V.G.10 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 (-40 to 120°C).
- Effectively no co-transport of molecular species with proton.
- Reduction of fuel cell overvoltage.
- Durable, good mechanical strength and stable.

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, Program Plan:

(A) Durability
(C) Performance

Technical Targets

The goal is to make a stable electrolyte membrane that has a proton conductivity greater than 0.1 Siemen/cm at 120°C when supplied gases with low 25 to 50% relative humidity (RH) and greater than 0.0005 S/cm at –40°C.

Accomplishments

Proton Conduction in Membranes

ASU has made dozens of membranes and sent to Bekktech four of its best membranes based on electrochemical impedance spectroscopy (EIS) measurements using dry gas done at ASU. Conductivities at different RHs was determined by Bekktech for one membrane (ASU #2, 4-23-08) that was made with crosslinked hydroxy ethyl cellulose filled with 60 wt% ethylammonium nitrate (EAN), and its proton-conductivities at 120°C and at 30°C were:

- 20 and 6 mS/cm at 25% RH
- 70 and 30 mS/cm at 50% RH
- 160 and 40 mS/cm at 75% RH

respectively. These conductivities exceeded the conductivities of the standard Nafion® (NRE-212) membrane and the high temperature conductivities are approaching the DOE targets of 100 mS/cm at 25 to 50% RH.

Fuel Cell Performance with PEMs based on Ionic Liquid Concepts

Membranes with leachable and non-leachable ions were tested.

- Leachable: Two stable membranes were made from:
  - A crosslinked hydroxyethyl cellulose membrane filled with leachable 60 wt% of a mixture of six moles NH_4NO_3 and four moles $NH_4CF_3SO_3$. This gave a fuel cell with open circuit potential of 0.7 volt and a short circuit current of 47 mA/cm^2. This is a stable protic ionic liquid (pIL)-based membrane.
  - A crosslinked 20 wt% polyammonium styrenesulfonic acid and 60 wt% ionic mixture of six moles NH_4NO_3 and four moles $NH_4CF_3SO_3$ and gave an open circuit voltage of 0.55 V and short circuit current of 67 mA/cm^2.
- Non-leachable: Two non-crosslinked membranes with fixed ions were supported on an alumina

Anodisc for mechanical support. These two membranes were:

- Polysiloxane with pendant sulfonic acid groups each reacted with methyl amine that gave an open circuit voltage of 0.5 V and short circuit current of 12 mA/cm^2.
- Polysiloxane with pendant amine groups each reacted with methane sulfonic acid that gave an open circuit voltage of 0.43 V and short circuit current of 10 mA/cm^2.

The membranes had low open circuit voltages because they were water-soluble and suffered gas crossover. Still these early fuel cell results show the concept of a salt-based proton conducting membrane is feasible.

A New Class of stable pIL electrolytes, e.g., fluorinated pyridine triflates, was made with high conductivity and stable high fuel cell performance:

- At 80°C, 2-fluoropyridinium triflate (2-FPTf) gave $\sigma = 4x10^{-3}$ Scm^{-1} and gave a better polarization curve in a hydrogen/oxygen fuel cell than aqueous 85% phosphoric acid over all current densities.
- Discovering these fluorinated pILs is a breakthrough towards high performance PEMs based on protic salts that operate stably at high temperatures.

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Introduction

A membrane that conducts protons without the need for water would allow for a more efficient, compact and lighter weight PEM fuel cell. A state-of-the-art PEM fuel cell uses water as an ionizing solvent and operates below 80°C. This requires complex humidifiers to retain solvent water, large radiators to reject waste heat and lowers the performance of platinum catalysts because at high potentials in the presence of solvent water, platinum oxides form that inhibit air cathode activity so that fuel cell efficiency drops from the theoretical 95% to no higher than ~65%. These deficiencies present formidable barriers to the use of fuel cells as power sources.

This project is directed at making a membrane with proton-containing salts to conduct protons from -40 to 120°C. At ASU it was discovered that water-free pIL electrolytes and crystalline solid versions can have high proton conductivities (e.g., σ [25°C] >10 mS/cm which increases in an Arrhenius fashion as the temperature is increased up to over 200°C). The pIL electrolytes are formed when a proton is transferred from a Brönsted acid to a Brönsted base. The high proton conductivity of a protic salt evidently results from the rotational freedom of the nearly symmetrical constituent ions and from having an optimal difference in pKa (~14) of the component acid and base.

