2007 DOE Hydrogen Program Review

Protic Salt Polymer Membranes:
High-Temperature Water-Free Proton-Conducting Membranes

D. Gervasio

Arizona State University

May 16, 2007

Project ID # FC 16

Overview

DOE Hydrogen Program

Timeline

- Start: January 15, 2006
- End: January 14, 2011
  - go/no go end of year 3
- 25% completed

Barriers

- Barriers addressed by this project from the HFCIT Program Multi-Year Program Plan
  - (A) Durability
  - (C) Electrode Performance

Budget

- Total project funding $1,500K
  - DOE: 80%, Contractor: 20%
- Funding received in FY06
  - $150,000
- Funding for FY07
  - $300,000

Partners

- Arizona State University
- University of Akron
- Boeing

- DOE Technology Development Manager: Nancy Garland
- DOE Project Officer: Jill Gruber
- ANL Technical Advisor: Thomas Benjamin

Objectives

To make proton-conducting solid polymer electrolyte membrane (PEM) materials having:

- 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

Approach

SYNTHESIS

Proton-conducting PEMs are being made that are based on protic salt electrolyte concepts.

Protic ionic liquids (PILs) will be used to model membranes.

Acid and base moieties & polymer properties varied to optimize properties of a protic salt membrane (PSM).

- Liquid sorbed membranes
- Membranes with covalently and electrostatically immobilized ions are being made.

CHARACTERIZATION

The first goals are to make stable liquid and then membrane electrolytes with:
conductivity > 0.2 Siemen/cm at 120°C and > 0.0005 S/cm at –20°C.

Mechanism of proton conduction is being determined to guide electrolyte/membrane making.

The conductivity and thermal & 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 investigated three NMR methods:

1. pulse field gradient NMR to determine the diffusivity of ions,
2. multipulse solid state NMR to measure the molecular motion and interactions of species in membranes,
3. electrochemical NMR to measure distribution of species during proton conduction.

Plan & Progress

DOE Hydrogen Program

30% complete

- **Task 1: PIL Design and Testing**
  - mixed acid and base moieties as electrolyte
  - models for high temp (120°C) membrane

10% complete

- **Task 2: Proton Conducting Membranes**
  - 2.1.1 - Porous support with a PIL
  - 2.1.2 - PIL swollen in polymers
  - 2.2 - Immobilized PIL polymer

30% complete

- **Task 3: Temp Dependence of Electrolyte**
  - Conductivity, durability and wettability of electrolytes
  - at T = 120°C, 100°C, 80°C, 20°C and -20°

15% complete

- **Task 4: Proton Conduction by NMR**
  - 4.1 Pulsed field gradient NMR
  - Electrochemical NMR (eNMR)
  - eNMR Hittorf

15% complete

- **Task 5: Iterate Synthesis**
  - stability

5% complete

- **Task 6: Membrane Demonstration**

Technical Accomplishments/ Progress/Results

- Accomplishments/progress with high temperature electrolytes
  - Conductivity:
    - high in liquid and liquid filled membranes
  - Fuel cell Performance
    - High voltage in liquids at modest current densities ($\leq$ 10 mA/cm^2)
    - Not yet tested in STABLE PIL-based membranes

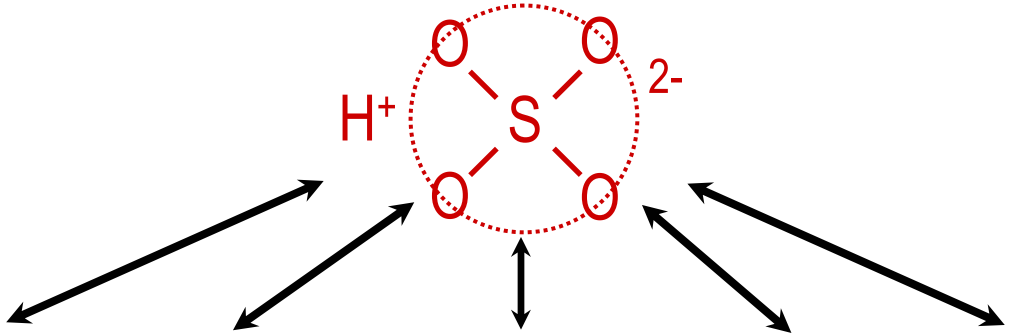
- Found stable PIL electrolytes with high conductivity but need to show high fuel cell performance with these

- Made first non-leachable PIM from polysiloxane sulfonic acid paired with methyl amine

