it is well established that proton conductivity is affected by membrane hydration level and relative humidification within the system. Figure 2 shows the stable proton conductivity of two candidate ion-pair membranes independent of relative humidity at 80°C. As shown, sample 65Qt shows higher or matches the Nafion reference (N212 H⁺) up to 50% relative humidity. The NanoSonic ion-pair membranes does show an influence of ion exchange capacity on proton conductivity, 36Qt <<65Br <65Qt. Testing is ongoing on a NanoSonic membrane with different ion exchange capacity (i.e., degree of functionalization) that may show even more enhanced performance.

Proton-conducting membranes able to operate at or above 120°C offer many benefits for fuel cell operations, including better tolerance to fuel impurities, improved electrode kinetics, higher ionic conductivities, and reduced requirements for heat and water management. Maintaining membrane hydration at the DOE target of 120°C is very difficult, however, which is one reason current commercially available and other alternative/developmental membranes may not work. Experiments investigating the influence of temperature on proton conductivity in membranes are being performed.

Figure 3 shows the influence of temperature and relative humidity on proton conductivity for a NanoSonic ion-pair membrane and Nafion. As expected, Nafion demonstrates good proton conductivity at 100% relative humidity at temperatures up to 100°C (blue line). At 120°C, however, Nafion proton conductivity quickly drops due to membrane dehydration or membrane mechanical failure; 120°C is above Nafion's plasticized glass-transition temperature, as found in literature. Nafion conductivity at 80°C is greatly influenced by relative humidity as observed at 20% and 70% (open blue circles).

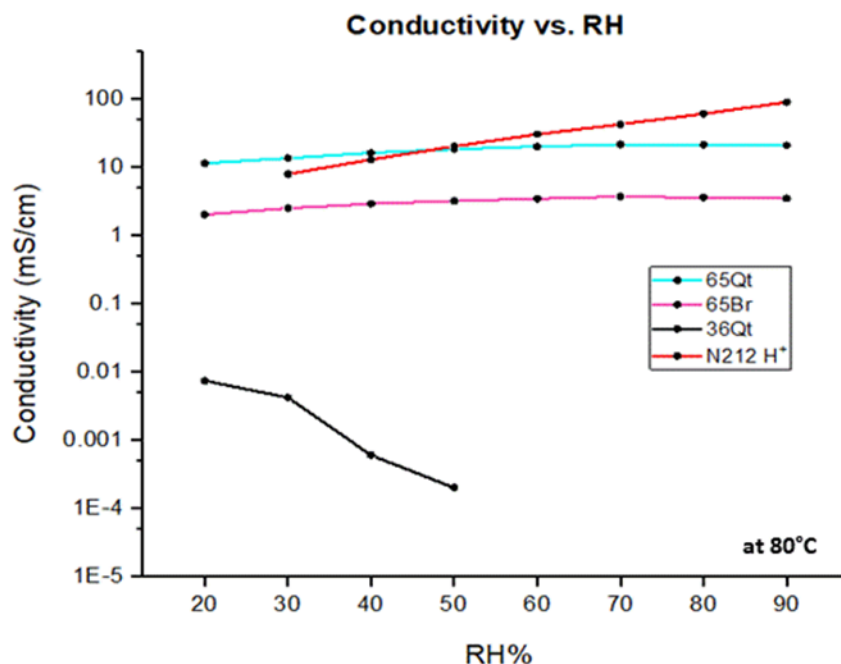


Figure 2. Influence of relative humidity on proton conductivity on NanoSonic ion-pair membranes and Nafion (N212) control

