DOE Hydrogen Program

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

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Organization: Arizona State University
in collaboration with
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Arizona State University;
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University of Akron

Date: Tue, May 19, 2009
Time: 11:30 am

Project ID
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Overview

Timeline

- January 15, 2006
- January 14, 2011
  - go/no go end of year 3
  - March 2009
- 60% 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
  - $300,000
- Funding for FY07
  - $300,000
- Funding for FY08
  - $300,000

Partners

- Arizona State University (lead)
- University of Akron (sub-contractor)
- Boeing

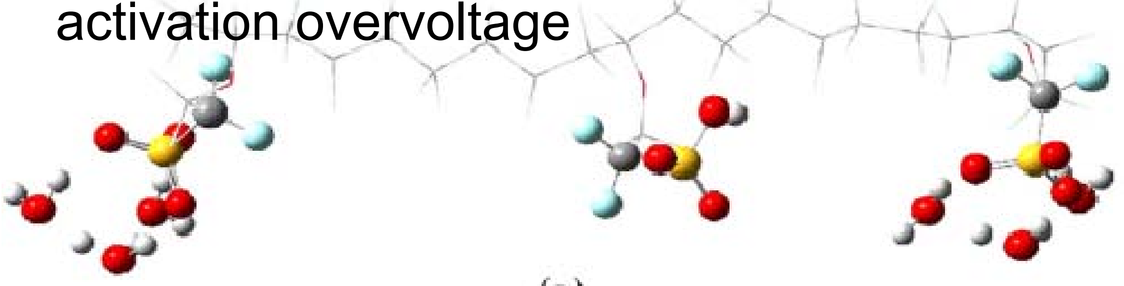
- DOE Technology Development Manager: Donna Lee Ho
- DOE Project Officer: Greg Kleen
- ANL Technical Advisor: Thomas Benjamin

Relevance

OBJECTIVE:

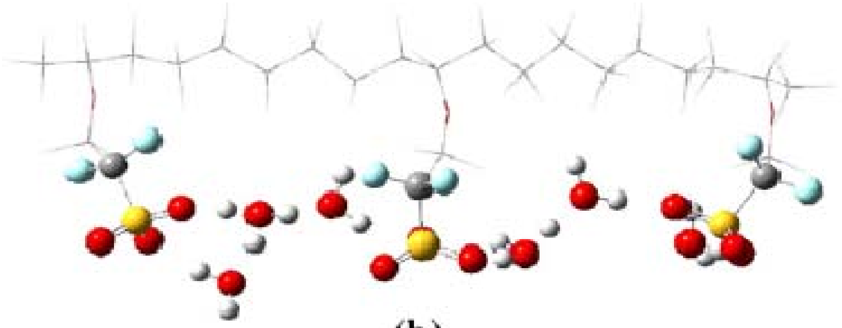
To make a solid water-insoluble anhydrous proton-conducting electrolyte membrane that has good

- *DURABILITY* by virtue of having
  - proton conductivity that surpasses the 2009 target of > 0.1 S/cm at 120^{o}C and 50% RH
  - effectively having no co-transport of molecular species with proton
  - good mechanical strength and chemical stability
- *ELECTRODE PERFORMANCE* by assisting catalyst to promote reduced activation overvoltage



(a)

a) Non-conducting
Low water form



(b)

b) Conducting
High water form

The water solvated acid membrane only conducts proton under conditions (b) pendant acid and waters are in contact with adjacent units

Relevance

Benefits

High conductivity and Lower activation overvoltage lead to higher efficiency

No co-transport of water and higher temperature operation lead to elimination of bulky humidifier and radiator

Approach

SYNTHESIS OF "DRY" PROTON ELECTROLYTE MEMBRANEs (PEMs)

- PEMs are being made based on "solvent free" liquid salts called ***protic ionic liquid (pIL) concepts***.
- ***pILs*** can be ***used to model membranes*** (stability, conductivity).
- ***Acid and base moieties*** are ***varied*** to optimize electrolyte properties.
- ***Polymers*** are ***varied*** to optimize membrane solubility for water insoluble membranes with a high density (low EW) of covalently and electrostatically bound non-leachable ions.

CHARACTERIZATION

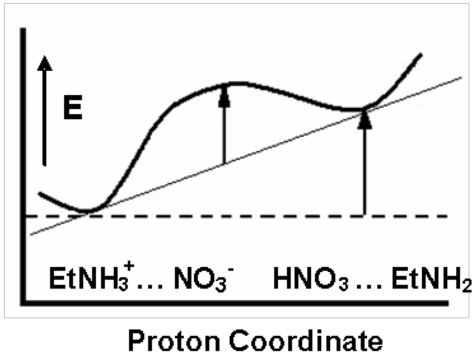
- Proton conductivity characterized by electrochemical impedance spectroscopy (EIS) from -20 to 120^{o}C
- Thermal oxidative stability of electrolytes measured by Thermal Gravimetry (TGA) from -20 to 120^{o}C
- Electrochemical stability and electrode polarization surveyed by cyclic voltammetry on Pt
- Fuel cell performance/stability estimated by steady state I/V curves
- The mechanism of transport of protons, anions, and molecules investigated 3 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. MRI while passing current to measure time-dependent distribution of species during proton conduction.

Approach/Milestones

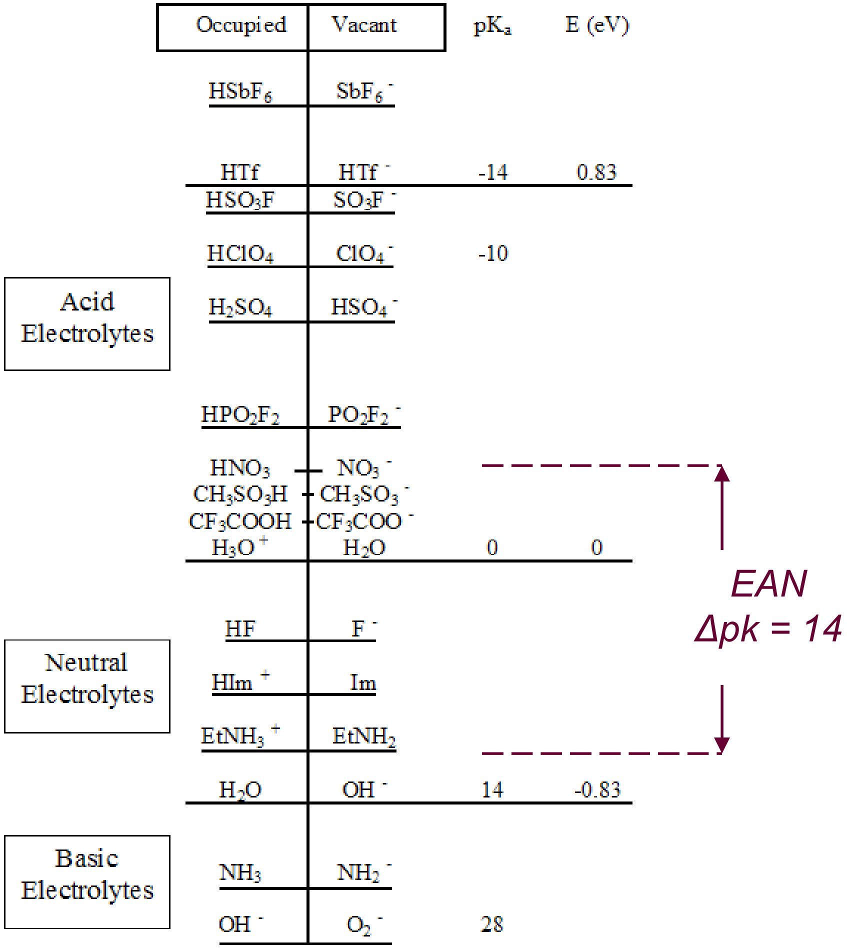
Month/Year	**Milestone for Go/No-Go Decision**
Jan-09	Milestone: 2 kinds of high temperature proton-conducting protic salts membranes were made into MEAs and tested in fuel cells: (i) membranes filled with leachable protic ionic liquids and (ii) membranes with non-leachable salt moieties Determine conductivity of membrane at 0 to 50% 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 water and other free solvents.
Feb-09	Milestone: Complete initial round of MEA fabrication and testing with selected new polymers (4 sent to Bekktech for evalution and 2 more in progress) for external validation on the membrane conductivity at various temperatures and RH conditions.
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 eliminated by blending 70 wt% ITP with 30 wt% of a proton conducting organic polymer, PVPP, but at a cost of reduced conductivity.

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)
	$HSbF_6$	SbF_6^-		
	HTf	HTf^-	-14	0.83
	HSO_3F	SO_3F^-		
	$HClO_4$	ClO_4^-	-10	
Acid Electrolytes	H_2SO_4	HSO_4^-		
	HPO_2F_2	$PO_2F_2^-$		
	HNO_3	NO_3^-		
	CH_3SO_3H	$CH_3SO_3^-$		
	CF_3COOH	CF_3COO^-		
	H_3O^+	H_2O	0	0
	HF	F^-		
Neutral Electrolytes	HIm^+	Im		
	$EtNH_3^+$	$EtNH_2$		
	H_2O	OH^-	14	-0.83
Basic Electrolytes	NH_3	NH_2^-		
	OH^-	O_2^-	28	

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^{o}C) membrane

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

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°

30% complete

☐ **Task 4: Proton Conduction by NMR**

4.1 Pulsed field gradient NMR
4.2 Electrochemical NMR (eNMR)
4.3 eNMR Hittorf

75% complete

☐ **Task 5: Iterate Synthesis**

- to optimize stability, conductivity

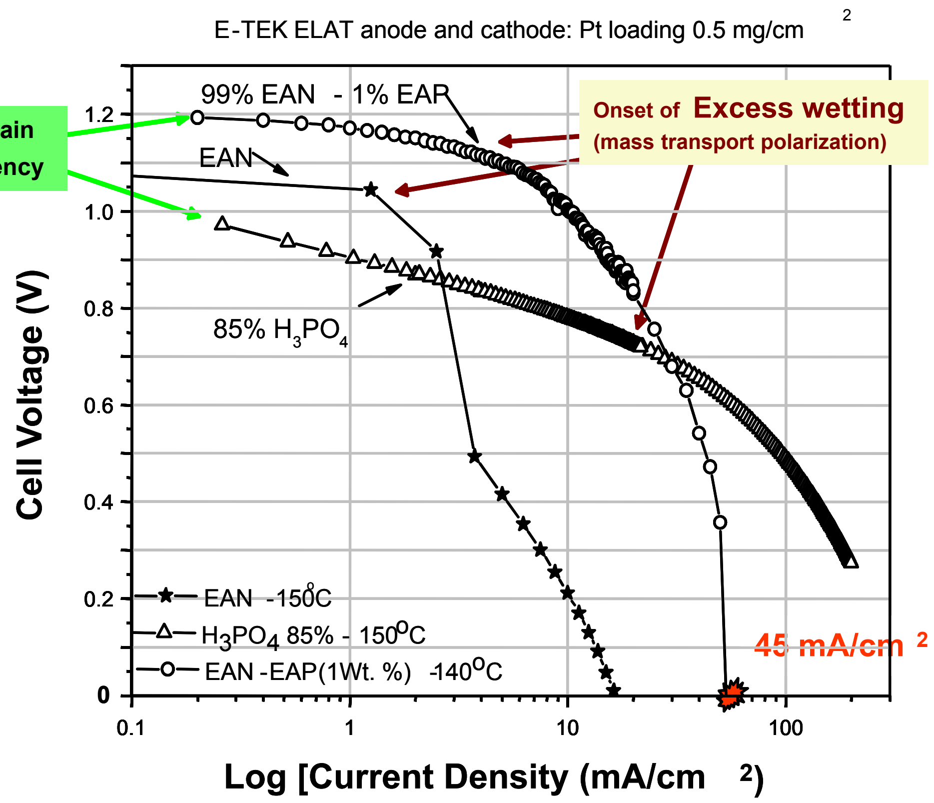
60% complete

☐ **Task 6: Membrane Demonstration**

- ASU sent 4 membranes to CFU
- 2 more in preparation

Technical Accomplishments FY08:
Fuel Cell with pIL and gas fed Porous Electrode

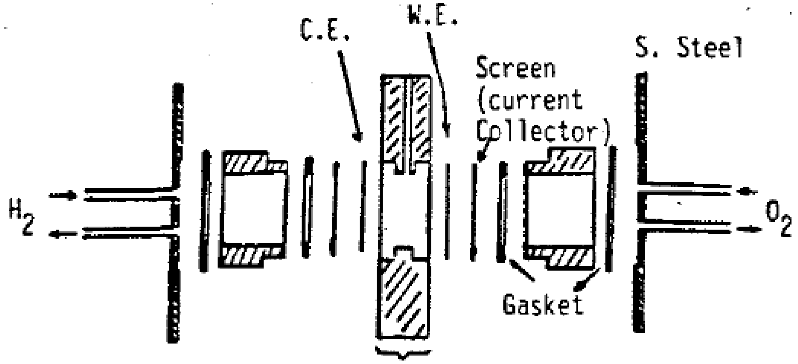
E-TEK ELAT anode and cathode: Pt loading 0.5 mg/cm^2