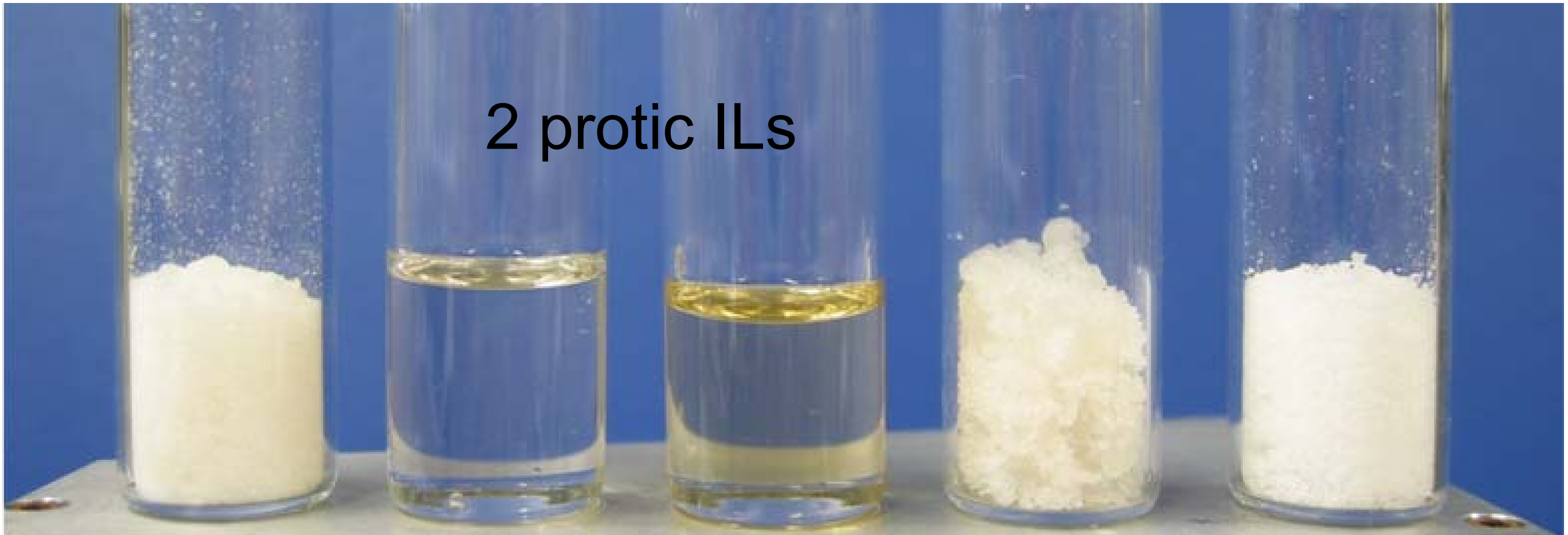
Two out of 5 salts below are PILs

DOE Hydrogen Program

$RN\text{-}HSO_4$



$[Bu_2NH_2]^+$ $[EtNH_3]^+$ $[Me_2NH_2]^+$ $[Me_3NH]^+$ $[Bu_3NH]^+$

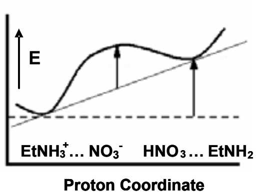


Photographs by Fumi Mizuno (who also made them)

PROTIC IONIC LIQUID (PIL) CONCEPTS

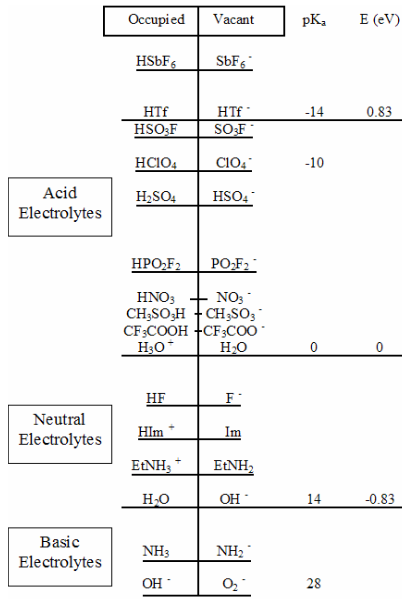
DOE Hydrogen Program

PILs belong to a new class of solvent-free proton-conducting electrolyte that can function at very high temperatures



Energy minima for ethyl ammonium nitrate (EAN) PIL with:
- proton transferred (Left)
- not transferred (Right),

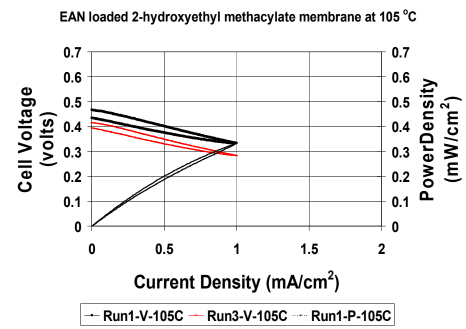
A protic ionic liquid (PIL) is made by transferring a proton from an acid to a base.



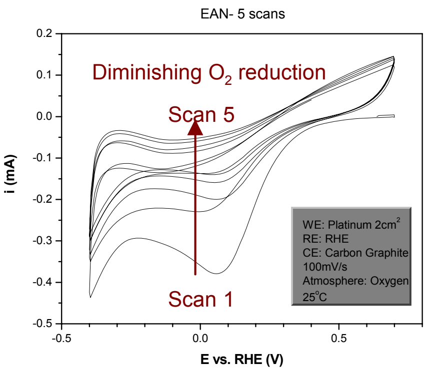
Gurney proton energy level diagram. For any pair of levels, the stable entities are upper right and lower left.

