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

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Project ID #FC176

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OBJECTIVE and APPROACH

To develop cost effective, durable hydrocarbon ionomers for proton exchange membrane (PEM) fuel cells to achieve the DOE's global goals for energy efficient transportation applications

Synthesize high molecular weight aromatic hydrocarbon membranes that will possess polar moieties along the polymer backbone and pendant quaternary ammonium groups. This innovative chemistry will facilitate the fabrication of stable phosphoric acid-doped ion pair membranes for PEM fuel cells capable of 120° C operation for transportation

PHASE II TECHNICAL OBJECTIVES

TECHNICAL OBJECTIVE 1	Synthesize and characterize aromatic poly(arylene benzonitriles) precursor membranes and composites containing highly basic functionality as high temperature polymer electrolyte membranes for fuel cells. 80% Complete
TECHNICAL OBJECTIVE 2	Empirically establish structure – property relationships of synthesized materials that will afford optimal membrane properties through monomer selection and compositional manipulation 70% Complete
TECHNICAL OBJECTIVE 3	Measure fuel cell performance of down-selected proton exchange membrane composites 30% Complete

Desirable Membrane Properties

- High ionic (protonic) conductivity but low electronic conductivity
- Low fuel and oxidant permeability
- Good thermal and oxidative stability
- Good mechanical properties
- Easy fabrication into membrane electrode assembly
- Low cost

Project Overview

Timeline and Budget

- Project Start Date: 04/10/2017
  (07/17/17 Contract Start)
- Project End Date: 012/10/2019
- Total Project Budget: $1,000,000
- Total DOE Funds Spent: $647,000

Technical Barriers

- Development of robust, low cost ionomers for PEMFCs for transportation capable of operating at 120°C
- Verification of membrane durability and fuel cell performance

Collaboration Partners

- Los Alamos National Laboratory (Testing, Evaluation, and Discussions)
- Nissan North America (Updates and Future In-kind Testing/Evaluation)

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Current Proton Exchange Membranes

Perfluorosulfonic Acid PEM

- Industry Benchmark
- High proton conductivity of up to 0.1 $S \cdot cm^{-1}$ under fully hydrated conditions
- Limited to <100°C
- Expensive

Hydrocarbon Ionomers

- Aliphatic ionomers
  - Inexpensive synthetic route
  - Lack thermal durability and chemical (oxidative) stability Limited to <80°C operation
- Aromatic ionomers
  - Variety Synthetic Route
  - Lower cost than Nafion
  - Limited to <100°C operation

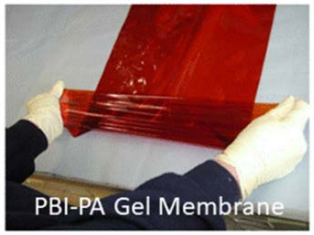
Phosphoric Acid-Polybenzimidazoles

Attributes:

- Nitrogen (N and N-H) atoms in the polymer structure yield basic PBIs
  - Basic character allows for complexation to phosphoric acid
- Acid-Base membrane composites overcomes the dependence on water and/or humidification for conductivity
  - Capability of proton conductivity for fuel cell operation at temperatures greater than 140 °C
- Reported conductivity up to 0.2 S/cm

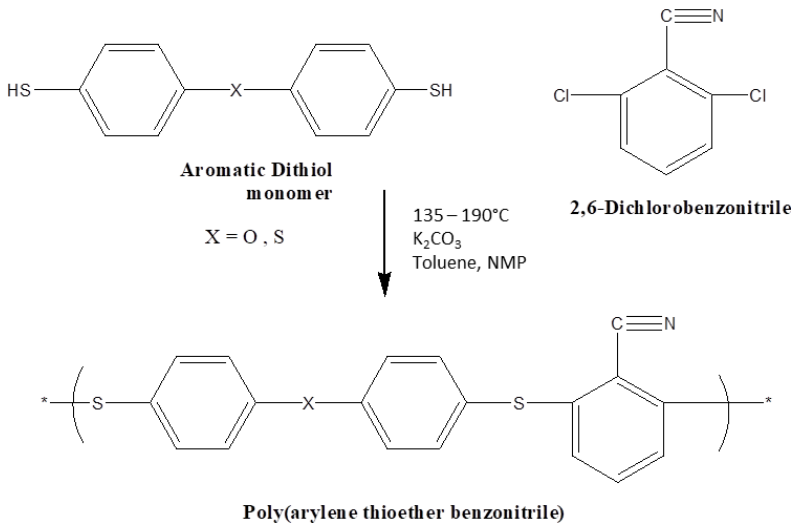
Reported Issues:

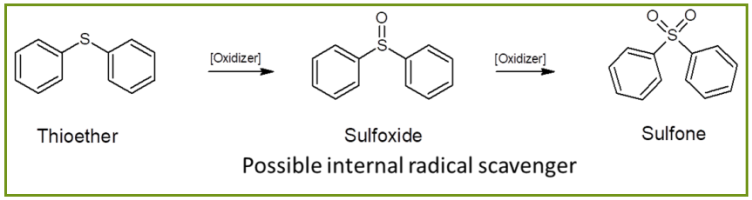
- Difficult to Solvate
- Gel Membranes (up to 90wt% PA) have creep and compression issues
- Mechanical property variations
- Reported pinhole formation and film thinning
- Operation: 140 to 180°C may not suitable for transportation
- High phosphoric acid loss
- Expensive



❖ PFSA and Hydrocarbon ionomers fuel cell performance is greatly dependent upon hydration/humidification

Synthesis and General Properties of Poly(thioether benzonitrile)





Properties

- Noted Thermal Stable
  - ✓ High T_g and T_m
- Excellent Oxidative Stability
- Excellent Hydrolytic Stability
- Easy Processing
  - ✓ Thermal or Solvent Casting

