

V.M.12 Protic Salt Polymer Membranes: High-Temperature Water-Free Proton-Conducting Membranes

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Objectives

The project objective is to make new proton-conducting solid polymer electrolyte membrane (PEM) materials with the following properties:

- High proton conductance at high temperature (up to 120°C).
- Effectively no co-transport of molecular species with proton.
- Reduction of fuel cell overvoltage.
- Good mechanical strength and chemical stability.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (C) Performance

Technical Targets

The goals are to make stable membrane electrolytes with: conductivity >0.2 Siemen/cm at 120°C and >0.0005 S/cm at -20°C. Mechanism of proton conduction is to be determined using nuclear magnetic resonance (NMR) methods to guide electrolyte/membrane making. The electrolyte/membranes are to be conductive, and thermally and oxidatively stable from -20 to 120°C.

Table 1 (below) summarizes the conductivity of typical electrolytes made in this project at Arizona State University.

TABLE 1. Progress Towards Meeting Technical Targets for High Temperature Proton Conducting Membranes for Transportation Applications

Electrolyte	Comment	Conductivity (Siemen cm ⁻¹)	
		Target	ASU result
Ethyl ammonium nitrate (EAN)	Liquid	0.2 at 120°C	0.1
Protic Ionic Membranes			
polysiloxane with pendant propyl sulfonic acid plus methyl amine (8:1)	Non-leachable	0.2	0.0001
polysiloxane with pendant propyl amine plus methyl sulfonic acid (4:1)	Non-leachable	0.2	0.0001
polysiloxane with pendant ethyl amine plus methyl sulfonic acid (4:1)	Non-leachable	0.2	0.001
polysiloxane with pendant propyl amine plus methane sulfonic acid (1:1) and swollen with 60 wt% EAN	Leachable plasticizer	0.2	0.01
polysiloxane with pendant propyl sulfonic acid plus methyl amine (1:1) swollen with 60% NH ₄ NO ₃ -NH ₄ CF ₃ SO ₃ eutectic mixture	Leachable plasticizer	0.2	0.05

The data in Figures 1 and 2 show the temperature dependence of the conductivity of the liquid and solid membranes, respectively. All conductivity data is taken

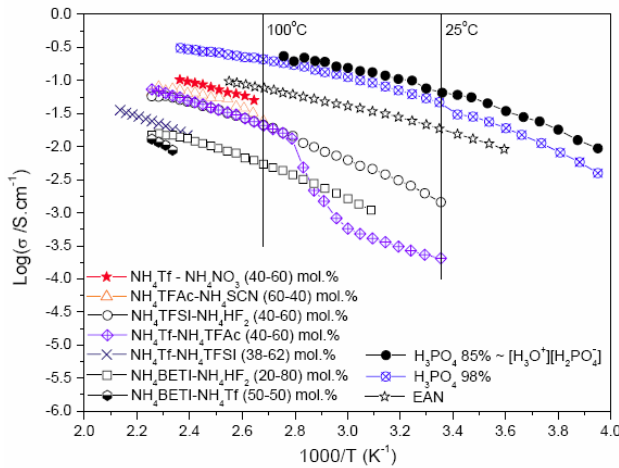


FIGURE 1. Ionic Conductivities of Protic Ionic Liquids Compared to Liquid Phosphoric Acid

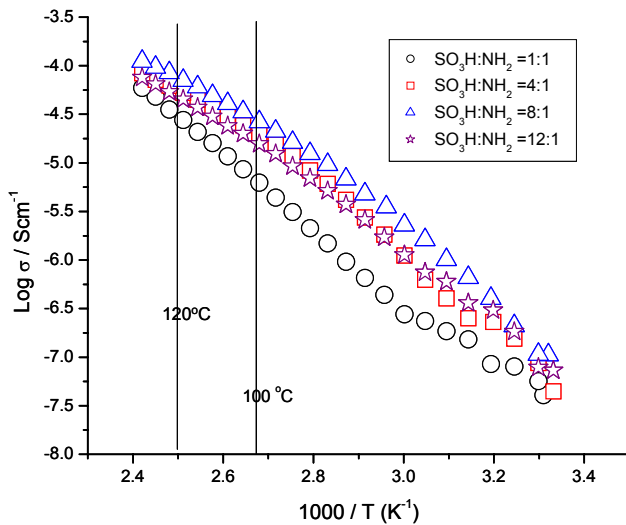


FIGURE 2. Ionic Conductivities of self standing membranes of dry polysiloxane with pendant propyl sulfonic acid groups neutralized with methylamine. Conductivity is 10-4 Siemen cm⁻¹ for 1 methyl amine per 8 pendant propyl sulfonic acids.

at 0% relative humidity over the specified range of temperatures.

