

Protic Salt Polymer Membranes:

High-Temperature Water-Free Proton-Conducting Membranes

Name: Don Gervasio (PI)

Organization: University of Arizona

gervasio@email.arizona.edu

in collaboration with

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

Arizona State University;

W. Youngs (co-PI)

University of Akron

Tuesday, 8 June 2010 6:30-8:30 PM

Project ID: FC060

Overview

Timeline

- January 15, 2006
- January 14, 2011
 - go/no go end of year 3
 - go/no go March 2010
- 80% 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
 - \$300,000
- Funding received in FY09
 - \$300,000
- Funding received in FY10
 - \$300,000 (pending go/no-go)

Barriers

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

Partners

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

- DOE Technology Development Manager: Kathi Epping
- DOE Project Officer: Greg Kleen
- ANL Technical Advisor: Thomas Benjamin

Relevance

OBJECTIVE:

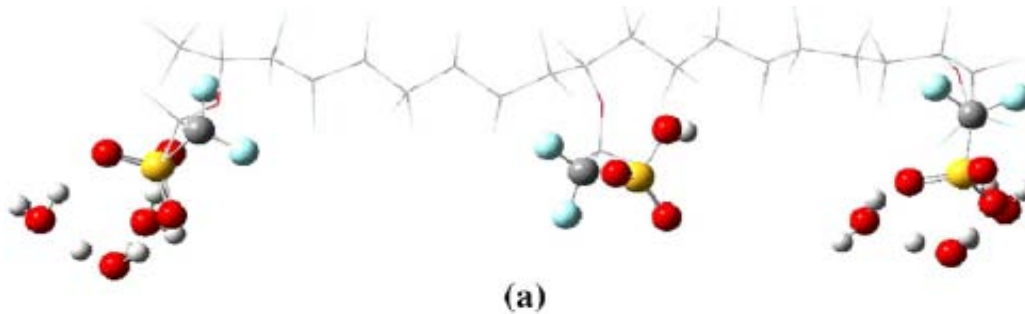
to make a **solid water-insoluble anhydrous proton-conducting electrolyte membrane** that has good

o *MEMBRANE PERFORMANCE*

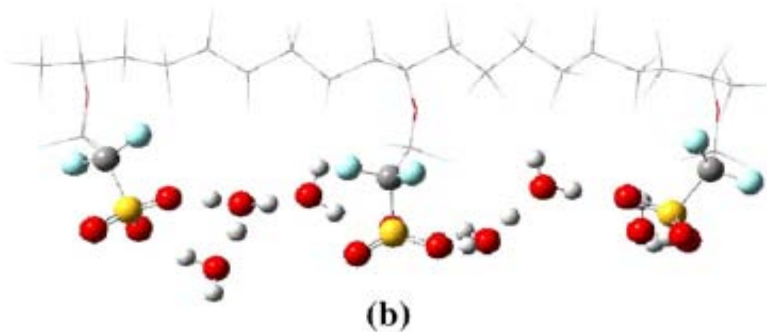
- proton conductivity that surpasses the 2009 target of $> 0.1 \text{ S/cm}$ at 120°C and 50% RH
- effectively having no co-transport of molecular species with proton
- good mechanical strength and chemical stability

o *ELECTRODE PERFORMANCE*

- assisting catalyst to promote reduced activation overvoltage



a) Non-conducting acid PEM
Low water form



b) Conducting acid PEM
High water form

Acid membrane: A hydrated acid membrane conducts proton with co-transport of water only under condition (b), in which a repeat unit of pendant acid and 3 or more waters contacts an adjacent repeat units.

Salt membrane: A salt repeat unit contacts adjacent salt unit to conduct proton with no co-transport of water.

Relevance

Benefits

Water-independent highly proton-conducting membrane with Lower activation overvoltage leads to higher efficiency

No co-transport of water and higher temperature operation lead to elimination of bulky humidifier and radiator for a more compact and efficient power-generating system.

Approach

SYNTHESIS OF “DRY” PROTON ELECTROLYTE MEMBRANES (PEMs)

- PEMs made based on “solvent free” liquid salts called *protic ionic liquids (pILs)*.
- *pILs used to model ionic membranes* (stability, conductivity).
- *Acid and base moieties in pIL are varied* to optimize electrolyte properties.
- *Inorganic and organic polymer moieties are varied* for
 - 1) reducing membrane water solubility
 - 2) increasing density of covalently and electrostatically bound (non-leachable) ions to promote both
 - i) mechanical stability
 - ii) high proton-conductivity in solid membranes.

CHARACTERIZATION of PEMs

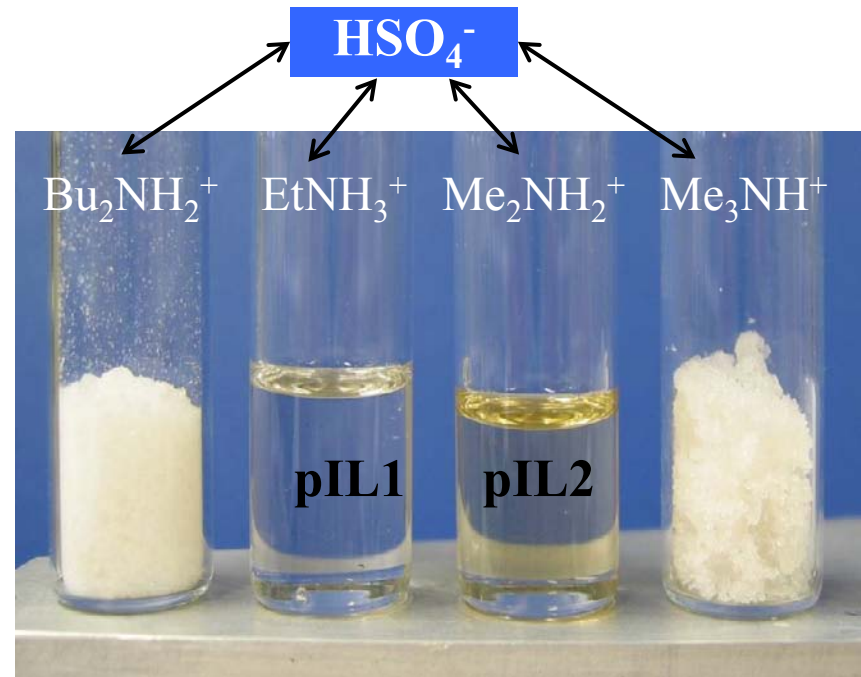
- Proton conductivity by electrochemical impedance spectroscopy (EIS) from -20 to 120°C
- Thermal oxidative stability of electrolytes by Thermal Gravimetric Analysis (TGA) from -20 to 120°C
- Electrolyte stability and electrode polarization by voltammetry on Pt and non-Pt catalysts
- Fuel cell performance/stability by steady state I/V curves
- The mechanism of transport of protons, anions, and molecules by 3 NMR methods:
 1. Pulse-field-gradient NMR to determine the diffusivity of ions,
 2. Multi-pulse 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