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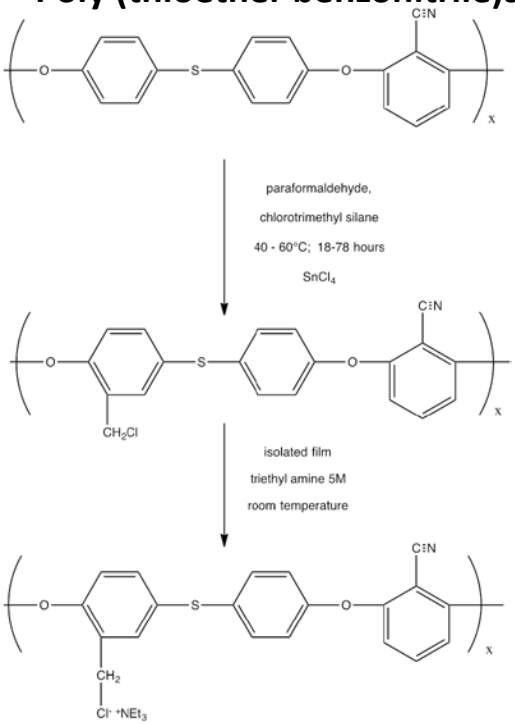
Introduction of Pendant Quaternary Ammonium for Ion Pair Formation with Phosphoric Acid

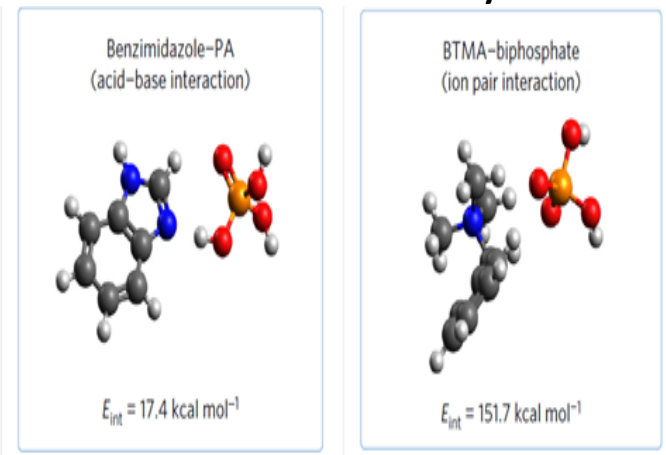
Chemical Functionalization of Poly (thioether benzonitrile)s



^{31}P NMR Spectrum showing the Influence of Phosphoric Acid in presence of Polar Moiety#

#Changes in phosphorous chemical shift suggest nature of interactions

Calculated Interaction Energy between Benzimidazole and Tetramethyl ammonium moiety$



*Water-Phosphoric Acid = 12.6 kcal/mol, only 5 kcal/mol difference in PBI-PA

- Ion Exchange Capacity Control
- Quaternary Ammonium complexes with H_3PO_4 to allow wider range of operation temperatures and aid acid retention

$Ref: KS Lee, JS Spendelow, C. Fujimoto, YS Kim, Nature Energy, 2016, **1**, 1.

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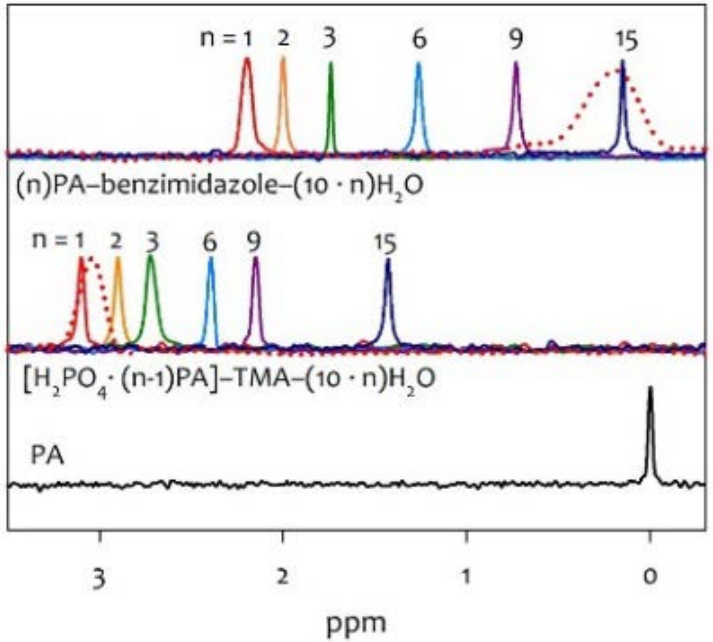
Influence of Water on Phosphoric Acid-Basic Moiety on Polymer Interaction (^{31}P NMR)

The impact of the number of phosphoric acid (PA) on the cluster interaction energy of the hydrous <u>phosphoric acid complex</u>



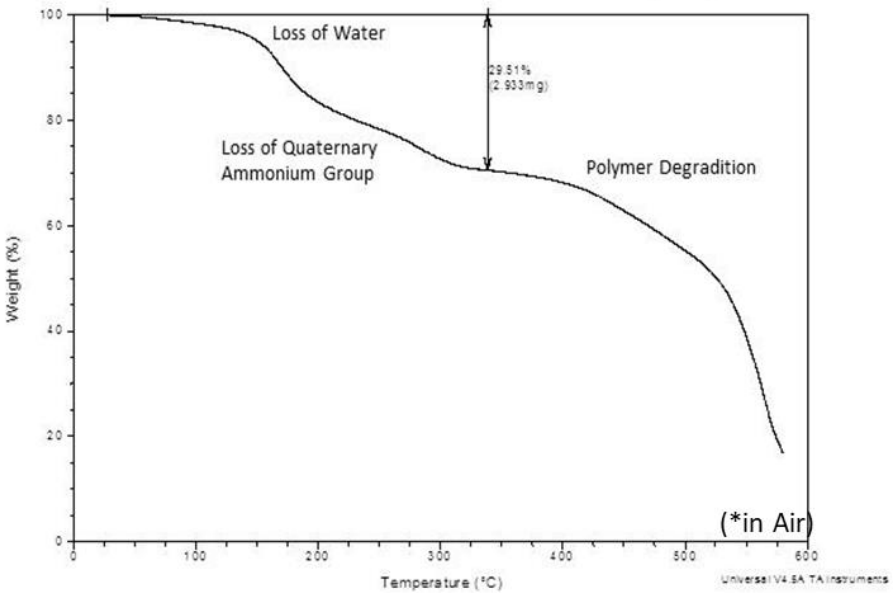
- The impact of the number of PA on the cluster interaction energy of the hydrous PA complex is shown: For both the hydrous phosphoric acid-benzimidazole and biphosphate-trimethyl ammonium, the interaction energy gradually decreases as the number of PA increases (different from what is observed in the anhydrous systems)

