

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

D. Gervasio (PI)

C.A. Angell, R. Marzke, J. Yarger (co-PI)

Arizona State University;

W. Youngs (co-PI)

University of Akron

June 9, 2008

Project ID #FC 17

Overview

Timeline

- January 15, 2006
- January 14, 2011
 - go/no go end of year 3
- 60% completed

Budget

- Total project funding \$1,500K
 - DOE: 80%, Contractor: 20%
- Funding received in FY06
 - \$300,000
- Funding for FY07
 - \$300,000
- Funding for FY08
 - \$200,000/\$300,000

Barriers

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

Partners

- Arizona State University
- University of Akron
- Boeing

- DOE Technology Development Manager: Terry Payne
- DOE Project Officer: Reginald Tyler
- 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

Milestones

| Month/Year | Milestone or Go/No-Go Decision |
|------------|---|
| Jan-08 | Milestone: 2 kinds of high temperature proton-conducting protic salts membranes were made into MEAs and tested in fuel cells: (i) leachable protic ionic liquid filled membrane and (ii) membranes with non-leachable salt moieties covalently and electrostatically bound to the polymer. Determine conductivity of membrane at 0 to 25% RH and the full range of temperature (-40 to 120°C) and compare to target of 0.1 S/cm . Determine conductivity in absence of free solvents. |
| May-08 | Milestone: Complete initial round of MEA fabrication and testing with selected new polymers (1 done 3 more sent in progress) to provides external validation and information on the catalyst behavior under low RH conditions. |
| Nov-08 | Milestone: Design targets defined and measured for conductivity (0.05 to 0.2S/cm) and gas permeability (< 2mA/cm ² measured with a catalyst coated membrane for both hydrogen and oxygen crossover) for high-temperature, low RH operation without external humidification. |
| Nov-08 | Milestone: Design targets defined and measured for conductivity (0.05 to 0.2S/cm) and gas permeability (< 2mA/cm ² measured with a catalyst coated membrane for both hydrogen and oxygen crossover) for high-temperature, low RH operation without external humidification. |

Approach

SYNTHESIS OF “DRY” PROTON ELECTROLYTE MEMBRANES (PEMs)

PEMs are being made based on “solvent free” *protic ionic liquid (pIL) concepts*.

pILs can be *used to model membranes* (stability, conductivity) and to *act as a plasticizers* in membranes.

Acid and base moieties & polymers are *varied* to optimize properties *in 2 kinds of PEMs*.

1. pIL filled membranes (pIL act as leachable plasticizers)
2. Membranes with covalently and electrostatically non-leachable immobilized ions are being made.

CHARACTERIZATION

Proton conductivity characterized by electrochemical impedance spectroscopy (EIS) from -20 to 120°C

Thermal & oxidative stability of these electrolytes are measured by Thermal Gravimetry (TGA) from -20 to 120°C

Electrochemical stability and chemical reduction polarization are surveyed by cyclic voltammetry on Pt

Fuel cell stability and performance is estimated by short term steady state I/V curves

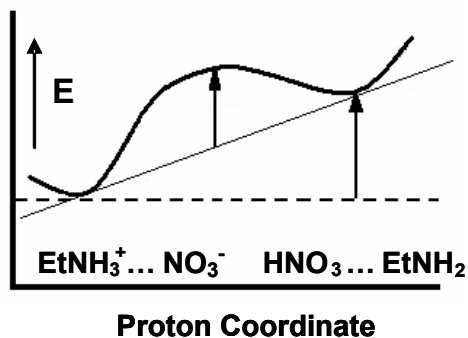
The mechanism of transport of protons, anions, and molecules investigated three NMR methods:

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.

PROTIC IONIC LIQUID (pIL) CONCEPTS

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

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



Energy Diagram for the EAN (ethyl ammonium nitrate) pIL with:

- proton transferred (Left)
- not transferred (Right),

| | Occupied | Vacant | pK _a | E (eV) |
|----------------------|-----------------------------------|--|-----------------|--------|
| Acid Electrolytes | HSbF ₆ | SbF ₆ ⁻ | | |
| | HTf | Tf ⁻ | -14 | 0.83 |
| | HSO ₃ F | SO ₃ F ⁻ | | |
| | HClO ₄ | ClO ₄ ⁻ | -10 | |
| | H ₂ SO ₄ | HSO ₄ ⁻ | | |
| | HPO ₂ F ₂ | PO ₂ F ₂ ⁻ | | |
| | HNO ₃ | NO ₃ ⁻ | | |
| | CH ₃ SO ₃ H | CH ₃ SO ₃ ⁻ | | |
| | CF ₃ COOH | CF ₃ COO ⁻ | | |
| | H ₃ O ⁺ | H ₂ O | 0 | 0 |
| Neutral Electrolytes | HF | F ⁻ | | |
| | HIm ⁺ | Im | | |
| | EtNH ₃ ⁺ | EtNH ₂ | | |
| Basic Electrolytes | H ₂ O | OH ⁻ | 14 | -0.83 |
| | NH ₃ | NH ₂ ⁻ | | |
| | OH ⁻ | O ₂ ⁻ | 28 | |

EAN
Δp_k = 14

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

Plan & Progress

60% complete

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

33% complete

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

50% 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

75% complete

- ☐ **Task 5: Iterate Synthesis**
 - to optimize stability, conductivity

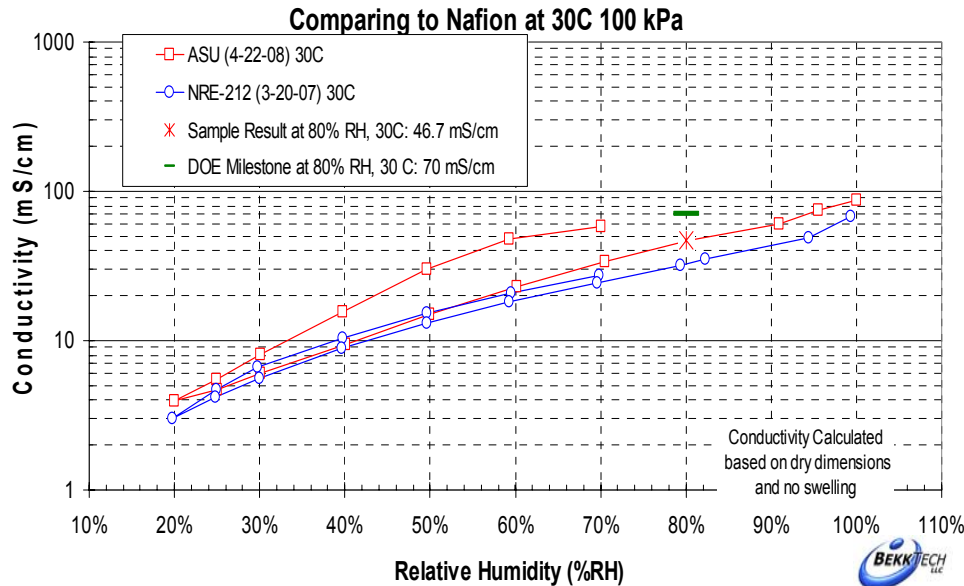
50% complete

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

50% complete

- ☐ **Task 6: Membrane Demonstration**
 - ASU sent 4 membranes to CFU

Technical Accomplishments: Proton Conductivity

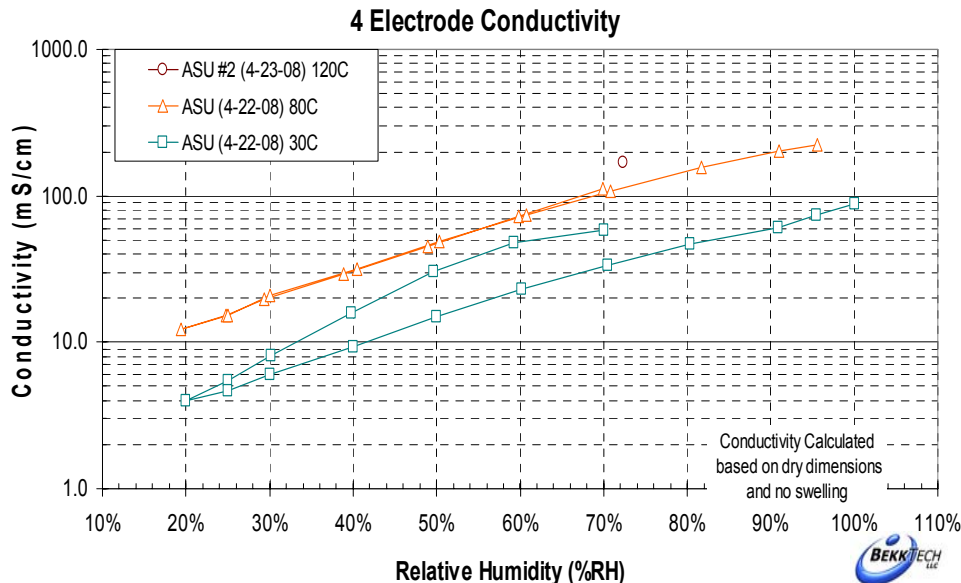


ASU membrane characterized by BEKKTECH and graphically reported here is:

Crosslinked hydroxyethyl cellulose (HEC) with 60wt% ethylammonium nitrate (EAN).