Ionic Liquid and protic Ionic Liquids (pILs) Properties

- “Ionic Liquids” are salts with melting points below 100°C
- Protic Ionic Liquids (pILs) have mobile protons and are made when a proton is transferred from a Bronsted acid to a Bronsted base
- Low vapor pressures
- High ionic conductivity
- Excellent solvating properties
- Thermally stable
- Useful for both high and low temperature applications.
- pILs tailored by choosing base and acid
- Solvent-free proton-conducting electrolytes

Examples of 2 hydrogen sulfate pILs



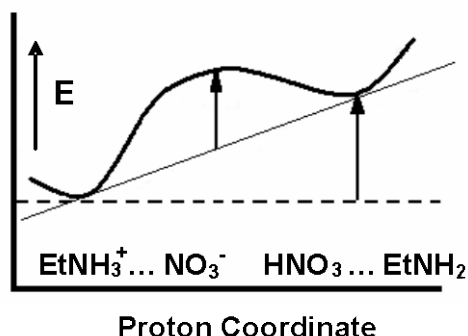
Membranes are modeled by pILs and made with immobilized pIL moieties.

PROTIC IONIC LIQUID (pIL) CONCEPTS: Gurney Diagram

Energetics of proton transfer

□ 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),

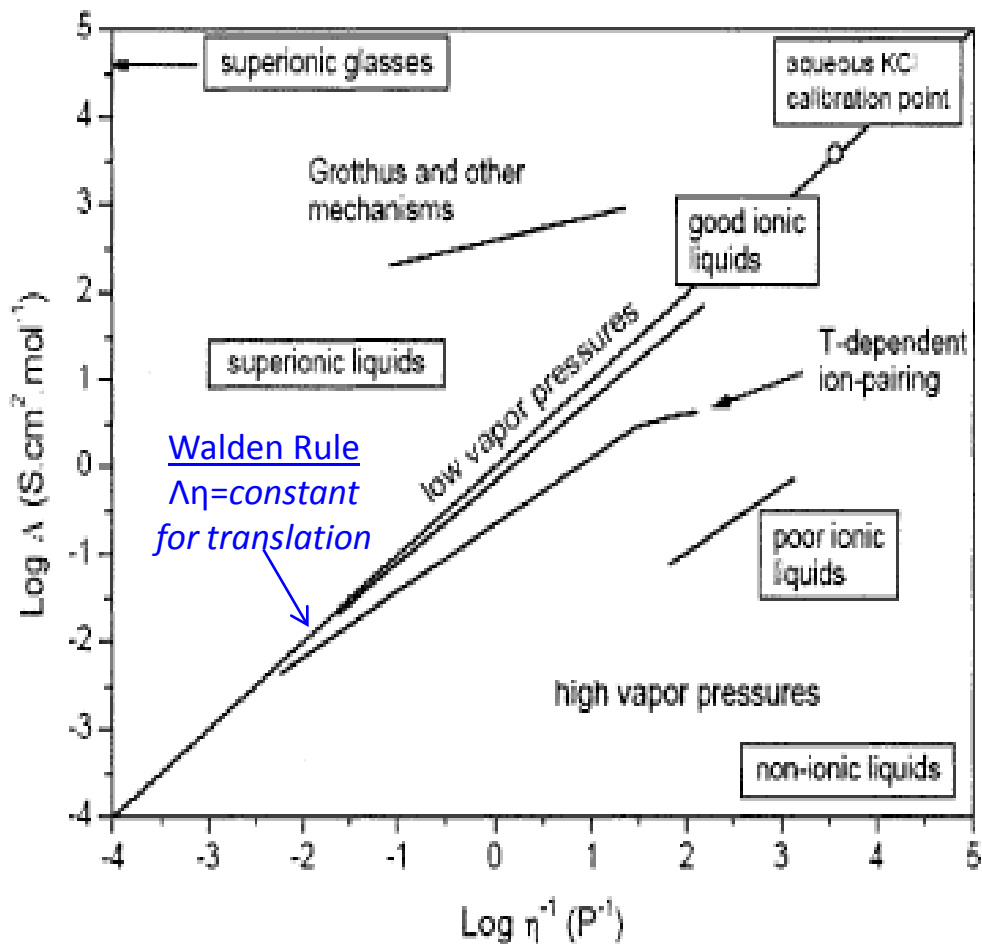
	Occupied	Vacant	pK _a	E (eV)
Acid Electrolytes	HSbF ₆	SbF ₆ ⁻		
	HTf	Tf ⁻	-14	0.83
	HSO ₃ F	SO ₃ F ⁻		
	HClO ₄	ClO ₄ ⁻	-10	
	H ₂ SO ₄	HSO ₄ ⁻		
	HPO ₂ F ₂	PO ₂ F ₂ ⁻		
	HNO ₃	NO ₃ ⁻		
	CH ₃ SO ₃ H	CH ₃ SO ₃ ⁻		
	CF ₃ COOH	CF ₃ COO ⁻		
	H ₃ O ⁺	H ₂ O	0	0
Neutral Electrolytes	HF	F ⁻		
	HIm ⁺	Im		
	EtNH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

EAN
Δpk = 14

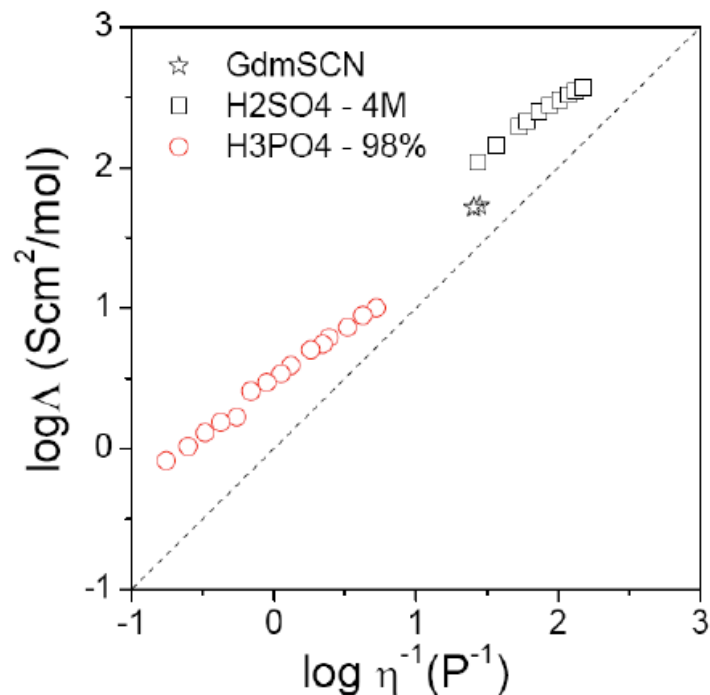
Gurney proton energy level diagram.
For any pair of levels, the stable entities are upper right and lower left.