But EAN is NOT stable for long

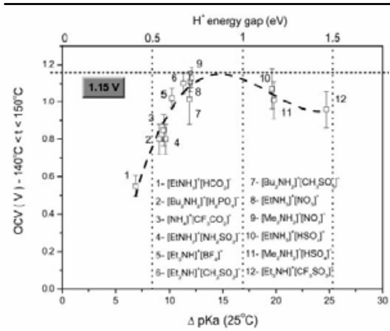
EAN degrades in membrane fuel cell



Degradation validated by voltammetry



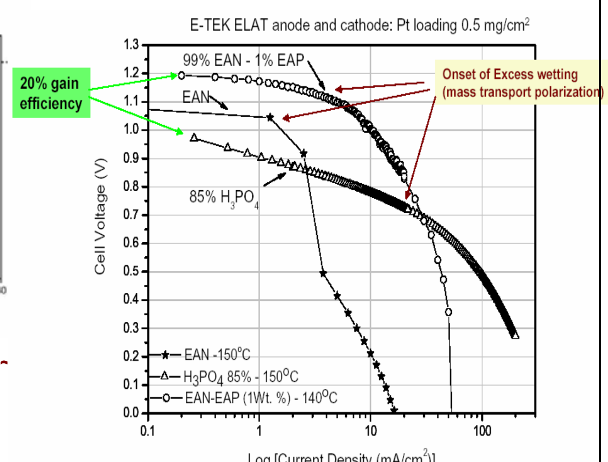
What to do?
Tailor the electrolyte for stability!



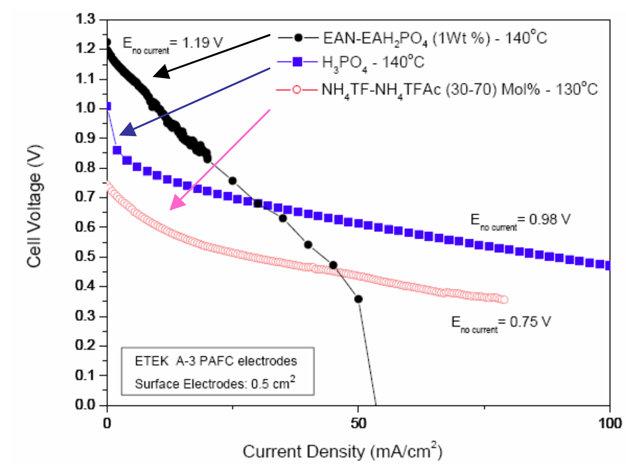
Correlation between OCV & ΔpKa constituents of PILs; Select ΔpKa = ~ for an effective PIL.

Protic Ionic Liquids promote: superior fuel cell properties …

- **High open circuit voltage (OCV),**
- **High efficiency operation**
- **High power operation**



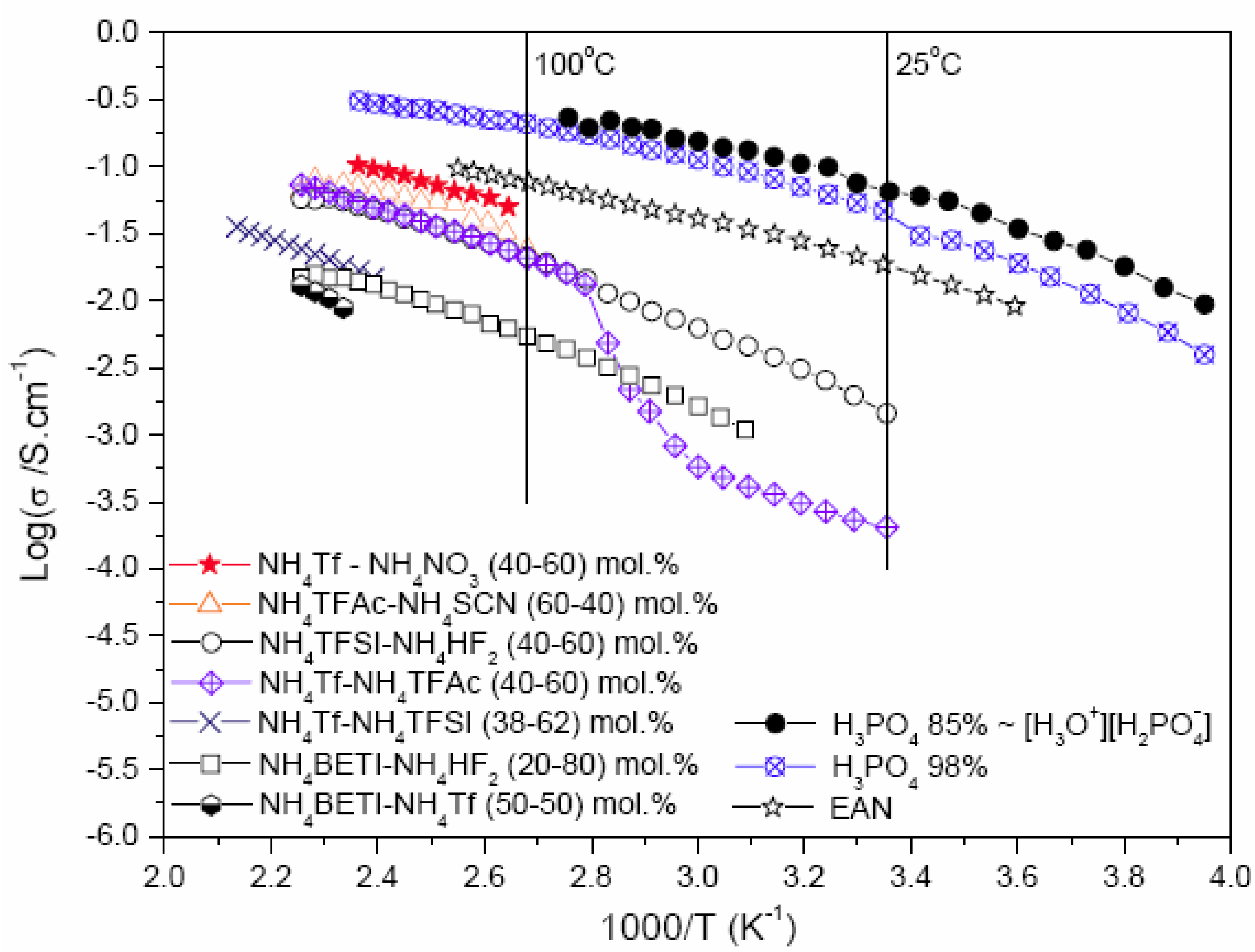
20% higher performance with EAN than H_3PO_4