Accomplishments

- Proton Conductivity:
 - High in protic ionic liquid (PIL) and PIL-filled membranes with no humidification over the range of temperatures (0.1 S/cm).
 - Lower with all solid membranes (0.001 S/cm).
- Fuel Cell Performance:
 - High voltage in liquids at modest current densities (<10 mA/cm²).

- Not yet tested in stable PIL-based membranes.
- Found stable PIL electrolytes with high conductivity but need to show high fuel cell performance with these.
- Made first non-leachable protic ionic membrane (PIM) from polysiloxane sulfonic acid paired with methyl amine and polysiloxane methyl amine paired with acids especially, sulfonic acid, without and with PIL plasticizers, which enhance membrane conductivity.



Introduction

Membranes are being made that conduct protons without the need for water in the membrane and that operate from -20 to 120°C to make high temperature polymer electrolyte membrane fuel cells that convert hydrogen to electrical energy in an efficient, lightweight and compact device.

Liquid solvent-free electrolytes have been found at Arizona State University with ionic conductivities exceeding those of most aqueous solutions at ambient and high temperatures and recently some have shown excellent fuel cell electrolyte properties. These new fuel cell electrolytes are salts that are formed from transfer of a proton between molecular Brönsted acids and Brönsted bases. For electrodes reactive to protons, these electrolytes have a proton transference number (t_p) of unity even if the proton transport mechanism is vehicular. Crystalline solid versions have also been observed having ionic conductivities exceeding those for most liquid electrolytes (e.g., σ @ 25°C >10 mS/cm). The high proton conductivities of the protic salt are evidently associated with the rotational freedom of their nearly symmetrical constituent ions and the differences in pKa of their component acids and bases. The protic ionic liquids and solids may in some cases be “dry proton” conductors, though this is not yet established. Two types of solid PEMs are being developed: (i) ionic liquid filled PEMs consisting of bi-phasic porous matrices filled with water immiscible ionic liquids immobilized by capillary forces and ionic liquids sorbed in polymers; and (ii) non-leachable PEMs consisting of novel polymers and polymer blends with no plasticizers which allow all acid and base moieties to be immobilized by covalent and electrostatic binding. Acid and base moieties as well as polymer properties are being systematically varied to optimize properties. This new approach for making PEM materials is expected to lead to a fuel cell operating at temperatures up to 120°C with high efficiency and high power density. Meeting these objectives will help “break through” the barriers, which have long delayed the use of fuel cells as power sources.

Approach

The approach has two parts: 1) synthesis of membranes and 2) characterization of the membranes for conductivity, stability and mechanism of proton conduction.

SYNTHESIS: Proton-conducting PEMs are being made that are based on protic salt electrolyte concepts. PILs are being used to model membranes and as plasticizers for improving performance of membranes. Acid and base moieties and polymer properties are being varied to optimize properties of the two PIMs: i) liquid sorbed membranes, and ii) membranes with covalently and electrostatically immobilized ions.

CHARACTERIZATION: The goals are to make first, a stable liquid and second, membrane electrolytes with: conductivity >0.2 Siemen/cm at 120°C and >0.0005 S/cm at -20°C . The mechanism of proton conduction is being determined to guide electrolyte/membrane making. The conductivity, and thermal and oxidative stability of these electrolytes are being measured from -20 to 120°C . Proton conduction is being characterized by electrochemical impedance spectroscopy (EIS). The mechanism of transport of protons, anions, and molecules were investigated using three NMR methods: 1) pulse field gradient NMR to determine the diffusivity of ions in liquid and solid states, 2) multipulse solid state NMR to measure the molecular motion and interactions of species in solid membranes, and 3) electrochemical NMR to measure distribution of species during proton conduction in solid membranes.

Results

Two types of new proton conducting membranes were made:

1. membranes with non-leachable ions formed from polymer with pendant base (acid) with added acid (base), and
2. membranes above doped with added protic ionic liquid.

Figure 3 shows the scheme for making protic ionic membranes from polysiloxanes. Similar polyphosphazenes are being made but there are no results to report yet. For the polysiloxanes, every Si in the polymer has an ionic pendant group of either alkyl sulfonic acid or alkyl amine in which alkyl chain is propyl or ethyl. Pendant sulfonic acid was reacted with base (methyl amine) to make a protic salt polymer. Pendant alkyl amine was reacted with acid (typically the best acid was methyl sulfonic acid) to make a protic salt polymer. The protic salt polymer could then be made into a freestanding crosslinked (or not) PIM. Representative conductivity of the membranes was measured as is summarized in Table 1.