- This suggests that there may be more involved in the PA loss than simple extraction by water

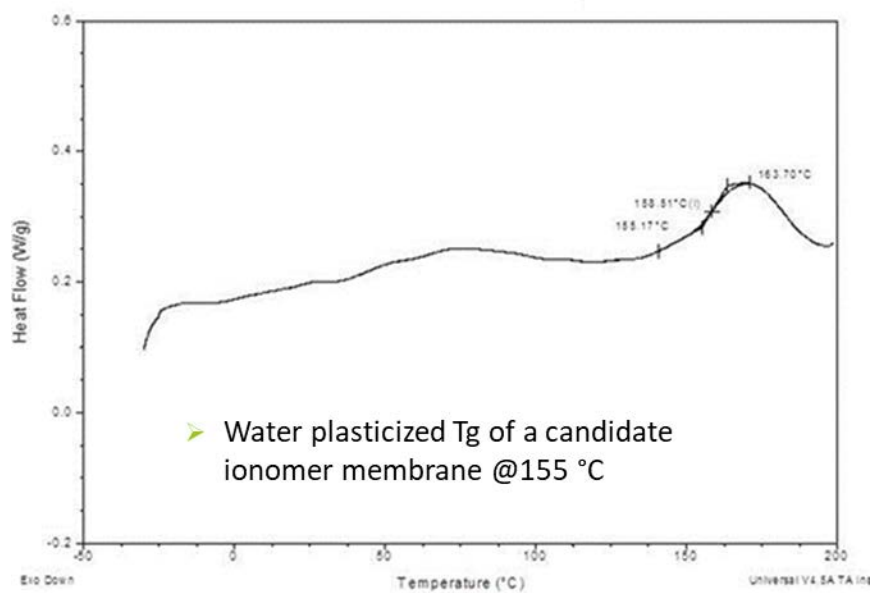
Used with author's permission: "The energetics of phosphoric acid interactions reveals a new acid loss mechanism", Albert S. Lee, Yoong-Kee Choe, Ivana Matanovic and Yu Seung Kim, *J Material Chem*, accepted 2019.

Thermal Analyses of Poly(thioether benzonitriles)

Thermooxidative Stability determined via <u>Thermogravimetric Analysis (TGA)</u>



Thermal Transition examined via <u>Differential Scanning Calorimetry (DSC)</u>



* Glass transition temperature of copolymers depend on composition and degree of functionalization
* Water plasticization results in up to 30 °C Tg depression in some copolymers
    - ✓ Plasticized Tg of NanoSonic down-selected ionomer membranes range 150 – 190 °C

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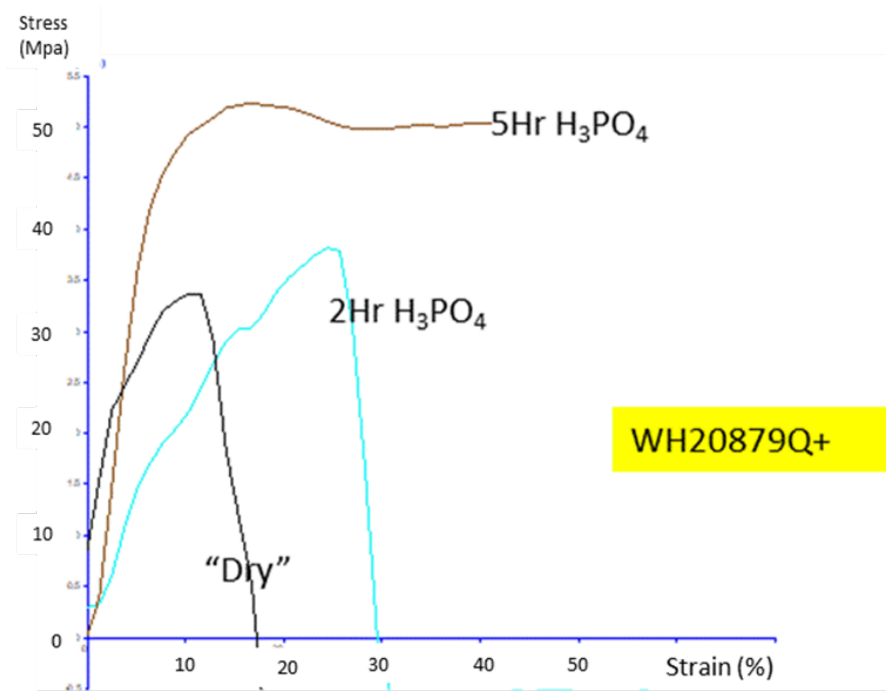
Fully Hydrated Quaternary Ammonium Poly(thioether benzonitrile) Copolymers Display Good Mechanical Properties



*Mechanical Strength is influenced by copolymer composition and degree of functionalization

