

V.D.6 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).
- Effectively no co-transport of molecular species with proton.
- Reduction of fuel cell overvoltage.
- Durable, 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, Program Plan:

- (A) Durability
- (C) Electrode Performance.

Technical Targets

The DOE goal is to make a stable electrolyte membrane that has a proton conductivity greater than 0.1 S/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

The DOE targets and summary of the major works and accomplishments in 2009 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 (HT PEM).

Item	Description
DOE targets	Make a membrane with conductivity of 0.1 S/cm at 0 to 50% RH at 120°C. Determine and report best membrane conductivity by February 2009
Summary of ASU work	Liquid and polymeric high-temperature proton-conducting protic salt membranes were made and tested for conductivity and stability in fuel cell conditions, namely: (i) pILs protic ionic liquids, and (ii) pIMs protic ionic membranes with non-leachable salt moieties. Selected new membranes were sent to Beektech for external validation of conductivity at various temperatures and RH conditions.
Accomplishments Feb-09	A neat indium tin phosphate (ITP) membrane was made that has conductivity 0.16 S/cm from 25°C to greater than 120°C and 0% RH. Crossover in pure ITP membrane eliminated by blending 70 wt% ITP with 30 wt% of a proton conducting organic polymer (polyvinyl pyridinium phosphate, PVPP) but at a cost of reduced conductivity.



Introduction

A membrane that conducts protons up to 120°C without the need for water would allow for a more efficient, compact and lighter weight PEM fuel cell. Presently PEM fuel cell electrolyte membranes need water as an ionizing solvent. Consequently, this requires operation below 80°C, 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. The project aims to make a membrane with anhydrous proton-containing salts to conduct protons from -40 to 120°C and to study the fundamental mechanism of proton conduction in these salt membranes. At ASU it was discovered that neat protic ionic liquid (pIL) electrolytes and crystalline solid versions have high proton conductivities from ambient temperatures to over 200°C. A salt electrolyte forms when a proton is transferred from a Brønsted acid to a Brønsted 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 of the acid and base.

Approach

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

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. Polymers, acids and bases have been varied to optimize proton conduction, stability and other PEM properties. The liquid and solid membrane salt-electrolytes are characterized for proton conductivity by electrochemical impedance spectroscopy (EIS) in thermostatted cells and for stability by thermal gravimetric analysis and by monitoring fuel cell performance in time. The mechanism of the transport of protons, anions, and molecules is being 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

The team has been developing new water-free proton-conducting salt membranes. Electrolytes made to date include: the liquid salts, called pILs, polymeric salt membranes with (leachable) and without (non-leachable) pILs added, and solid ceramic membranes of non-stoichiometric ITP ($\text{In}_{0.1}\text{Sn}_{0.9}\text{P}_2\text{O}_7$) alone as well as ceramic blended with a non-leachable organic salt PVPP.

Types of salt electrolytes made to date:

1. Protic ionic liquids (pILs).
2. Polysiloxane (PS) solid PEMs.
3. PS PEMs filled with pILs.
4. Cellulose PEMs filled with pILs.
5. PVPP PEMs.
6. ITP ceramic PEMs.
7. PVPP and ITP blended PEM.
8. Phosphazene trimer (PT) – polyimide (PI) blended PEMs.
9. Polyphosphazene (PP) – PI-blended PEMs.

The best membranes from the standpoint of conductivity were polymers filled with pILs and ceramic ITP membranes [2]. Polymer membranes filled with pILs have conductivity approaching the DOE Go/No-Go targets. Insoluble ceramic membranes made from ITP have proton conductivity over a broad temperature range that apparently exceeded the DOE Go/No-Go targets (Figure 1).

Studies of pILs have helped understand and develop solid proton-conducting ionic membrane electrolytes (pIMs). As seen in Figure 2, the conductivity for the solid poly vinyl pyridinium phosphate ($\text{PVP-H}_3\text{PO}_4$) membrane is high even in the absence of water at high temperatures. This high conductivity (measured by EIS) is attributed to close proximity of one pendant salt group to another, so that protons can be passed by direct contact of these salt groups. Precisely how protons are passed is the subject of ongoing NMR studies. Although the PVPP has high proton conductivity, Figure 2 shows that it is not quite as high as for the analogous liquid vinyl pyridinium phosphate pIL ($\text{Py-H}_3\text{PO}_4$) or 2-fluoro pyridinium triflate (2-FPyTf) as a function of