20% gain efficiency

Onset of **Excess wetting** (mass transport polarization)

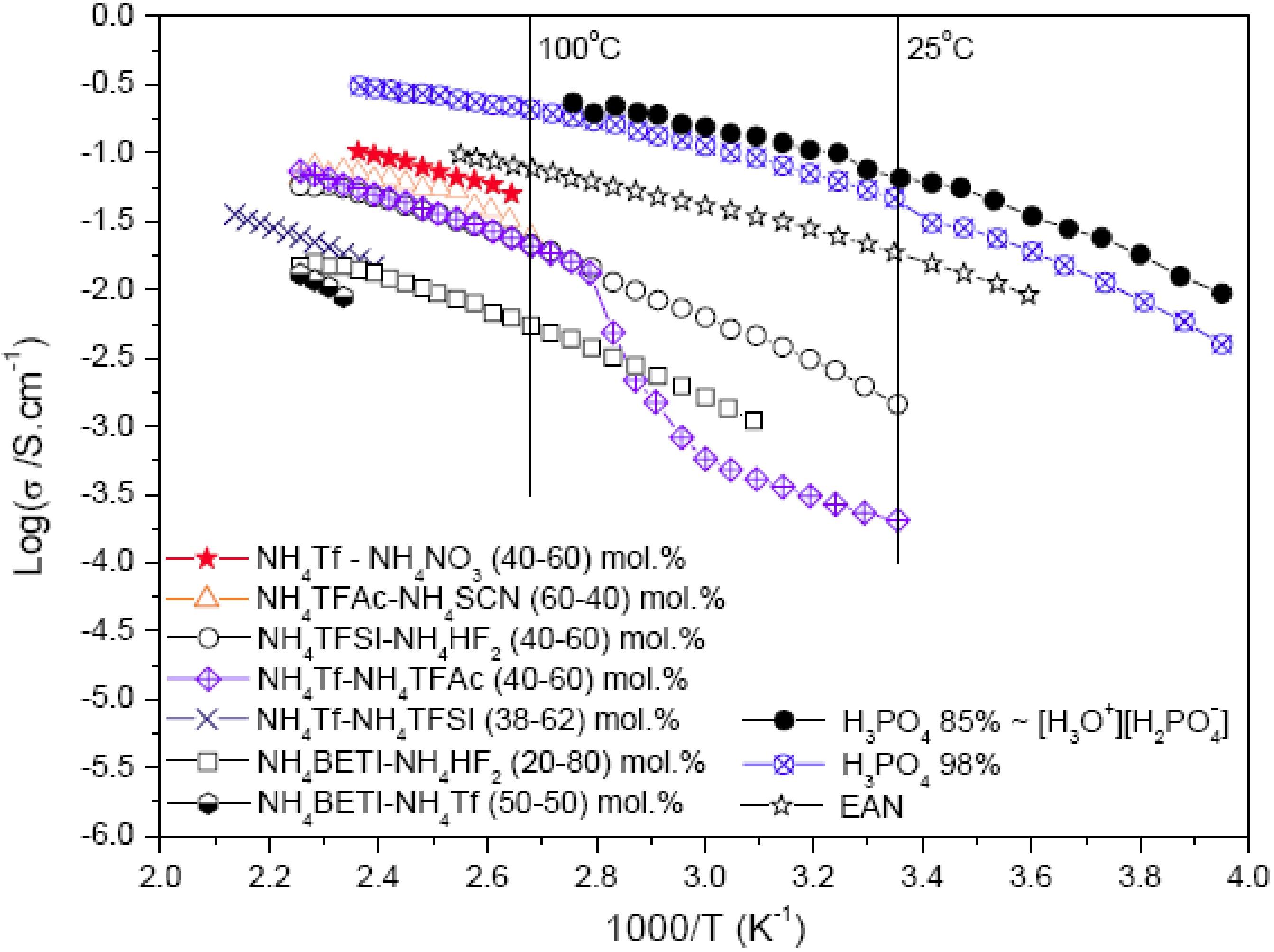
~~45 mA/cm~~ 2



Liquid Electrolyte Cell

- *Fuel cells with protic salts still show* ***better performance than with 85% H_3PO_4***
- ***New material goal, a more stable and non wetting electolyte***

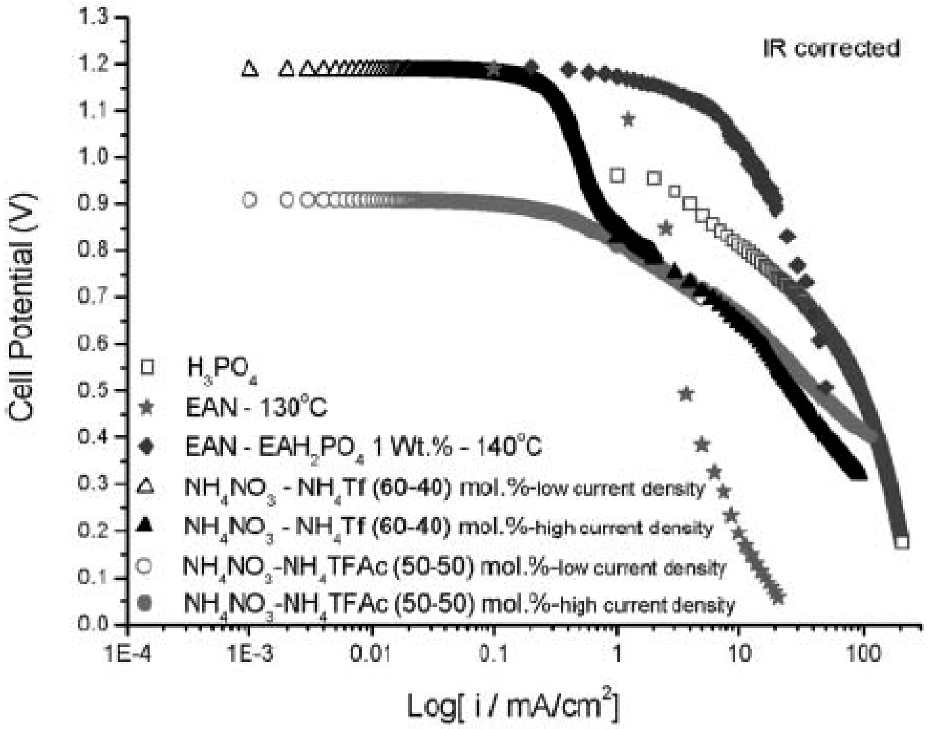
Technical Accomplishments FY08:
: Arrhenius plot of conductivity of ammonium salt mixtures



Technical Accomplishments FY08:
: *Fuel Cells with New Stable PIL Electrolytes*

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.

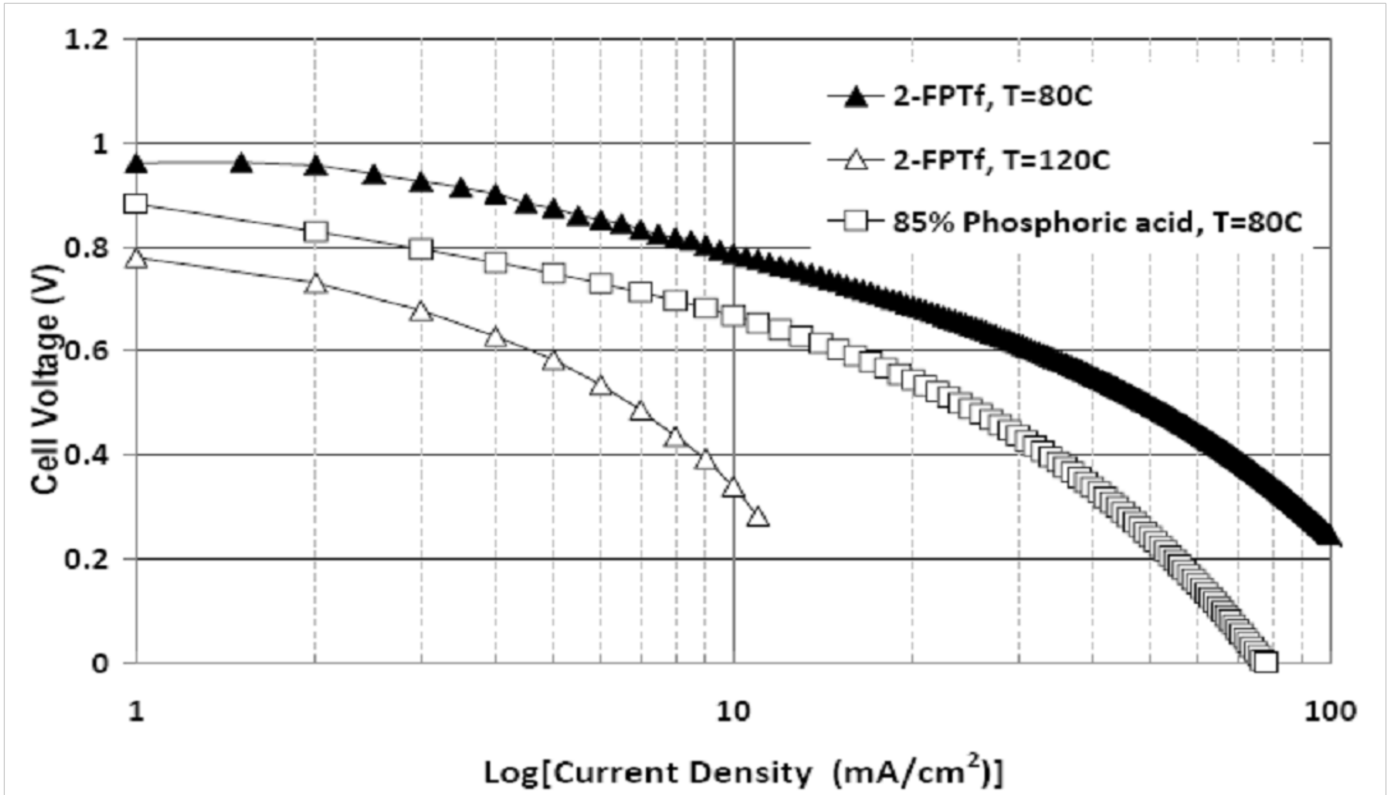
* Beyond the potential enhancement performance of an ionic protic liquid, a non-hydrous electrolyte allows for a greater array of catalysts and electrodes to be considered for use in a proton exchange fuel cell.

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

Technical Results: More Efficient and Stable Fuel Cell

with an Electrochemically and Physically stable pIL, 2-FPTf



STEADY STATE I/V curves for H_2 and O_2 fed to Pt-catalyzed porous electrodes in 2-FPTf electrolyte at 80C and 120C and 85% phosphoric acid electrolyte at 80C. σ(2-FPTf) = 4x10^{-3} Scm^{-1} A = 0.5 cm^2, $t^{electrolyte}$ = 0.3 cm.

Why is fuel cell better with this salt electrolyte ??

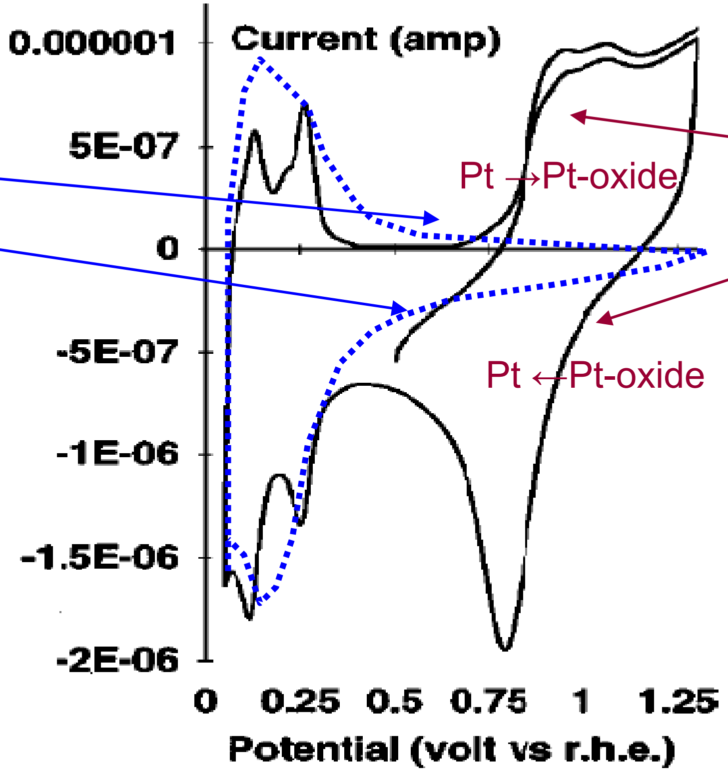
Technical Results:Cyclic voltammogram of Pt surface in:

- **aqueous sulfuric acid electrolyte** **(solid black line)**
- **versus protic salt** **(dotted blue line).**

With protic salt electrolyte

There is
- no Pt-oxide formation
- nor reduction

to impede O_2 reduction.