Two types of solid polymer electrolyte membranes are being developed: (i) ionic liquid filled PEMs, consisting of: (i-a) bi-phasic porous matrices filled with ionic liquids immobilized by capillary forces or (i-b) ionic liquids absorbed in polymers and (ii) non-leachable PEMs, consisting of non-leachable novel polymers in which all acid and base moieties are 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

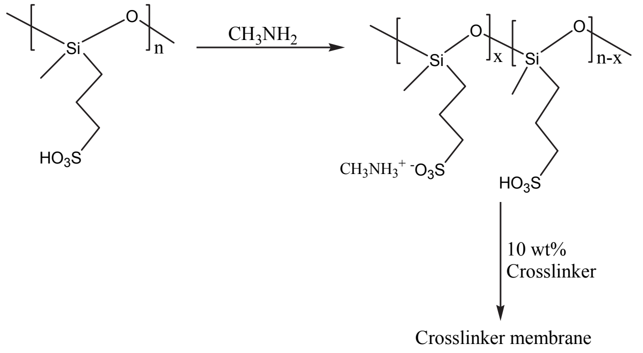
The approach has two parts: synthesis of membranes and characterization of the membranes for conductivity, stability and mechanism of proton conduction.

Syntheses: Proton-conducting PEMs are made that are based on protic salt electrolyte concepts. Protic ionic liquids are being used to model membranes and as plasticizers for improving performance of membranes. Acid and base moieties and polymer performance are being varied to optimize properties of two kinds of membranes, i) a membrane with an absorbed pIL and ii) a membrane with covalently and electrostatically bound ions.

Characterization: The conductivity and thermal and oxidative stability of these electrolytes are being measured from -40 to 120°C. Proton conductance is characterized by EIS thermostated by using a newly constructed Peltier device. Stability is screened by thermal gravimetric analysis. The mechanism of the transport of protons, anions, and molecules is investigated by three nuclear magnetic resonance (NMR) methods: 1) pulse field gradient NMR to measure 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

Many proton-conducting membranes have been made at ASU using polysiloxane and cellulose polymer backbones [1]. Recently polyphosphazenes have been prepared but there are no conductivity results to report yet. Two kinds of membrane were made: 1) membranes with non-leachable ions formed from polymer with

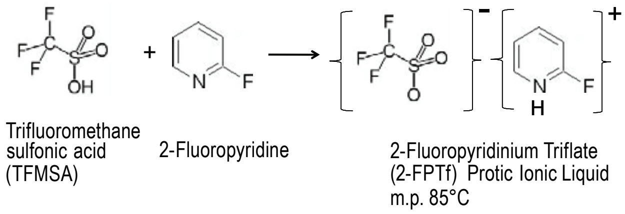


SCHEME I

pendant base (acid) with added acid (base) and 2) membranes above doped with added protic ionic liquid.

Scheme I shows how protic ionic membranes are made from polysiloxanes. Every Si in the polysiloxane has a pendant ionic group of either acid or base. Pendant acid (sulfonic acid) was reacted with base (methyl amine) to make a protic salt polymer. A pendant base was reacted with an acid to make an isomeric protic salt polymer. The protic salt polymer was made into a freestanding protic ionic membrane (pIM). The polysiloxanes and cellulose backbones were unfortunately found to be water soluble, so new work is focused on using water insoluble polyphosphazene backbones.

Trifluoromethanesulfonic acid (TFMSA) monohydrate perfluorinated electrolyte is well known to have good stability and promotes high potentials for oxygen reduction on Pt [2]. Unfortunately TFMSA monohydrate electrolyte wets Teflon®, so it has never been successfully used in Teflon®-bound Pt-catalyzed porous gas-fed fuel cell electrodes. However, recently, a stable high-performance fuel cell has been attained using a fluorinated pIL, 2-FPTf [3]. The 2-FPTf is formed by mixing 1 mole of 2-fluoropyridine and 1 mole of triflic acid as shown in Scheme II.