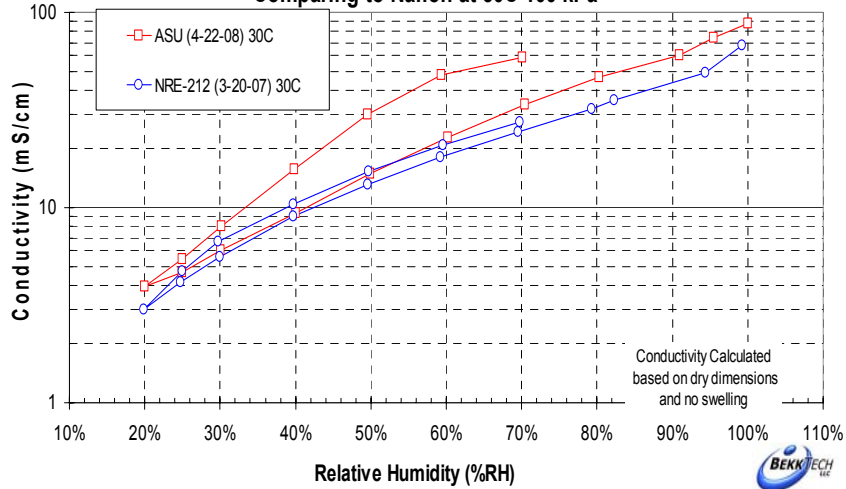
There are three more membranes soon to be characterized by BEKKTECH:

- I. Crosslinked hydroxyethyl cellulose (HEC) containing 40wt% EAN,
- II. HEC containing 60wt% mixture of NH_4NO_3 and $\text{NH}_4\text{CF}_3\text{SO}_3$ (6:4),
- III. and crosslinked polysiloxane membrane containing 40wt% EAN

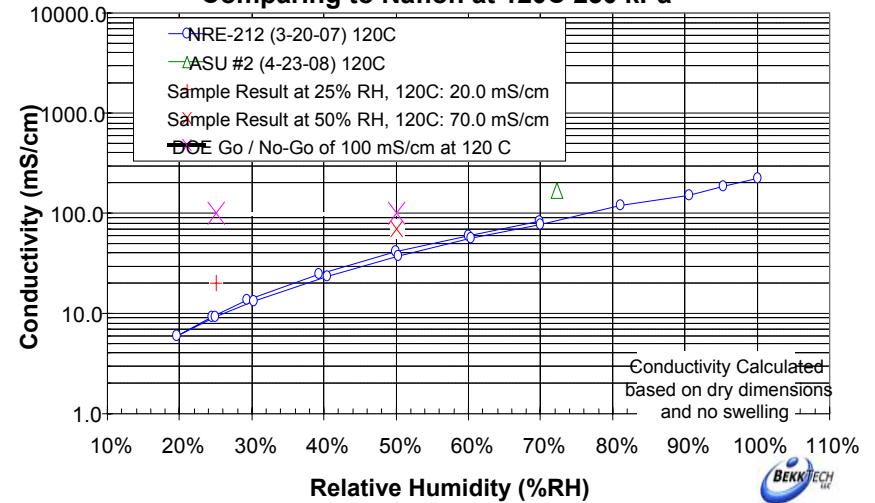


Technical Accomplishments: Proton Conductivity

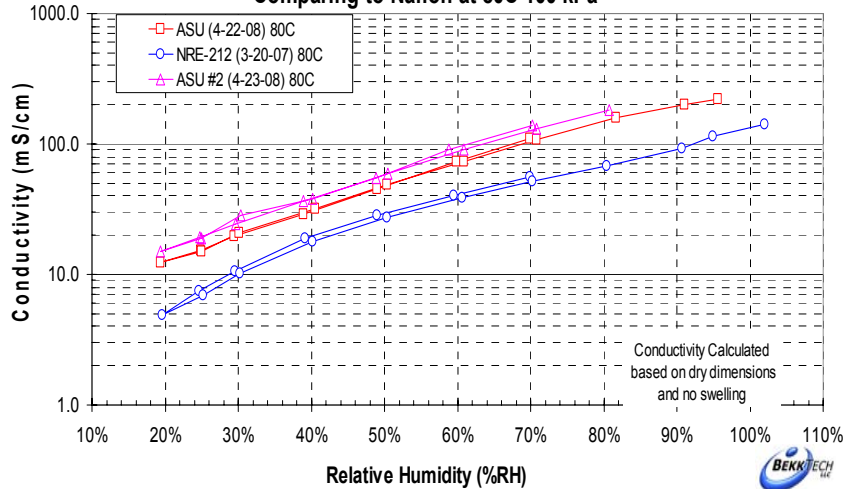
Comparing to Nafion at 30C 100 kPa



Comparing to Nafion at 120C 230 kPa



Comparing to Nafion at 80C 100 kPa



Proton conductivity determined by BEKKTECH for ASU's Protic Salt Membrane

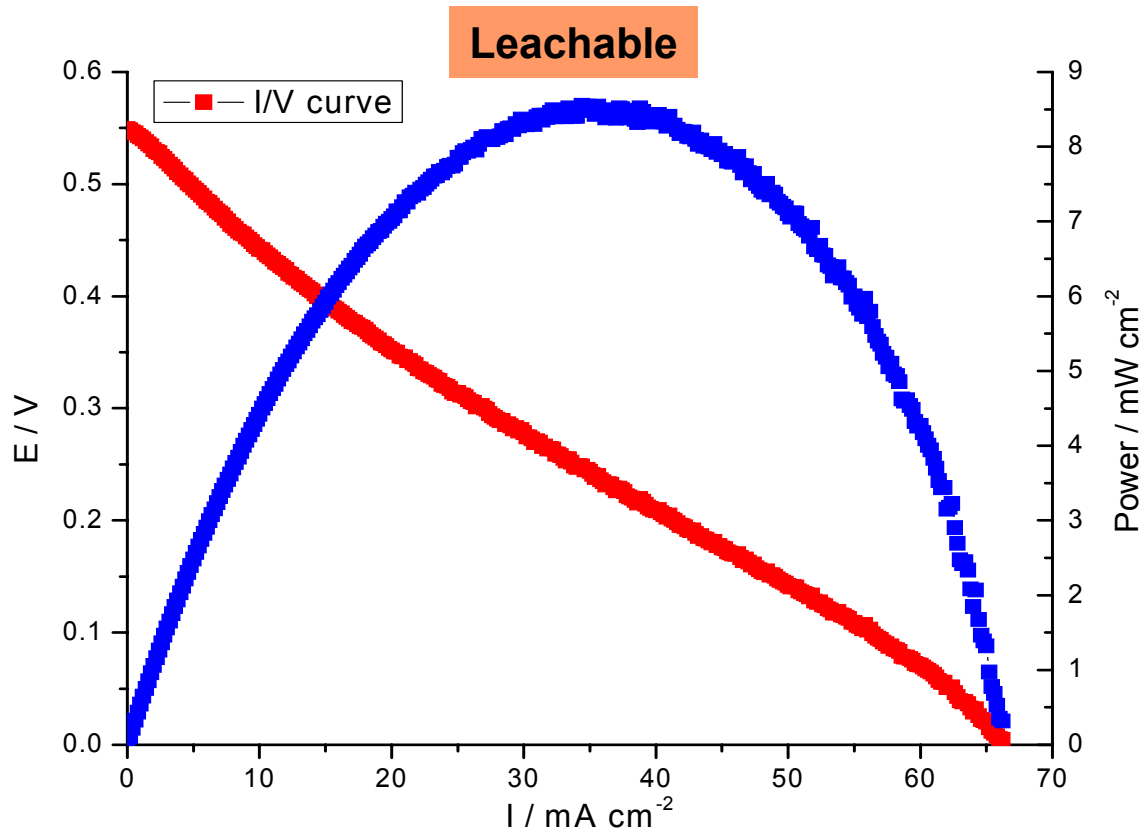
Crosslinked hydroxy ethyl cellulose (HEC) with 60wt% ethylammonium nitrate (EAN)

- is similar to the limited conductivity data obtained by ASU
- is representative of many of the Protic Salt Membranes with "sorbed" plasticizer and
- is comparable to the DoE target.

Technical Accomplishments: Fuel Cell Performance

Need to test in fuel cell

Best Protic Salt Membrane to date: composite polymer with **60 wt%** Eutectic plasticizer