- Ion Pair Membrane Tensile Strength : 5 - 60 MPa
- Percent Elongation: > 10%

* Sample full saturated (deionized water) shows very good mechanical strength

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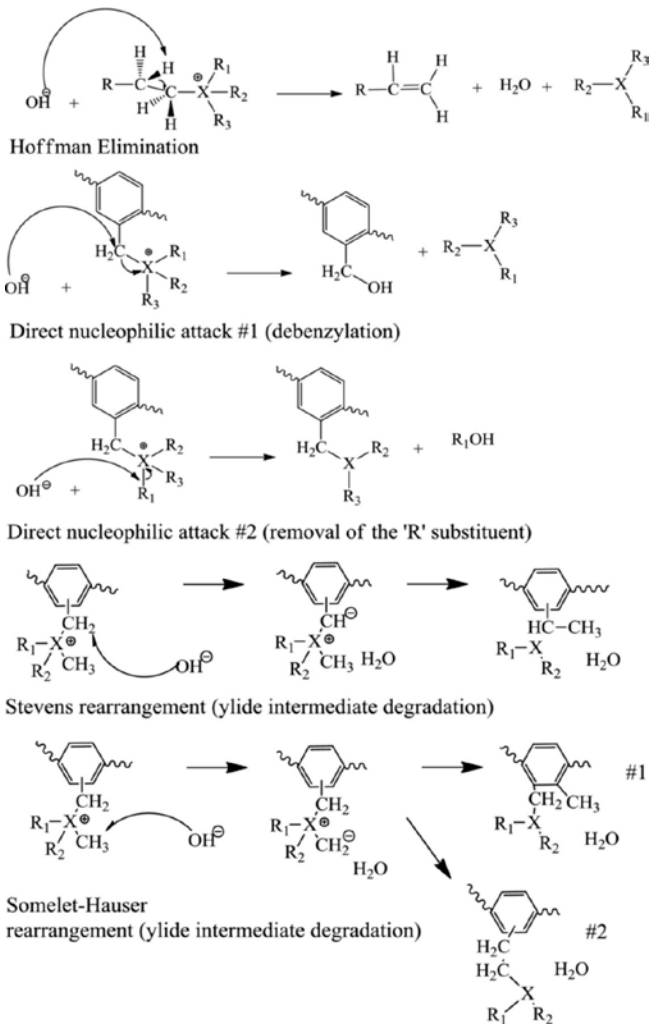
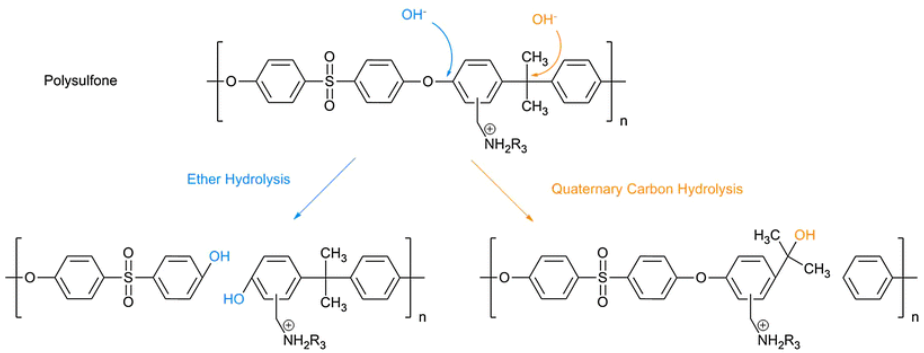
Detrimental Polymer Degradation Pathways in Anion Exchange Membranes are Not Valid in NanoSonic Ion Pair Membranes





No similar degradation pathways available in phosphoric acid

Fenton Reagent Oxidative Stability of Quaternary Ammonium- containing Poly(thioether benzonitrile)

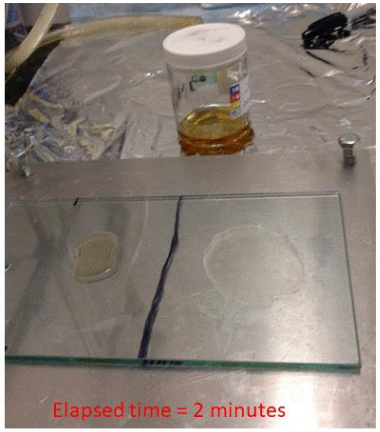
Room Temp@ 24Hours :	<1 wt% loss
70°C@ 24Hours:	~5wt% loss*
70°C@ 48Hours:	~8wt% loss*

- Sample (IEC: 1.2) in 4ppm $FeSO_4$ in 3% H_2O_2
- Evaluation in ion pair form was difficult to discern weight loss and structural change due to PA/H_2O presence

* Comparable to literature PBI values

Fabrication of Very Thin, Mechanically Durable Membranes via Solution Casting

Cleaned Glass Side with 1ml polymer solution



Surface Prepped Glass Side With 1ml polymer solution

A proprietary surface treatment for glass substrates improves wettability and minimizes membrane defects during fabrication.
Scalable process: demonstrated on 4ft x 8ft glass surface

Most films are released easily by immersion in DI Water

0.02mm = 0.78mil

The surface treated glass substrates affords very thin membrane fabrication (14-30 µm) which may improve overall PEM performance (electrochemical reactions) and reduce PEM cost

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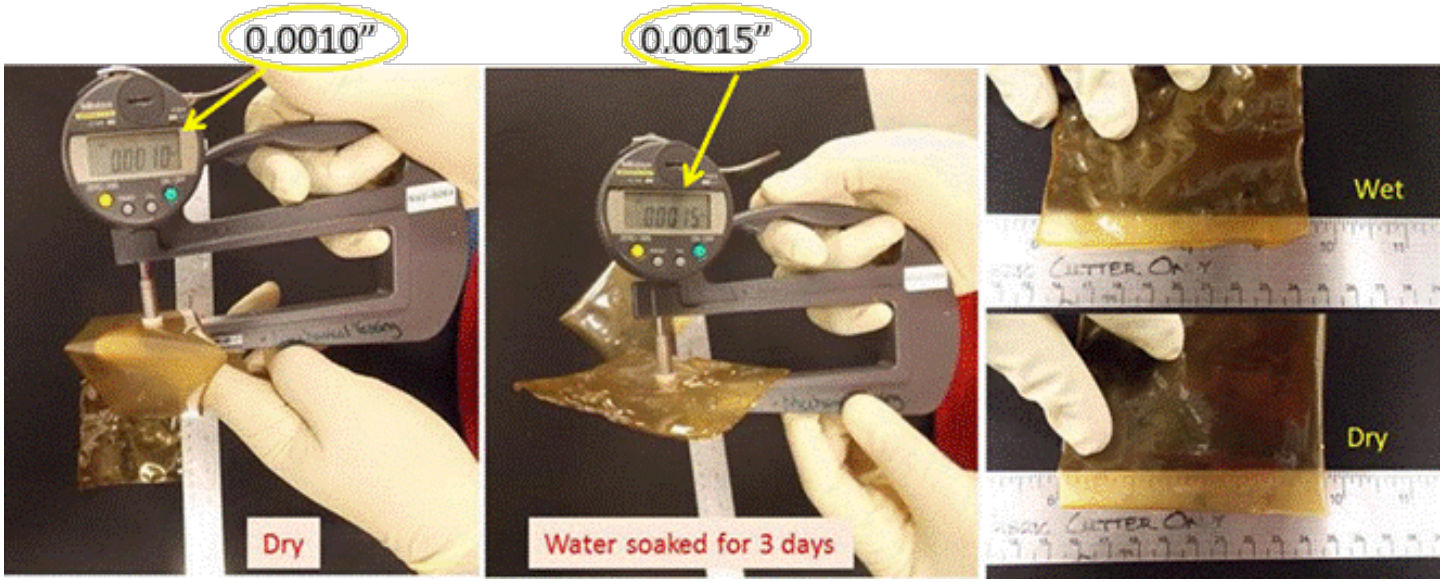
NanoSonic's Quaternary Ammonium Functionalized Ionomers show Exceptional Dimensional Stability