SCHEME II

Figure 1 shows steady-state polarization curves for Pt catalyzed hydrogen and oxygen fed fuel cells with aqueous 85% phosphoric acid and neat 2-fluoro pyridinium triflate liquid electrolytes. These curves are not corrected for resistive losses. Improved fuel cell performance with 2-fluoro pyridinium triflate electrolyte is similar to that found previously with EAN. However, the 2-fluoro pyridinium triflate electrolyte differs from EAN electrolyte in two important ways. First, there is no nitrate in 2-FPTf electrolyte. Up until 2-FPTf, all high performance pILs had nitrate, which could imply radical chemistry. Second, the 2-FPTf is stable under fuel cell operating conditions over all current densities for many hours for low temperature operation and up to 80°C. The enhanced performance is attributed to lower oxygen reduction polarization because Pt is metallic and catalytically active at potentials as high as 1.2 V vs. reference hydrogen electrode (RHE). The increased stability with 2-FPTf is attributed to fluorine being substituted for H in reactive bonds and that it does not wet Teflon®. Unlike EAN, 2-FPTf does not suffer mass-transport losses at higher current densities, so the effects of lower oxygen reduction polarization extend to higher current densities.

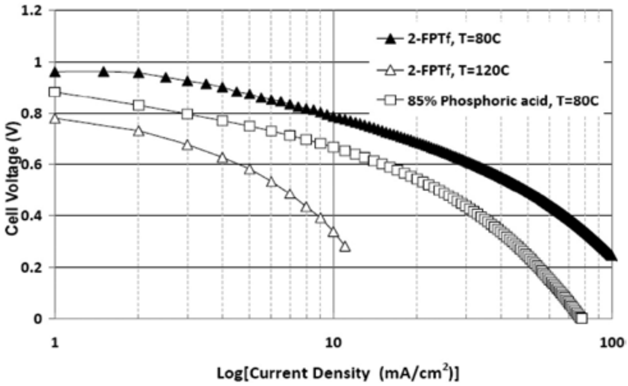


FIGURE 1. Polarization curves for fuel cell fed H_2 and O_2 on gas-fed Pt-catalyzed porous electrodes in 2-FPTf electrolyte at 80°C and 120°C and 85% phosphoric acid electrolyte at 80°C. σ(2-FPTf) = $4x10^{-3}$ Scm^{-1}, A = 0.5 cm^2, $t^{electrolyte}$ = 0.3 cm.

The lower oxygen reduction polarization was confirmed by the voltammetry of Pt in 2-fluoropyridinium triflate at 80°C (Figure 2), which shows the onset for oxygen reduction near the reversible potential of 1.2 V vs. RHE. The oxidation current above 1.2 V is not for Pt-oxide formation or electrolyte oxidation, but is for oxidation of water in the diffusion layer. This is another sign that oxygen reduction is reversible in the 2-FPTf [4]. A perfluorinated pIL, has been made by reacting perfluoro pyridine with bis perfluoromethyl sulfonyl imide, and is expected to be even more stable than 2-FPTf and will extend operation to temperatures higher than 80°C. The results with fluorinated pIL electrolytes give a strategy for making advanced membrane electrolytes, namely, using highly oxidized (fluorinated, oxygenated, nitrogen substituted etc.) pendant bases and reacting these with fluorinated acid. This strategy is being pursued by using polyphosphazenes with pendant tri- and tetra-azole groups which are reacted with fluorinated acids, like triflic acid, fluoroboric acid and bis(trifluomethylsulfonyl) imide, to give a pIM.

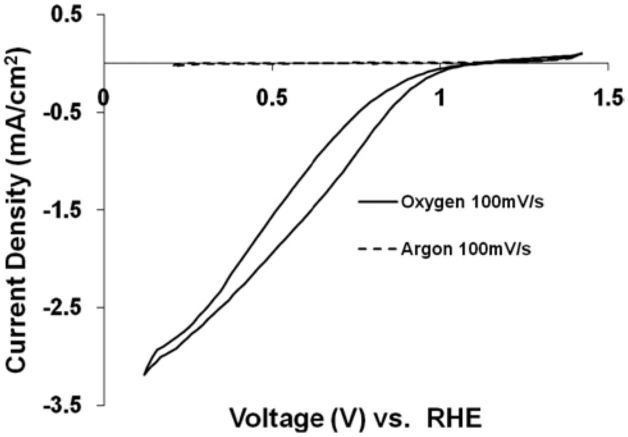


FIGURE. 2. Voltammetry of Pt in neat 2-FPTf at 80°C under dry oxygen and argon at a total gas pressure of 1 atm. Scan Rate = 100 mV/s. Electrode Area = 0.1 cm^2.