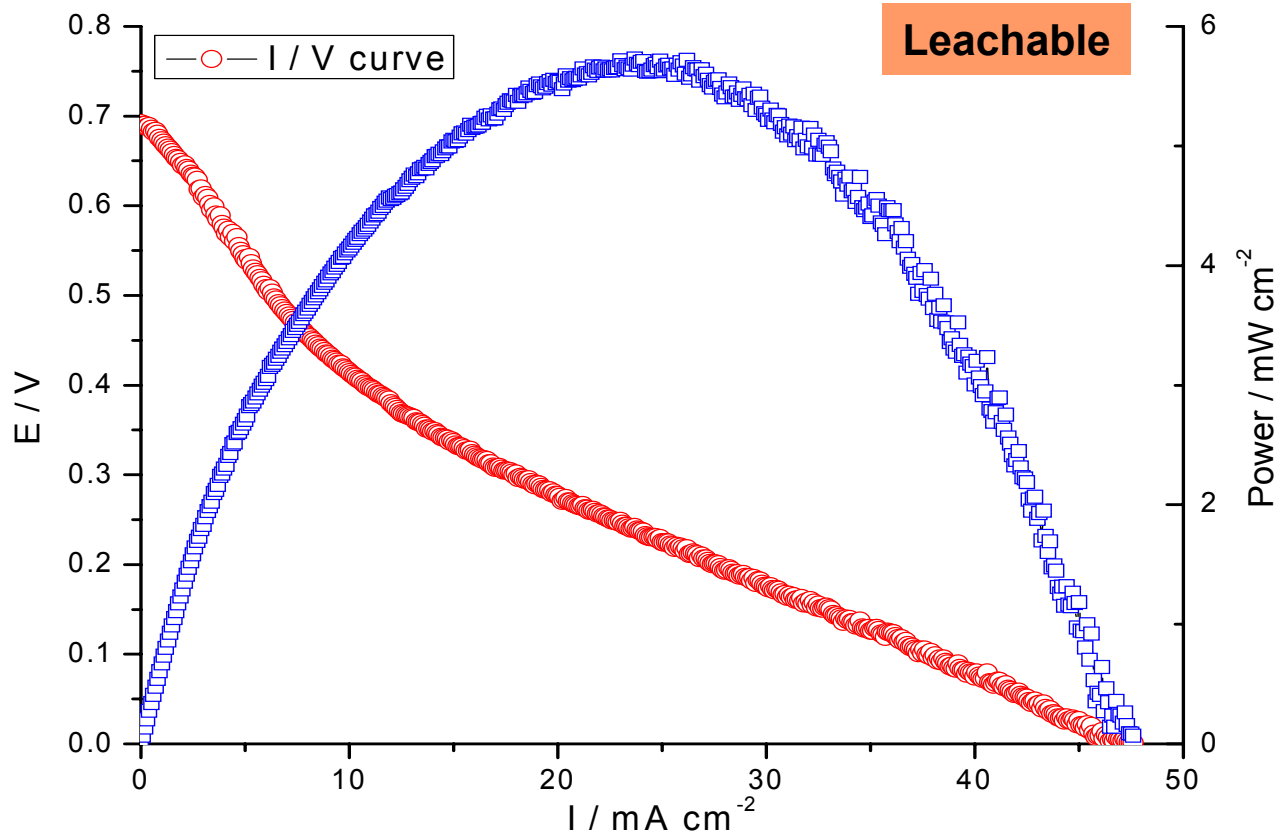


Polarization Curve for Hydrogen/ Oxygen Fuel Cell with a crosslinked hydroxyethyl cellulose membrane containing 20wt% polyammonium styrenesulfonic acid and 60wt% ionic mixture of 6 NH_4NO_3 and 4 $\text{NH}_4\text{CF}_3\text{SO}_3$.

$T = 125^\circ\text{C}$; $P^{\text{total}} = 1 \text{ atm}$. $P(\text{H}_2\text{O}) = 24 \text{ torr}$ in H_2 and O_2 feeds.

Technical Accomplishments: Fuel Cell Performance

Another Protic Salt Membrane with **60wt%** of Eutectic Salt Plasticizer



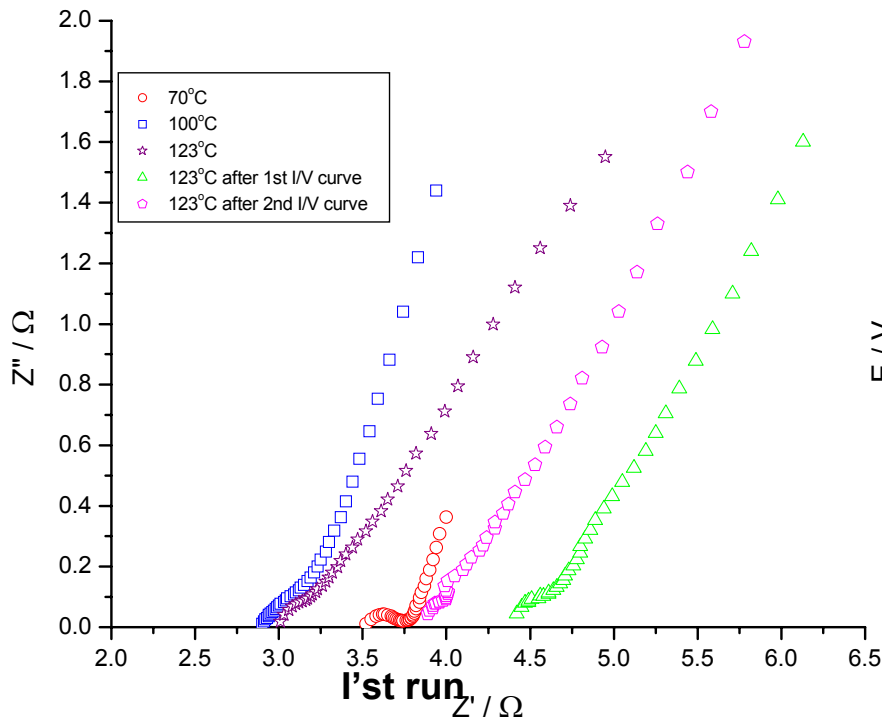
Polarization Curve for Hydrogen/Oxygen Fuel Cell with crosslinked hydroxyethyl cellulose membrane containing 60wt% ionic mixture of 6 moles NH_4NO_3 and 4 moles $\text{NH}_4\text{CF}_3\text{SO}_3$.

Cell was tested at 138°C with $P(\text{H}_2\text{O}) = 24$ torr in H_2 and O_2 feeds.

Technical Accomplishments

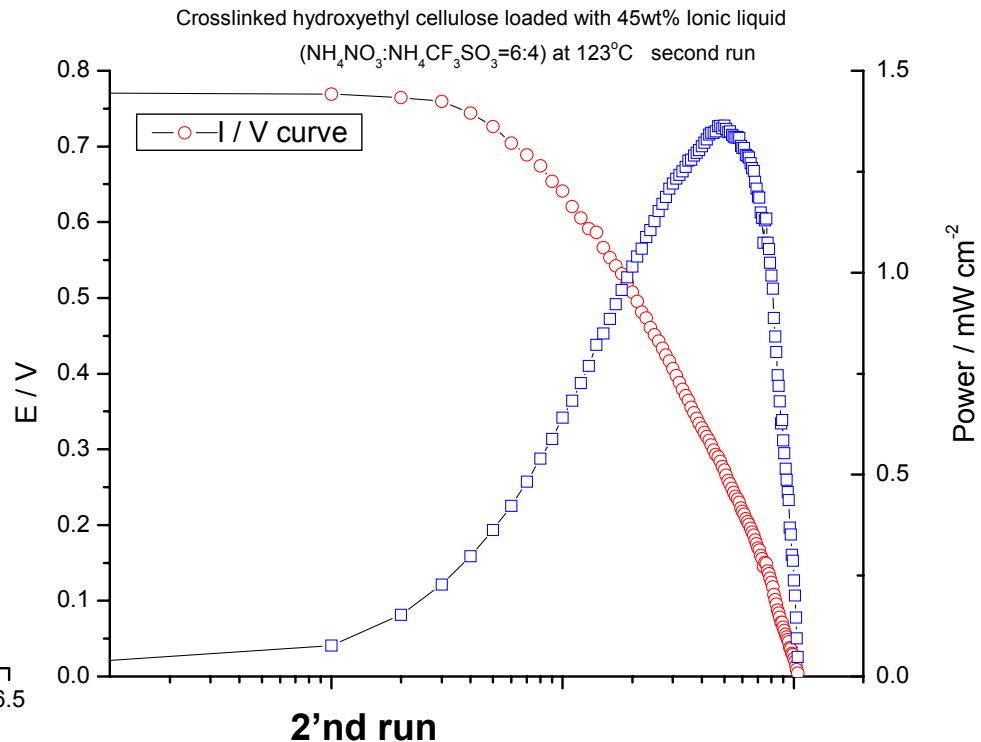
Protic Salt Membrane with **45wt%** of Eutectic Salt Plasticizer