- Candidate polybenzonitrile-based membranes demonstrated low volumetric changes (swelling) possibly due to secondary interaction with backbone moieties
  - Comparable sulfone references shows >300% swelling changes
- PEMs show very good "wet-dry cyclic" durability/stability (up to 50 cycles)

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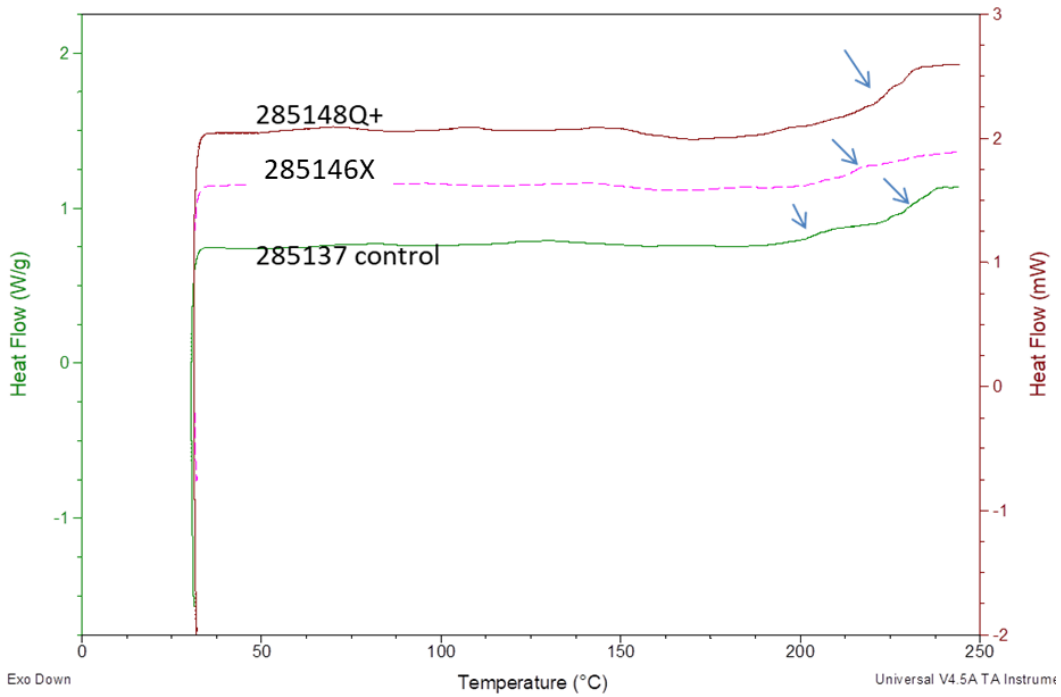
Glass Transition: High Tg Functionalized Ionomer PEM Copolymers suitable to Higher Temperature Applications

*Glass transition is a function of copolymer structure and composition. Tg range: 150 – 250 °C

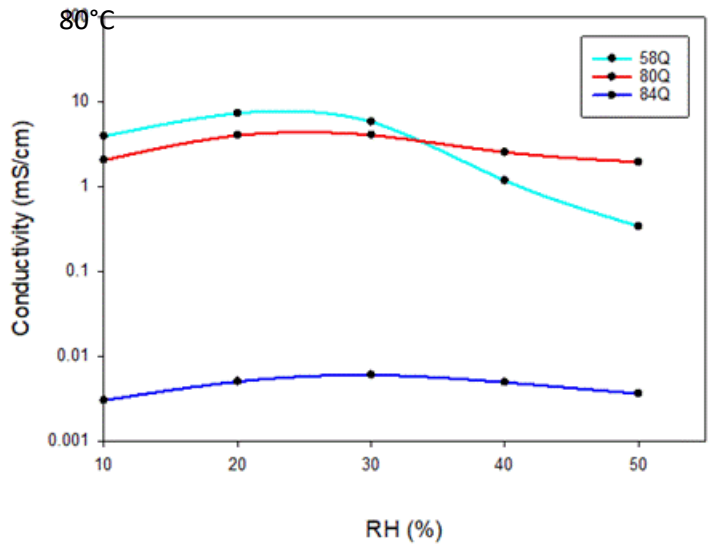


*Tg increases with bulky side group introduction

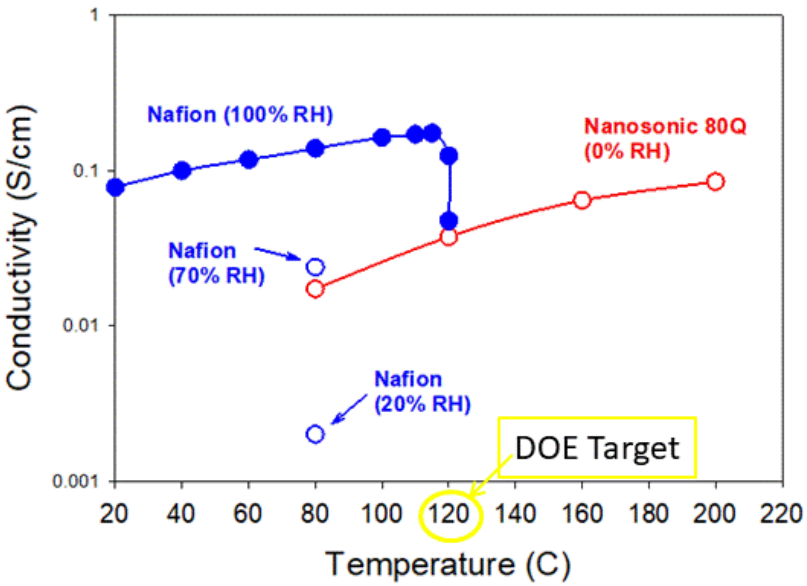
- Sample 285148Q+ Hydrated Tg = 195 °C. The hydrated Tg signifies the upper temperature stability for the plasticized membrane.

