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

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Relevance and Approach

Polymer electrolyte membrane (PEM) fuel cells are a leading candidate to power zero emission vehicles. PEM fuel cells are also of interest for stationary power applications, including primary power, backup power, and combined heat and power. Commercial PEM technology is primarily based on expensive perfluorosulfonic acid ionomers. Hydrocarbon membranes represent a lower-cost alternative, however, previously reported materials display low performance and durability which limit these ionomers' utilization.

To develop cost effective, durable hydrocarbon ionomers for proton exchange membrane fuel cells to achieve the DOE's goals for energy efficient transportation applications, NanoSonic is developing 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

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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.
TECHNICAL OBJECTIVE 2	Empirically establish structure – property relationships of synthesized materials that will afford optimal membrane properties through monomer selection and compositional manipulation
TECHNICAL OBJECTIVE 3	Measure fuel cell performance of down-selected proton exchange membrane composites

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Project Overview

Timeline and Budget

- Project Start Date: 04/10/2017
  (07/17/17 Contract Start)
- Project End Date: 04/10/2019
- Total Project Budget: $1,000,000
- Total DOE Funds Spent: $260,325

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

Partners

- Los Alamos National Laboratory
- US Fuel Cell
- Nissan North America

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Desirable Properties of Proton Exchange Membranes

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

Current Proton Exchange Membranes

Perfluorosulfonic Acid: Nafion®

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

Sulfonic Acid-containing Hydrocarbon Polymers

- 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

* Fuel Cell performance is dependent upon hydration/humidification of membrane

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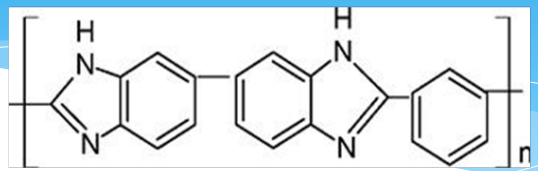
Phosphoric Acid-doped Polybenzimidazoles (PA-PBIs)



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 100 °C
- Excellent conductivity up to 0.2 S/cm

Reported Concerns:

* Difficult to Solvate
* Reported Pinhole formation and film thinning
* Operation: 140 to 180°C, not suitable for transportation
* High acid leaching by water and phosphoric acid evaporation
* Mechanical Property Variations
* Expensive

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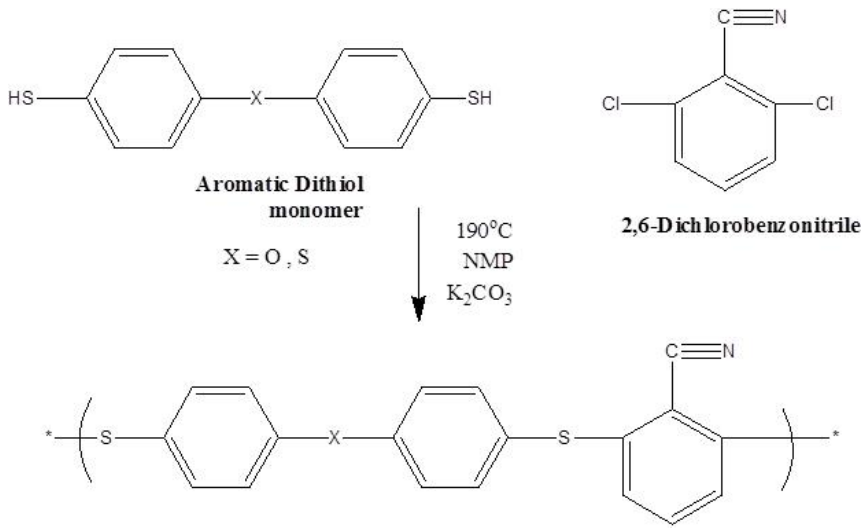
Synthesis and Properties of Poly(thioether benzonitrile)