PROTIC IONIC LIQUID (pIL) CONCEPTS: Walden Plot

Physiochemical classification of ion conductors



Example of proton hopping pIL



Walden plots of selected electrolyte systems, including anhydrous pIL guanidinium (Gdm⁺) thiocyanate (SCN⁻) showing superionic (proton hopping) character.

Milestones

MILESTONES

Year 1: Make protic ionic liquids with enhanced stability (fluorocarbon, deactivated hydrocarbon, etc.) and evaluate proton conductivity and oxidative stability.

Year 2 (3Q): Demonstrate conductivity of 0.07 S/cm at a maximum of 80% relative humidity at 100 °C.

Year 3 (3Q) also Go/No Go Decision Point: Demonstrate conductivity of greater than 0.1 S/cm at 100 °C and 1.5 kPa water vapor partial pressure (50% relative humidity measured at room temperature).

Year 4: Establish acid/base pairs for ionic liquid electrolyte with long term (> 5000 h) stability.

Year 4 (3Q) Go/No Go Decision Point: Demonstrate conductivity of greater than 0.1 S/cm at 120 °C and 50% relative humidity using an ITP blend, as measured by Bekktech.

Year 5: Demonstrate a membrane with no leachable species at a maximum of 1.5 kPa water vapor partial pressure (50% relative humidity measured at room temperature) with a proton conductivity of greater than 0.1 S/cm at 120 °C > T > 80 °C with conductivity greater than 0.07 S/cm at 20 °C and 0.01 S/cm at -20 °C, with no noticeable chemical degradation for 5000 hours.

Plan & Progress

80% complete

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

80% complete

- ☐ **Task 4,8: Proton Conduction by NMR**
 - 4.1 Pulsed field gradient NMR
 - 4.2 Electrochemical NMR (eNMR)
 - 4.3 eNMR Hittorf

80% complete

- ☐ **Task 2: PEMs based on pIL concepts**
 - 2.1.1 - Porous support with a pIL
 - 2.1.2 - pIL swollen in polymers
 - 2.2 - Immobilized pIL polymer

90% complete

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

80% 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°

75% complete

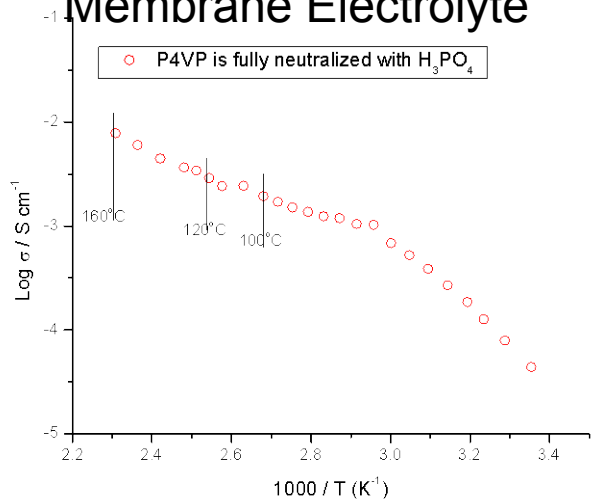
- ☐ **Task 6,7,9: Membrane Demonstration**
 - Sent 6 membranes to Bekktech & CFU
 - more in preparation
 - ITP, Akron polymer and composites of these

Technical result YR3: Liquid versus Solid Membrane “dry” H⁺ conductor

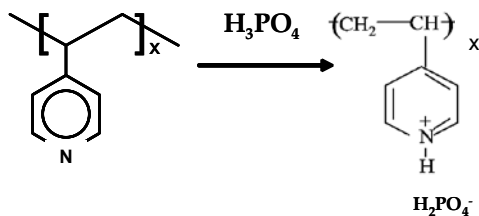
pIL and solid salt PEM are SIMILAR! Conductivity drops only 1/2 decade pIL → PEM

Solid poly vinyl pyridine with 1 H₃PO₄ per 1 pyridine

Solid Non-Leachable
Membrane Electrolyte

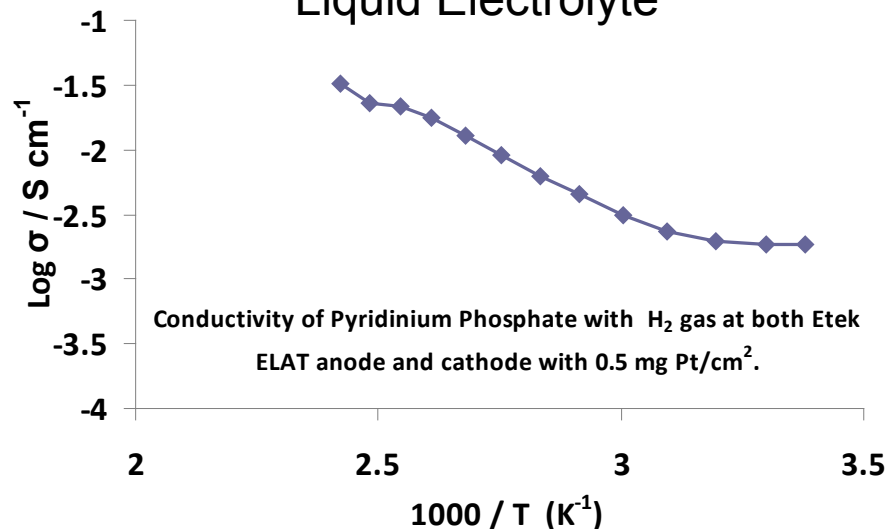


Conductivity of non-leachable solid poly vinyl pyridine with 1 H₃PO₄ per 1 pyridine proton conducting PEM as a function of temperature.

