V.D.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 up to 120°C) and up to 50% relative humidity (RH).

• Effectively no co-transport of molecular species with proton.

• Reduction of fuel cell overvoltage.

• Durable, good mechanical strength and stability.

Technical Barriers

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

(A) Durability
(C) Performance

Technical Targets

The DOE goal is to make a stable electrolyte membrane that has a proton conductivity greater than 0.1 Siemen centimeter^{-1} at 120°C when supplied gases with low 25 to 50% RH and greater than 0.01 at -20°C.

Accomplishments

The DOE targets and summary of the major works and accomplishments in 2009 and 2010 for achieving the DOE technical targets are summarized in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Making a Proton-Conducting High Temperature Polymer Electrolyte Membrane

Item	Description
DOE Targets	• Make a membrane with conductivity of 0.1 S/cm at 0 to 50% RH over the full range of temperature (-40 to 120°C). • Determine and report best membrane conductivity by February 2009. • Determine and report best fuel cell performance by February 2010.
Current Year Summary	• Liquid and polymeric high temperature proton-conducting protic salt membranes were made and tested for conductivity and stability in fuel cell conditions, namely: • (i) Seven new stable fluorinated protic ionic liquids (pILs). • (ii) Protic ionic membranes (pIMs) with non-leachable salt moieties. • Selected new inorganic indium tin phosphate (ITP) membranes were sent to Scribner and Bekktech for validation of conductivity at various temperatures and relative humidities.
Accomplishments February 2009	• A neat ITP membrane [1] was made that has conductivity of 0.16 S/cm from 25°C to greater than 120°C and 0% RH. • Crossover in pure ITP membrane was eliminated by blending 70 wt% ITP with 30 wt% of a proton-conducting organic polymer, polyvinyl pyridinium phosphate (PVPP) [2], but at a cost of reduced conductivity.
Accomplishments 2010	• Improved synthesis and processing of ITP and organic polymer blended membranes. Mixing of reagents during heating was found to be critical for reproducibly making ITP. • Membrane samples were sent to Scribner and Bekktech for conductivity testing

Scribner and Associates checked the conductivity of an indium tin phosphate ($In_{0.1}Sn_{0.9}P_2O_7$ or ITP) sample that was 1.23 mm thick x 12 mm diameter. This sample was tested using electrochemical impedance spectroscopy (EIS) in a H_2 atmosphere at 30, 80, and 120°C from 20 to 95% RH and the result are shown in Figure 1. The conductivity was evaluated from the impedance data using an equivalent circuit model and the ITP data taken at 80°C, 70% RH with this model gives a membrane resistance of 0.754 ohm, which corresponds to a conductivity of ~140 mS/cm. The conductivity was found by Scribner to decrease when the temperature was raised to 120°C, which was unexpected, because for tests done at Arizona, the conductivity increased smoothly with increasing temperature from room temperature up to 250°C.

✧   ✧   ✧   ✧   ✧

Introduction

A membrane that has high proton conductance at temperatures up to 120°C without the need for water would allow for a more efficient and compact PEM fuel cell. Presently PEM fuel cell electrolyte membranes need water as an ionizing solvent which results in three consequences: 1) operation below 80°C and complex humidifiers to maintain solvent water, 2) large radiators to reject waste heat, and 3) lower performance of platinum catalysts. 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 three consequences of using water present barriers to the use of fuel cells as power sources. This project aims to make a membrane with anhydrous proton-containing salts to conduct proton from -40 to 120°C and to study
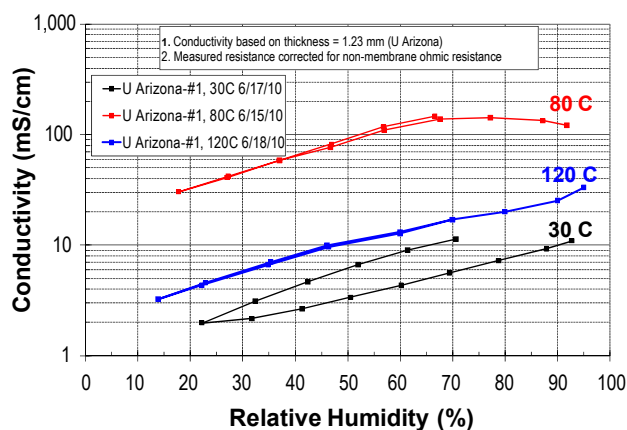
the fundamental mechanism of proton conduction in these salt membranes. Our team discovered that neat pIL electrolytes and crystalline solid versions have high proton conductivities from ambient temperatures to over 200°C. A pIL forms when a proton is transferred from a Brönsted acid to a Brönsted base. The high proton conductivity of a protic salt evidently results from: i) the rotational freedom of the nearly symmetrical constituent ions and, from ii) having an optimal difference in pKa of the constituent acid and base.