NEW Stable but lower performance ELECTROLYTE NH_4TF-NH_4 TFAc

Total polarization curve (no IR correction) for fuel cell with NH4Tf-NH4TFAc electrolyte compared to EAN and 85% H3PO4 measured in the same cell geometry. ETEK Pt catalyzed porous gas-fed electrodes. Pt-loading = 0.5 mg/cm2. Anode feed: H2. Cathode feed: O2.

Arrhenius plot of conductivity of ammonium salt mixtures

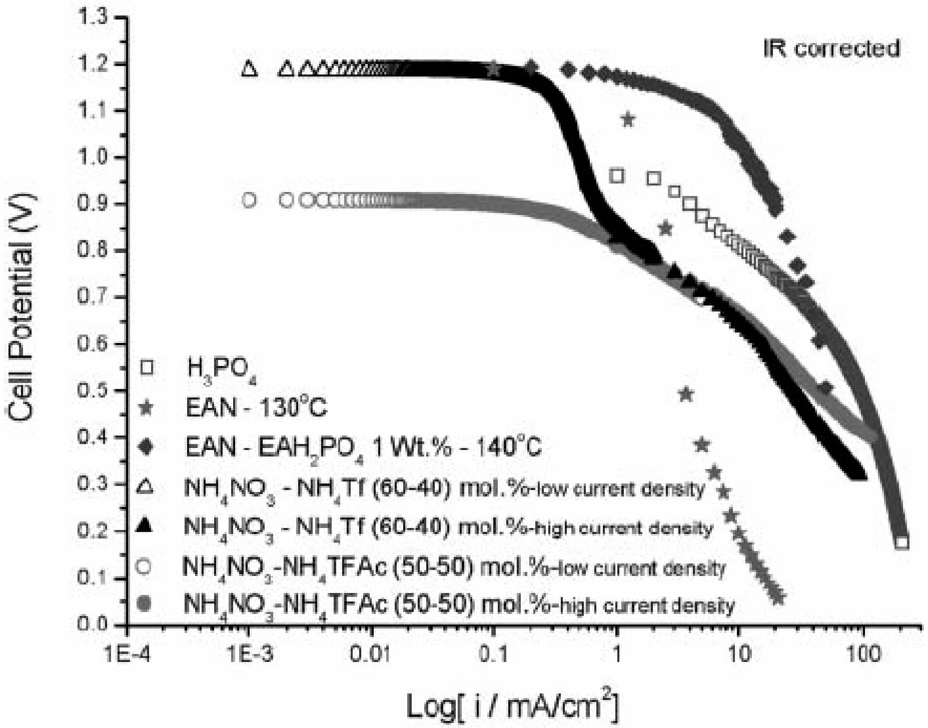


Fuel Cells with New Stable PIL Electrolytes

DOE Hydrogen Program

binary ammonium salt mixtures:

- trifluoromethansefulonate (triflate, Tf) + trifluoroacetate (TFAc),
- trifluoroacetate + nitrate,
- triflate + nitrate.



A Tafel plot, cell potential (V) versus log of current density, for a series of inorganic binary ammonium salts, an organic ammonium salt, and phosphoric acid. The plateau at low current density indicates barrier free electroreduction.

Data from: Binary inorganic salt mixtures as high conductivity liquid electrolytes for > 100°C fuel cells, Jean-Philippe Belieres, Don Gervasio and C. Austen Angell, *Chem. Commun.*, 2006, 4799.