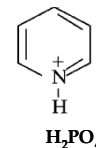


Liquid pyridinium phosphate

Analogous
Liquid Electrolyte

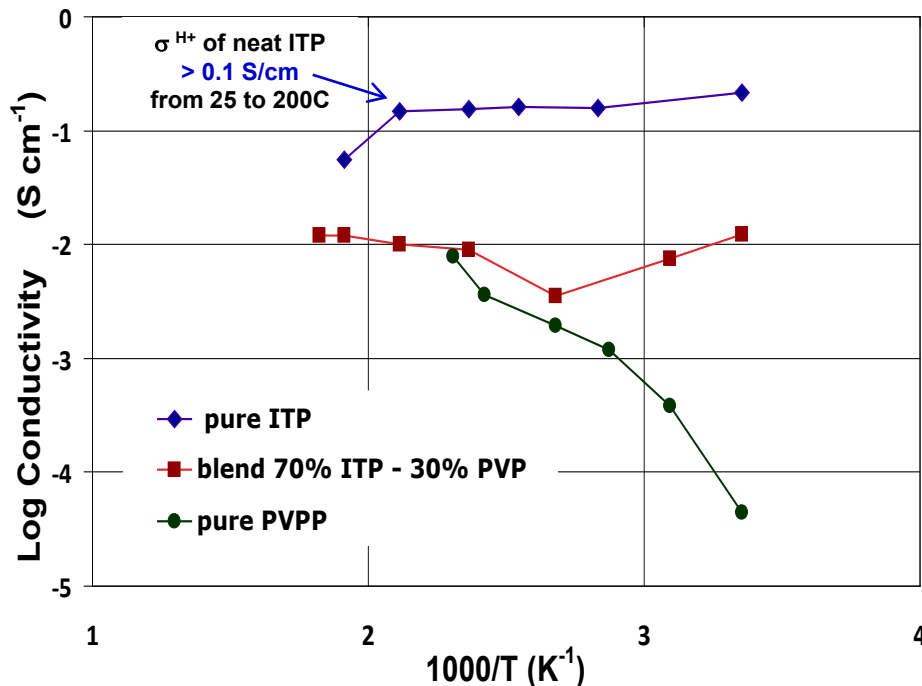


Conductivity of liquid pyridinium phosphate as a function of temperature, H₂ gas fed to both anode and cathode. Electrodes are E-tek ELAT with 0.5 mg Pt/cm².

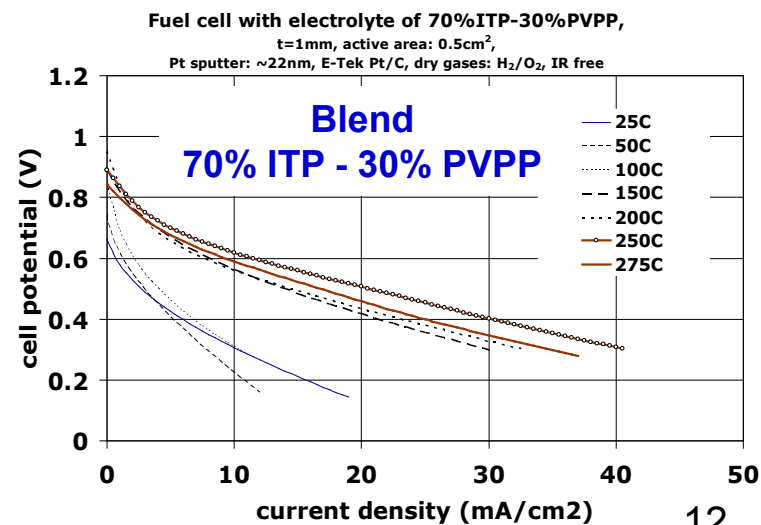
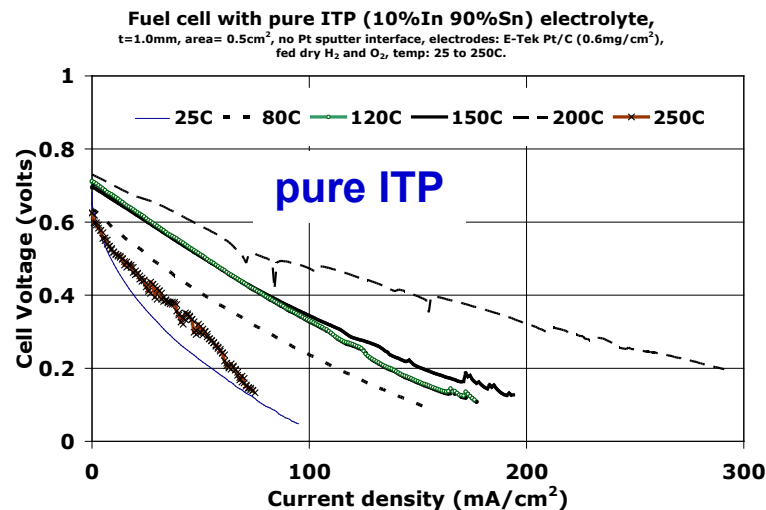


Technical Result YR 3: Solid Ceramic, Organic and Ceramic/Organic “dry” proton-conducting Polymer Membranes

Proton conductivity



Fuel Cell Polarization



Conclusions YR 1-3 research

- The best conductivity results with pure ITP membrane ($>0.1\text{ S/cm}$). The highest conductivity found for ITP-PVPP blend was $\sim 0.014\text{ S/cm}$ @ 275C.
- There was a drop in conductivity between 25C and 100C due to drop in PVPP conductivity.
- Pure ITP (10% In 90% Sn) has better conductivity than the ITP-pVPP blended pellet, since the conductivity of pure PVPP is lower than pure ITP.
- Pure ITP showed higher power but higher crossover (lower OCV) than ITP-PVPP blend.
- Finding a suitable ITP-polymer blend is desirable to stop crossover in pure ceramic ITP

Year 5 Objectives

The objective of year 5

Inorganic and organic acids and bases in protic salt membrane systematically varied to optimize proton-conductivity, stability, adsorption on Pt and mechanical properties for a high performance fuel cell.

Statement of Work for year 5

1. Develop understanding fundamental salt electrolyte properties.

E.g., proton activity and compatibility with various electrocatalysts by studying liquid protic salts as models to membranes, using 3-electrode voltammetry with a reference electrode.

2. Make polymer electrolyte membranes (PEMs) with non-leachable protic salts.

Immobilize acid and base moieties by covalent and electrostatic binding in organic polymer and compound with insoluble ceramic, indium tin phosphate (ITP, $\text{In}_{0.1}\text{Sn}_{0.9}\text{P}_2\text{O}_7$) for organic / inorganic polymer composite membrane that is flexible yet still has a high conductivity from low (sub 25°C) to high (above 120°C) temperatures and with no (0% RH) to high (100% RH) humidification.

3. Produce a water-insoluble proton-conducting organic-salt polyphosphazene membrane.

Special effort to make a free standing membrane made from a polyphosphazene backbone with immobilized pendant salt to make an organic polymer that can be formed alone or with ITP.

4. Probe molecular structure and dynamics in protic salts using Nuclear Magnetic Resonance (NMR).

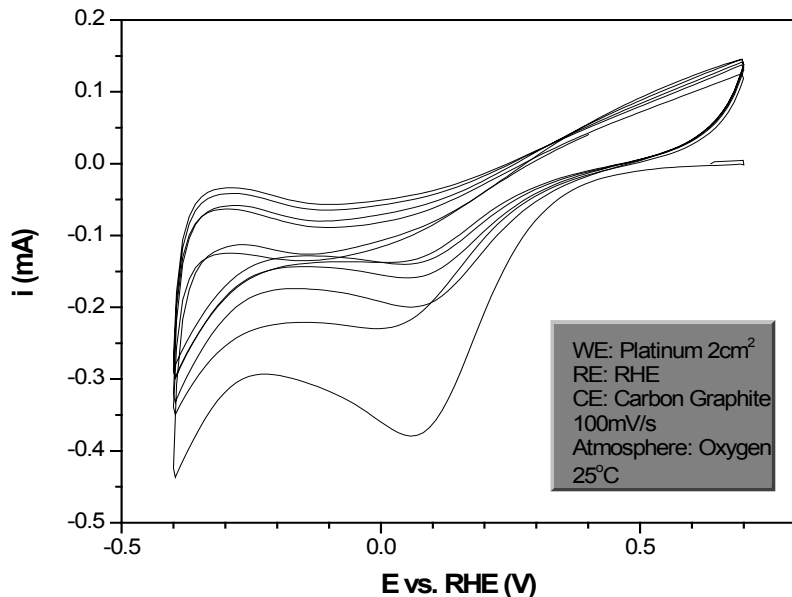
This is to gain insight into modes of diffusion of ions or molecules in new neat proton-conducting liquid and solid salt electrolytes.