EIS for H⁺ conductivity



Leachable

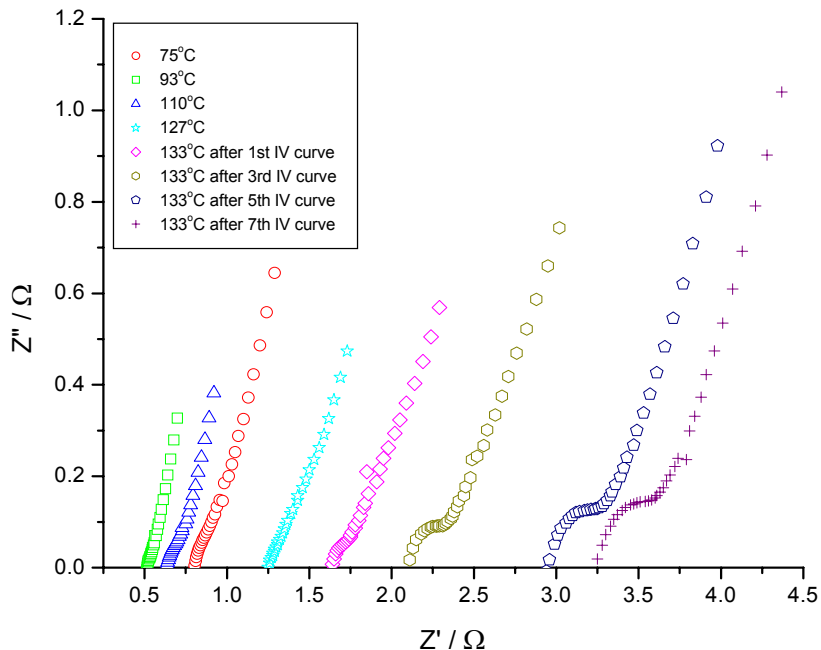
Fuel Cell I/V Curve



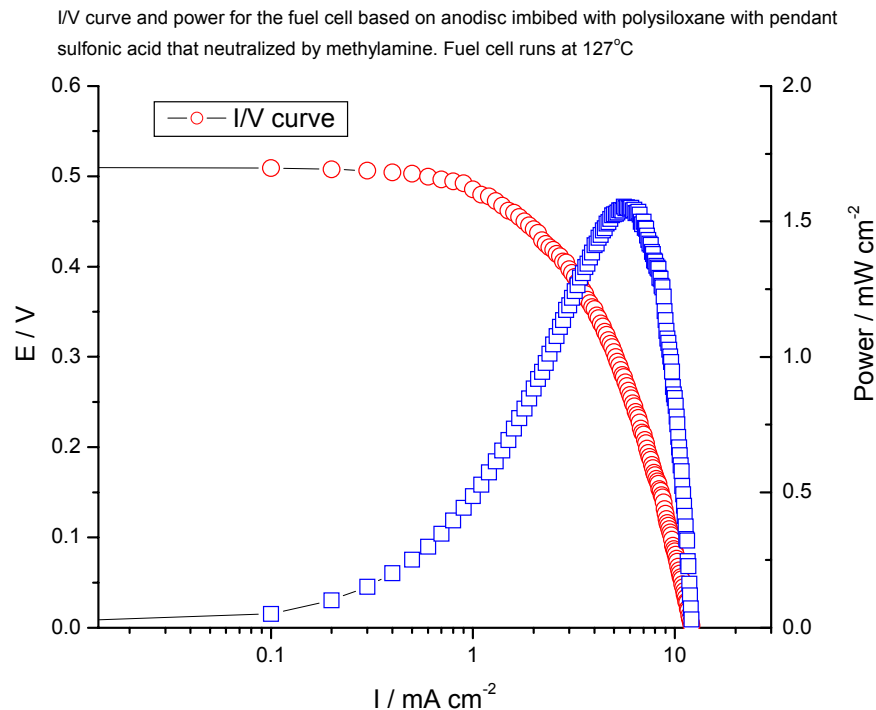
Impedance and Fuel cell Polarization with a crosslinked hydroxycellulose membrane filled with 45wt% of ionic liquid consisting of NH₄NO₃:NH₄CF₃SO₃ at 123°C. ETEK ELAT electrodes with 0.5 mg-Pt/cm² and ambient pressure. NO HYDRATION.

Technical Accomplishments: non-leachable PEM 1

EIS for H⁺ conductivity



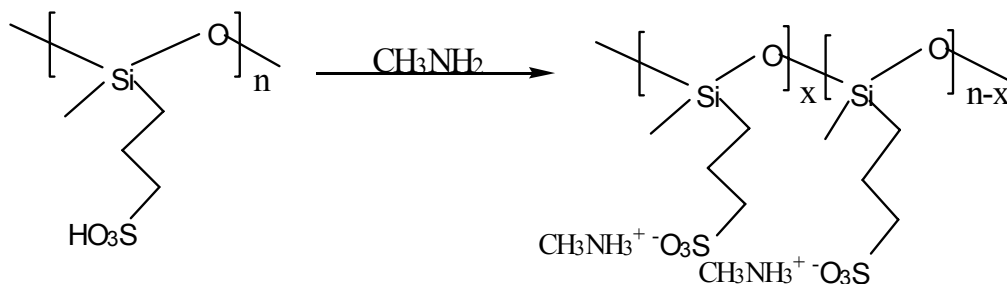
Fuel Cell I/V Curve



Impedance and polarization curves for “dry” non leachable membranes consisting of an Anodisc (Whatman alumina membrane, $t = 60$ micron, pore diameter = 100 micron) filled with solid polysiloxane with pendant sulfonic acid that fully neutralized with methylamine

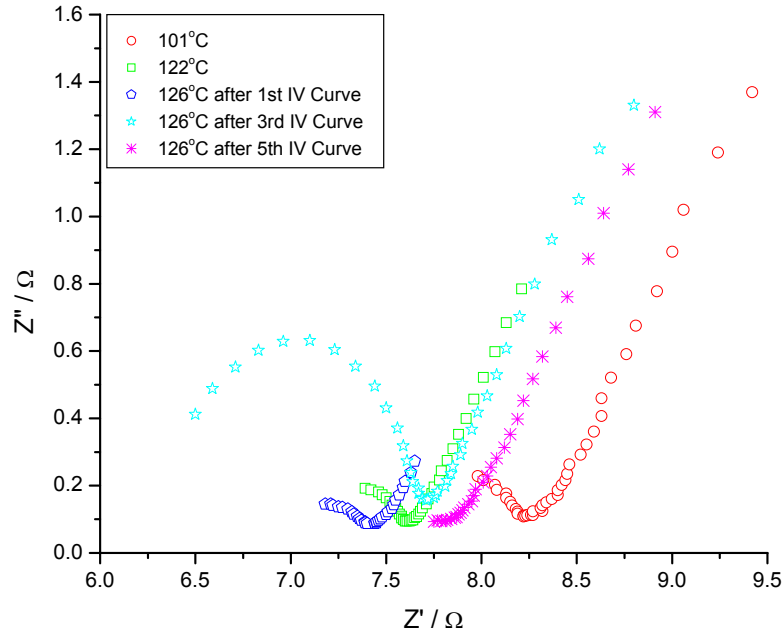
Non-leachable

Pendant sulfonic acid polymer fully neutralized with methyl amine

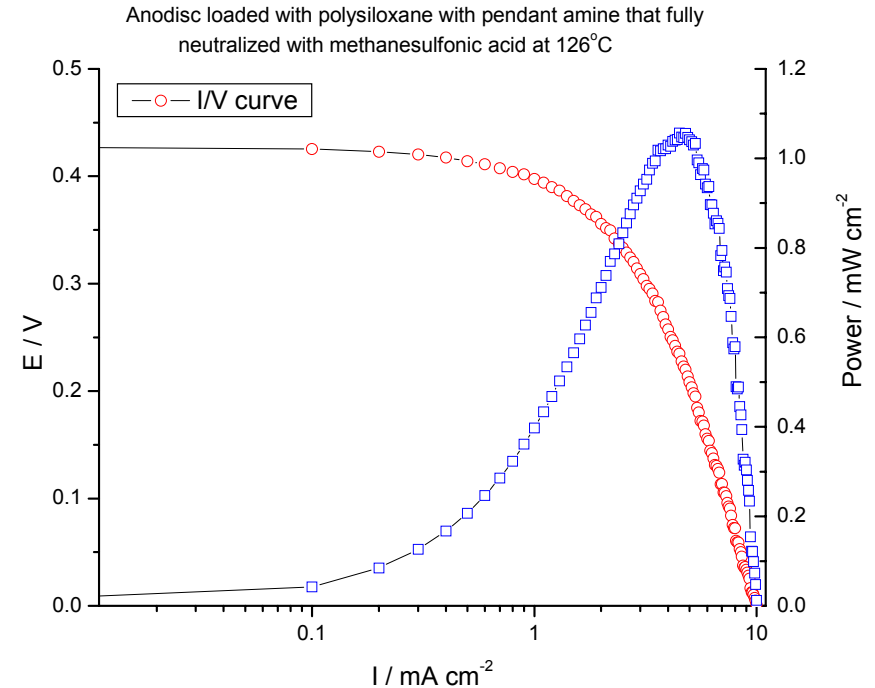


Technical Accomplishments: Non-leachable PEM 2

EIS for H⁺ conductivity



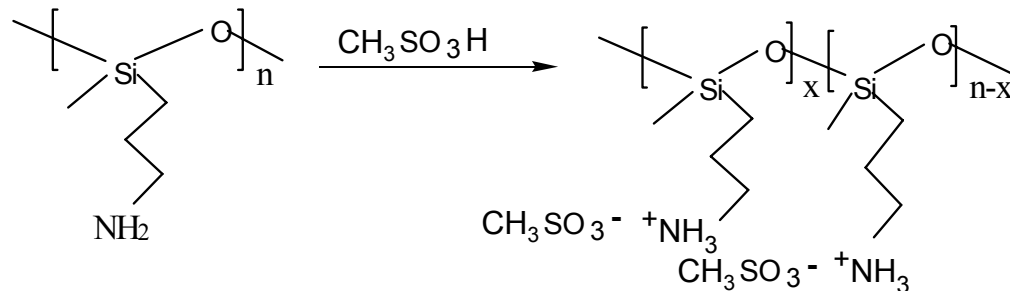
H₂ / O₂ Fuel Cell I/V Curve



Impedance and polarization curves for “dry” non leachable membranes consisting of an Anodisc (Whatman alumina membrane, $t = 60$ micron, pore diameter = 100 micron) filled with solid polysiloxane with pendant amine fully neutralized with methylsulfonic acid.