Influence of Ion Exchange Capacity and Relative Humidity on Conductivity of Ion Pair PEMs via Chloromethylation Route

Conductivity vs. Relative Humidity



Conductivity at Relative Humidity compared to Nafion



- Ion exchange capacity and copolymer structure influences conductivity
- Many samples demonstrated stable proton conductivity over a wide range of relative humidity
- NanoSonic ionomer shows conductivity with zero humidification at 120°C-DOE target while Nafion (at 100% RH) is displaying loss of membrane stability

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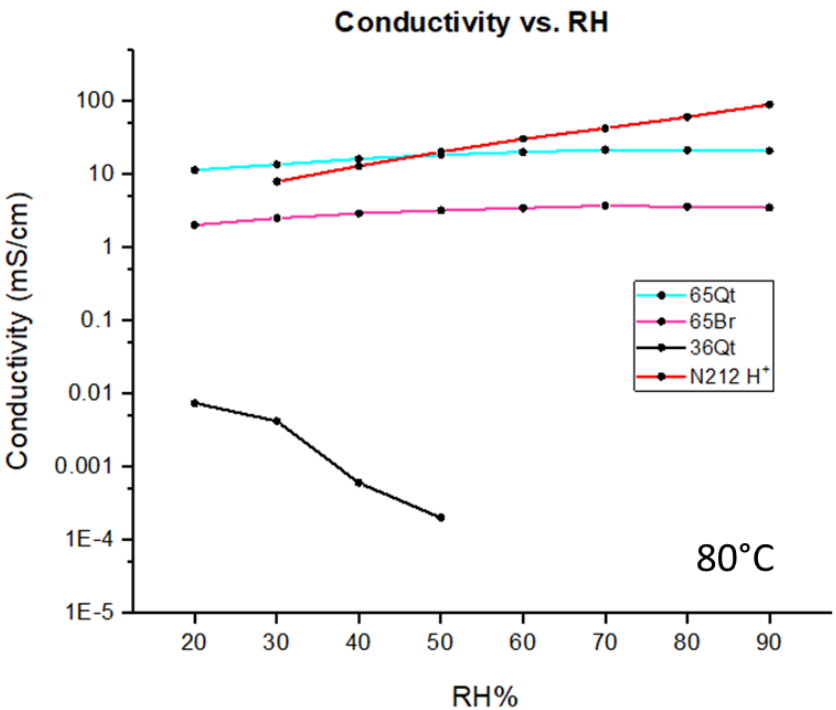
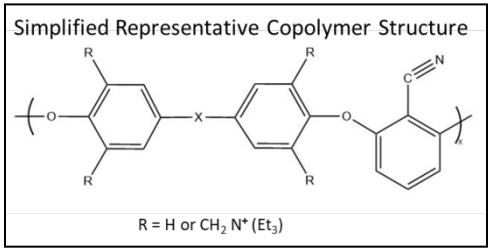
Conductivity vs. Relative Humidity for Ion Pair PEM via Copolymerization much Higher than those via Chloromethylation

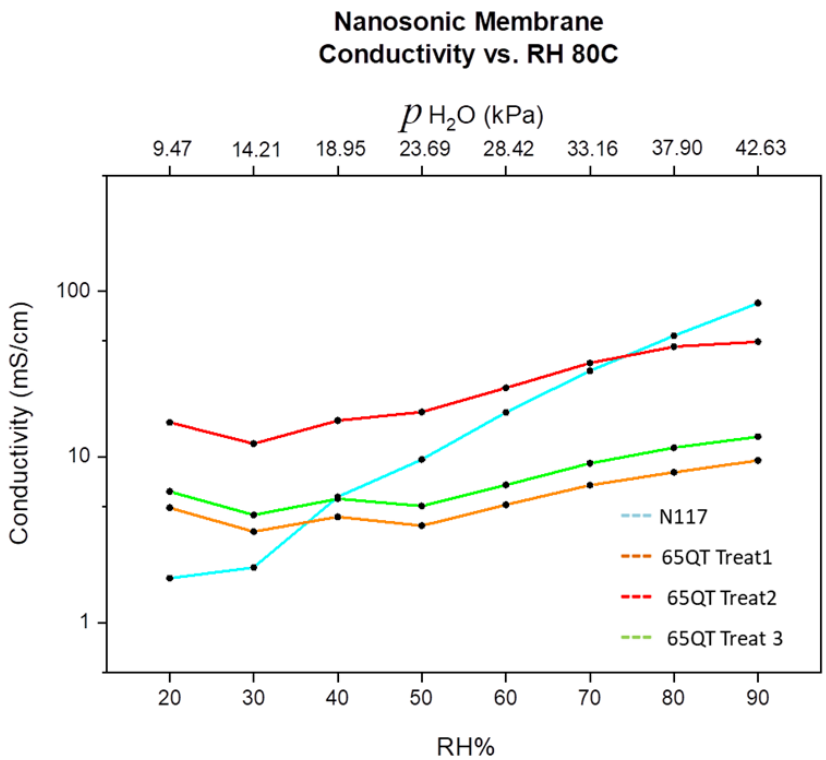


- Phosphoric Acid (85%) doping at RT
- Samples equilibrated at least 30mins prior to measurement



- Samples show stable conductivity over RH range
- Sample 65Q+ shows reasonable conductivity for application, matching Nafion 212 at 50% RH
  - Conductivity expected to be higher at higher temperatures
- Achieved IEC and proton conductivity significantly higher than those via chloromethylation routes. Polymer structure is also different due to pre-functionalized comonomers.