Technical Result YR4:

1. Continued focus on understanding fundamental salt electrolyte properties: stability

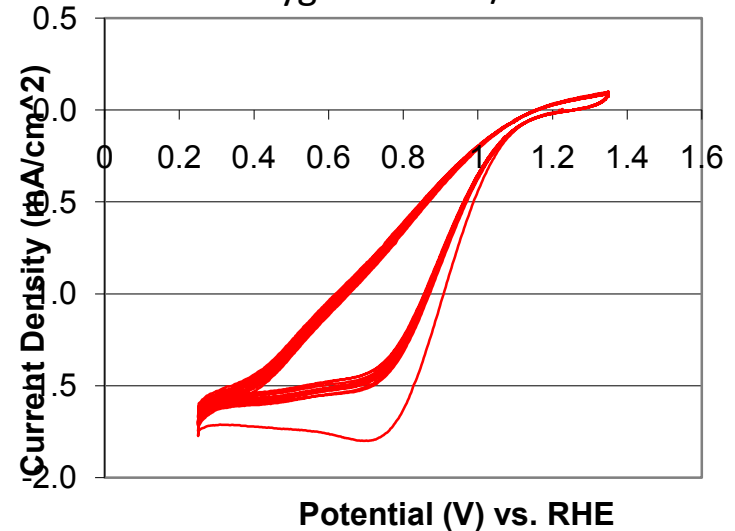
- Synthesizing ionic liquids with functional groups that are perfluorinated and rich in electronegative heteroatoms (like N) will have a stabilizing effect on the electrolyte.
- Electrochemically stable electrolytes will lead to longer lived, higher efficiency fuel cells.

EAN under oxygen at 25°C, 100mV/s



O₂ reduction diminishing as low surface area Pt is "poisoned" by decomposing EAN in minutes

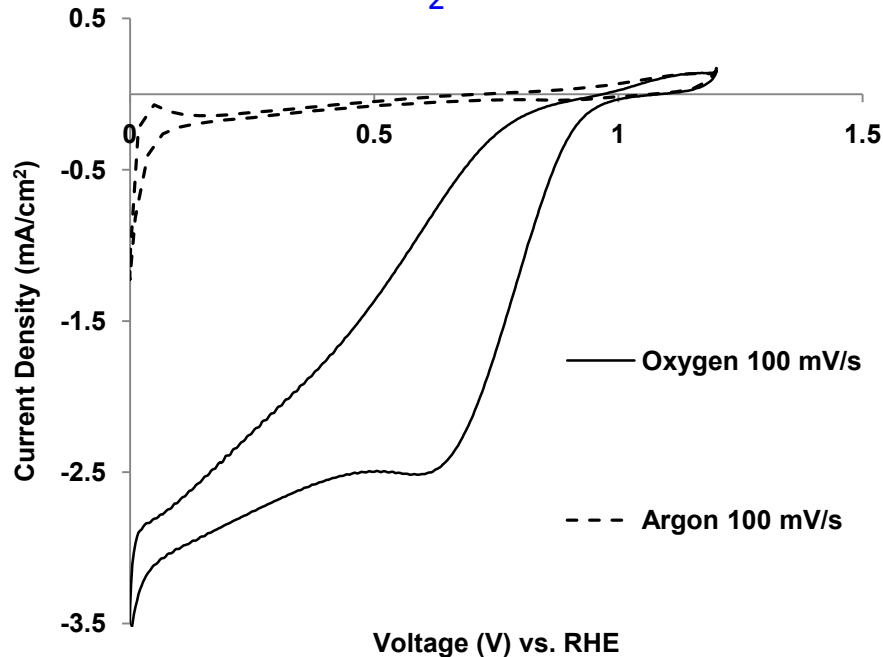
2-Fluoro-pyridinium triflate under oxygen 100mV/s 80°C



Voltammetry of 2-Fluoropyridinium triflate shows that it is stable after 100 cycles.

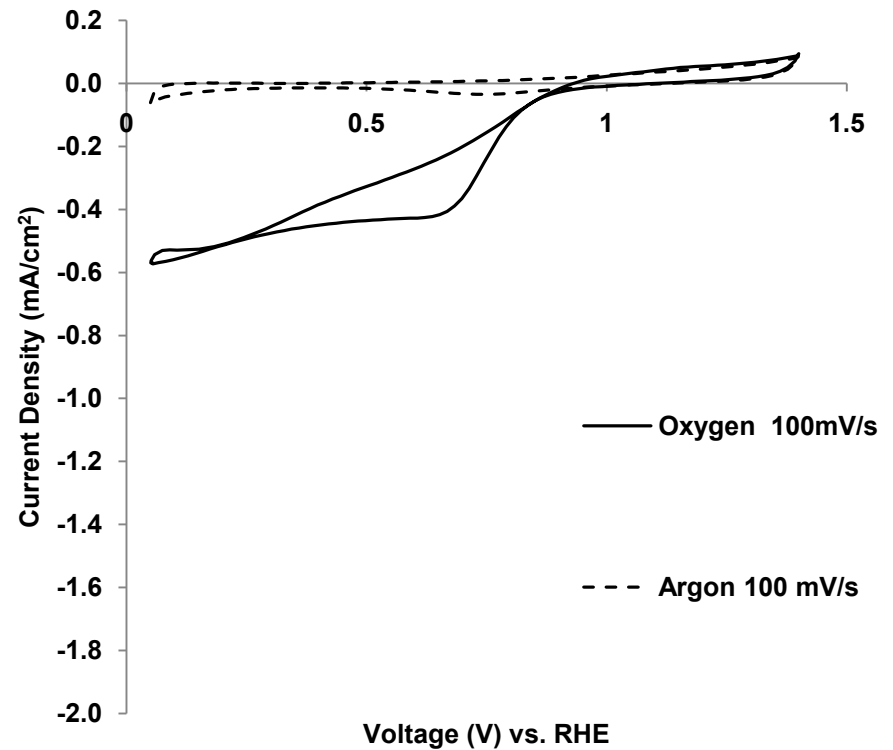
Technical Result: Effect of Water on PIL

1H₂O:1 TFMSA



1:1 TFMSA:H₂O cyclic voltammogram of Pt at 80°C under Ar (dashed line) and O₂ (solid line). P_{gas} = 1 atm. Scan rate = 100mV/s. Electrode area = 0.1 cm².