With aqueous electrolyte

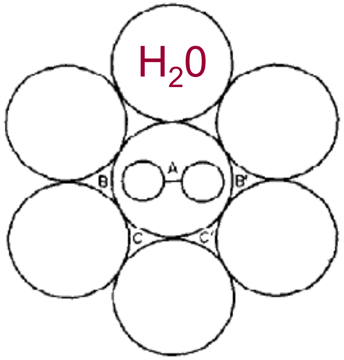
Pt-oxide formation

$Pt + H_2O \rightarrow Pt\text{-}OH + H^+ + e^-$

Pt-oxide reduction

$Pt\text{-}OH + H^+ + e^- \rightarrow Pt + H_2O$

Pt-oxide impedes O_2 reduction.

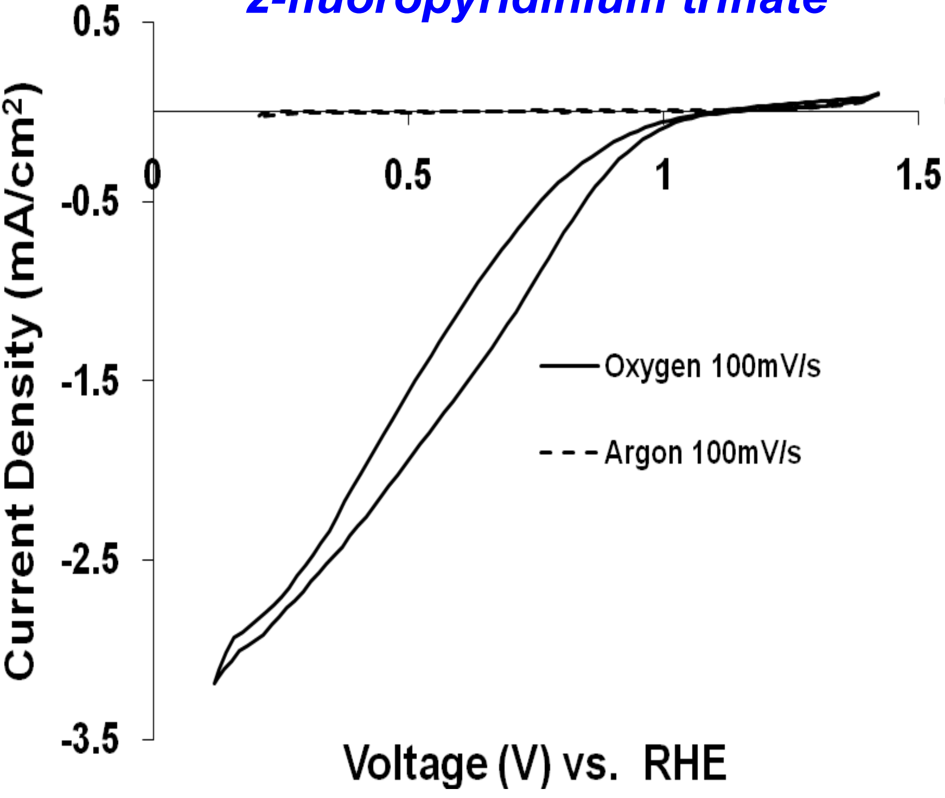


Low water activity makes Pt a better <u>cathode</u> electrocatalyst

Technical Results: Voltammetry of Pt with Oxygen in:

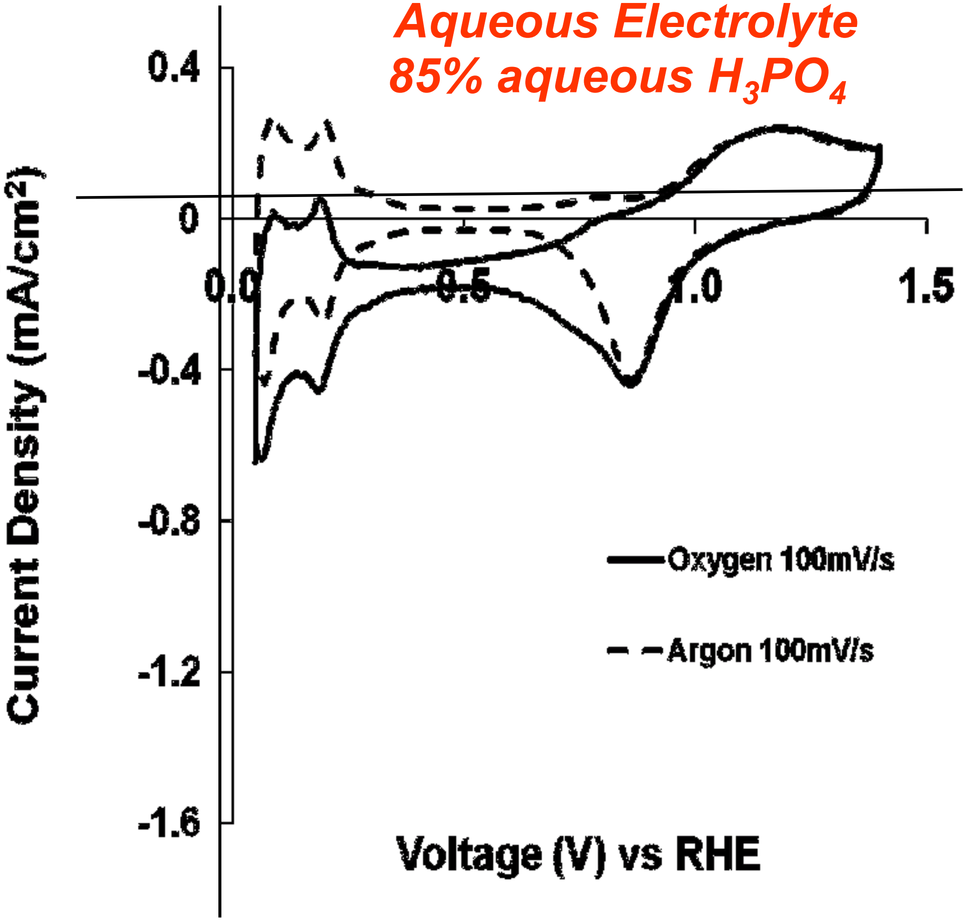
Salt Electrolyte

2-fluoropyridinium triflate



Aqueous Electrolyte

85% aqueous H_3PO_4



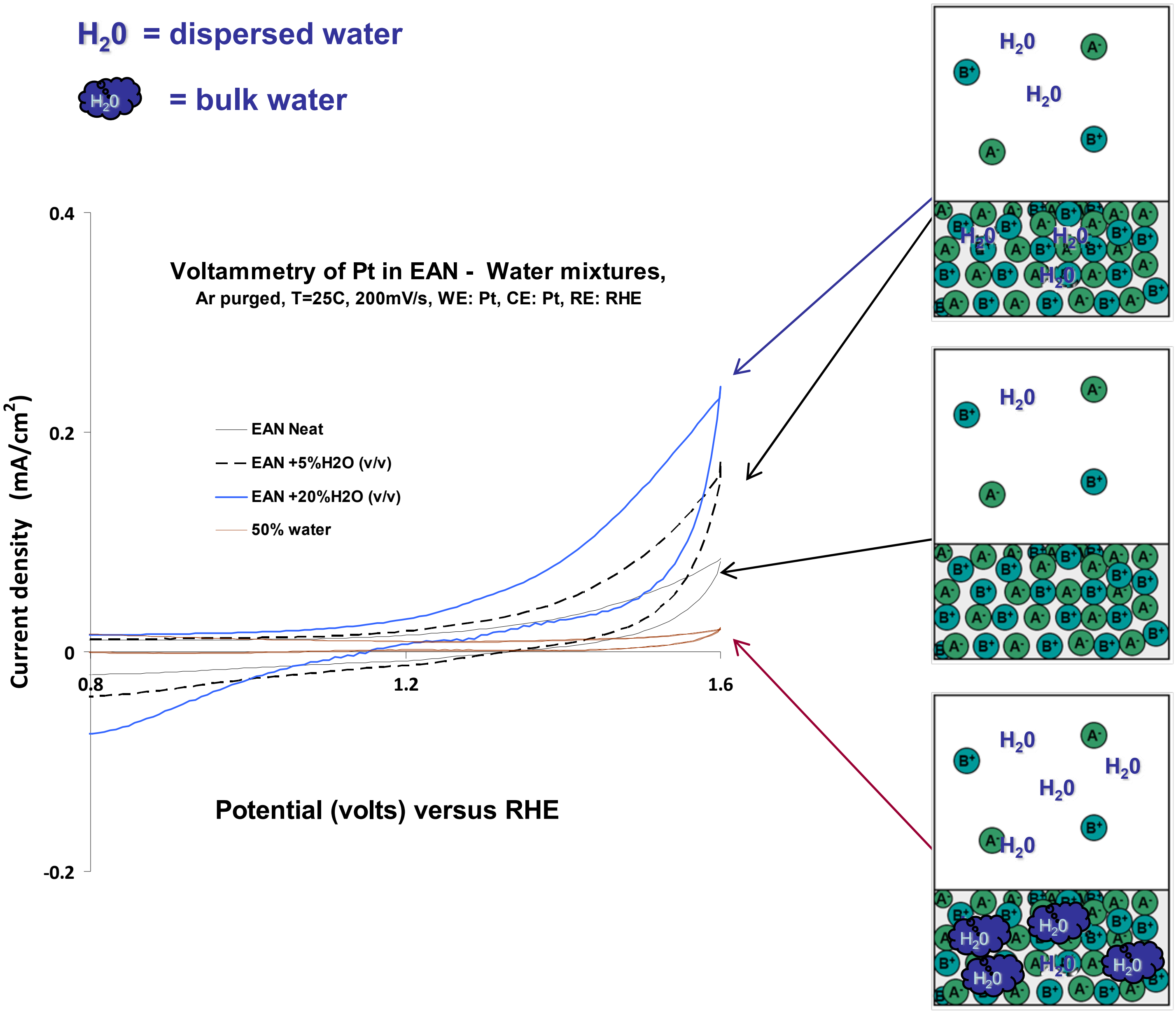
Voltammetry of Pt in 2-fluorpyridium triflate shows:

- Stable after 100 cycles in presence of O_2
- O_2 reduction starts near thermodynamic limit [1.18V at 80°C]
- Oxidation current at E>1.18V *is not for electrolyte oxidation* *its for water oxidation to O_2*

Technical Results: Effects of Dispersed and Bulk Water

H_20 = dispersed water

H_20 = bulk water



Voltammetry of Pt in EAN - Water mixtures,
Ar purged, T=25C, 200mV/s, WE: Pt, CE: Pt, RE: RHE