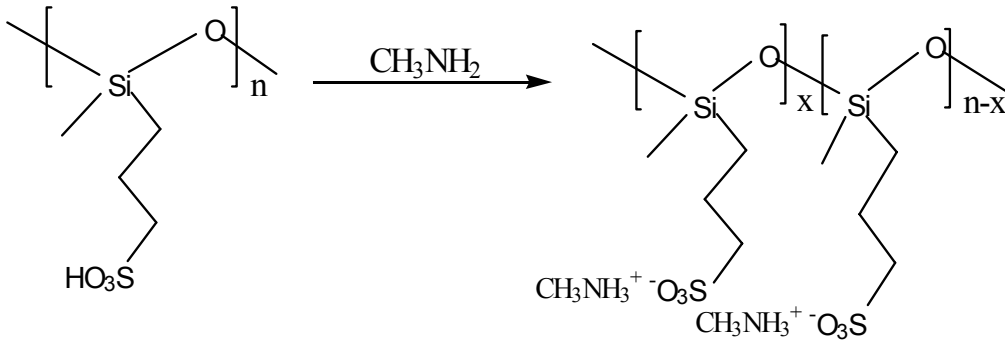
Non-leachable

Pendant propyl amine polymer fully neutralized with methyl sulfonic acid

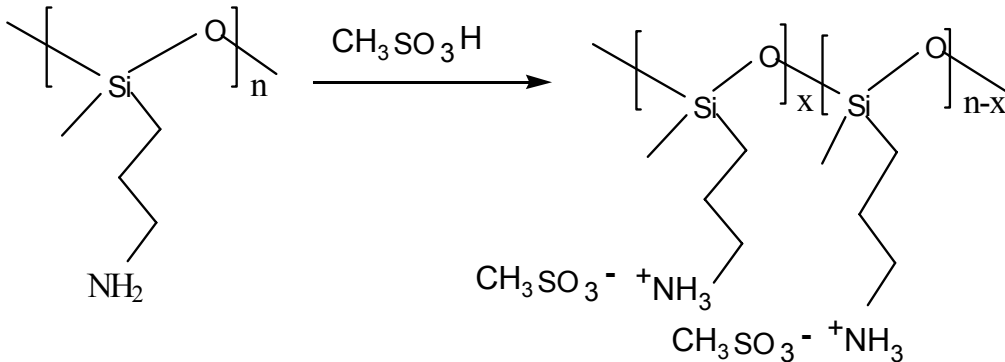


Technical Accomplishments: non-leachable PEMs

Two non-leachable protic salt polymer membranes



1. Pendant sulfonic acid polymer fully neutralized with methyl amine



2. Pendant propyl amine polymer fully neutralized with methyl sulfonic acid

Critique of non-leachable PEM

Pro: These data do illustrate the concept of using a *protic-salt membrane* as a “dry” proton-conductor and as a fuel cell membrane.

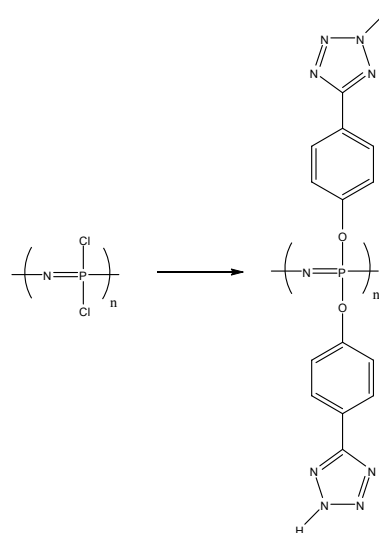
Con: The data indicate the membrane has limited stability (soft and water soluble) resulting in low performance (low open circuit voltage OCV, 0.45V, and low power, 2mW/cm²) in a fuel cell probably due to reactant crossover or/and possibly poisoning of Pt from decomposition of organics in this PEM.

What's next?

Technical Accomplishments: Poly-phenoxy-phosphazenes

1. With azole directly bound to phenoxy ring.

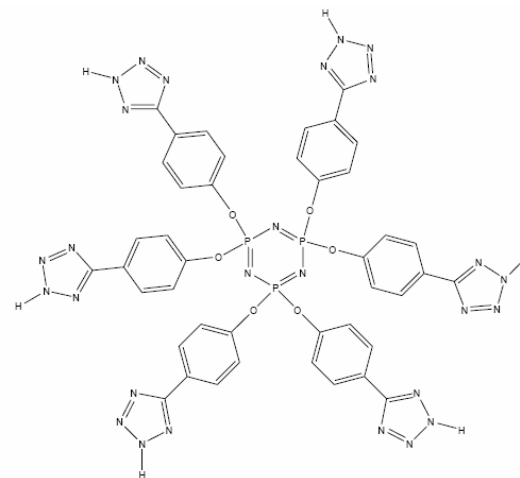
- i. hexakis(4-cyanophenoxy)cyclotriphosphazene
- ii. hexakis(4-tetrazolylphenoxy)cyclotriphosphazene
- iii. hexakis[4-(1,2,4-triazol-1-yl)phenoxy]cyclotriphosphazene
- iv. hexakis[4-(imidazol-1-yl)phenoxy]cyclotriphosphazene
- v. poly[bis(4-cyanophenoxy)phosphazene]
- vi. poly[bis(4-tetrazolylphenoxy)phosphazene]
- vii. poly[bis(4-(1,2,4-triazol-1-yl)phenoxy)phosphazene]
- viii. poly[bis(4-(imidazol-1-yl)phenoxy)phosphazene]



1.vi.

2. With methylene units between the azole and the phenoxy ring.

- i. hexakis(4-(1H-imidazol-1-ylmethyl)phenoxy)cyclotriphosphazene
- ii. hexakis(4-(1H-1,2,4-triazol-1-ylmethyl)phenoxy)cyclotriphosphazene 4-(1H-1,2,4-triazol-1-ylmethyl)phenol
- iii. hexakis(4-(1H-5-methyltetrazol-1-ylmethyl)phenoxy)cyclotriphosphazene 4-(1H-5-methyltetrazol-1-ylmethyl)phenol
- iv. [N3P3(p-O-C6H4-CH2C3N2Cl2)6]
- v. [N3P3(p-O-C6H4-CH2OH)6]
- vi. [N3P3(p-O-C6H4-CHO)6]
- vii. [N3P3(p-O-C6H4-CH2OH)6]
- viii. 4-(1H-1,2,4-Triazol-1-ylmethyl)phenol
- ix. [N3P3(p-O-C6H4-CH2Br)6]

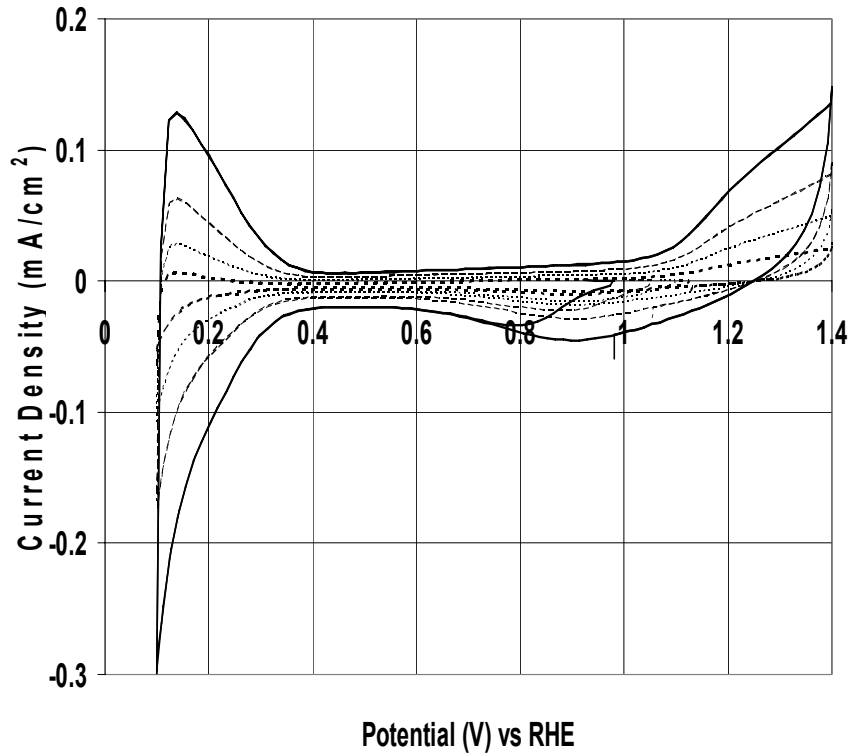


1.ii.

Syntheses of substituted poly phenoxy phosphazene have been developed to give low equivalent weight frameworks with a variety (imidazole, triazole and tetrazole) of pendant bases with a wide range of pK suitable for reacting with a variety of acids for optimizing proton conductivity of salt membranes.