50 waters per triflic acid

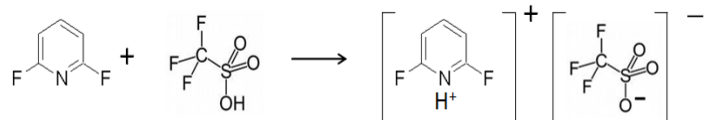


1M Triflic Acid cyclic voltammogram of Pt at 80°C under Ar (dashed line) and O₂ (solid line). P_{gas} = 1 atm. Scan rate = 100mV/s. Electrode area = 0.1 cm²

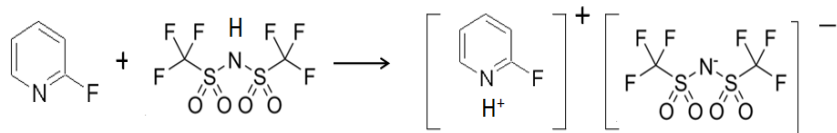
Technical Result: Stable pILs Investigated



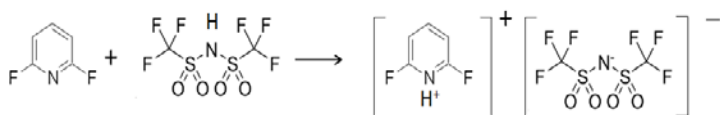
YR3 -2-Fluoro-pyridinium triflate (2-FPTf)



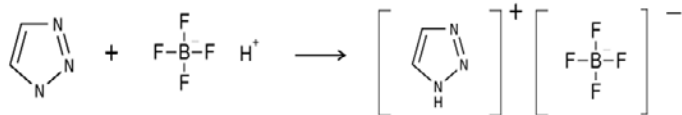
YR4- 2,6 –difluoro pyridinium triflate (2,6 –dFPTf)



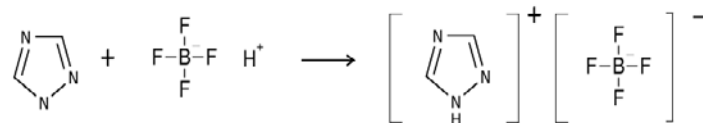
YR4- 2-fluoro-pyridinium trifluoromethyl sulfonylimide (2-FPTfSi)



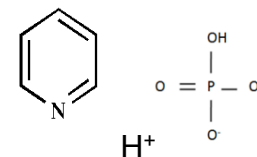
2,6 – difluoro-pyridinium trifluoromethyl sulfonylimide (2,6-dFPTfSi)



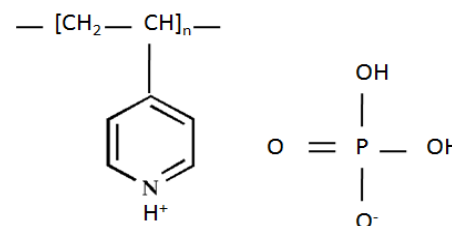
1,2,5 triazole fluoroborate (1,2,5-tABF₄)



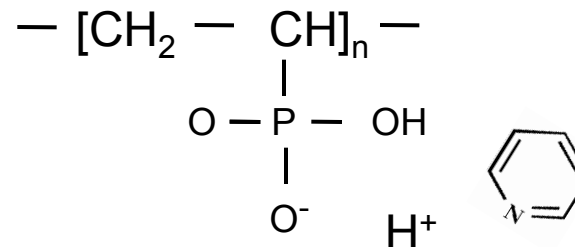
1,2,4 triazole fluoroborate (1,2,4-tABF₄)



Pyridinium phosphate ionic liquid



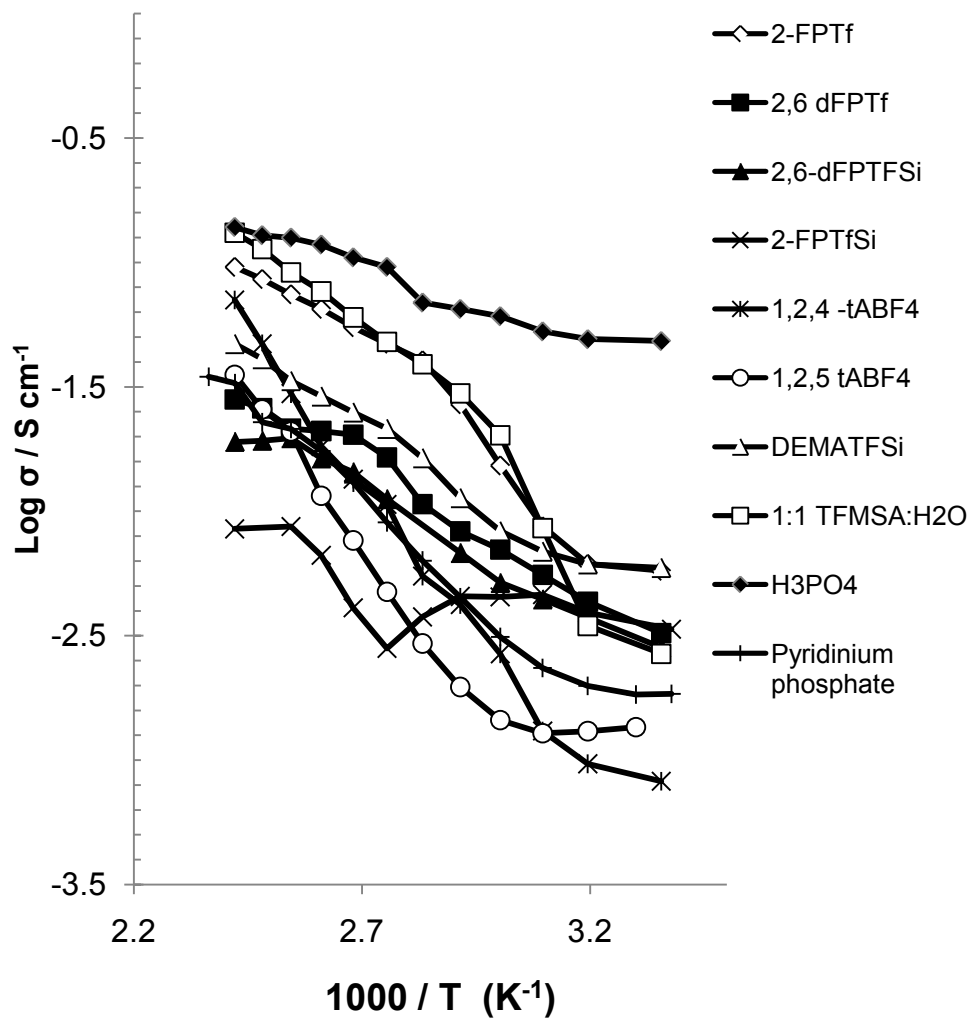
YR3 - Poly-4-vinylpyridinium phosphate (PVPyP)