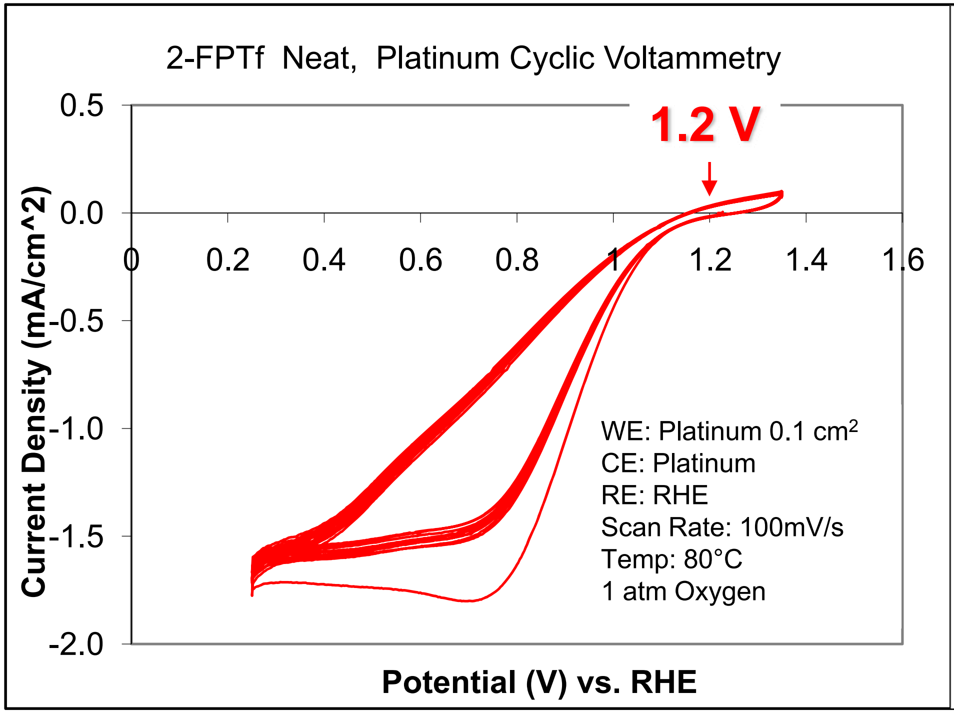
5 to 20% Dispersed H_20 in IL

Trace H_2O in Neat IL

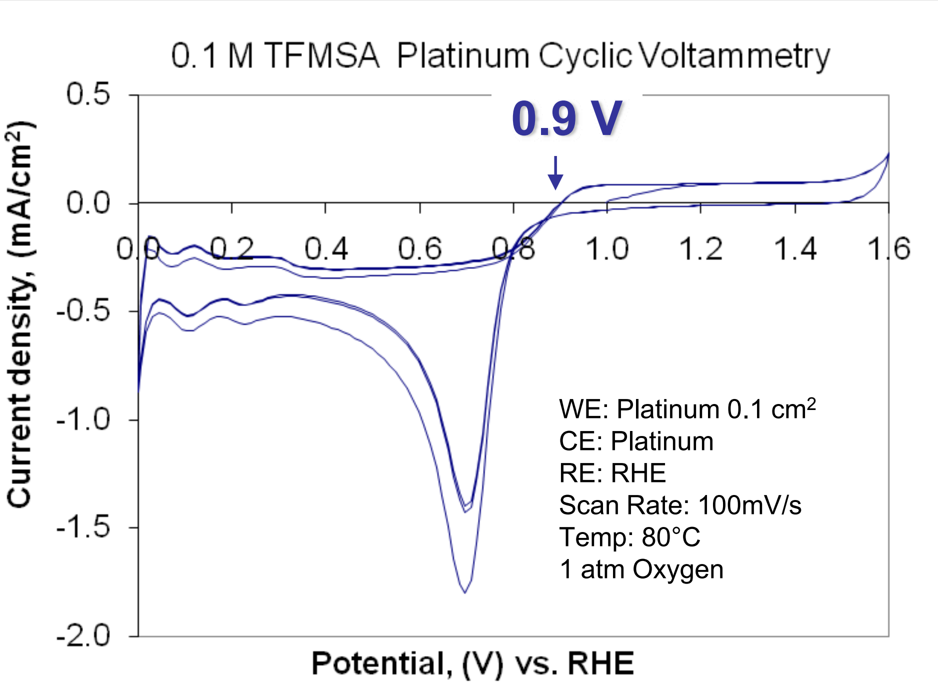
50% Dispersed and Bulk H_20 in 50% IL

Technical Results:
Voltammetry of Pt in Fluorinated Ionic Liquid Electrolytes:

without bulk water

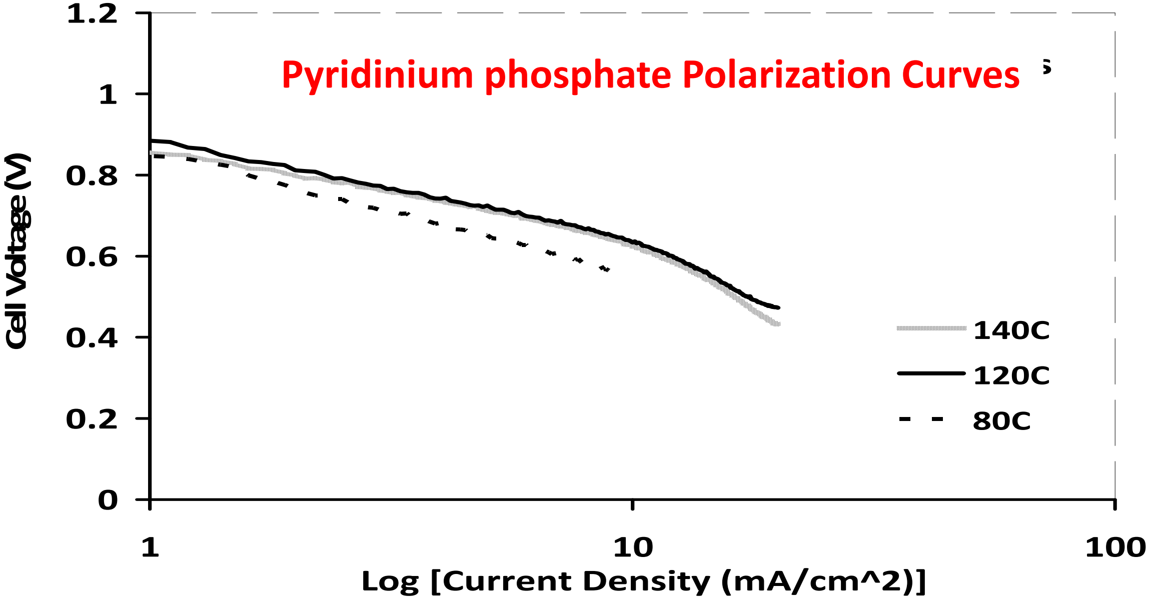


with bulk water



- **Voltammetry of 2-Fluoropyridinium triflate shows that it is stable after 100 cycles.**
- **Oxygen reduction starts near the thermodynamic limit for ORR [1.18V at 80°C]**

Technical Results: hydrocarbon pIL vs fluorocarbon pIL

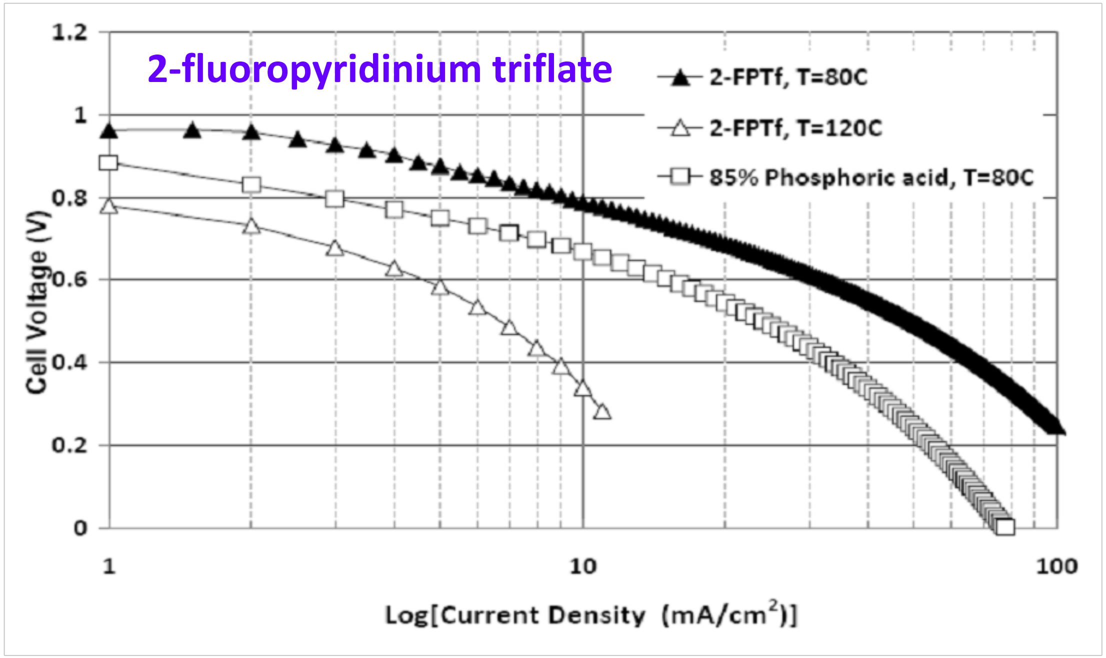


<u>Hydrocarbon</u>

- **Stronger adsorbing**
- ***Lower* power**

<u>Fluorocarbon</u>

- **Weaker adsorbing**
- ***Higher* power**

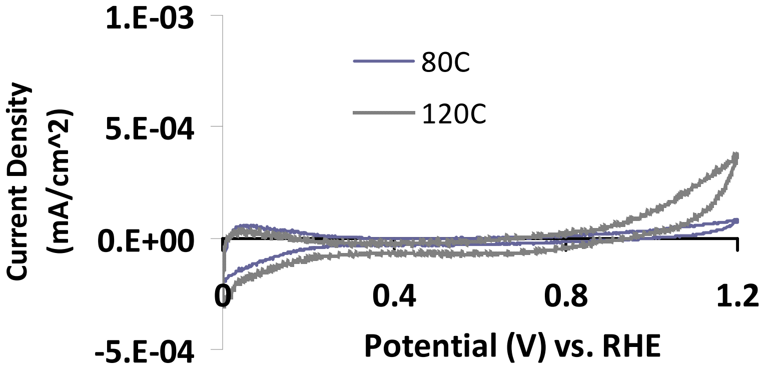


Technical Results: Voltammetry of hydrocarbon and fluorocarbon Ionic Liquid Electrolytes

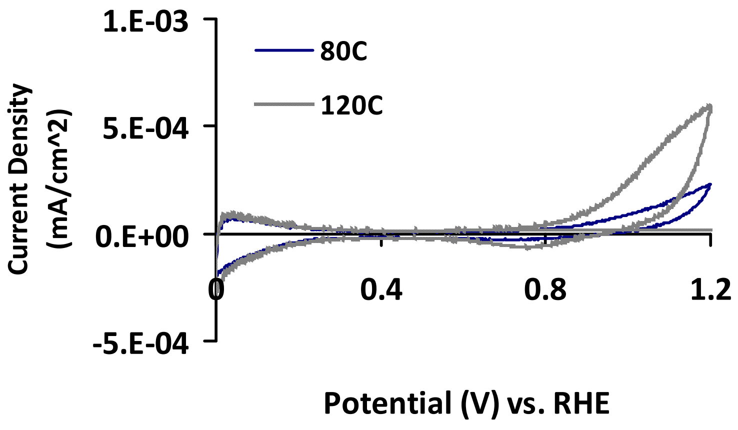
Voltammetry of Pt in pyridinium phosphate shows:

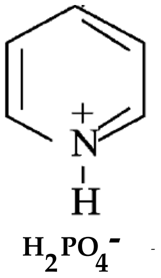
- **Oxidatively unstable**
- **Lower O2 reduction current**

Pt Voltammetry in Pyridinium Phosphate under Oxygen Scan Rate = 100 mV/s



Pt Voltammetry in Pyridinium Phosphate under Nitrogen Scan Rate = 100 mV/s

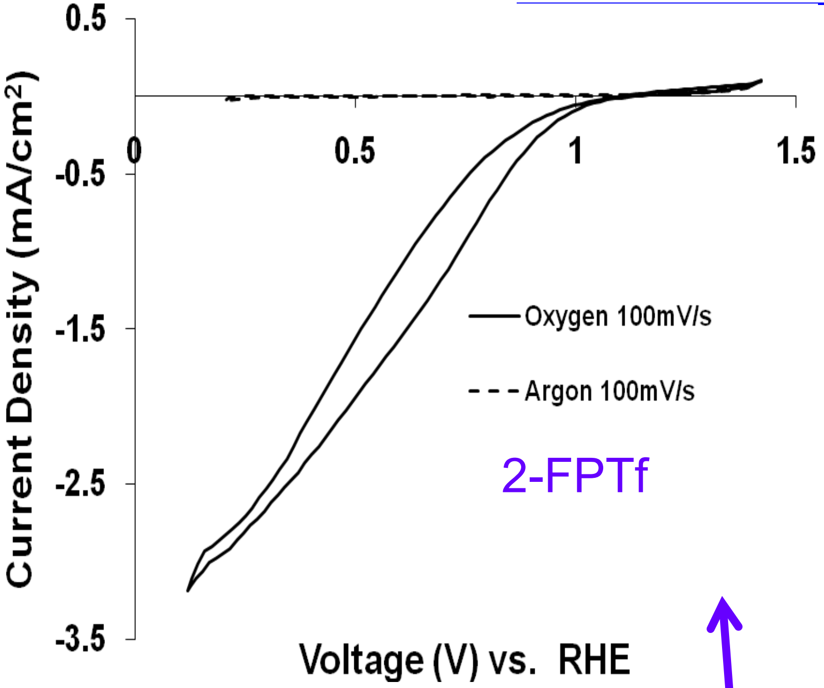


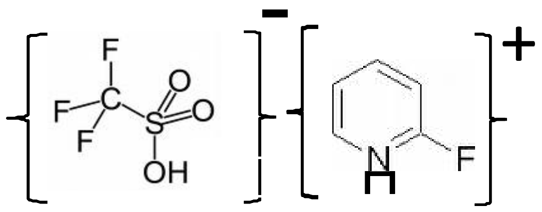


Pyridinium Phosphate

Voltammetry of Pt in 2-fluorpyridium triflate shows:

- Stable after 100 cycles in presence of O_2
- O_2 reduction starts near thermodynamic limit [1.18V at 80°C
- Oxidation current at E>1.18V *is for water oxidation to O_2*





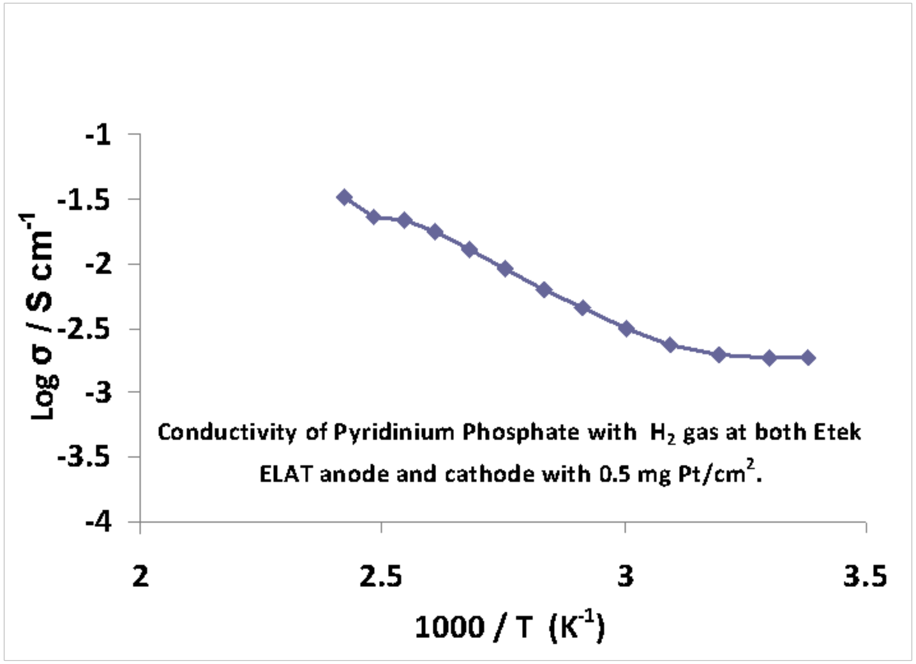
2-Fluoropyridinium triflate

Technical Results:
Conductivity of Liquid hydrocarbon vs fluorcarbon pIL

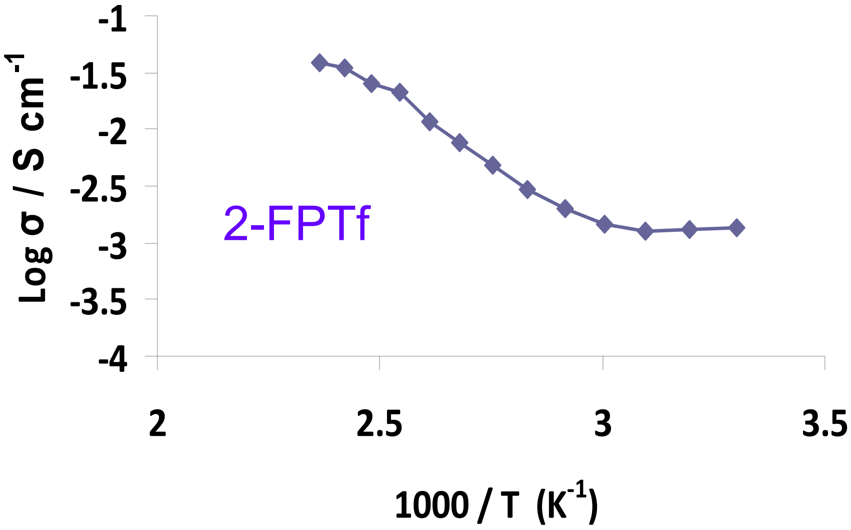
as a function of temperature, dry H2 gas fed to ETEK ELAT Pt anode and cathode

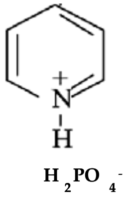
Liquid hydrocarbon pIL
pyridinium phosphate (PP)

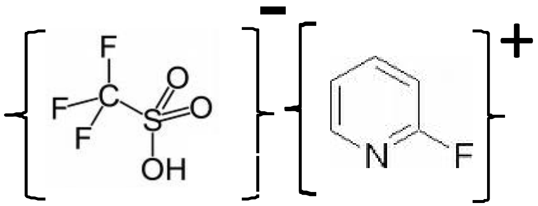
Liquid fluorocarbond
Fluoropyridinium triflate2-FPTf



Conductivity of Pyridinium Phosphate with H_2 gas at both Etek ELAT anode and cathode with 0.5 mg Pt/cm^2.





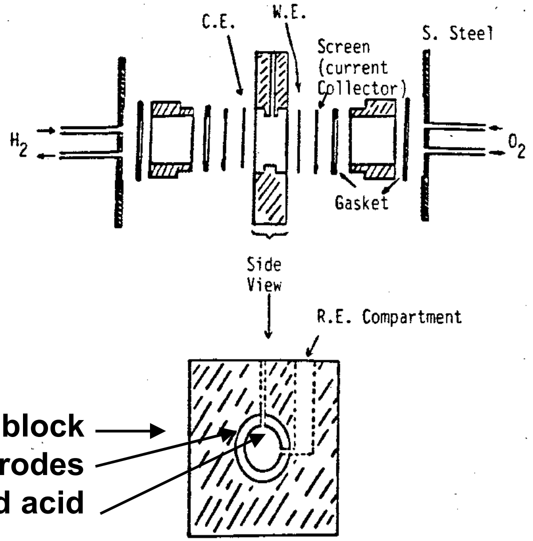


About the same

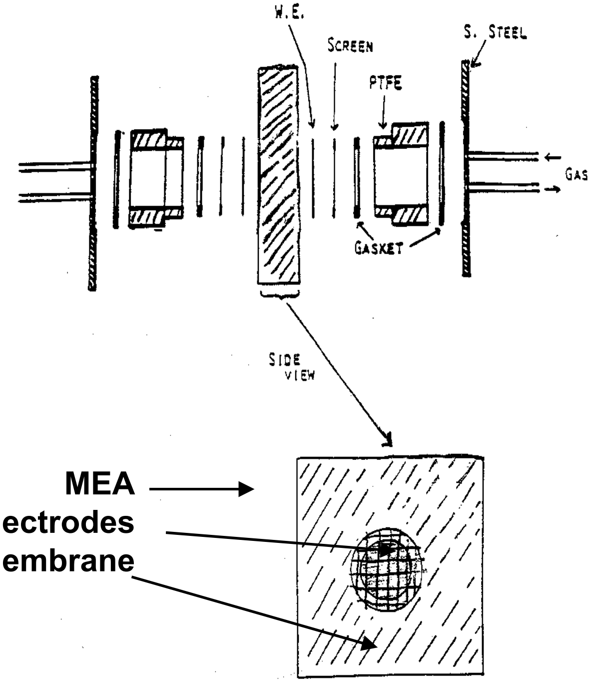
Technical Accomplishments:

a stable & conductive membrane with immobilized ions in membrane

Schematic Diagram of Liquid vs Solid PEM Fuel Cell



Teflon block
Holds electrodes
Contains liquid acid



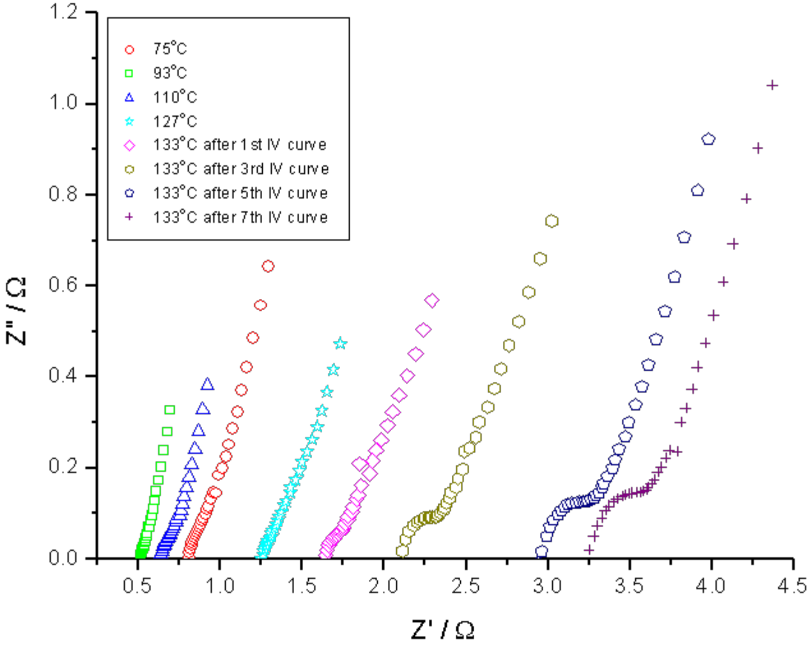
MEA
With electrodes on membrane

micro fuel cell with liquid electrolyte, like phosphoric acid.

micro fuel cell with PEM electrolyte, like Nafion®.

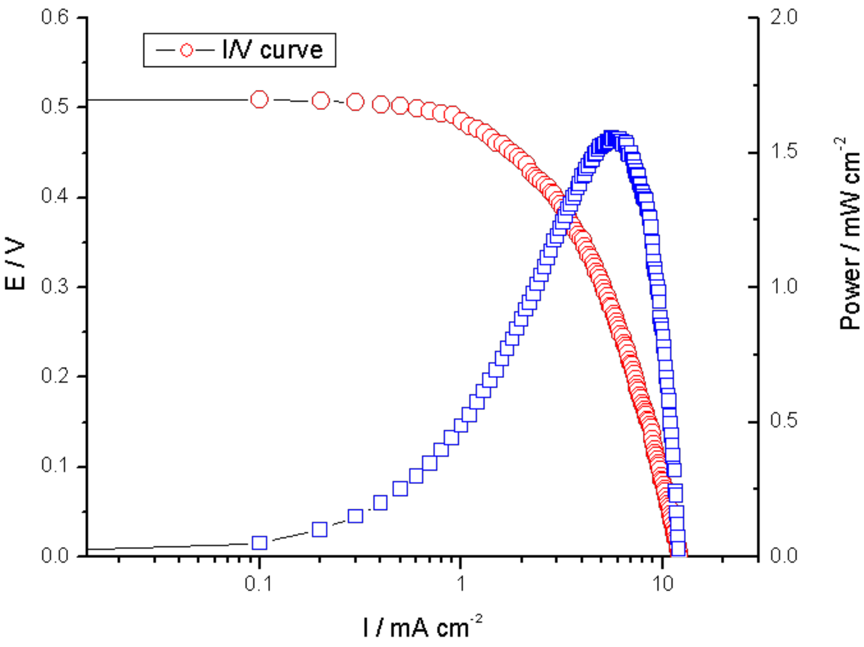
FY08: Technical Accomplishments: non-leachable PEM 1

EIS for H^+ conductivity



Fuel Cell I/V Curve

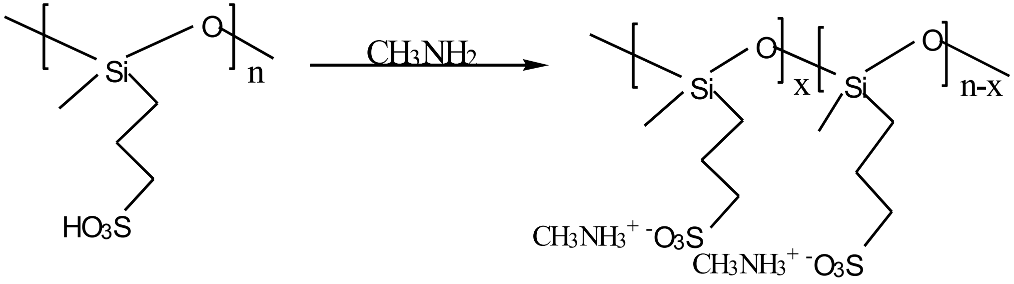
I/V curve and power for the fuel cell based on anodisc imbibed with polysiloxane with pendant sulfonic acid that neutralized by methylamine. Fuel cell runs at 127°C