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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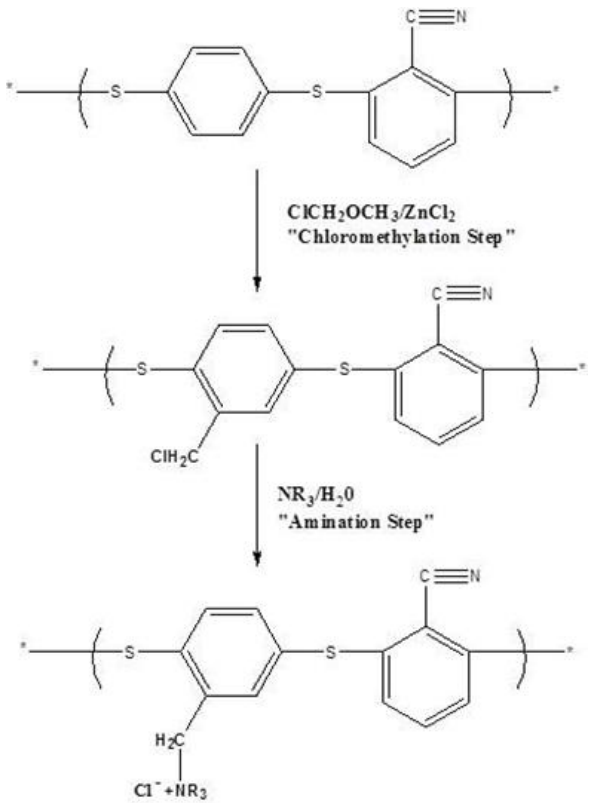
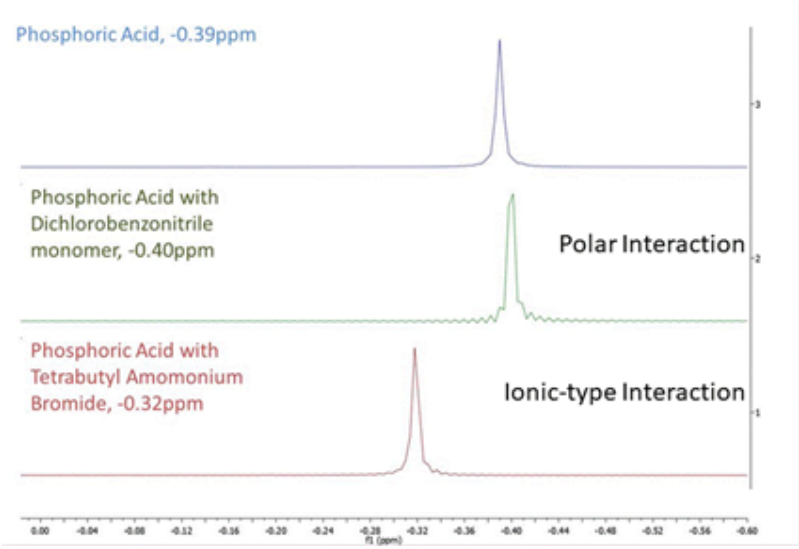
Introduction of Pendant Quaternary Ammonium as Phosphoric Acid Complex Site

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

- Ion Exchange Capacity Control
- Quaternary Ammonium complexes with H_3P0_4 to allow wider range of operation temperatures and aids acid retention