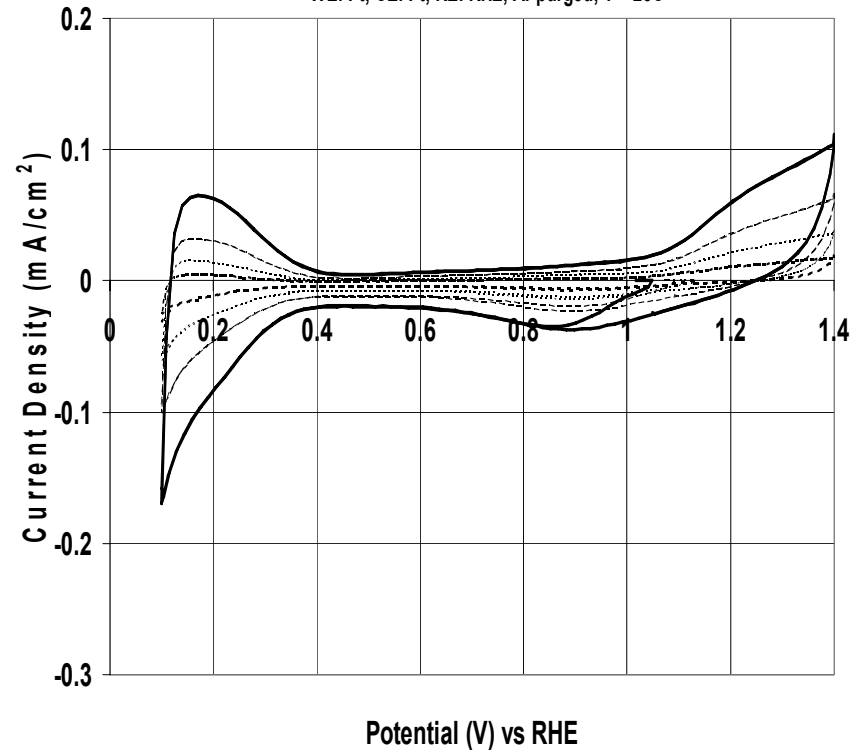
Technical Accomplishments: Pt voltammetry under Ar, Stability Test

1:1 Triflic acid:water (2mL);
WE: Pt; CE: Pt; RE: RHE; Ar purged; T = 25C



— 200mV/sec - - - 100mV/sec ····· 50mV/sec ····· 20mV/sec

1:1 Triflic acid:water (2mL) + triazolyl phenoxy trimer (1.2mg);
WE: Pt; CE: Pt; RE: RHE; Ar purged; T = 25C



— 200mV/sec - - - 100mV/sec ····· 50mV/sec ····· 20mV/sec

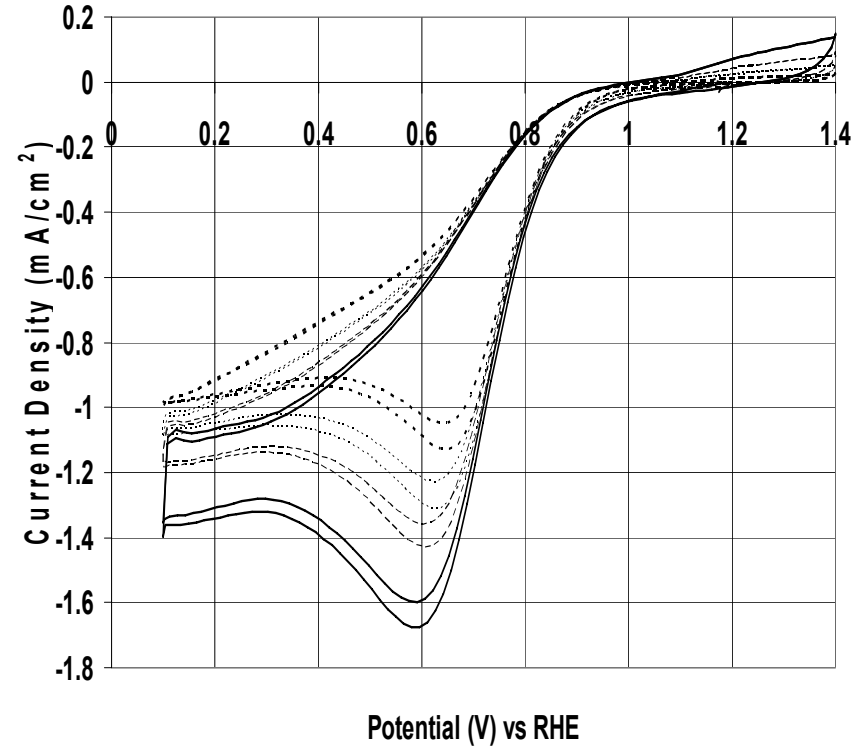
Observations: Cyclic Phosphazene 1.ii. adsorbs but does not decompose.

Conclusion: Phenoxyphosphazene is suitable as a building block for a fuel cell polymer electrolyte membrane (PEM).

Technical Accomplishments: Pt voltammetry under O₂, Activity Test

1:1 Triflic acid:water (2mL);

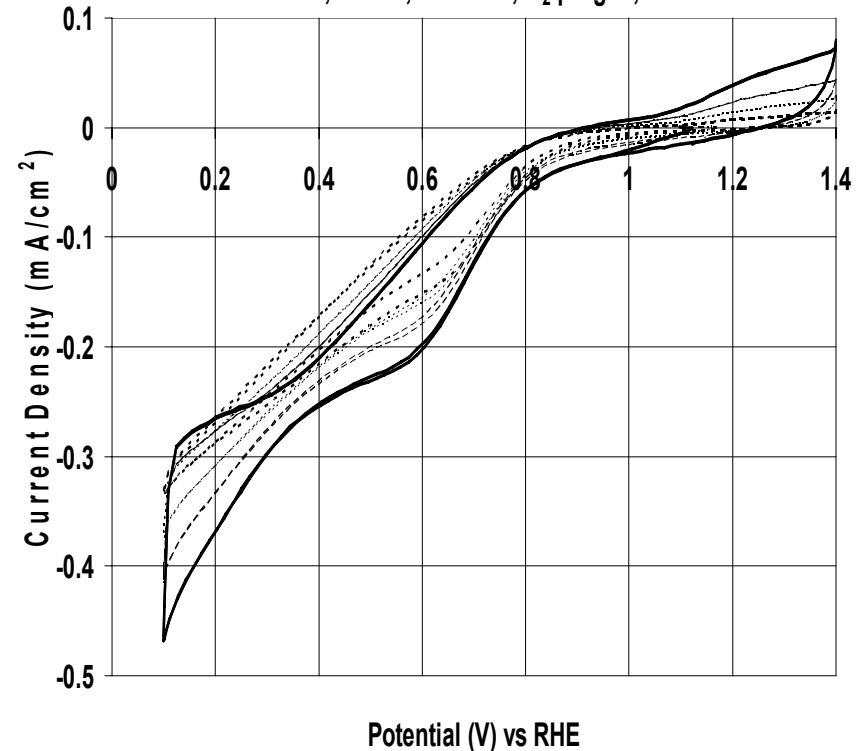
WE: Pt; CE: Pt; RE: RHE; O₂ purged; T = 25C



— 200mV/sec --- 100mV/sec 50mV/sec -.-. 20mV/sec

1:1 Triflic acid:water (2mL) + triazolyl phenoxy trimer (1.2mg);

WE: Pt; CE: Pt; RE: RHE; O₂ purged; T = 25C



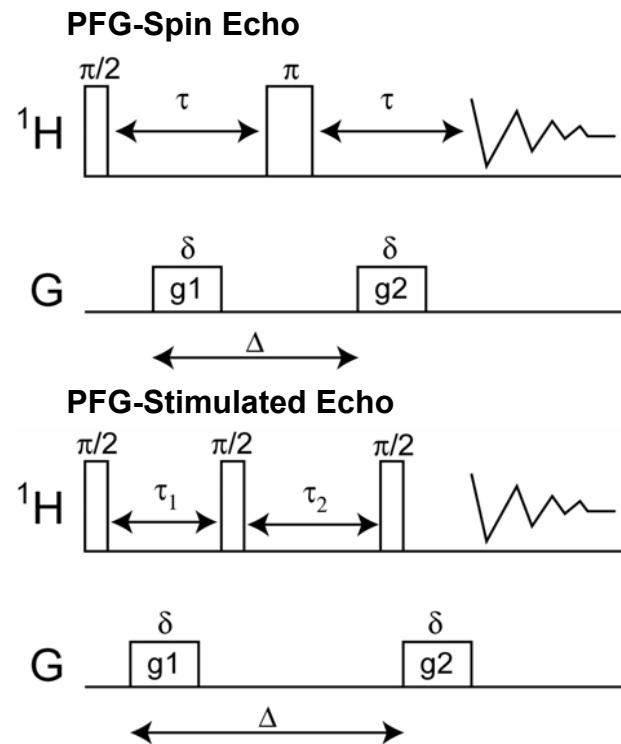
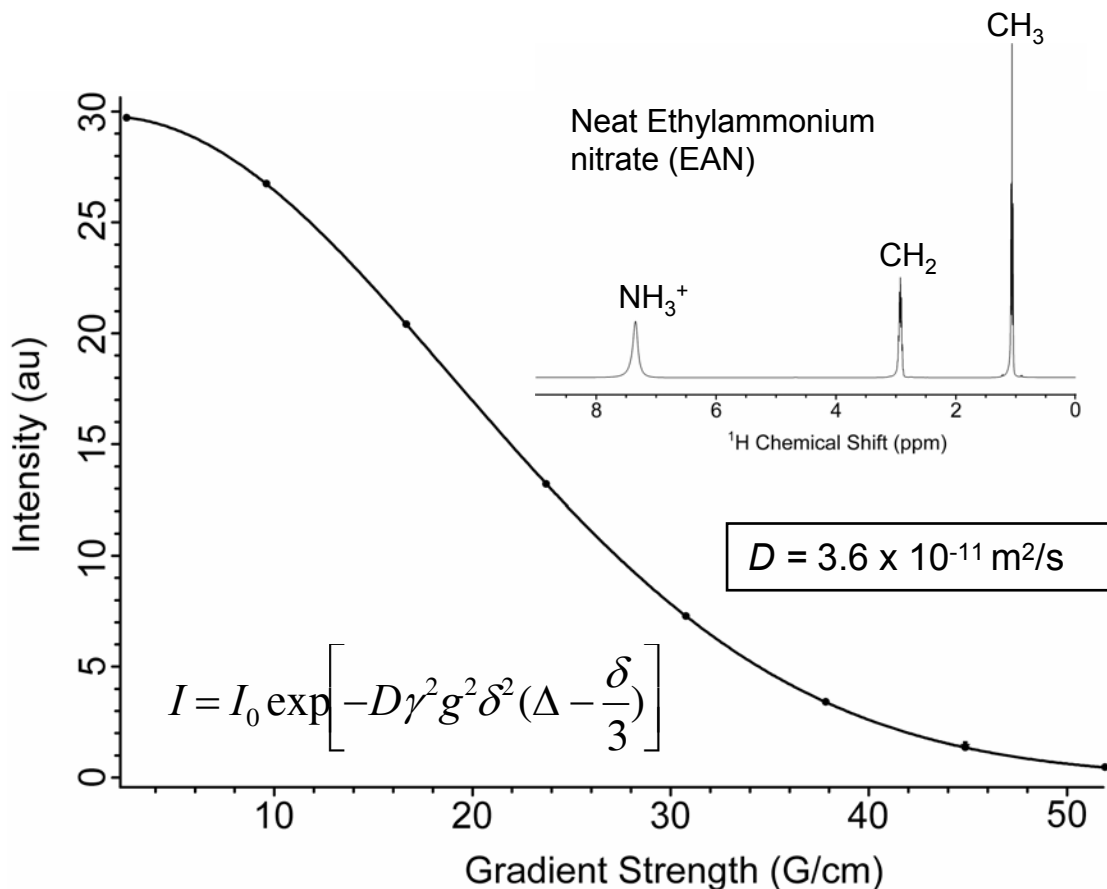
— 200mV/sec --- 100mV/sec 50mV/sec -.-. 20mV/sec