Twenty phosphazene compounds have been made. The polyphosphazenes are especially attractive, because in general, they are not water soluble, so a PEM fuel cell can operate in the presence of liquid water without disturbing the membrane electrode assembly stability due to excessive swelling. Good electrolyte stability and oxygen reduction are expected for this new polyphosphazene system based on a stringent test of these properties, namely, the voltammetry of Pt in a polyphosphazene model (a phosphazene trimer, called hexakis [4-(1,2,4-triazol-1-yl) phenoxy] cyclo tri phosphazene) mixed with liquid triflic acid monohydrate under (a) Ar and (b) oxygen atmospheres. In this liquid electrolyte, no electrolyte decomposition was found, but oxygen reduction at high potentials was found.

Indium Tin Phosphate (ITP, $In_{0.1}Sn_{0.9}P_2O_7$,)

Indium tin phosphate (ITP) is a water-insoluble proton-conducting ceramic. We intend to blend ITP with low amounts (10 to 30 wt%) of Viton (DuPont™), a water insoluble elastomeric fluorinated binder, to make a flexible water-insoluble proton-conducting membrane. The indium and tin in ITP can be mixed in non-stoichiometeric ratios, like $In_{0.1}Sn_{0.9}P_2O_7$, to form mainly a proton conductor (90%) but also an oxide conductor (10%). ITP can be considered a solid ceramic pIL. Over the past year we have been investigating the properties of this interesting material. A non-stoichiometric indium tin phosphate (ITP, $In_{0.1}Sn_{0.9}P_2O_7$) powder was prepared by mixing 0.9 moles of tin oxide, 0.1 moles of indium oxide and 2 moles of phosphoric acid in a platinum crucible and heating to 300°C. The powder is ceramic that is insoluble in all solvents. The powder was pressed into a pellet at room temperature with a Carver press using seven tons of pressure. The pellet was tested as a ceramic solid-state proton conductor. Before the conductivity test, each side of the pellet was treated with 22 nm of Pt by sputter deposition. The platinized pellet was sandwiched between two gas-fed Pt-catalyzed E-tek ELAT electrodes (Pt loading = 0.5 mg/cm^2) and then was mounted in a Teflon® cell using Viton gaskets to make a gas tight seal. Active area was 12 mm x 1.0 mm. The electrodes were fed pure dry H_2 gas at ambient pressure and the through membrane conductivity was measured using electrochemical impedance spectroscopy. The high frequency real axis intercept was considered to be the areal proton resistance. Preliminary results of the proton conductivity for $In_{0.1}Sn_{0.9}P_2O_7$ are given in Table 1.

TABLE 1. Proton Conductivity of Indium Tin Phosphate ($In_{0.1}Sn_{0.9}P_2O_7$,)

Temperature (°C)	1,000/T (K^{-1})	Log G (S/cm)	Conductivity (mS/cm)
25	3.35	-3.93	0.12
80	2.83	-4.00	0.09
100	2.68	-3.48	0.33
120	2.54	-3.77	0.17
160	2.31	-3.55	0.28
185	2.18	-3.48	0.33
200	2.11	-3.68	0.21

The conductivity increased with temperature. The increase was erratic, probably due to poor particle contact in the pellet, because the neat powder was cold pressed at 25°C. Preliminary H_2/O_2 fuel cell data showed low open circuit voltage (0.6 V) and cell voltages but sustains fairly high currents (100s of mA/cm^2). This low open circuit voltage could be due to crossover in the poorly sintered membranes. Filling with Viton binder should eliminate membrane porosity and gas crossover. In the future we will examine the conductivity of a neat ITP membrane and a membrane of ITP powder bound by Viton as a function of pressing temperature from 25°C up to 300°C. Derivatives like indium tin arsenate (ITA) and mixtures of ITP/ITA are also being prepared. Substitution with arsenic should not be hazardous as these ceramics are insoluble. Arsenic substitution should improve proton conductivity as arsenic acid is know to be a solid state proton conductor and lattice distortion of ITP by As is expected to favor lattice and therefore proton mobility.

Conclusions and Future Directions

Conclusions

- Protic salt electrolytes do not require water to conduct protons and behave like non-aqueous electrolytes even with 20% water, because water is dispersed in the pIL and its reactivity is not like “bulk” water.