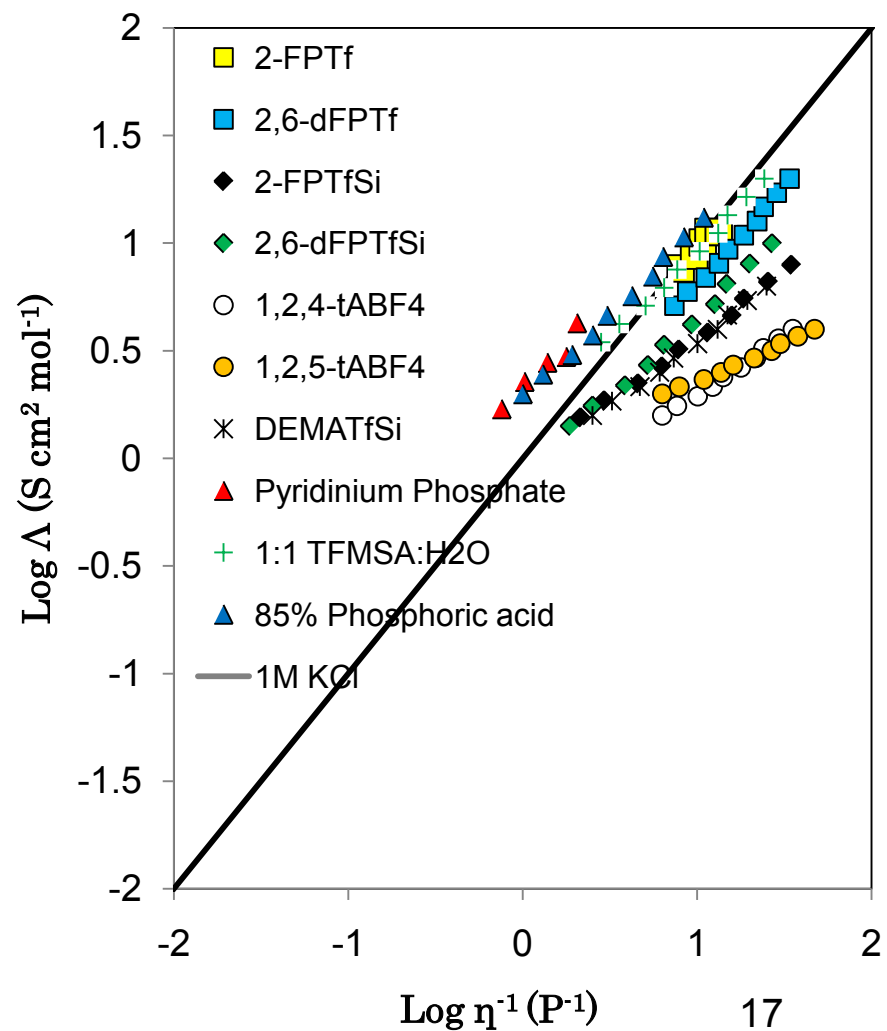
YR4 – Polyvinylphosphonate pyridinium (PVPPy)

Technical Result: Conductivity of Fluorinated pILs

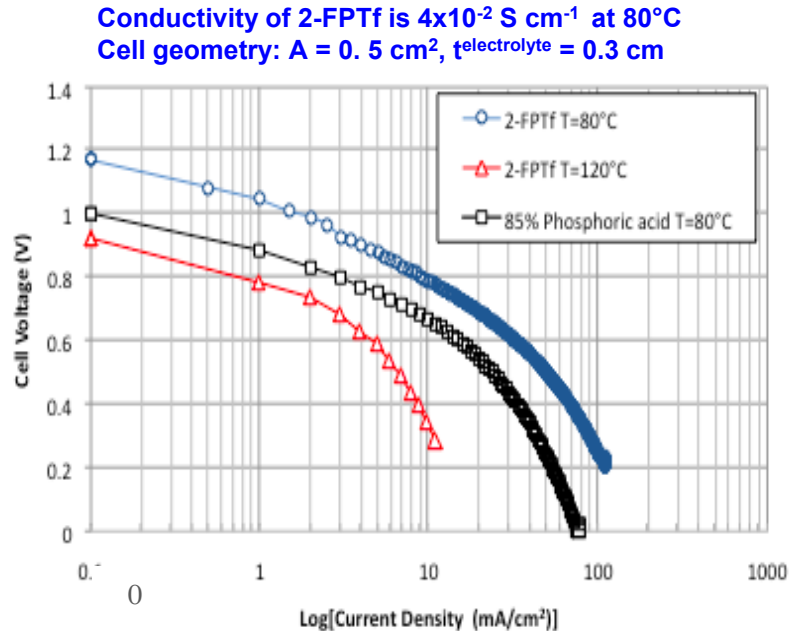
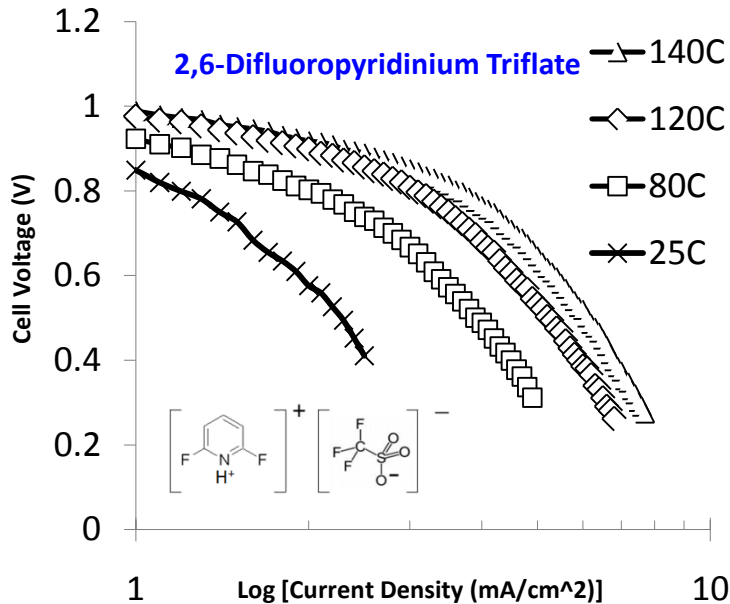
Arrhenius Plot