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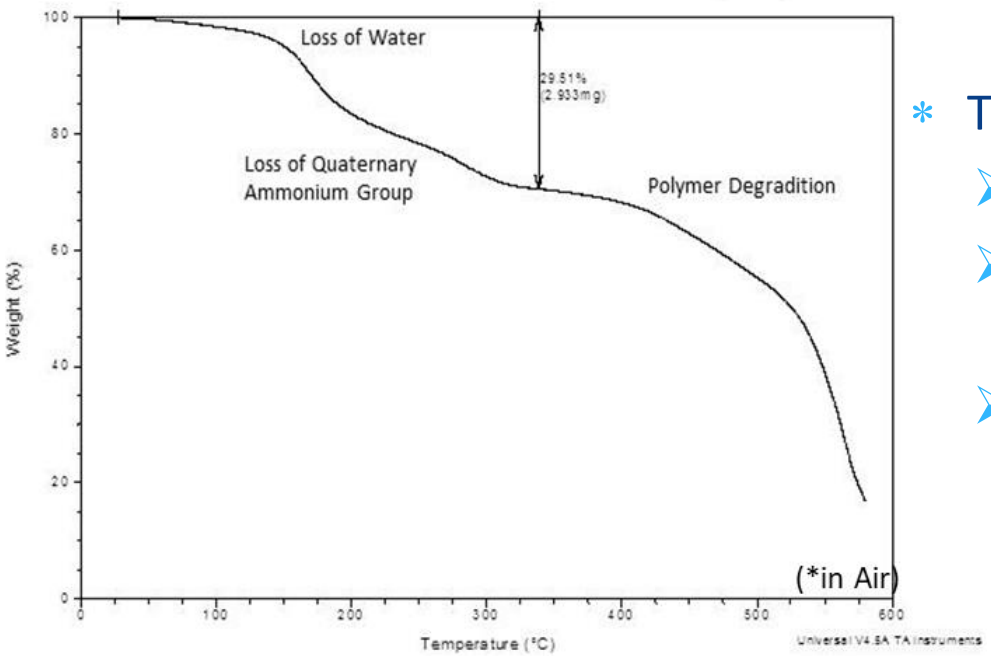
Thermogravimetric Analysis shows High Thermooxidative Stability of Quaternary Ammonium Copolymer



* TGA experiments shows:
  - Water retention >120 °C
  - Quaternary Ammonium Stability to 200 °C
  - Polymer backbone stability >400 °C

* Sample soaked in deionized water for 72 hours prior to TGA testing

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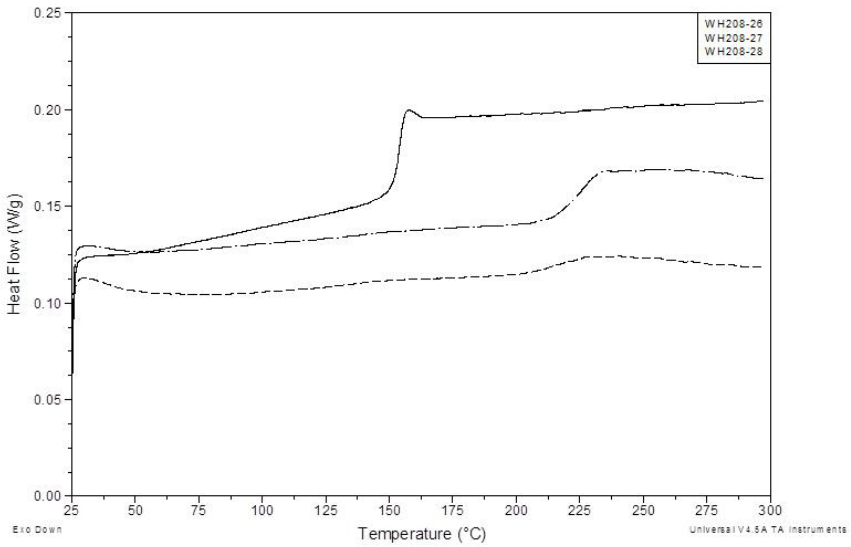
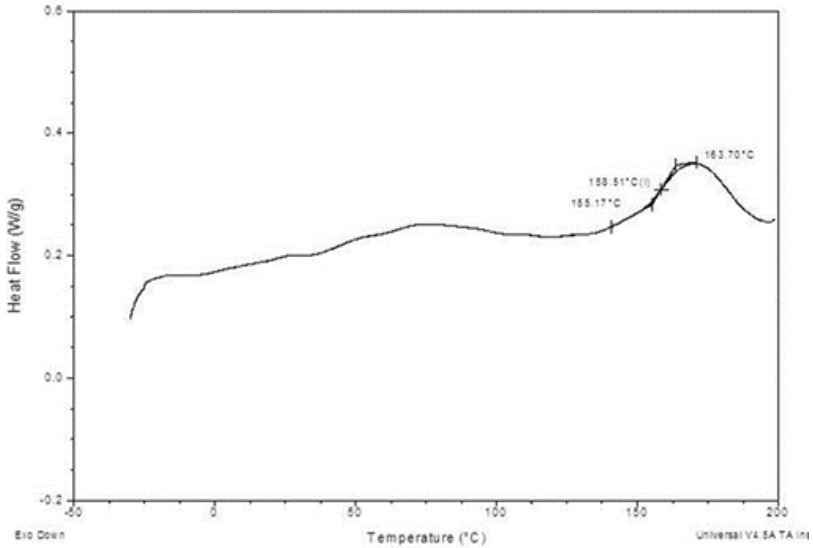
Thermal Properties of Poly(thioether benzonitriles) Films: Glass Transition (Tg)