Observations: Cyclic Phosphazene 1.ii. adsorbs but does not decompose even in the presence of Pt and O₂. Adsorption diminishes O₂ reduction by ~ factor of 6. NOT a problem with phosphazene covalently immobilized in polymer.

Conclusion: Phenoxyphosphazene is suitable as a building block for a fuel cell polymer electrolyte membrane (PEM).

Technical Accomplishments: NMR

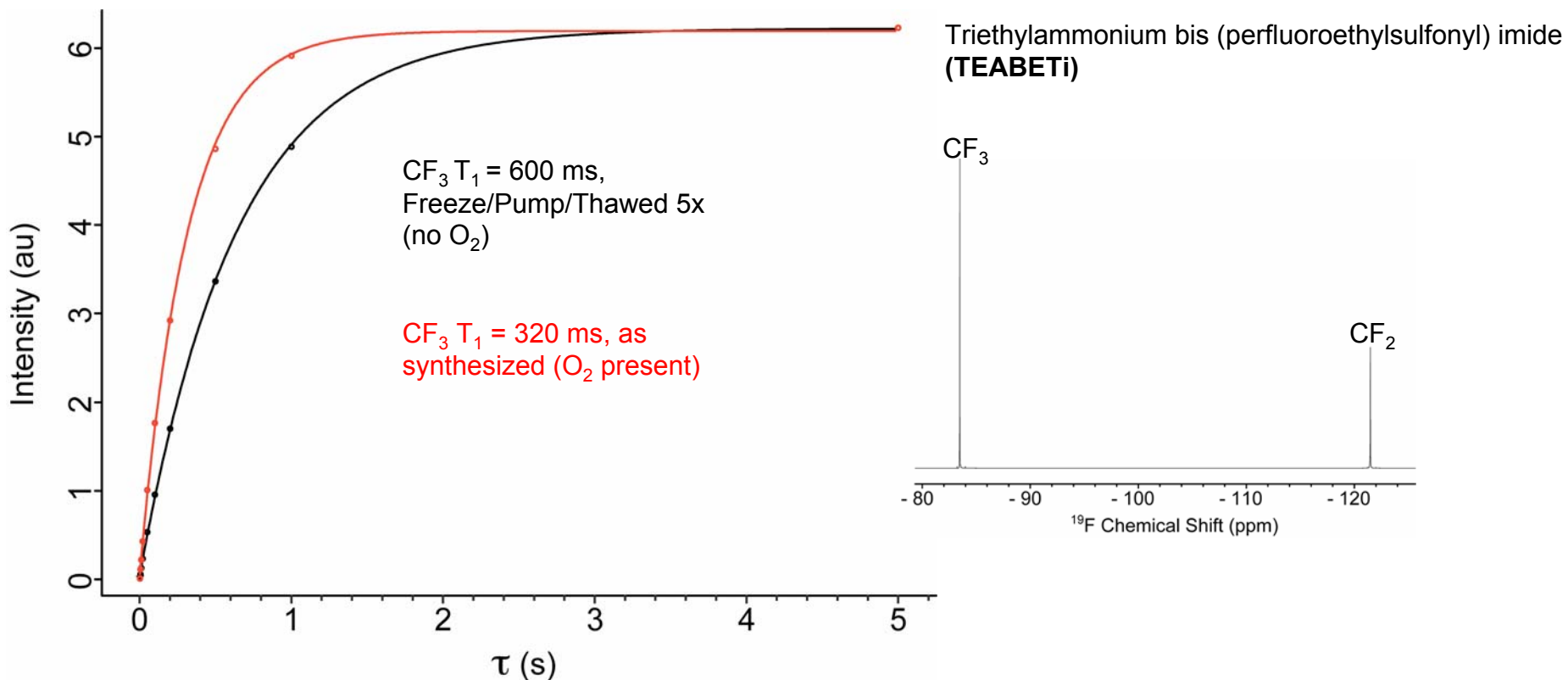
PFG Self-Diffusion Measurements on ILs



- ❑ PFG spin echo D measurements are limited by T_2 relaxation
- ❑ PFG stimulated echo is limited by T_1 relaxation (in viscous ionic liquids $T_1 \gg T_2$)
- ❑ Stimulated echo D measurements on EAN resulted in identical D for all ^1H sites

Technical Accomplishments: NMR

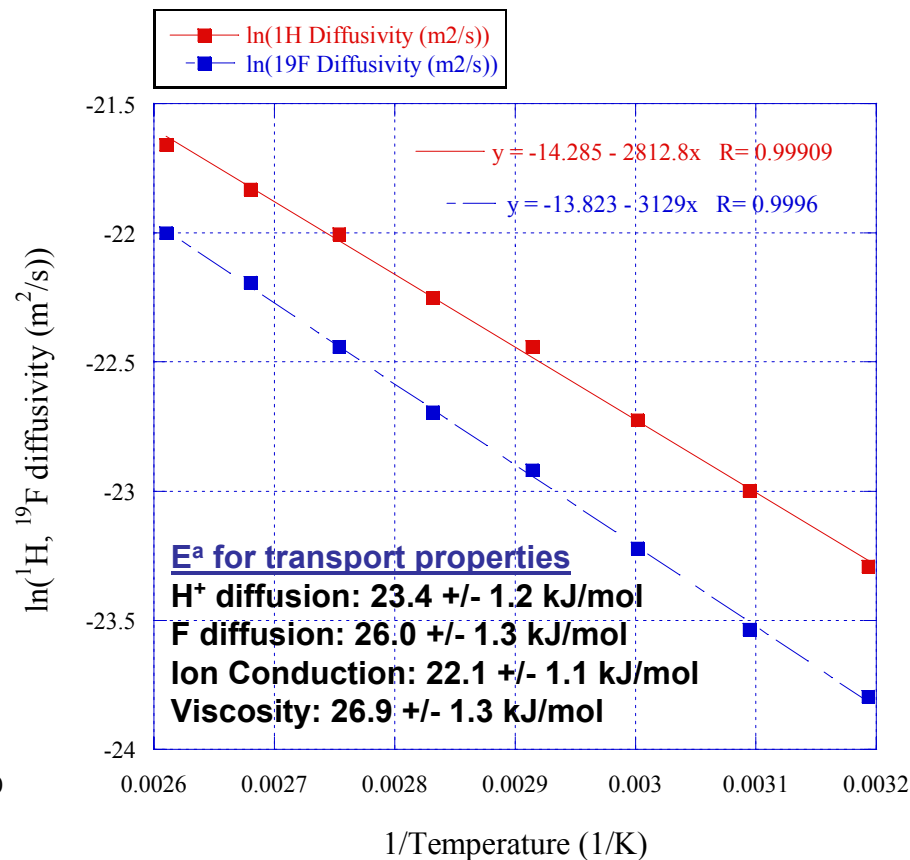
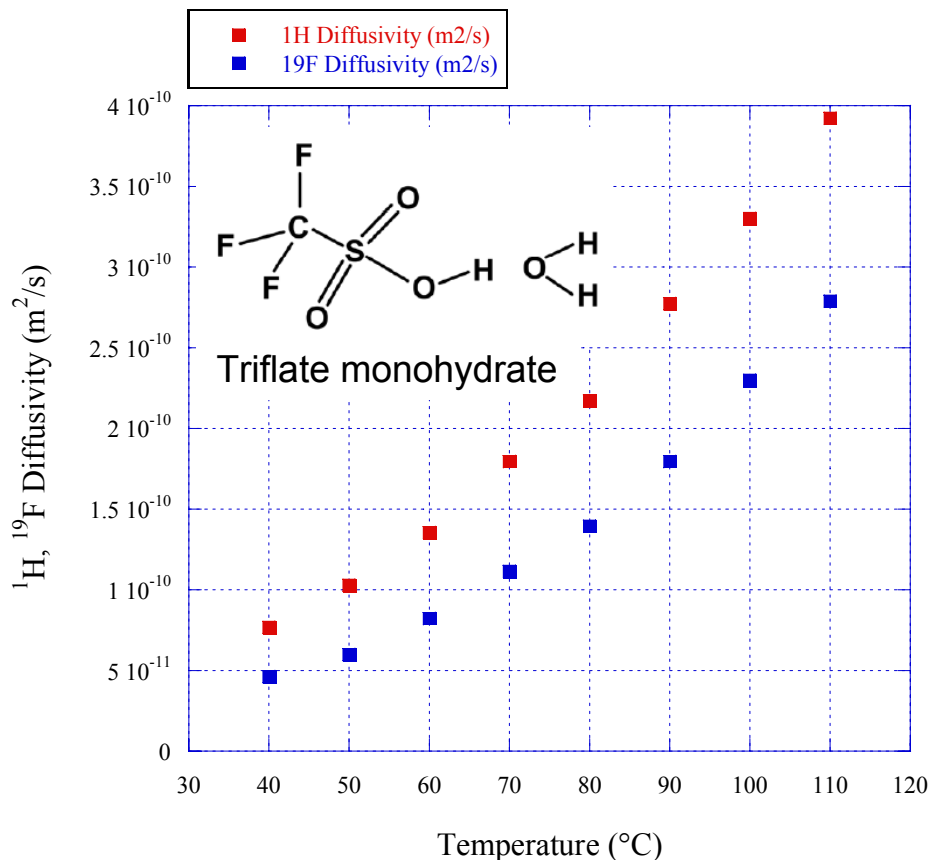
^{19}F NMR T_1 Relaxation Enhancement to Probe O_2 Presence in ILs