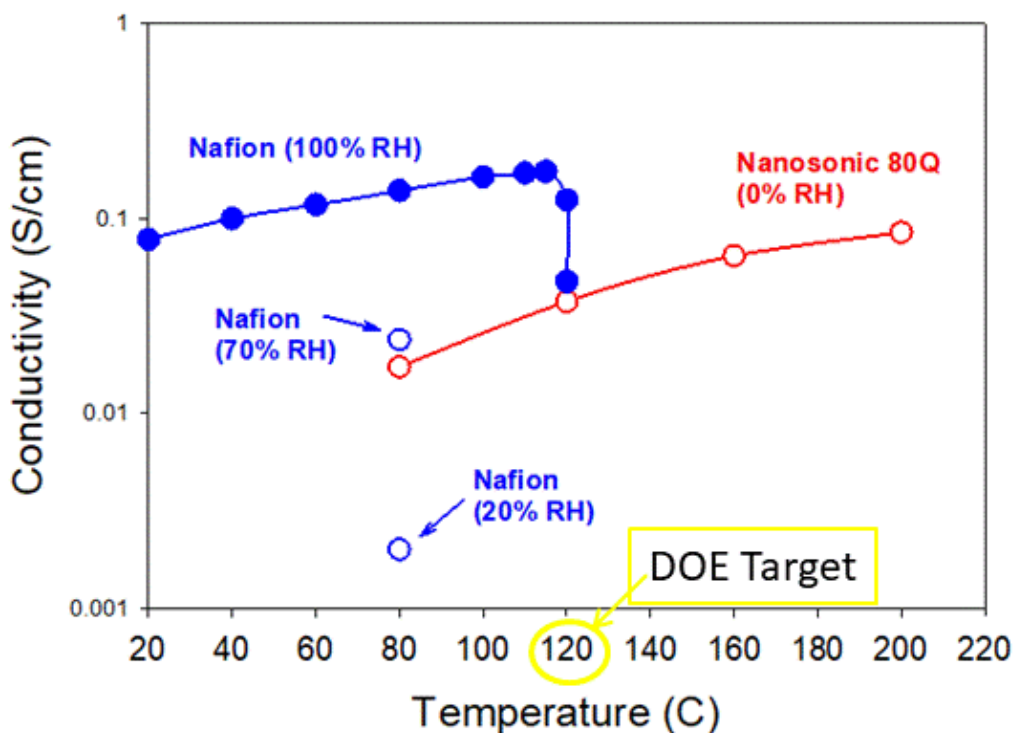


Figure 3. Influence of temperature and relative humidity on proton conductivity on NanoSonic ion-pair membranes and Nafion control

NanoSonic ion-pair membrane “80Q” shows progressively increasing proton conductivity, starting at 120°C even at no humidification (0% relative humidity). Not shown in the graph—but of importance to note—Nafion has no appreciable conductivity at 0% relative humidity. This study is ongoing with down-selected ion-pair membranes with different copolymer compositions and higher initial conductivity. All NanoSonic ion-pair membranes candidates must display hydrated glass-transition temperatures greater than 160°C to account for the plasticization effect of the phosphoric acid and water.

NanoSonic ion-pair membranes have been fabricated into membrane electrode assemblies and demonstrate successful operation at the DOE target temperature, 120°C and higher. Figure 4 displays a NanoSonic ion-pair membrane that was successfully fabricated into a membrane electrode assembly and the preliminary data collected by Yu Seung Kim’s group (our Los Alamos National Laboratory partner). Membrane-to-electrode ionomer interface is critical for efficient operation of the membrane electrode assembly. Progress is being made to optimize membrane electrode assembly fabrication and fuel cell test-stand qualification at Los Alamos National Laboratory.

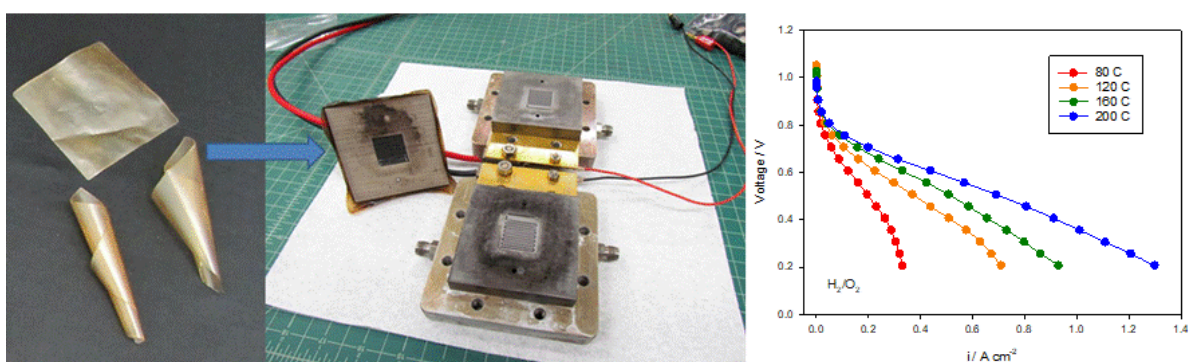


Figure 4. Exemplary NanoSonic ion-pair membrane in a fuel cell test cell with preliminary voltage-current data

CONCLUSIONS AND UPCOMING ACTIVITIES

Proton-conducting membrane copolymers based on a novel ion-pair concept have been developed. A new surface treatment for glass substrates have been employed to fabricate durable, thin membranes (<25 μm) from common laboratory solvents. The ion-pair membranes show exceptional dimensional stability and durability to wet-dry cycling. The ion-pair copolymer membranes show stable proton conductivity independent to relative humidity and at DOE target (120°C) temperature and higher. Fabrication and testing of membrane electrode assemblies of the ion-pair copolymer membranes is ongoing with promising preliminary success. New functionalized copolymer compositions are being synthesized to further understand structure-property relationships as test results are analyzed to guide the development of the optimal proton conduction ion-pair membrane.

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.