Differential Scanning Calorimetry Thermogram of Thioether Benzonitrile Copolymers



Water plasticized Tg of a candidate ionomer membrane is >155 °C



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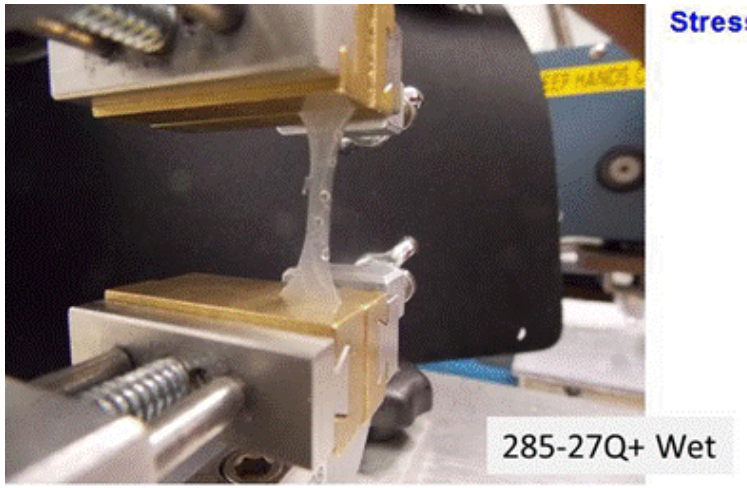
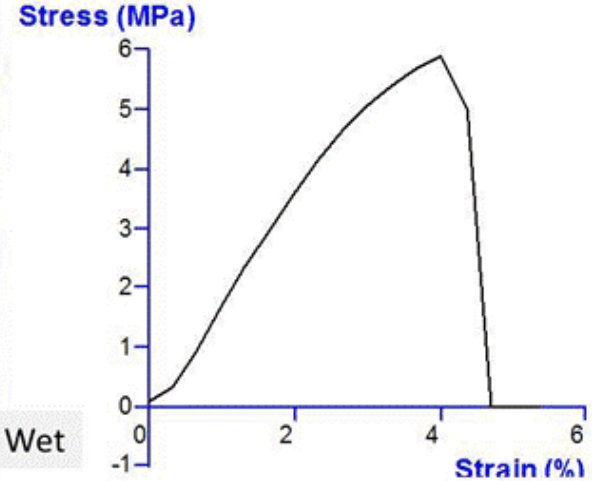
Fully Hydrated Quaternary Ammonium Poly(thioether benzonitrile) Copolymers Display Good Mechanical Properties





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

- Tensile Strength: 5-30 MPa
- Percent Elongation: 4-15

* Sample full saturated in deionized water for 72 hours prior to testing

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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

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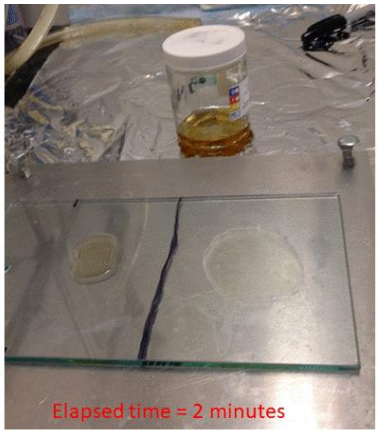
Fabrication of Very Thin yet Mechanical Durable Membranes on Treated Glass Substrates