- Because O_2 is paramagnetic it will greatly impact NMR T_1 relaxation
- NMR T_1 measurements can be used to determine which ionic liquids and which sites in those ionic liquids are influenced by O_2 presence
- TEABETi (10 F) showed a significant change in T_1 with O_2 present compared to TEATFSi (6 F)
 - This is attributed to the larger number of F in TEABETi

Technical Accomplishments: NMR

Activation energies, E^a , for all transport properties in triflate monohydrate, a model pIL



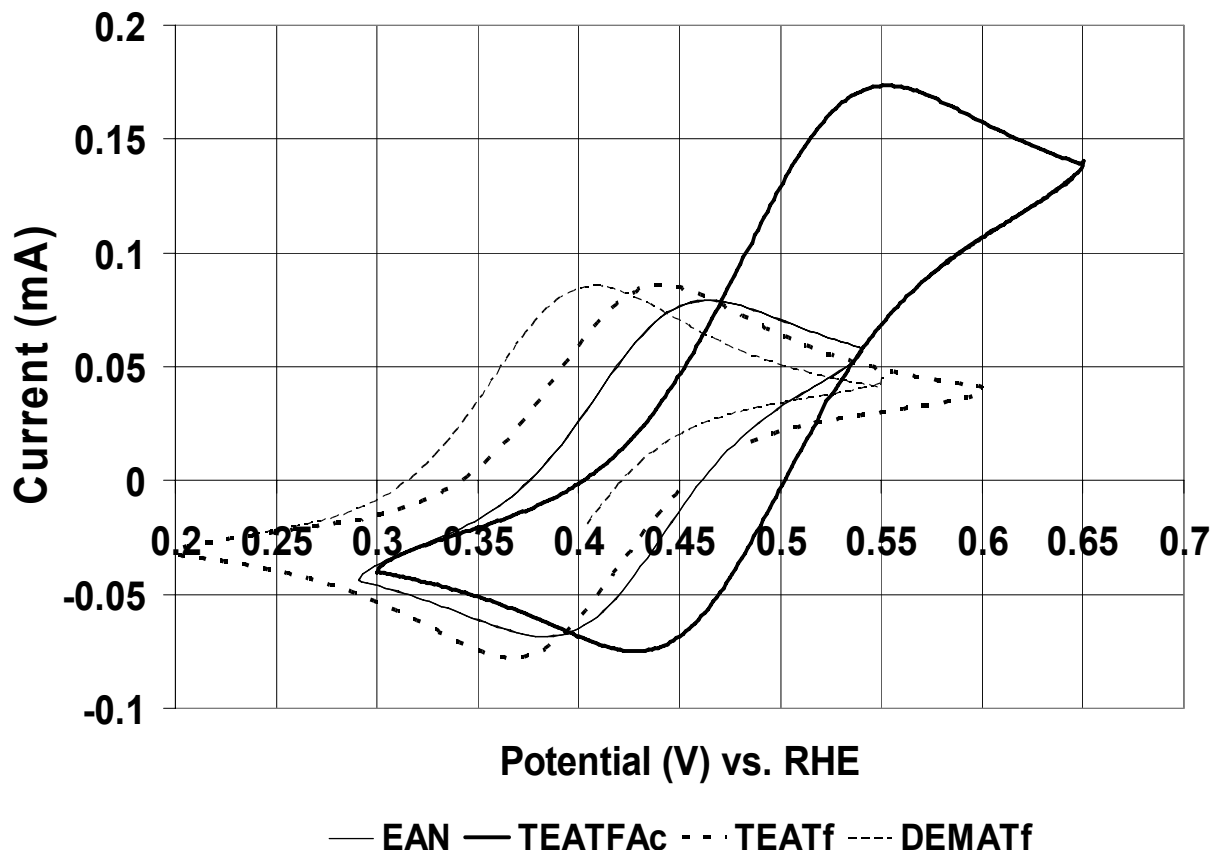
- That proton has 1.5x's higher diffusivity and lower E^a than F over the range of temperatures indicates H^+ hopping can occur in a pIL.
- Similar studies underway for another pIL, fluoropyridinium triflate.

Technical Accomplishments: solution voltammetry of ferrocene

Determining proton activity in protic ionic liquids

Solution voltammetry of ferrocene in 4 ionic liquids

Ar purged, T = 25 °C, SR = 100mV/s, WE: Pt, CE: Pt, RE: RHE

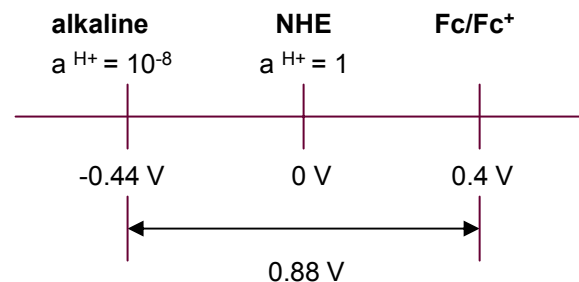


The acidity function H can be defined by

$$-H_{GF} = \log a^{H^+} + \log (f^{Fc}/f^{Fc^+})$$

- GF refers to the electrodes used (Glass, Ferrocene)
- f is the activity coefficient
- a^{H^+} is the activity of proton
- shift of 56 mV is ~ 1 pH unit

From: "Acidity Functions of Aqueous Fluorinated Acid Solutions". R. Cox, U. Krull, M. Thompson, K. Yates, *Anal. Chimica Acta*, 106 (1979) 51-57



- $E^{1/2}$ (ferrocene) vs RHE = 0.4, corresponds to a proton activity of 1 (1M in H^+ , or pH = 0)
- $E^{1/2}$ (ferrocene) vs RHE > 0.4, corresponds to a proton activity < 1 (more basic, pH > 0)
- $E^{1/2}$ (ferrocene) vs RHE < 0.4, corresponds to a proton activity > 1 (more acidic, pH < 0).

Future Work

- 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 leachable ionic liquids
 - ib. leachable 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.
 - a. Polyphosphazenes: low EW, heat-melt formed and water insoluble membranes.

- Echem NMR and FTIR
 - Continue pulse field gradient for H⁺ mobility of new materials
 - NMR Imaging under H⁺ current (“NMR Hittorf”) experiment to investigate distribution of species during proton conduction

- Voltammetry of Pt and other metal electrodes in PILs to investigate:
 - Pt-oxide formation
 - Adsorption of pIL on Pt
 - Check for O₂ reduction activity on Pt and non-Pt catalysts
 - Measure potential shift versus standard potential of “solvent shielded” metal complexes (e.g., for ferrocene, E^o = 0.4V vs NHE) in a pIL to determine proton activity in pIL and its component acid and base. Gives a reliable prediction of pK and rational basis for finding $\Delta pK = 14$.

Summary

- ❑ **Relevance: Help develop energy efficient fuel cell using protic salt electrolyte membranes**
- ❑ **Approach: Protic salt membrane 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**
 - **Lower corrosion and Pt particle growth**
 - **Simplified Fuel Cell: no humidifier, smaller radiator**
- ❑ **Technical accomplishments: Status of Protic Ionic Liquids (PILs)**
 - **High Conductivity and Fuel Cell Activity Found in some PILs**
 - **Stable PILs found**
 - **Need to combine high activity and stability**
 - **Demonstrated proton conductivity and fuel cell performance in leachable and non-leachable membranes**
 - **Synthesized new poly-phosphazene polymer with pendant nitrogen heterocycles**
- ❑ **Proposed Future Work:**
 - **Heat-melt cast poly-phosphazene polymer with pendant nitrogen hetero cycles into a water insoluble membrane and then react with triflic (and other) acids to form protic salt membranes. Test H⁺-conductivity and fuel cell performance**
 - **Continue NMR characterization of proton mobility.**
 - **Finish NMR imaging of membranes under proton current.**