Influence of Acidification Process: Tetra Quaternary Ammonium Ion Pair PEM Conductivity vs. Relative Humidity



Treatment 1 Room Temp, T1
Treatment 2 Heated Process
Treatment 3 Room Temp, T2

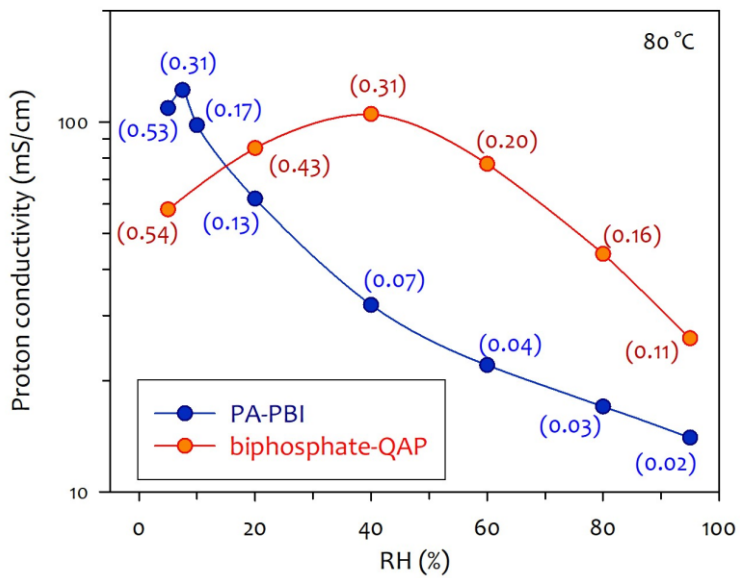
Morphology may be playing a role

- ✓ **PEM Conductivity Milestone: 80 mS/cm at water vapor pressure at 20 kPa and 80 °C**
- ✓ **H2/O2 Fuel Cell Durability Milestone: <10%current density loss at 0.6V at 120°C after 100 start-stop cycling**

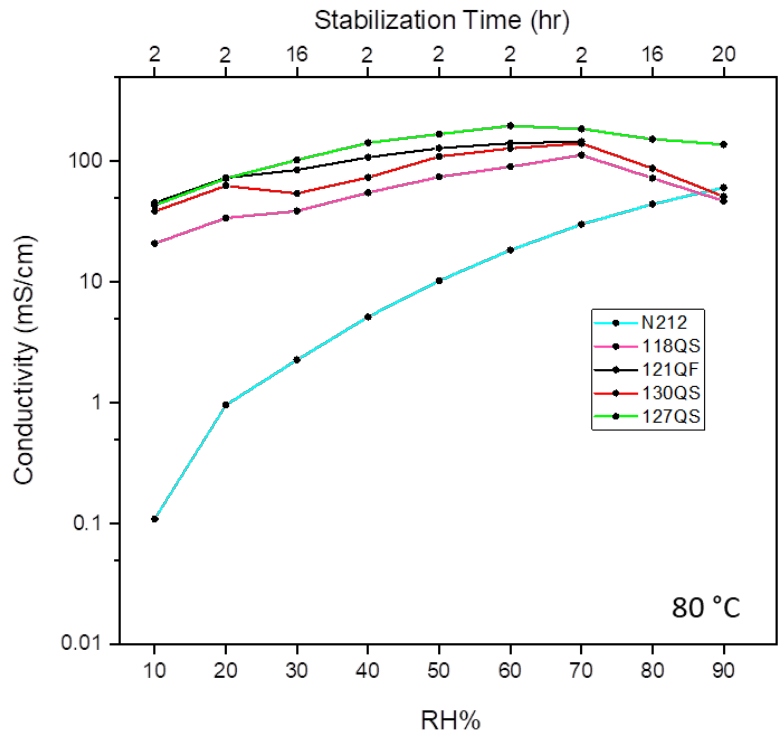
Conductivity Data: NanoSonic Ion Pair Copolymers as Function of RH

- **Milestone: Conductivity > 100 mS/cm under humidified conditions**

Conductivity Data of Phosphoric Acid-Polybenzimidazole and Quaternary Ammonium containing Polyphenylene-Ion Pair*



New NanoSonic Ion Pair Ionomeric Copolymers show Exceptional Conductivity compared to Nafion

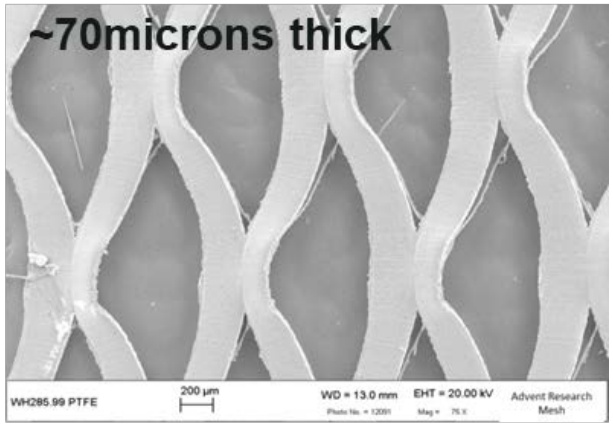


This data may suggest the maximum RH value of stable operation: PBI@ ~7.5%, QA-Polyphenylene @ ~40%, NanoSonic Ion Pair @ ~70%

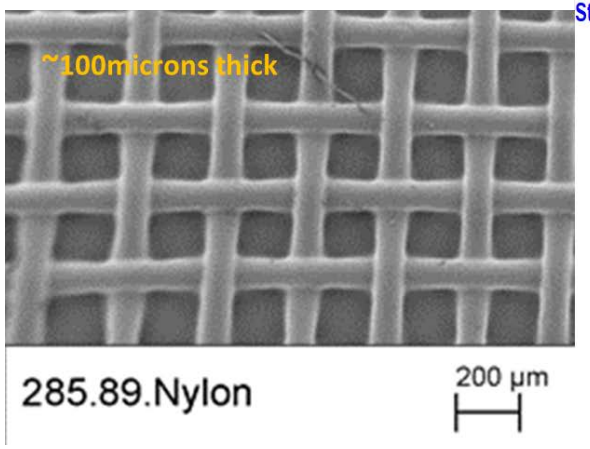
*Used with author's permission: "The energetics of phosphoric acid interactions reveals a new acid loss mechanism", Albert S. Lee, Yoong-Kee Choe, Ivana Matanovic and Yu Seung Kim, *J Material Chem*, accepted 2019.