Approach

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

Proton-conducting PEMs are being made based on concepts developed with pILs. The pILs are used to model membranes to help select acid and base moieties. Polymer backbones, acids and bases have been varied to optimize PEM proton conduction, stability, and other properties. Liquid and solid membrane salt-electrolytes are characterized for proton conductivity by EIS and for stability by thermal gravimetric analysis (TGA) and by monitoring fuel cell performance in time. The mechanism of the transport of protons, anions, and molecules in pILs and protic ionic membranes (pIMs) is being investigated by: 1) pulse field gradient nuclear magnetic resonance (NMR) to measure the diffusivity of ions in liquid and solid states, 2) multipulse solid-state NMR to measure the molecular motions and interactions of species in solid membranes, and 3) electrochemical NMR to measure distribution of species during proton conduction in solid membranes.

Results

The preparation and processing of the ceramic (ITP) membranes [1] were further developed so that these high-performance advanced materials can be made reproducibly. These ITP ceramic materials and blends with organic polymers, like PVPP [2] and polyphosphazenes (PPhz) have shown proton conductivities in excess of 0.1 S/cm.

Preparation and Performance of ITP

A mass of indium oxide (0.5027 g), tin oxide (4.8933 g) and aqueous phosphoric acid reagents (85%, 12.1685 g) were mixed in a ceramic crucible while stirring at 300°C for approximately 1 hour and then calcined in the crucible (uncovered) at 650°C for 2.5 hours. The calcined material was ground in a mortar and pestle and then cold pressed at 6,000 lbs for 1 minute to form a pellet membrane. The pellet was heated at 200°C for 1 hour. Each side of the membrane

FIGURE 1. Test done at Scribner for Through-Plane Conductivity of a Pure ITP membrane (J7, U. of Arizona#1) at 30, 80 and 120°C from 0 to 100% RH.

pellet surfaces was coated with a 20 nm thick Pt layer by direct current sputtering. The ITP membrane was then characterized for proton conductivity as shown in Figure 2.

Recently a new inorganic/organic composite was made using 90 wt% ITP with 10 wt% of organic binder PVPP. The conductivity is shown in Figure 3.
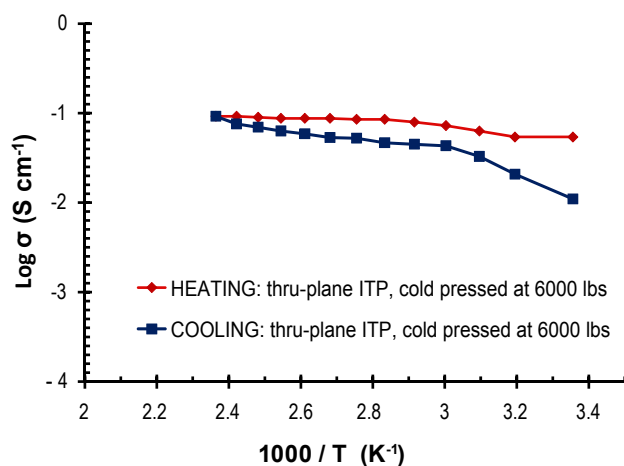
FIGURE 2. Arrhenius plot of pure ITP membrane under a dry hydrogen atmosphere measured thru-plane by EIS from 50 kHz to 10 Hz. Alternating current modulation amplitude: 50 mV. Membrane thickness = 1.65 mm, active area = 0.484 cm^2, thickness sputtered Pt = 20 nm. E-TEK electrodes (0.5 mg of Pt per cm^2) gas diffusion layer. Pt screen current collectors. Formulation J4 with sputtered Pt on ITP membrane.
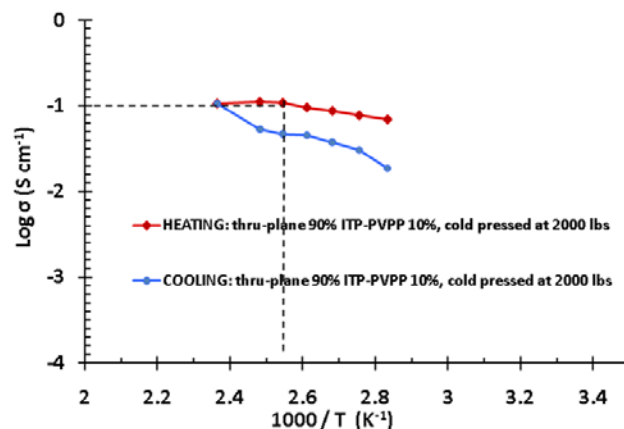
FIGURE 3. Arrhenius plot of the proton conductivity of a 90% ITP with 10% PVPP membrane measure through-plane. EIS measured using a PAR 2273 over a frequency range of 500k-1 Hz using an alternating current modulation amplitude of 10 mV. Thickness =1.5 mm. Equilibrated with humidified H$_2$ gas (RH 70%). Pt sputtered 20 nm (active area 0.5 cm^2) E-TEK Pt/C (0.5 mg/cm^2) gas diffusion layers and Pt current collectors.