Cleaned Glass Side with 1ml polymer solution



Surface Prepped Glass Side With 1ml polymer solution

A new surface treatment for glass substrates was developed to improve wettability and minimize membrane defeats during fabrication

Most films are released easily by immersion in DI Water

0.02mm = 0.78mil

The surface treated glass substrates affords very thin membrane fabrication (<20µm)which may improve overall PEM operation (electrochemical reactions) and reduce PEM cost

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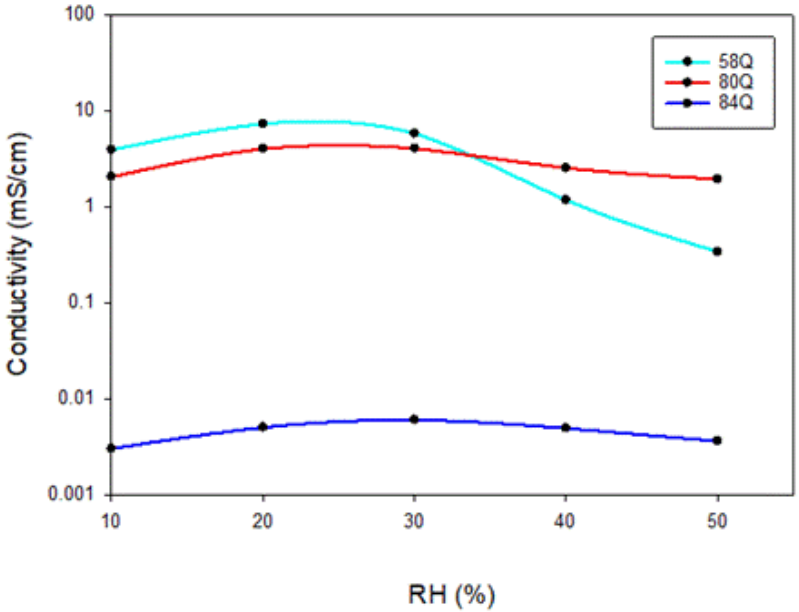
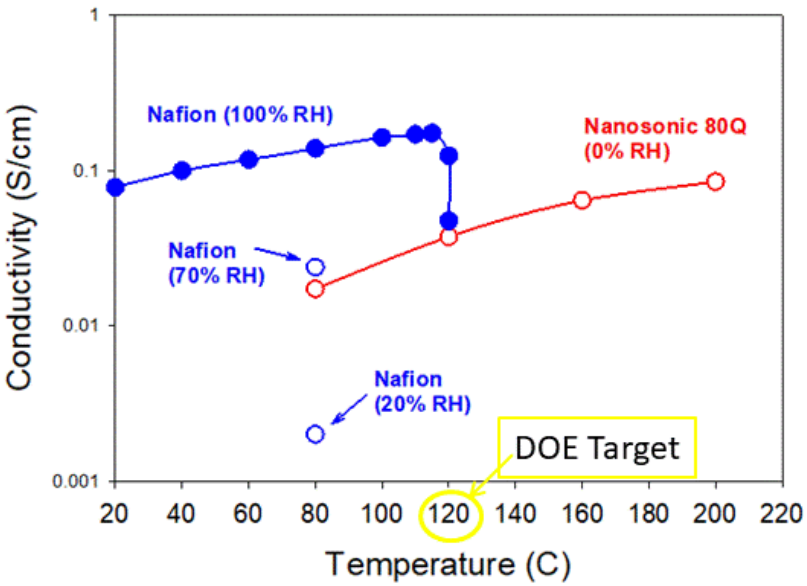
Influence of Ion Exchange Capacity and Relative Humidity on Conductivity of Select PEMs