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

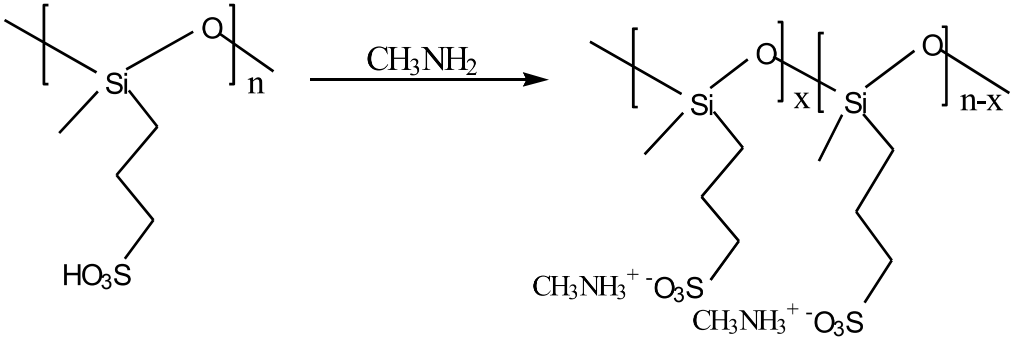
Non-leachable

Pendant sulfonic acid polymer fully neutralized with methyl amine

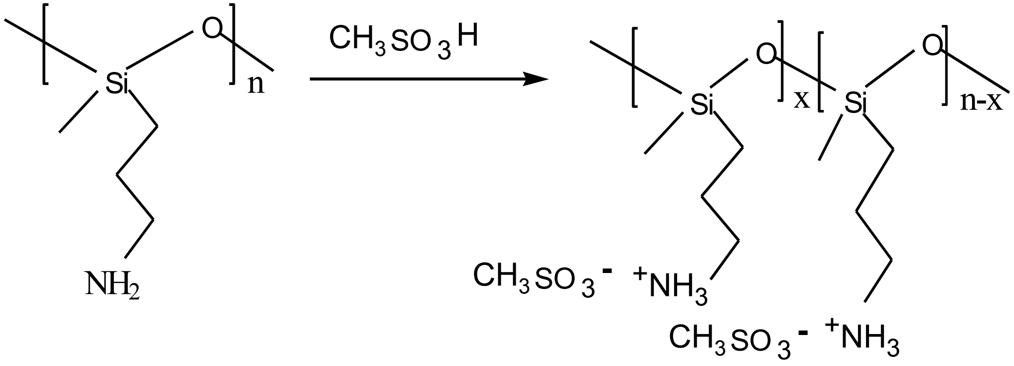


Summary on non-leachable Siloxane-based PEMs

Two non-leachable siloxane 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

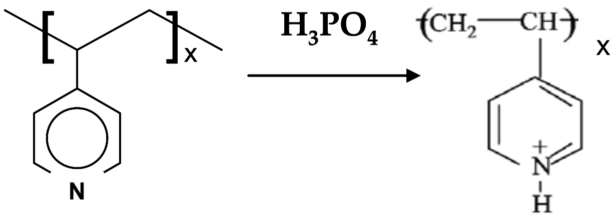
Pro: These data illustrate using a *protic-salt membrane* as a “dry” proton-conductor in a fuel cell membrane.

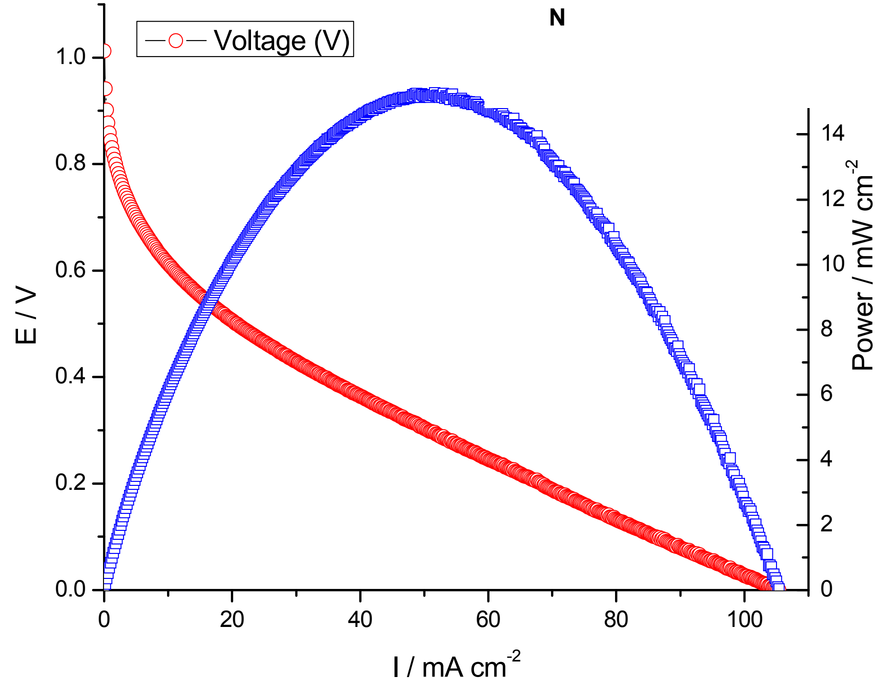
Con: siloxane membranes have limited physical stability (soft and water soluble) resulting in low performance (low open circuit voltage OCV, 0.45V, and low power, 2mW/cm^2) in a fuel cell due to reactant crossover in this PEM.

What’s next?

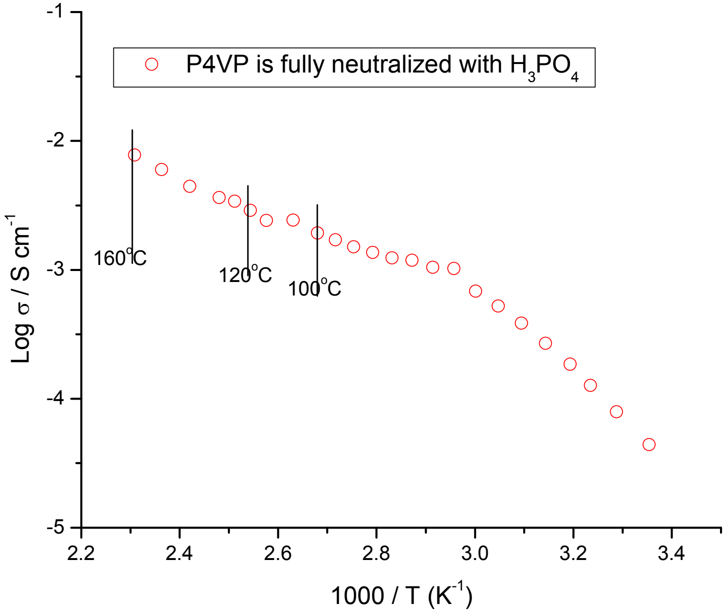
FY09: Technical Accomplishments: non-leachable PEM

Poly Vinyl Pyridinium Phosphate (PVPP)





I/V curve for H_2/O_2 fuel-cell with poly vinyl pyridine fully neutralized with phosphoric acid. Pt loading =0.5 mg/cm² E-Tek ELAT electrodes. σ =0.005 S/cm. Temp. = 162°C;

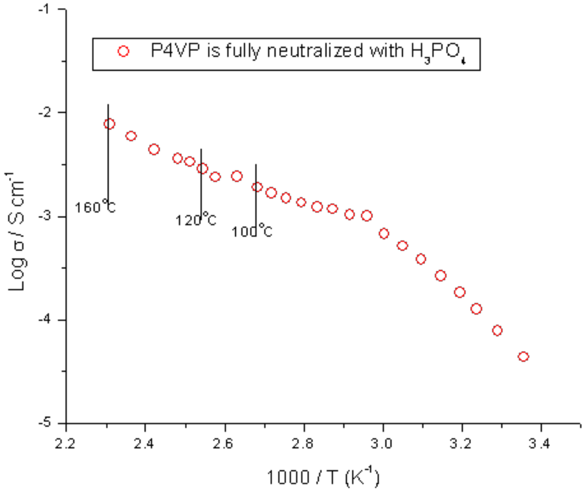


Conductivity of poly vinyl pyridine with 1 H3PO4 per 1 pyridine as a function of temperature.

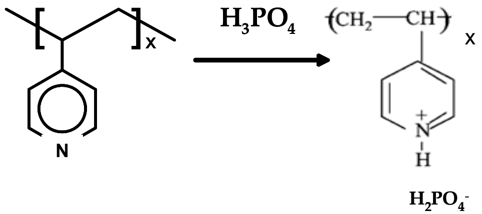
FY09: Technical result: Liquid versus Solid Membrane of Pyridine Phosphate

Poly vinyl pyridine with 1 H_3PO_4 per 1 pyridine

Solid Non-Leachable
Membrane Electrolyte

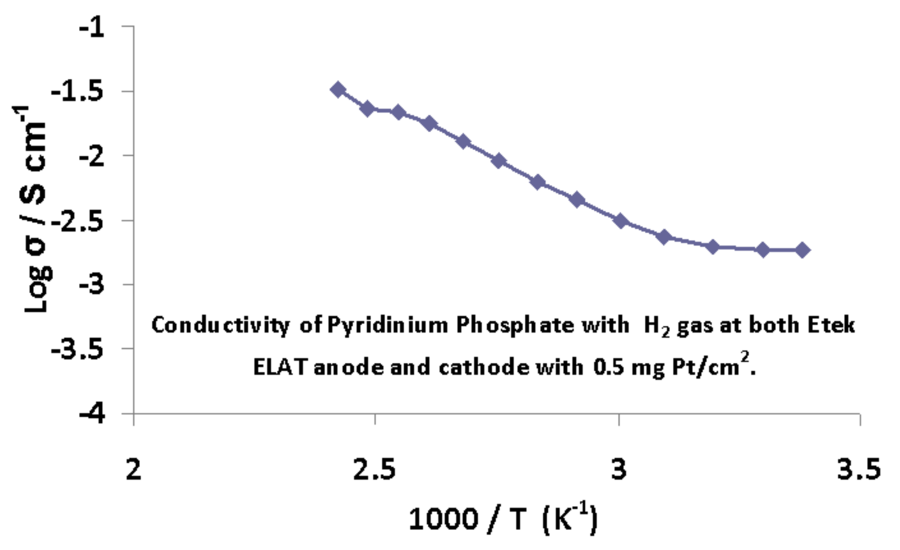


Conductivity of non-leachable solid poly vinyl pyridine with 1 H_3PO_4 per 1 pyridine proton conducting PEM as a function of temperature.



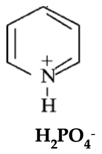
Liquid pyridinium phosphate

Analogous
Liquid Electrolyte

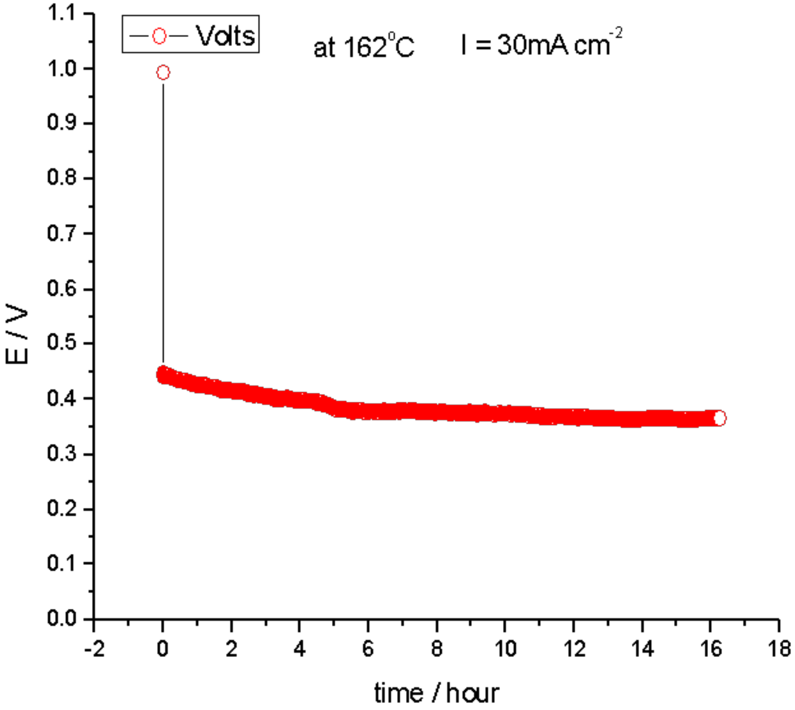


Conductivity of liquid pyridinium phosphate as a function of temperature, H_2 gas fed to both anode and cathode. Electrodes are E-tek ELAT with 0.5 mg Pt/cm^2.