Summary of recent results

* New stable electrolyte found

* Tafel plots of the fuel cell data for ionic liquids indicate barrier free O_2 reduction at low currents probably due to the low water activity of the salts.

* The inorganic ammonium salts exhibit more polarization at intermediate loads, probably due to adsorption but remain stable through higher cell loads.

* Beyond the potential enhancement performance of an ionic protic liquid, a non-hydrous electrolyte allows for a greater array of catalysts and electrodes to be considered for use in a proton exchange fuel cell.

What's next?

• Further tailor mixtures with non – adsorbing components for higher performance

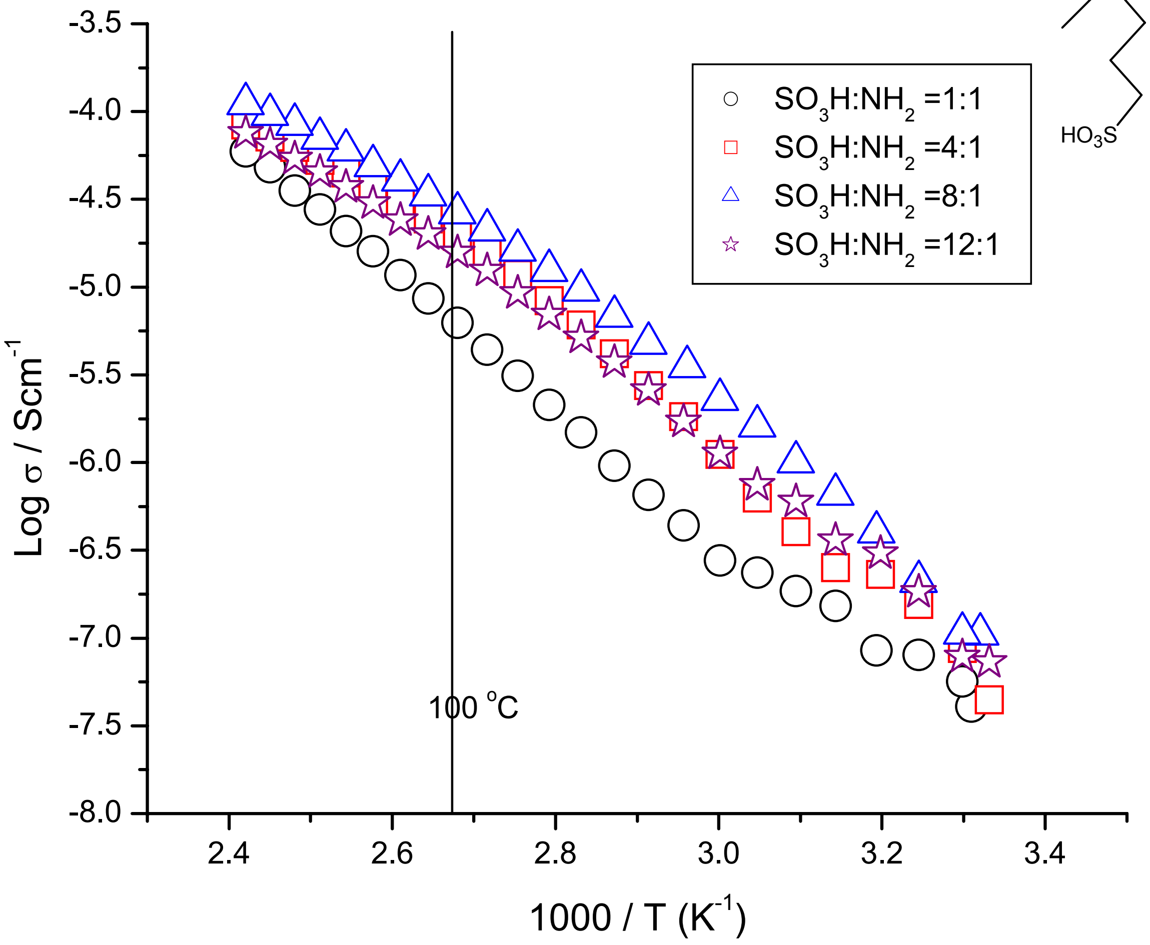
• Continue fuel cell test of membranes loaded with salt mixtures

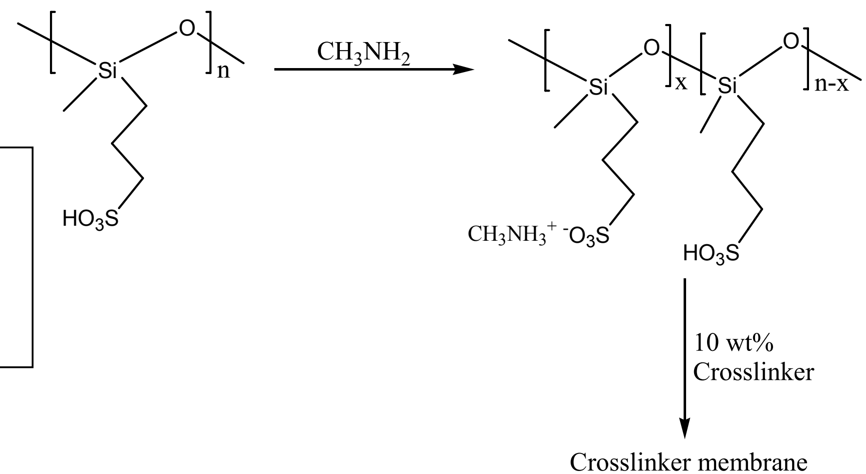
• Make polymeric forms of salt mixtures

Non-Leachable Polysiloxane Protic Ionic Membrane (PIM)