- No bulk water inhibits formation of Pt-OH on the Pt 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:
  - A fuel cell with 2-FPTf, proton-conducting pIL gives higher performance than with the best industrial liquid acid electrolyte, aqueous 85% phosphoric acid.
  - Need to fill a membrane support to make pIL loaded membrane and test for mechanical strength for suitability in fuel cell.
- Status of pIMs:
  - Sulfonated polysiloxane with methyl amine gives first pIM.
- Need to further improve conductivity, physical stability.
  - Syntheses of similar poly phosphazenes are in progress.

Future Directions

The planned work for next year and anticipated accomplishments are to:

- Make PEMs based on:
  - i. Siloxane, cellulose and polyphosphazene polymers filled with fluorinated ionic liquids like 2 -FPTf.
  - ii. Polyphosphazene with pendant azoles and reacted with fluorinated acid to give non-leachable PEMs with all acid and base moieties to be immobilized by covalent and electrostatic binding.
- Test indium tin phosphate with Viton binder for conductivity and in a fuel cell.
- Use electrochemical NMR (eNMR) to characterize proton conductivity in membranes. NMR will be used to study solid membranes:
  - To investigate motions during proton conduction by 2-D NMR.
  - To investigate distribution of species during different levels (currents) of proton conduction by eNMR Hittorf method.
- Use electrochemical Fourier transform infrared spectroscopy of Pt surface in protic ionic liquid electrolytes to investigate:
  - Pt-oxide formation with potential, electrolyte choice.
  - Adsorption of electrolyte on Pt as a function of electrode potential.

FY 2008 Publications/Presentations

1. **"Protic Salt Polymer Membranes: Water-Free Proton-Conducting Membranes"**, D. Gervasio, invited talk to the Southeast Regional Meeting American Chemical Society (SERMACS), Greenville, SC, October 26, 2007.
2. **"High temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFCs) for Portable Power in Large-Scale Energy Storage Devices",** D. Gervasio, Paper Number 195, 212th Meeting of the Electrochemical Society, Washington D.C., October 11, 2007.
3. **Study of Transport Properties of Trifluoromethanesulfonic acid monohydrate: Diffusivity, Conductivity and Viscosity,** Mohammed Abdullah, M.S. Thesis, Physics Department, Arizona State University, April, 2008.
4. **"High Temperature Fuel Cells using Ionic Polysiloxane Membranes With and Without Ionic Plasticizers",** X. Sun, D. Gervasio and C. Angell (Arizona State University) Paper Number 442, 213th Meeting of the ECS, May 18-22, 2008 Phoenix, AZ.
5. **"On the State of the Proton in Protic Ionic Liquids"**, J. Belieres, N. Byrne, D. Gervasio and C. Angell (Arizona State University) Paper Number 464, 213th Meeting of the ECS, May 18-22, 2008 Phoenix, AZ.
6. **"Stable Protic Ionic Liquid (pIL) Fuel Cell Electrolytes"**, J. Thomson, R. Marzke and D. Gervasio (Arizona State University) Paper Number 466, 213th Meeting of the ECS, May 18-22, 2008, Phoenix, AZ. Accepted in *Electrochemical Transactions*.
7. **"Characterization of Poly(dichlorophosphazene)s and their reactions to Poly(organophosphazene)s",** A. Leigh; S. Ekanayake; S. Moolsin; M. Panzer;, W. Youngs; C.Tessier; C. Wesdemiotis, The University of Akron, Akron, OH, Mass Spectroscopy Society Meeting, Poster Hall Code: WPJ Time Slot/Poster Number: 217 June 2008.

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1. **"High Temperature Fuel Cells using Ionic Polysiloxane Membranes With and Without Ionic Plasticizers",** X. Sun, D. Gervasio and C. Angell (Arizona State University), 213th Meeting of the ECS, May 18-22, 2008, Phoenix, AZ.
2. **"Electrochemical Behavior of Low Molecular Weight Hydrocarbons in Trifluoromethanesulfonic Acid Monohydrate",** A. Adams, R.T. Foley, J. Electrochem. Soc., 126, 775, 1979.
3. **"Stable Protic Ionic Liquid (pIL) Fuel Cell Electrolytes"**, J. Thomson, R. Marzke and D. Gervasio (Arizona State University), 213th Meeting of the ECS, May 18-22, 2008, Phoenix, AZ. Accepted in *Electrochemical Transactions*.
4. **"Efficient Water Electrolysis in Protic Ionic Liquids",** J. Thomson, J-P. Belières, C. Austen Angell and D. Gervasio, 214th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 12-17 (2008).