SIMILAR !



Technical Result: Cell voltage in time at constant load for a H_2/O_2 fuel-cell with a PVPP membrane



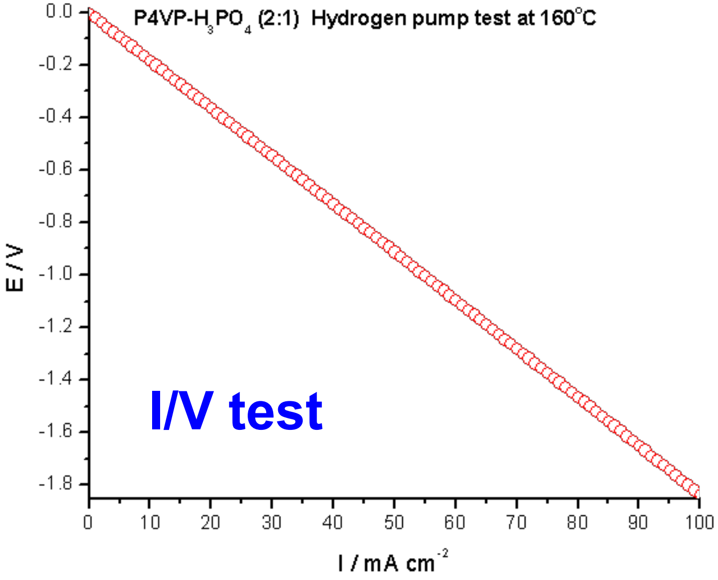
Cell voltage in time at constant load for a H_2/O_2 fuel-cell with a membrane made of polyvinylpyridine in which each pyridine is reacted with phosphoric acid. Pt loading =0.5 mg/cm^2 E-Tek ELAT electrodes. Load is 30 mA/cm^2. Temperature = 162°C.

The cell was run overnight under constant load of 30 mA/cm^2. After this overnight test, the polarization (I/V test) did not change.

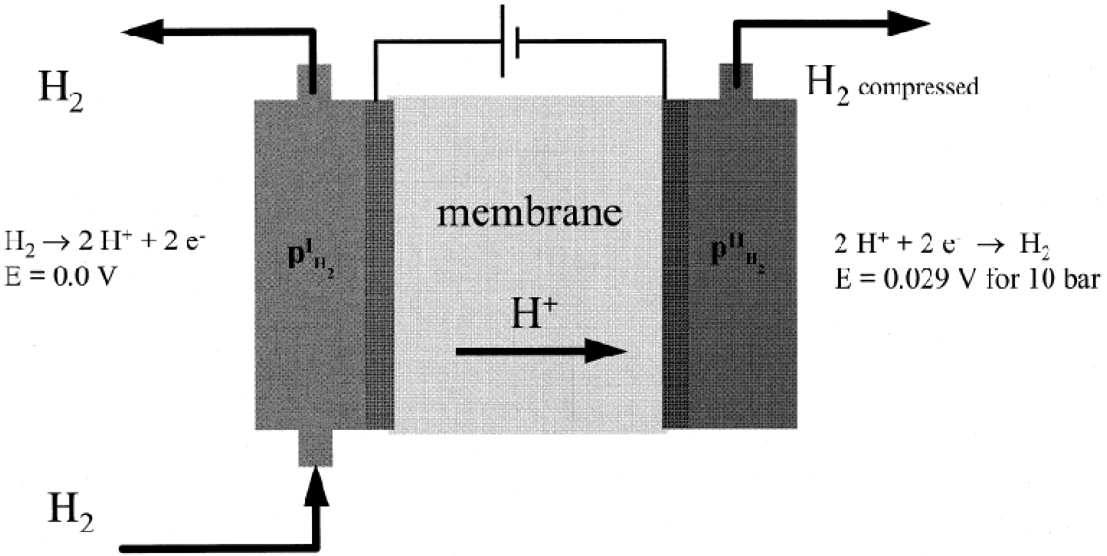
Overnight fuel cell stability while passing H^+ current

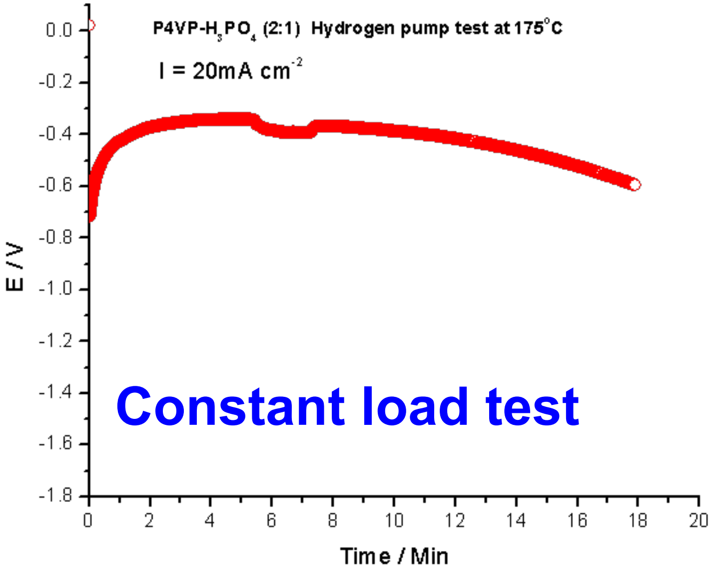
Strong evidence that the proton is hopping through this solid membrane that has no leachable ions or solvents.

Technical Result: E-chem H-Pump with PVPP membrane



I/V test





Constant load test

$V = V_0 + RT/2F \ln [p^{II}_{H2} / p^{I}_{H2}]$:

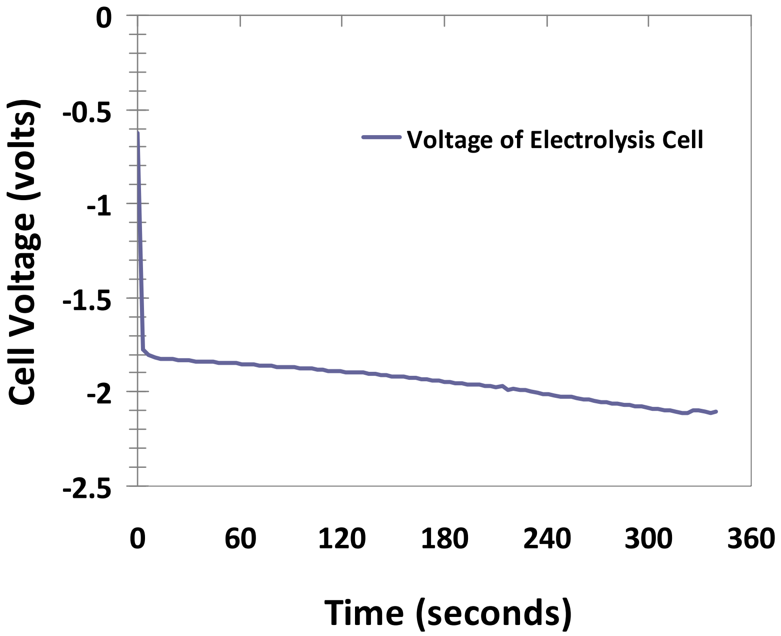
Electrochemical H_2 pressurization

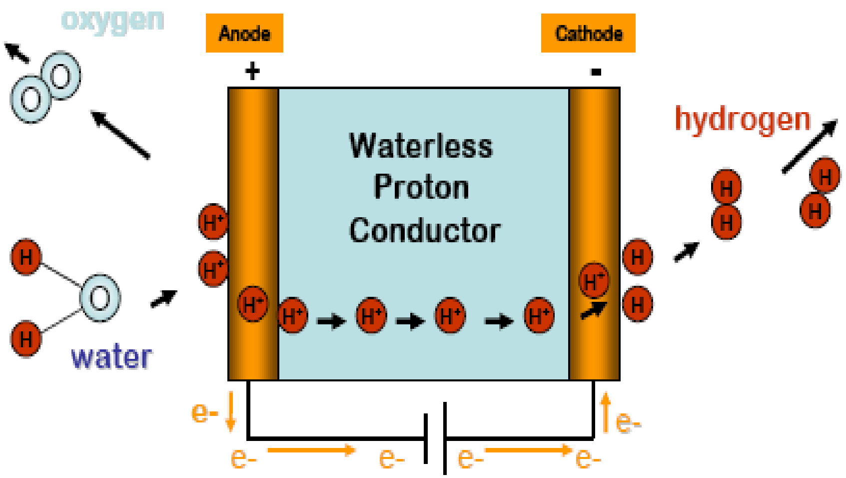
Pt loading =0.5 mg/cm^2 E-Tek ELAT electrodes.

Proton is the only ion being conducted

Technical Result: Galvanostatic electrolysis of water on Pt in PVPP PEM cell

PVPP membrane requires no water for H^+ conduction yet allows water electrolysis





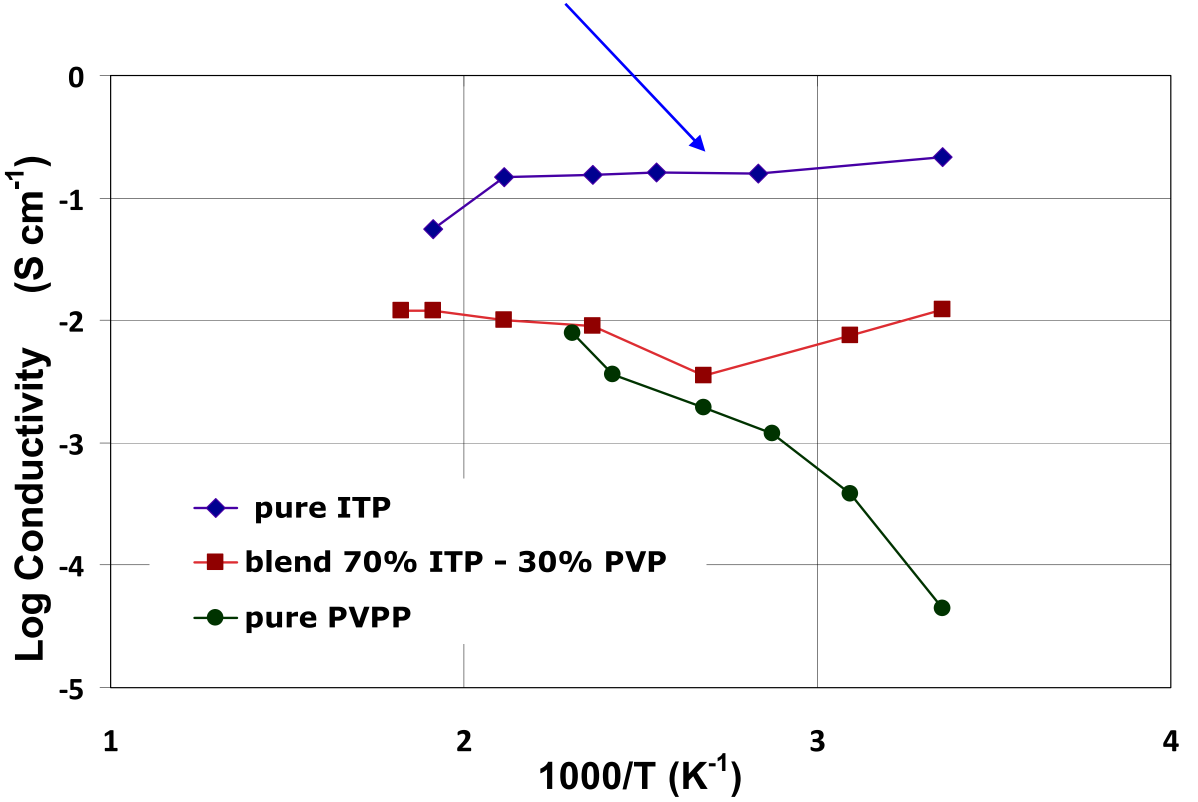
Cell voltage in time for the galvanostatic electrolysis of water on E-tek ELAT electrode with Pt loading of 0.5 mg/cm^2 used for anode and cathode with a solid electrolyte membrane (t=35 mil) of polyvinyl pyridinium phosphate (PV P$^+$: $H_2PO_4^-$; 1:1). Constant cell load current = 11 mA/cm^2, Cell Temperature = 150^{o}C, Argon flow humidified at 80^{o}C.