DOE Hydrogen Program

Ionic Conductivities of dry polysiloxane with pendant propyl sulfonic acid groups neutralized with methylamine



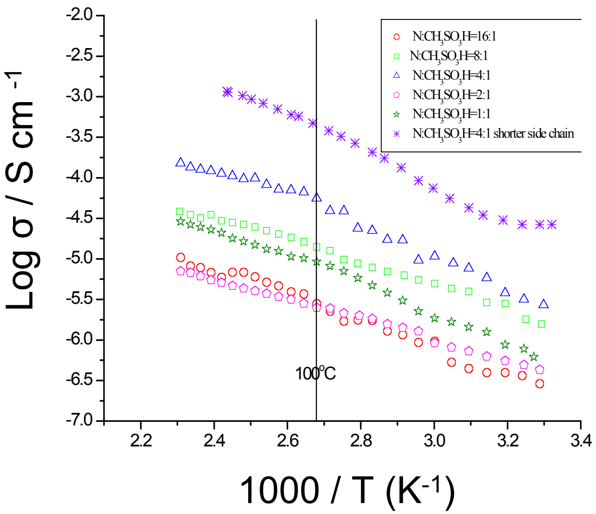


- **All samples are self standing films**
- **Maximum conductivity of $10^{-4.28}$ S cm^{-1} at 100°C is reached when 1 in every 8 acids is neutralized**

Polysiloxane Protic Ionic Membrane (PIM)

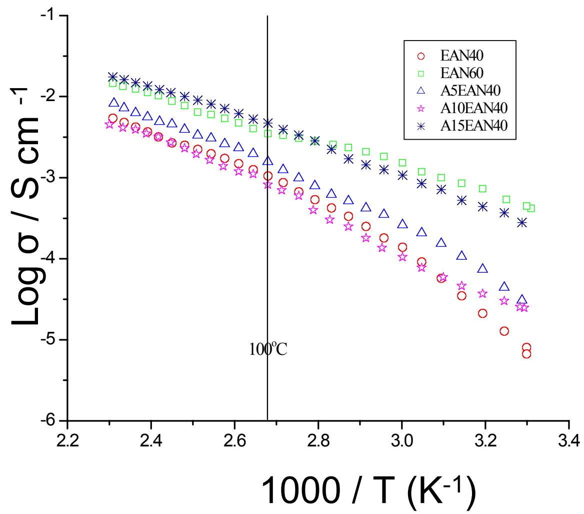
DOE Hydrogen Program

Non-leachable



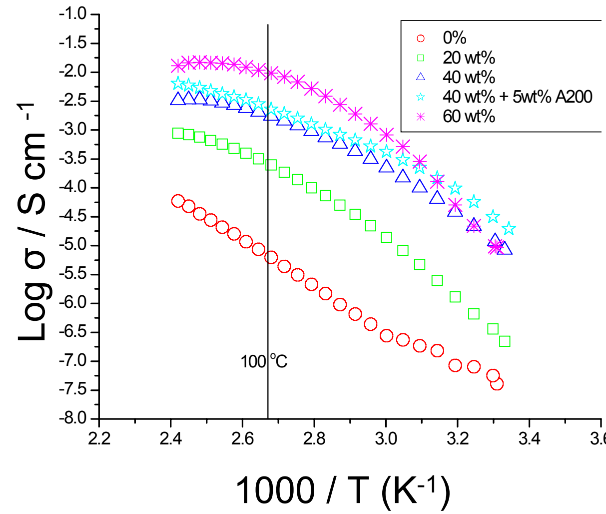
Conductivities of “dry” ionic siloxane polymers based on the neutralization of pendant propylamine groups to varying extents. Maximum conductivity is reached when 1 in every 4 amines (25%) is neutralized. When shorter sidechains are used the conductivity increases by almost one order of magnitude, *an unexpected effect which must be further investigated*

Leachable



Conductivity of crosslinked siloxane polymers with pendant propylamine groups neutralized with methane sulfonic acid and then swollen with EAN ($CH_3CH_2NO_3$) Conductivity at 60 wt% swell and 100ºC is almost 10^{-2} Scm^{-1}.