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 stability

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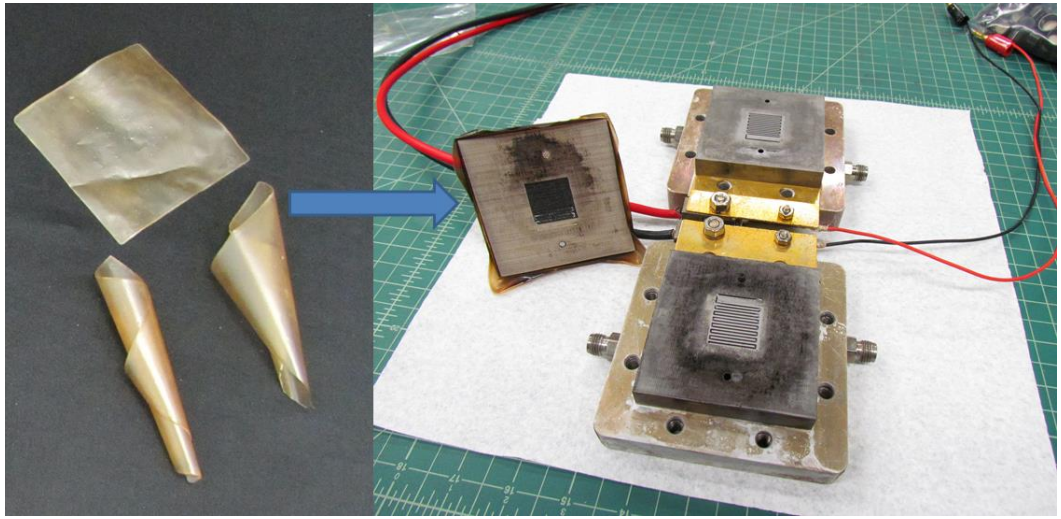
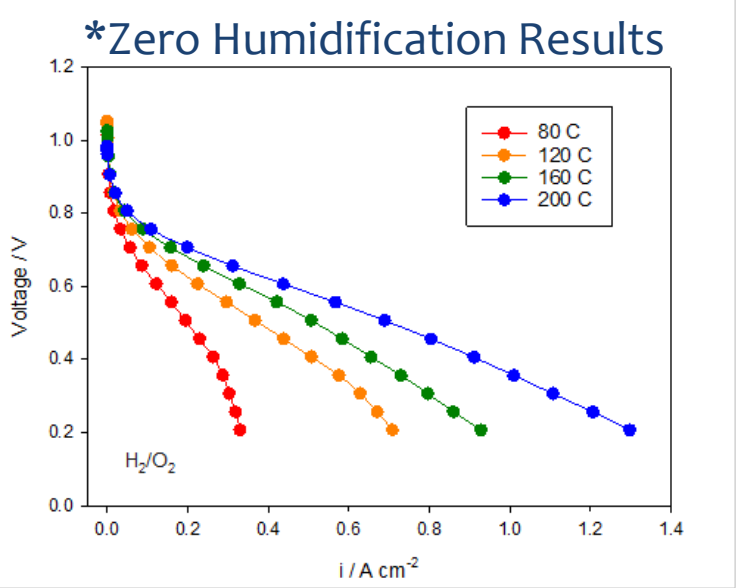
MEA Fabrication and Fuel Cell Test Stand Data