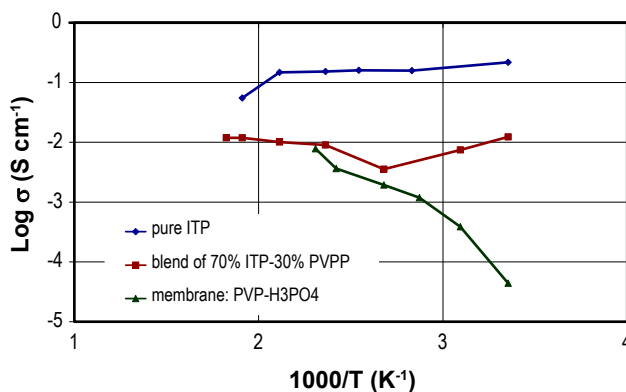


FIGURE 1. Conductivity determined by impedance spectroscopy for three electrolyte samples as a function of temperature. Electrodes E-Tek Pt/C (0.5mg/cm²) fed dry; H₂ gas, T = 25 to 275°C. Solid triangle: Solid membrane of poly vinyl pyridinium phosphate (PVP-H₃PO₄), Solid diamond: solid ceramic membrane of pure 10%indium 90%ITP. Solid square: a solid membrane of 70% ITP blended with 30 wt% PVP- H₃PO₄.

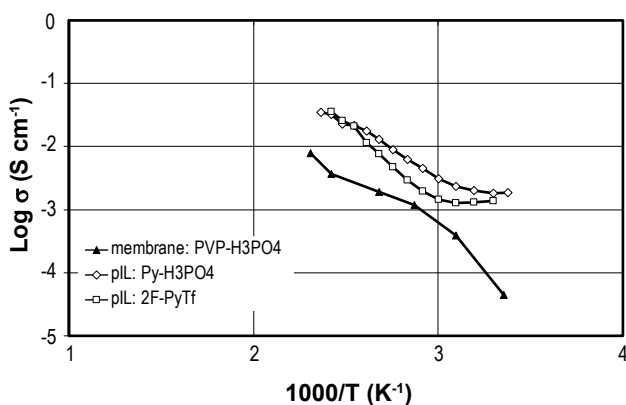


FIGURE 2. Conductivity determined by impedance spectroscopy for three electrolyte samples as a function of temperature. Electrodes E-Tek Pt/C (0.5mg/cm²) fed dry: H₂ gas, T=25 to 150°C. Solid triangle: Solid poly vinyl pyridinium phosphate (PVP- H₃PO₄) membrane, Open diamond: Liquid vinyl pyridinium phosphate pIL (P- H₃PO₄), Open square: Liquid 2-fluoro pyridinium triflate (2-FPyTf).

temperature. This is expected, as the polymer forbids proton conduction by salt translation and restricts conduction to “hopping” only. Fuel cell, hydrogen pumping and water electrolysis were done in cells using PVPP as the cell membrane, and these experiments were steady in time (for as long as days) which is only possible if proton is hopping in PVPP.

The best membranes from the standpoint of conductivity were made from pure and blended ITP and have conductivity apparently exceeding the DOE Go/No-Go targets (Figure 1). Figure 3 shows preliminary fuel cell performance for these two membranes. The highest power is with the pure ITP but the highest open circuit voltage is with the ITP blended with PVPP polymer. This later improvement is most likely due to decreasing of gas crossover when the pores of the porous ITP membrane are filled by PVPP polymer.

Conclusions and Future Directions

- 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
- The absence of bulk water reduces formation of Pt-OH on the Pt surface, accounting for the observed lower overpotential for oxygen reduction, higher cell efficiency, and possibly lower corrosion and Pt particle growth.
- Status of pILs
 - Fluorinated 2-fluoropyridinium triflate (2-FPTf) and non-fluorinated pyridinium phosphate are two new non-aqueous pIL electrolytes that gave high proton conductivity and good stability.

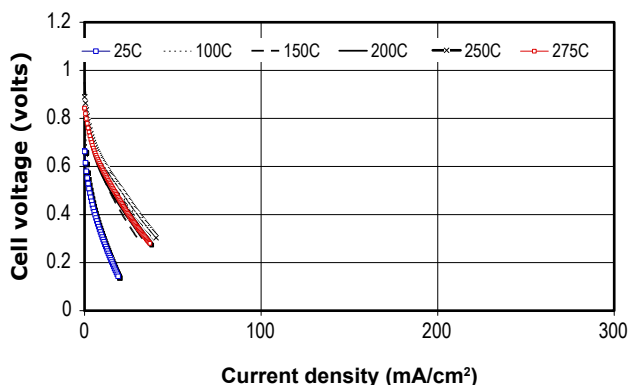
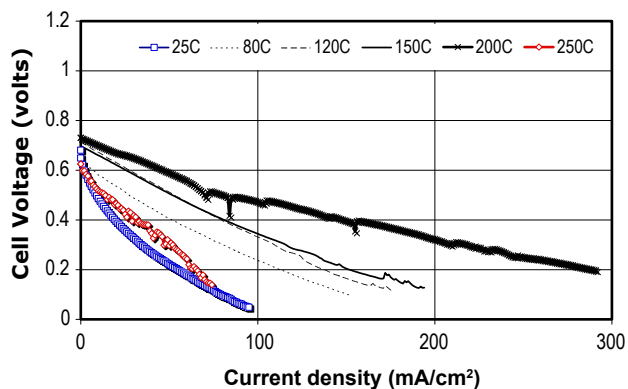