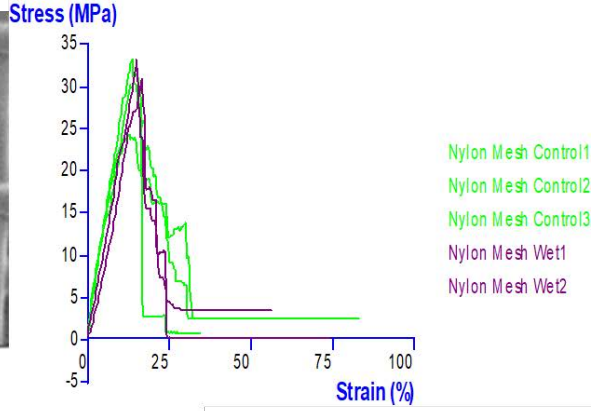
Thin Membrane Fabrication via Fabric Reinforcement: SEM Micrographs

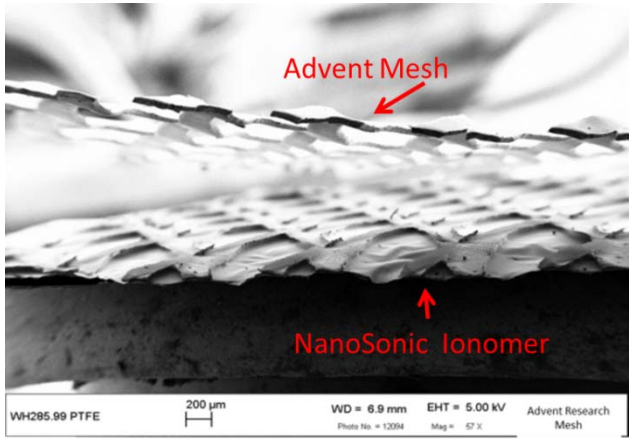
Advent Research Material ePTFE mesh is nonwoven



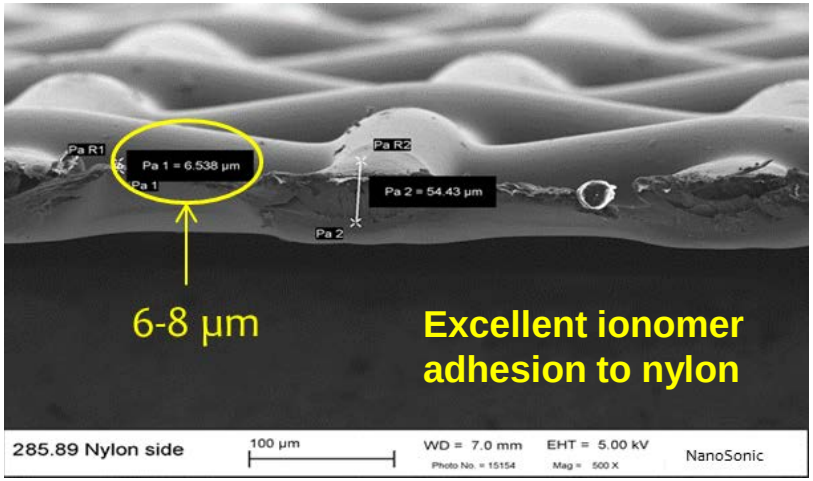
Candidate Membranes show excellent adhesion to Commercial Nylon woven mesh and excellent mechanical wet strength







NanoSonic ionomer shows complete delamination (no adhesion)



***Membrane is much thinner than any freestanding membrane we are able to prepare**

Project Summary

- High molecular weight copolymers with tailored compositions have been synthesized and yield tough films with very good thermal and thermo-oxidative stabilities
- Copolymerization route affords high molecular weight polymers with tailorable structure
  - Comonomer functionalization allows for molecularly-controlled membrane properties in a commercially viable process
  - ✓ Ion exchange capacity reproducibility better than chloroacylation routes
  - ✓ Protonic conductivity, swelling and dimensional stability and mechanical properties are influenceable
- Thin, freestanding membranes (14 - 30µm) were prepared via solution casting on treated glass substrates which may improve electrochemical kinetics and reduce membrane cost
  - Thin membranes are durable in both wet and dry state
  - Fabrication of fabric-supported membranes have also been demonstrated
  - Copolymer hydrated glass transition temperature of down-selected membranes are >150°C, assuring suitability for 120°C target operation
- Several of NanoSonic's ion pair copolymers show exceptional conductivity over the entire RH range tested
  - Conductivities are higher than Nafion and PA-PBI reference materials, up to 100mS/cm at 70% RH
  - Ion pair formation process shown to significantly influences conductivity
  - Select membranes show promising initial fuel cell performance (<10% current density loss at 0.6V at 120°C after 100 start-stop cycling)

Future Proposed Work

- Synthesize new copolymers and compositions via direct copolymerization of functionalized monomers for precise IEC control for optimum properties
- Correlate phosphoric acid imbibing and ion pair formation to stable conductivity across relative humidity range
- Compare and understand NanoSonic's copolymer structure(s) to more rigid structures previously reported with regards to a newly proposed phosphoric acid loss mechanism
  - Does morphology and/or polymer structure having significant influence on conductivity and phosphoric acid retention?
- Perform thermal and humidity testing in new environmental chamber
  - Evaluate membrane mechanical properties, acid retention, etc.
- Coordinate membrane fuel cell and durability evaluations at collaborator's laboratories

➢ Any proposed future work is subject to change based on funding levels.