Proton only conducted

Technical Result: Proton Conducting Membranes of Ceramic & Ceramic Organic Polymer Blend

Conductivity of neat ITP

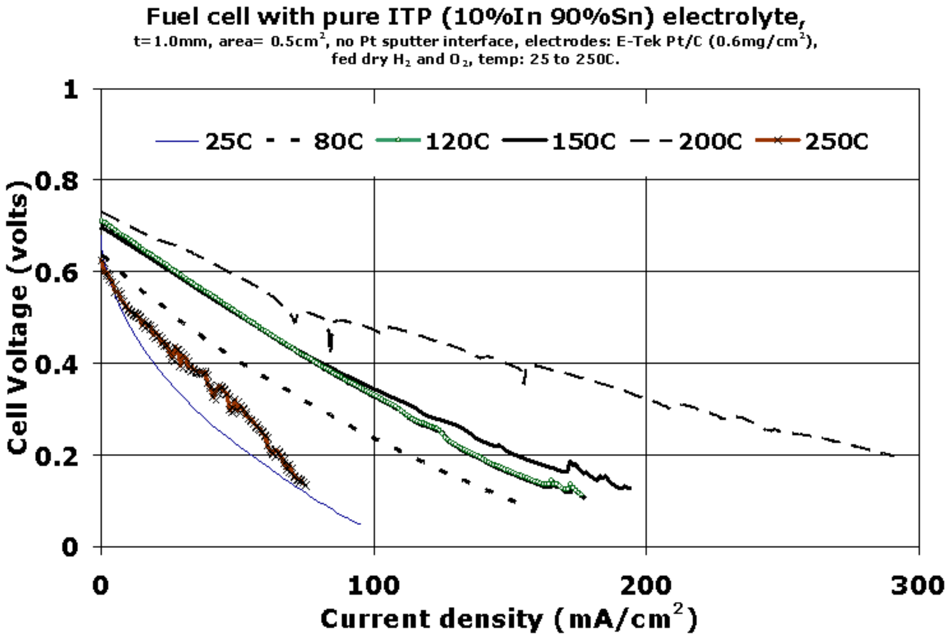
> 0.1 S/cm* from 25C to 200C



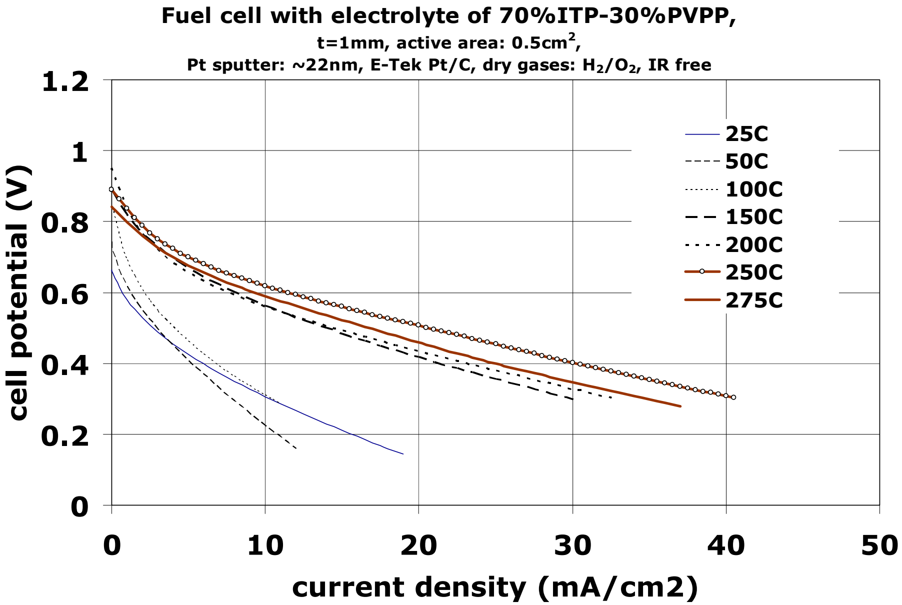
***Sample sent to Bekktech in March 2009**

Technical Result:
I/V curve for a fuel cell with neat ITP vs. a 70% ITP-30%PVPP membrane

Neat ITP


Fuel cell with pure ITP (10%In 90%Sn) electrolyte,
t=1.0mm, area= 0.5cm^2, no Pt sputter interface, electrodes: E-Tek Pt/C (0.6mg/cm^2), fed dry H_2 and O_2, temp: 25 to 250C.

Blend 70% ITP 30% PVPP


Fuel cell with electrolyte of 70%ITP-30%PVPP,
t=1mm, active area: 0.5cm^2,
Pt sputter: ~22nm, E-Tek Pt/C, dry gases: H_2/O_2, IR free

t=1mm, active area: 0.5cm^2 and electrode of ~22nm sputtered Pt
and
E-Tek GDL fed dry H_2/O_2, Room Temperature to 250C

Conclusions about Membranes with pure ITP and ITP-PVPP Blend

The best fuel cell results with ITP-PVPP blend were at T >200C, which is unusual … since TGA suggests that the PVPP organic compound should have decomposed.

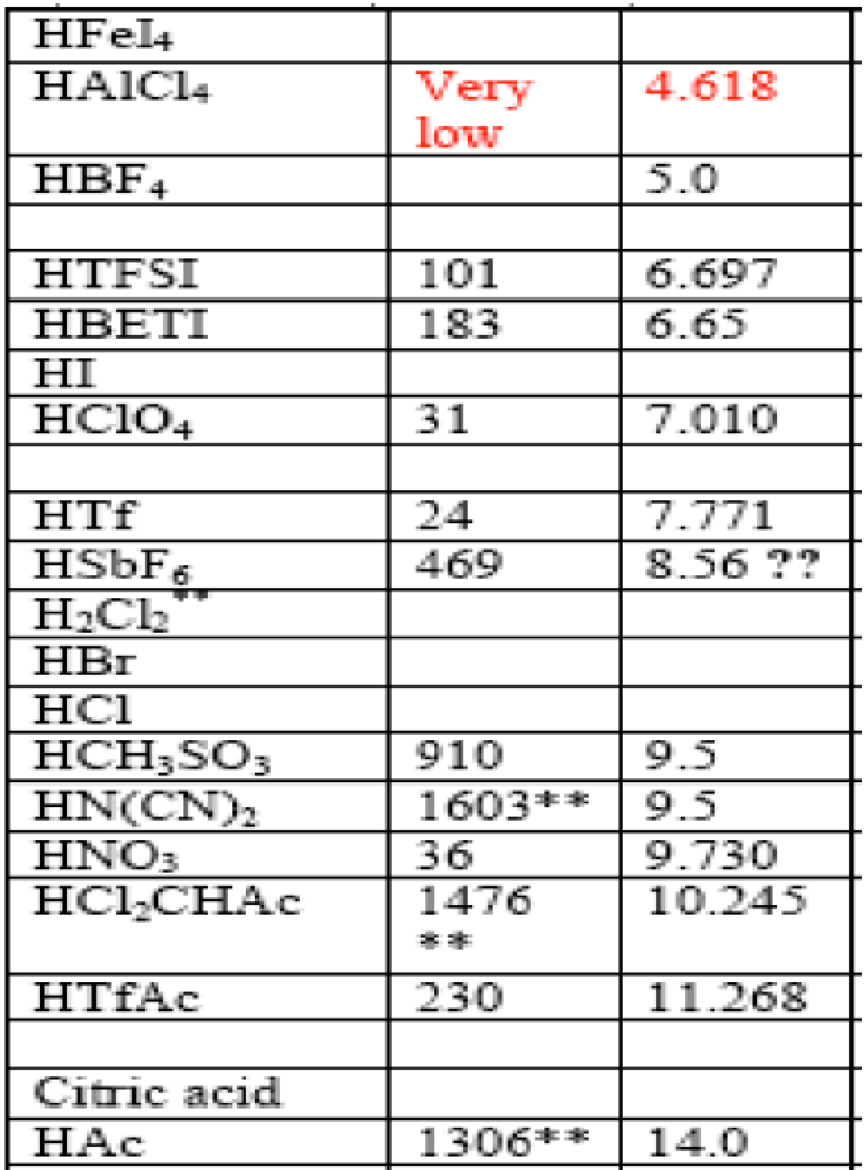
The highest conductivity found for ITP-pVPP blend was ~ 0.014 S/cm @ 275C.
There was an unexpected drop in conductivity between 25C and 100C.

Pure ITP (10% In 90% Sn), has better conductivity than the blended pellet, which is expected since the conductivity of pure PVPP is lower than pure ITP.

Pure ITP showed higher power than blend

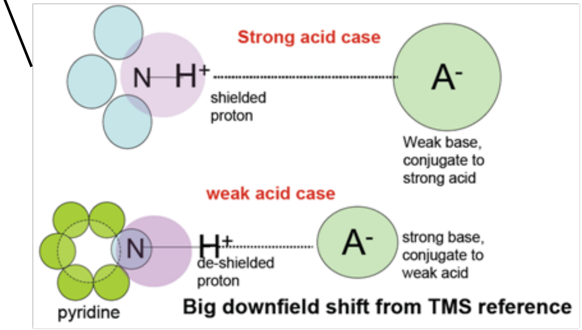
Still finding a suitable ITP-polymer blend is desirable to stop crossover in pure ceramic ITP

Technical Accomplishment: classifying strong- and super-acids
Table of *N-H Proton chemical shifts for pILs:



Acid	H_2O in pIL (ppm)	δ (N-H) (ppm)
$HFeI_4$		
$HAlCl_4$	Very low	4.618
HBF_4		5.0
HTFSI	101	6.697
HBETI	183	6.65
HI		
$HClO_4$	31	7.010
HTf	24	7.771
$HSbF_6$**	469	8.56 ??
H_2Cl_2		
HBr		
HCl		
HCH_3SO_3	910	9.5
$HN(CN)_2$	1603**	9.5
HNO_3	36	9.730
HCl_2CHAc	1476 **	10.245
HTfAc	230	11.268
Citric acid		
HAc	1306**	14.0

*for base diethylmethylamine (DEMA), pKa (aqueous) = 10.55



From: J.-P.Belieres in the I&EC division, Paper #82, ACS, Philadelphia, PA 2008

Chemical shift can be used for characterizing H+ environment

Future Work

- ☐ Continue to make and characterize pILs to model membranes
  - i. Focus on non-leachable PEMs consisting of novel polymers and polymer blends with ceramics which allow all acid and base moieties to be immobilized by covalent and electrostatic binding.
    - a. ITP
    - b. Develop Polyphosphazenes as low EW, heat-melt formed and water insoluble membranes, Polyvinyl pyridines (PVPP), fluorinated (PVPP)
    - c. Blends of a and b.

- ☐ 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 O_2 reduction activity on Pt and non-Pt catalysts
  - In situ Electrochemistry and FTIR to determine adsorption of hydrocarbon versus fluorocarbon pILs

Summary

- ☐ **Relevance: simpler more efficient fuel cell by using protic salt electrolyte membranes**

- ☐ **Approach: Protic salt membrane electrolytes conduct proton with no bulk water giving**
  - **simplified fuel cell with:**
    - **no humidifier**
    - **smaller radiator**
  - **little or no Pt-OH on Pt surface for:**
    - **Lower overpotential for oxygen reduction, therefore higher cell efficiency**
    - **Possibly lower corrosion of Pt and lower Pt particle growth**

- ☐ **Technical accomplishments: Status of Protic Ionic Liquids (pILs)**
  - **Designed pILs for high proton conductivity and fuel cell performance**
  - **Found stable pILs**
  - **Combined high activity and stability in some cases**
  - **Demonstrated proton conductivity and fuel cell performance in non-leachable protic salt polymer and ceramic membranes**
  - **Synthesized new poly-phosphazene polymer with pendant nitrogen heterocycles**
  - **ITP and polymer blends showed high proton conductivity from 25 to 200C**

- ☐ **Proposed Future Work:**
  - **Focus on pILs as guides to making non-leachable proton conducting salt membranes ITP, poly-phosphazenes, and blends**
  - **Continue NMR characterization of relative proton and counterion mobilities.**
  - **Chemical NMR imaging of membranes as a function of proton current.**

Collaborations

Project collaborators:

1. Don Gervasio (PI) in collaboration with C.A. Angell, R. Marzke, J. Yarger (co-PI) at Arizona State University
2. W. Youngs (co-PI) University of Akron
3. Industry, Boeing Co.