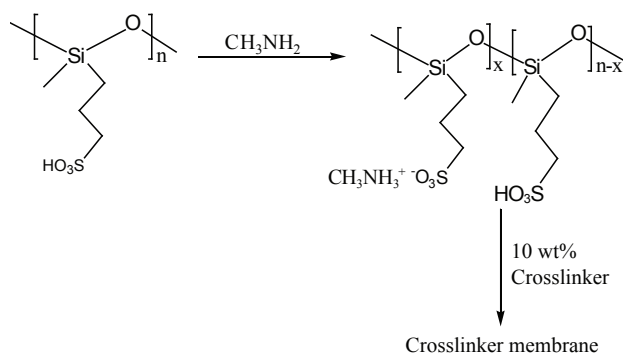


FIGURE 3. Scheme for Making Protic Ionic Membranes from Polysiloxanes

Conclusions and Future Directions

Conclusions

- Protic salt electrolytes are non aqueous proton conductors.
- No bulk water is expected to result in little or no Pt-OH on the surface, accounting for the observed: lower overpotential for oxygen reduction and higher cell efficiency possible with protic salt electrolytes, and possibly lower corrosion and Pt particle growth.
- Status of PILs:
 - High conductivity and fuel cell activity found in some PILs.
 - Stable PILs found.
 - Need to combine high conductivity and stability.
 - Need to fill a membrane support to make a PIL-loaded membrane and test for mechanical strength for suitability in a fuel cell.
- Status of PIMs:
 - Sulfonated polysiloxane with methyl ammine gives first PIM.
 - Need to raise conductivity.
 - Need to make suitable membranes for testing in fuel cells.
 - Synthesis of similar poly phosphazenes are in progress.

Future Directions

The planned work for next year and anticipated accomplishments are given below. We will:

- Continue to make and characterize two types of PIL-based PEMs:
 - Ionic liquid filled PEMs consisting of:

- bi-phasic porous matrices filled with water immiscible ionic liquids immobilized by capillary forces, and
- ionic liquids sorbed in polymers.
- Non-leachable PEMs consisting of novel polymers and polymer blends with no plasticizers which allow all acid and base moieties to be immobilized by covalent and electrostatic binding.
- Use electrochemical NMR to characterize proton conductivity in membranes. This involves:
 - Finishing setup of 3D gradient coils.
 - Display 2D NMR to investigate motions during proton conduction.
 - NMR Hittorf method to investigate distribution of species during different levels (currents) of proton conduction.
- Electrochemical Fourier transform infrared spectroscopy of Pt surface in PIL electrolytes to investigate:
 - Pt-oxide formation with potential, electrolyte choice.
 - Adsorption of electrolyte on Pt as a function of electrode potential.

2. Provisional Application Filed, ASU Case – M7-050, “Binary Inorganic Salt Mixtures as High Conductivity Liquid Electrolytes for >100C Fuel Cells”, Dear Drs. Angell, Belieres & Gervasio.

FY 2007 Publications/Presentations

1. “Inorganic salts as high conductivity electrolytes for >150°C fuel cells”, Jean-Philippe Belieres, Don Gervasio and C. Austen Angell, accepted in Chem. Commun., DOI: 10.1039/b611150e (2006).
2. “Proton transfer salts: A new class of solvent-free, involatile, fuel cell electrolytes”, D. F. Gervasio, J-P Belieres, and C. Austen Angell, American Chemical Society, Division of Fuel Chemistry, Fuel Cell Chemistry and Operation, San Francisco, CA, September 2006, Paper No. 171.
3. “Binary inorganic salt mixtures as high conductivity liquid electrolytes for high temperature fuel cells”, J.-P. Belieres, N. Byrne, X.-G. Sun, L. Holmes, G. Tucker, D. Gervasio, J. Yarger and C. A. Angell, 211th Electrochemical Society Meeting - Chicago, Illinois, May 2006, Ex. Abs. No. 321.
4. “High Temperature Proton Conducting Fuel Cell Membranes”, Chemistry Department Colloquium, University of Akron. September 26, 2006.

Special Recognitions & Awards/Patents Issued

1. “Binary inorganic salt mixtures as high conductivity liquid electrolytes for >100°C fuel cells”, J-P Belieres, D Gervasio and C A Angell, Chem. Commun., 2006, 4799. Chem Com HOT ARTICLE; Chemical Technology HIGHLIGHT ARTICLE.