Leachable

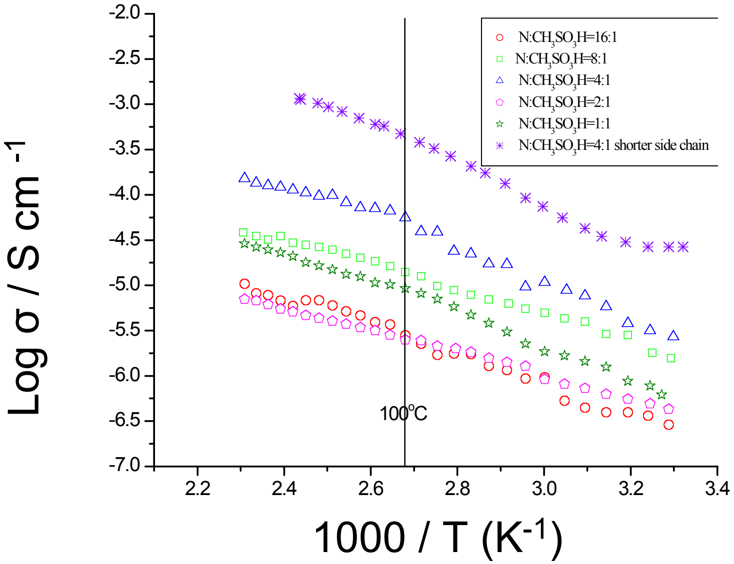


Conductivity of crosslinked siloxane polymer with pendant (propane) sulfonic acid, neutralized with methyl amine and then swollen with NH_4NO_3-$NH_4CF_3SO_3$ eutectic mixture. Conductivity at 60 wt% swell and 100ºC exceeds 10^{-2} Scm^{-1}.

Polysiloxane Protic Ionic Membrane (PIM)

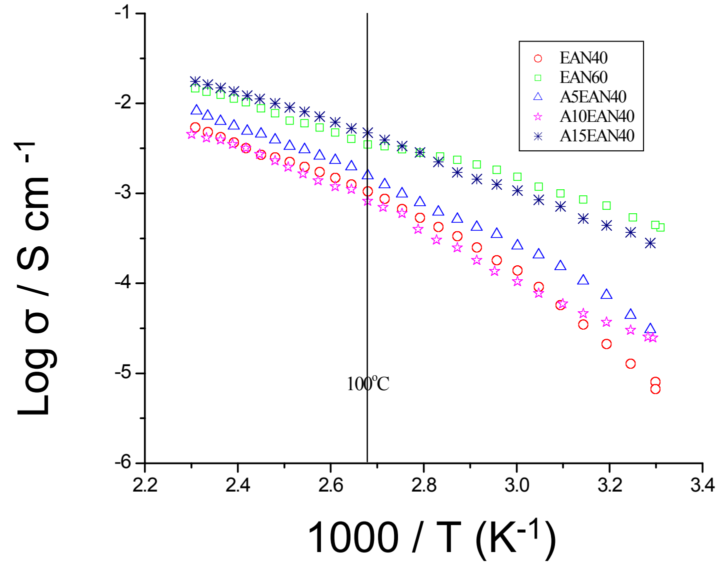
DOE Hydrogen Program

Non-leachable



Arrhenius plot of conductivity of crosslinked poly (N-2-aminoethyl)-3-aminopropyl-methyl siloxane) siloxane polymers of high mechanical strength containing variable proportions of methanesulfonic acid (from 1:1 to 16:1) as indicated in the legend. **Shortening the side chain leads to marked increases in conductivity**. We examined five different acids and found methane sulfonic acid gave the highest conductivity of the low cost acids.

Leachable



Ionic conductivity of crosslinked poly(N-2 aminoethyl)-3-aminopropyl-methylsiloxane) doped with methanesulfonic acid at the ratio $N:CH_3SO_3H$ =4:1 and containing different percentages of EAN and fumed silica A200. EAN40 stands for crosslinked film containing **40wt% EAN**; etc. A5EAN40 stands for crosslinked film containing 40wt% EAN and 5wt% A200 silica spheres; Likewise for A10 and A15.

Magnetic field gradient NMR

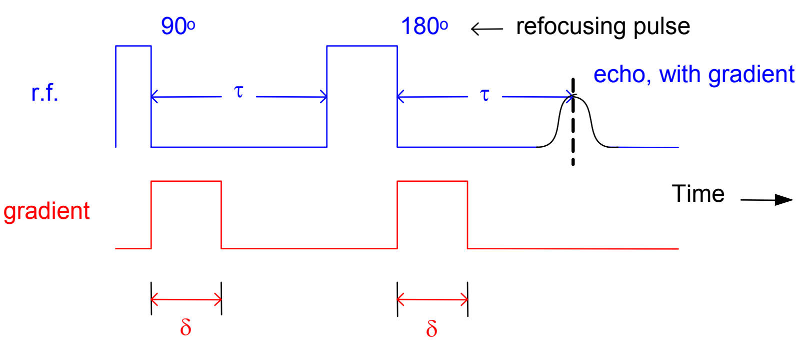
DOE Hydrogen Program

Diffusivity of Atoms and Molecules

Time dependence of the intensity I of the NMR signal of nuclei of ions diffusing at rate D, after a pulsed magnetic field gradient g is turned on at time 0, is:

$$I = I_0 e^{(-KDg^2t^3)}$$ (K is a known constant)