FIGURE 3. Fuel cells made with a pure ITP membrane (top) and a membrane with an ITP/PVPP blend (bottom).

- 2-FPTf is a non-aqueous proton-conducting pIL with higher hydrogen/oxygen fuel cell performance than aqueous 85% phosphoric acid as electrolyte.
- Status of pIMs
 - PVPP gives a non-aqueous membrane electrolyte that has temporally stable and high proton conductivity, but not as high as liquid PP.
 - Syntheses of similar water insoluble poly phosphazene membranes are in progress.
 - ITP has higher proton conductivity than the DOE target, and when blended with polymeric PVPP, gives no H₂/O₂ crossover but at the expense of conductivity.

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

- Make PEMs based on:
 - ITP with different ratios of non polar (VITON) and ionic (PVPP) polymer binders and test for proton conductivity and fuel cell performance.
 - PPs with pendant azoles and reacted with fluorinated acid to give tough flexible non-leachable PEMs with all acid and base moieties

- to be immobilized by covalent and electrostatic binding.
- Screen activity of non-platinum catalysts for promoting oxygen electroreduction in new fluorinated pILs.
 - 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-dimensional NMR.
 - to investigate distribution of species during different levels (currents) of proton conduction by eNMR Hittorf method.
 - Use electrochemical Fourier transform infrared spectroscopy and possible X-ray of the Pt surface in PIL electrolytes to investigate:
 - Pt oxide formation as a function of potential and electrolyte composition.
 - adsorption of electrolyte on Pt as a function of electrode potential.

4. “Characterization of Poly(dichlorophosphazene)s and their reactions to Poly(organophosphazene)s”; Alyson Leigh; Sujeevani Ekanayake; Supat Moolsin; Matthew Panzer; Wiley Youngs; Claire Tessier; Chrys Wesdemiotis, The University of Akron, Akron, OH, Mass Spectroscopy Society Meeting, Session: Materials and Polymers - Poster Hall Code: WPJ Time Slot/Poster Number: 217 June 2008.
5. “Study of Transport Properties of Trifluoromethanesulfonic acid monohydrate: Diffusivity, Conductivity and Viscosity, Mohammed Abdullah”, M.S. Thesis, Physics Department, Arizona State University, April, 2008.
6. “Characterization of protic ionic liquids: NH chemical shift”, J.-P. Belieres in the I&EC division, Paper no. 82, Am. Chem. Soc., Philadelphia, PA (2008). “Efficient Water Electrolysis in Protic Ionic Liquids”, Jeffery Thomson, Jean-Philippe Belières, C. Austen Angell and Don Gervasio, 214th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 12–17 (2008).
7. “Protic ionic liquids as probes for acidity of superacids”, in preparation.

Special Recognitions & Awards/Patents Issued

1. “Stable Protic Ionic Liquid (pIL) Fuel Cell Electrolytes”, Gordon Research Conference, Bryant College, Rhode Island, July 20, 2008. Accompanying poster presentation on July 23, 2008 was awarded one of 3 “Best GR Conference Posters”.
2. “Electrochemistry in Ionic Liquid Electrolytes”, Invited talk to the Chemical and Biochemical Engineering Department, Graduate Seminar Series, North Carolina State University, August 25, 2008.
3. “Electrochemistry in Ionic Liquid Electrolytes”, Invited talk to University of Warsaw, March 27, 2009, Warsaw, Poland.
4. “Electrochemistry in Ionic Liquid Electrolytes”, Invited talk to the 7th Spring Meeting of the ISE, Szczyrk, Poland March 23, 2009.

FY 2009 Publications/Presentations

1. “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, 213rd Meeting of the ECS, May 18–22, 2008 Phoenix, AZ.
2. “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, 213rd Meeting of the ECS, May 18–22, 2008 Phoenix, AZ.
3. “Stable Protic Ionic Liquid (PIL) Fuel Cell Electrolytes”, J. Thomson, R. Marzke and D. Gervasio (Arizona State University) Paper Number 466, 213rd Meeting of the ECS, May 18–22, 2008 Phoenix, AZ.

References

1. “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.
2. “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).