This 90% ITP and 10% PVPP blend showed over an order of magnitude greater conductivity than 70% ITP and 30% PVPP shown last year.

pILs

In addition to the work on ITP, a number of fluorinated and heterocycle rich pILs were synthesized including: 2-fluoro-pyridinium triflate (2-FPTf), 2,6–difluoro pyridinium triflate (2,6–dFPTf), 2-fluoro-pyridinium trifluoromethyl sulfonylimide (2-FPTfSi), 2-fluoro-pyridinium trifluoromethyl sulfonylimide (2-FPTfSi), 1,2,5 triazole fluoroborate (1,2,5-tABF$_4$), 1,2,4 triazole fluoroborate (1,2,4-tABF4), and guanadinium thiocyanate (GdSCN). These neat liquid salts had conductivity comparable to liquid aqueous electrolytes and were characterized in Walden plots (conductivity versus fluidity at different temperatures). Two of these, 2-fluoro-pyridinium triflate and guanadinium thiocyanate, displayed super protonic conductivity, that is, their proton conductivity increased with temperature more rapidly than their fluidity (inverse of viscosity) and both 2-FPTf and GdSCN showed proton conductivity >0.1 S/cm at 120°C and 0% RH. These two salts are recommended as the pendant groups in polymers for making a PEM with high conductivity with no need for hydration.

Non-platinum metals can be used for catalyzing oxygen electroreduction in these anhydrous proton conducting salts. In particular palladium and tungsten appeared good candidates as they had comparable oxygen reduction overpotentials as Pt as indicated by preliminary voltammetry experiments.

Conclusions and Future Directions

Conclusions

- Fiscal Year (FY) 2009: Protic liquid and solid salt electrolytes give "dry" proton-conducting membranes with conductivities found at Arizona to be $\geq$ 0.1 S/cm at 120°C and 0% RH but not confirmed at Bekktech or Scribner to date.
- FY 2010: More stable fluorinated liquid electrolytes show lower polarization for oxygen electro-reduction reaction.
- FY 2010: Non-aqueous electrolytes could enable use of non-Pt catalysts.
- FY 2009–FY 2010: Inorganic/organic polymer blends of dry proton conductors give non-porous proton-conducting membrane for *simplified* fuel cell operation in more compact system (no humidifier and smaller radiator).

Future Directions

- Make and test proton conductivity and fuel cell behavior for membranes based on:
  - ITP
  - blends of ITP and organic polymers
- Send to Bekktech for confirmation of conductivity found at Arizona State University.
- Correlate NMR and conductivity measurements.
- Study voltammetry of Pt on a solid salt (ITP) membrane electrolyte to find electrochemical active area of Pt in a salt membrane electrode assembly (MEA) and compare to the Pt area in a well-engineered MEA. Normalize performance in terms of electrode area for fair comparison of these two systems.
- Interpret voltammetry of Pt on ITP for Pt-oxide. If Pt-oxide free, consider inspection by X-ray irradiation to confirm if Pt stays metallic at high potential (1.2 V) or not. This X-ray work would be done with Dr. Deborah Myers at the Advanced Photon Source at Argonne National Laboratory.
- Optimize membranes from inorganic (ITP) and organic polymer blends:
  - Synthesis of ceramic/organic membranes of ITP and organic polymers (such as polyphosphazene triazoles with various immobilized salts).
  - Process ITP/polymer blend membranes for higher conductivity, flexibility, and toughness.
  - Test the ITP membrane conductivity as a function of humidification of gases and test samples after exposure to water (to probe for conductivity/performance changes if any free ions are removed).

Special Recognitions & Awards/Patents Issued

1. "Electrochemical Reduction in Ionic Liquids", Ph. D. Thesis, Jeffery Thomson, Materials Science, ASU, Advisor, D. Gervasio, 12 March 2010.

FY 2010 Publications/Presentations

1. "Fuel Cells with Neat Proton-conducting Salt Electrolytes", Don Gervasio, Ch. 20 in Fuel Cell Science: Theory, Fundamentals and Bio-Catalysis, Jens Norskov, Andrzej Wieckowski, Eds., John Wiley & Sons (2010).

2. "Catalysis of Electrode Reductions in Salt Electrolytes with Low-Water-Activity", D. Gervasio, University of Arizona, Tucson AZ, 85721, Ex. abs. 1757, Spring 2010 ECS meeting Vancouver, Canada.

References

1. "Intermediate-Temperature Proton Conduction in Al3+-Doped SnP2O7", A. Tomita, N. Kajiyama, T. Kamiyama, Masahiro Nagao, and Takashi Hibino, Journal of The Electrochemical Society, 154, B1265-B1269 (2007).

2. "Anhydrous Proton-Conducting Polymeric Electrolytes for Fuel Cells", S.R. Narayanan, Shiao-Pin Yen, L. Liu, and S.G. Greenbaum, J. Phys. Chem. B 2006, 110, 3942-3948.