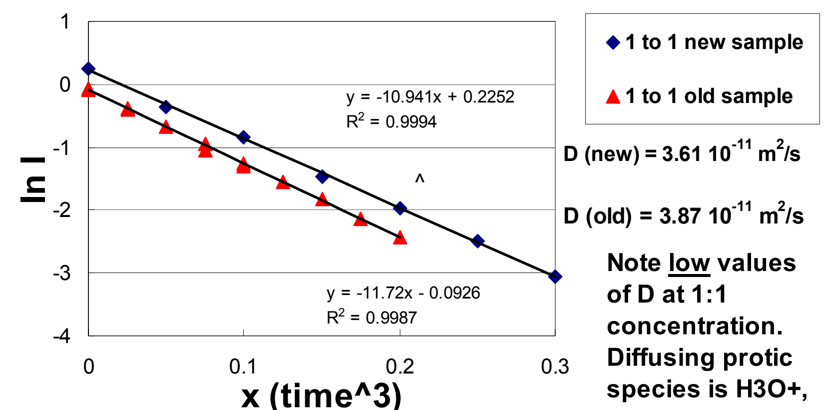
Measure attenuation $I(t)/I_0$ to determine D in a calibrated, pulsed gradient g, using the NMR spin echo sequence with gradient pulses: (Stejskal and Tanner, 1965)



Plot $\ln(I/I_0)$ vs. g^2 to obtain D.

Example:

TFMSA 1:1 diffusion at 299.5K, fresh and stored samples



Note low values of D at 1:1 concentration. Diffusing protic species is H3O+, not H+ ?

Water in Nafion® fuel cells recently visualized by MRI (R. Wasylishen et al., Chem. Phys. Chem. 2006,7,67-75)

Future Work

DOE Hydrogen Program

- Continue to make and characterize 2 types of PIL-concept based PEM:
  i. ionic liquid (IL) filled PEMs consisting of:
    ia. bi-phasic porous matrices filled with water immiscible ionic liquids immobilized by capillary forces and
    ib. 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.

- Echem NMR
  - Finish setup Gradient coils
  - 2 D NMR to investigate motions during proton conduction
  - Echem Hittorf to investigate distribution of species during proton conduction

- Echem FTIR of PILs to investigate:
  - Pt-oxide formation
  - Adsorption on Pt

High-Speed 1H MAS NMR to Investigate PEM Proton Conductivity

DOE Hydrogen Program

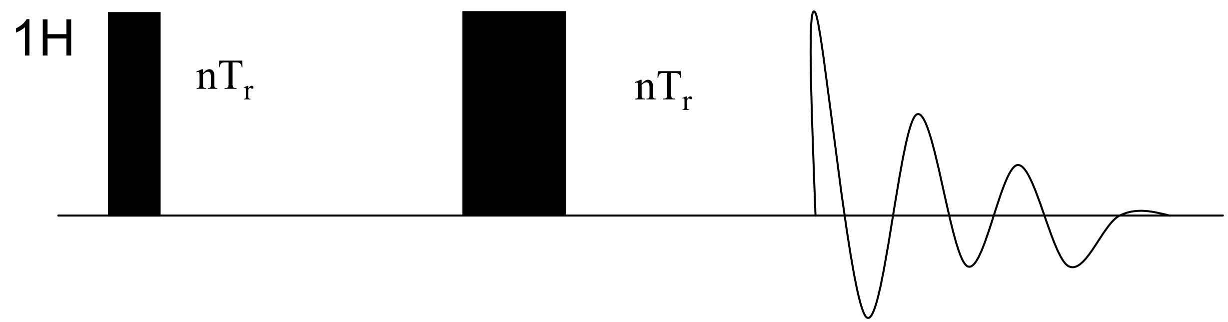
In progress

Solid-state MAS probes that exceed speeds of 35 kHz available to study PEM.

Coupling high-speed MAS with high-field NMR (800 MHz) yields high-resolution 1H NMR spectra in solids.

Combined with multiple pulse sequences will establish H+ structure and dynamics in PEM.

Spin-echo to Filter out Rigid Proton Signal in High-speed 1H MAS NMR



- **Complimentary to the DQ-filter is the conventional spin-echo pulse sequence**
- **This sequence can be used to filter out the rigid component of the NMR spectra**
- **The spin-echo technique will be implemented to investigate highly mobile ^1H species in PEM**
- **Measurements will be made as a function of temperature to extract the activation energy for proton hopping**

Summary

- Protic salt electrolytes are non aqueous proton conductors

- No bulk water means little or no Pt-OH on surface, expect:
  - Lower overpotential for oxygen reduction and higher cell efficiency possible with protic salt electrolytes
  - Lower corrosion and Pt particle growth

- Status of Protic Ionic Liquids (PILs)
  - High Conductivity and Fuel Cell Activity Found in some PILs
  - Stable PILs found
  - Need to combine 1 and 2
  - Need to fill support to make PIL loaded membrane and test in Fuel Cell

- Status of Proton conducting Ionic Membranes (PIMs)
  - Sulfonated polysiloxane with methyl ammine gives first PIM
    - Need to raise conductivity
    - Need to test in fuel cell