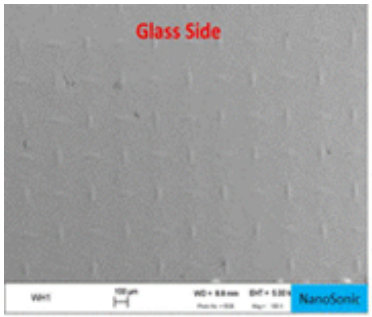


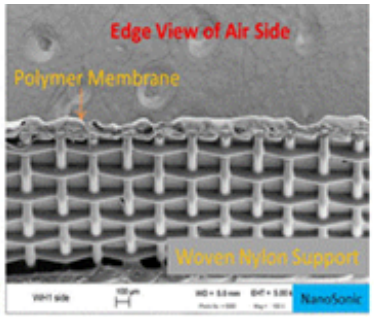


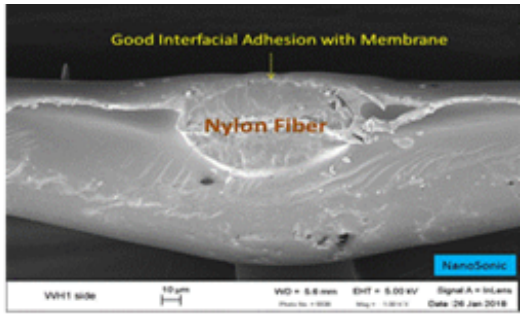
- NanoSonic's candidate membranes have been successfully doped with phosphoric acid and successfully fabricated into membrane electrode assemblies (MEAs) at LANL
- Candidate MEAs are being evaluated as a function of temperature and humidification
  - ✓ MEAs shows stable performance at 120 °C DOE target, even <u>without humidification</u>

Ongoing and Future Research

* NanoSonic has synthesized a new functionalized monomer that will allow a direct copolymerization approach to quaternary ammonium polymers which shall result in greater control of ion exchange capacity and conductivity
* Preliminary investigations using textile structural support has begun; this may further reduce membrane cost and maintain mechanical integrity. Ionomer-Nylon fabrics show good adhesion.







* Establish structure-property relationships with regards to copolymer composition and conductivity / fuel cell performance

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

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Project Summary

- High molecular weight poly(thioether benzonitrile) copolymers with tailored compositions have been synthesized and yield tough films from solution with good thermo-oxidative stability
- Chloroacylation functionalization of copolymers have successfully been demonstrated
  - Reaction conditions have been developed for reasonable reproducibility
- Fabrication of quaternary ammonium functionalized membranes have been demonstrated and characterization is ongoing
  - A surface treatment for glass substrates was developed to afford thin (<20µm) and mechanically durable PEMs which may improve electrochemical kinetics and reduce membrane cost
  - Hydrated glass transition temperature of down-selected membranes are >150°C, assuring suitability for 120°C target operation
  - Quaternary Ammonium functionalized PEMs display very low dimensional changes (swelling) and very good wet-dry cycling stability
- NanoSonic PEMs have successfully been fabricated into MEAs and evaluated at LANL in a fuel cell test stand
  - NanoSonic's ionomers display stable conductivity over a wide range of temperatures and relative humidities
  - NanoSonic's ionomer at 0% RH shows better conductivity than Nafion at 100% RH
  - NanoSonic's ionomer show good fuel cell stand performance at and above DOE 120°C operation target
- <u>The project was not reviewed last year.</u>

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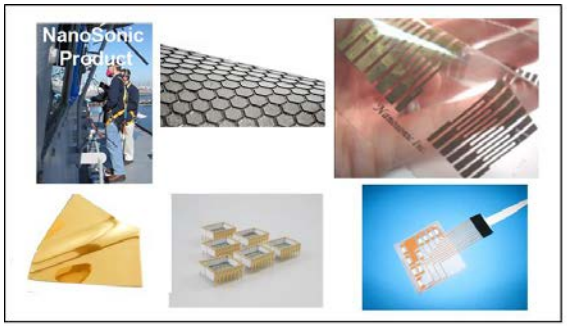
IP and Awards:

- NanoSonic has exclusively licensed nine patents covering electrostatic self-assembly (ESA) processing and use from Virginia Tech and is establishing its own intellectual property portfolio to enable process, material, and device commercialization
- R&D 100 Award for Metal Rubber™
- R&D 100 Award for HybridSil® Fire Blast
- Metal Rubber was recognized as one of NASA's top 13 nanotechnology products
- Micro Nano 25 Award for flexible electronics

R&D 100

MICRO NANO 25
The technologies of tomorrow

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