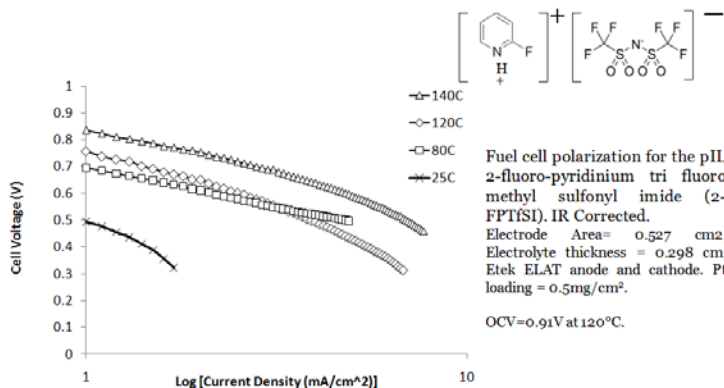
Walden Plot



Technical Result: Fuel Cell in Fluorinated pILs



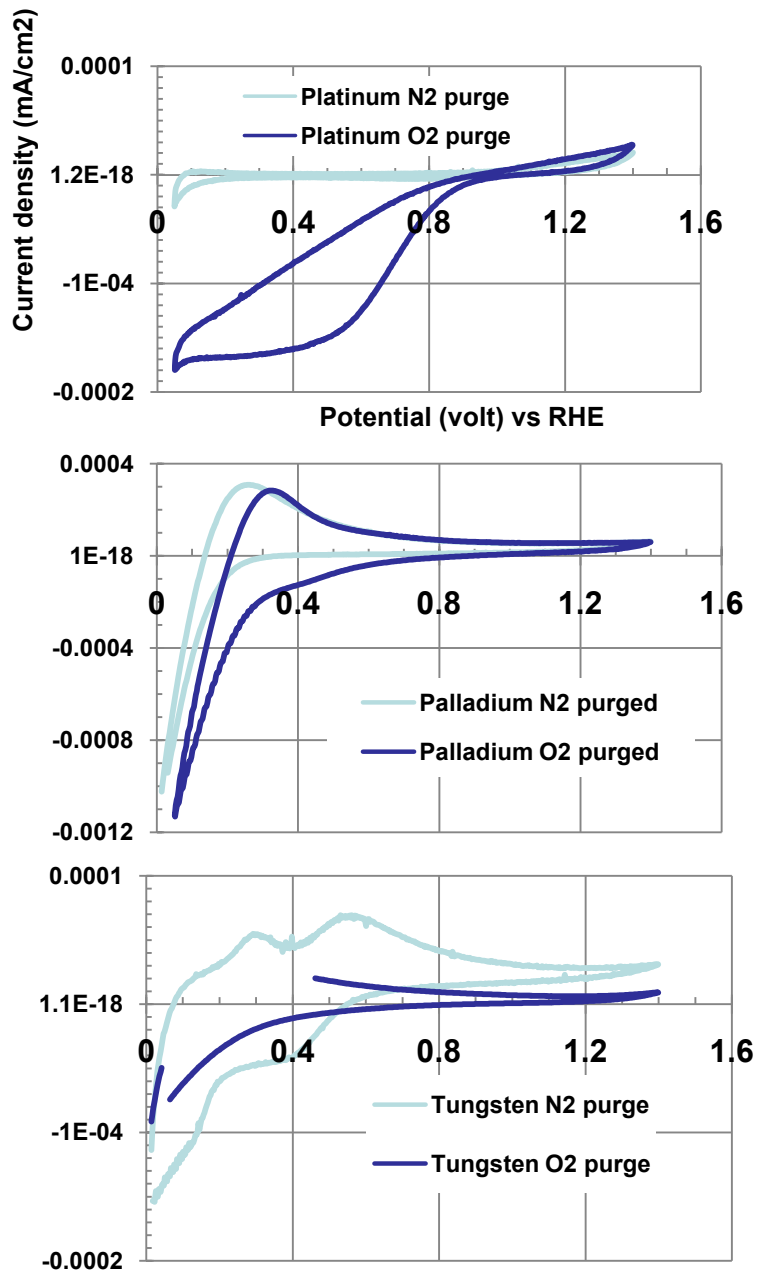
2-Fluoro-pyridinium Trifluoromethyl Sulfonylimide (2FPTFSI)



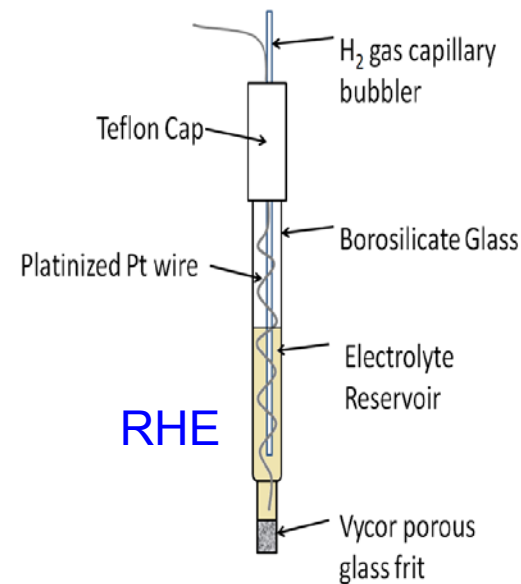
Conclusions on Stable Ionic Liquid Electrolytes

- Aqueous electrolytes cause high over potentials on a cathode
 - (e.g., Pt) at high potentials, due to metal oxide (e.g., Pt oxide) formation on the cathode surface which slows kinetics for oxygen reduction
- pILs are candidate electrolytes to lower ORR overpotential
- Fluorinated pILs are proton-conducting electrolytes which are stable under fuel cell operating conditions

Technical Result: O₂ reduction on Non-Pt metal catalysts



Wire diameter = 0.5 mm
Wire length = 1 cm
T = 25°C
SR = 50 mV/s
CE = Pt wire
Ref = RHE
Electrolyte = 2 FPTf



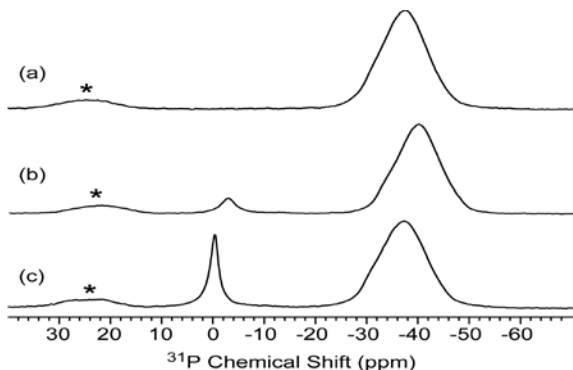
Summary

Pt, Pd, W, Au, Au Cu Al, Ti, Fe, Ni examined

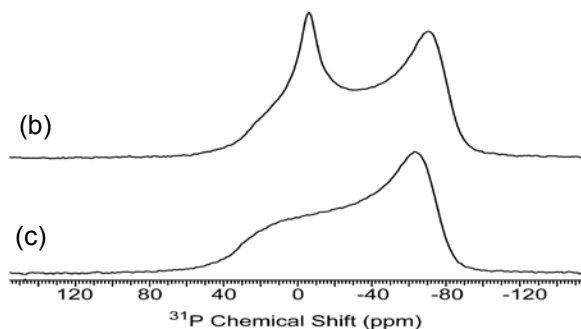
Pd and W are the only stable and active catalysts besides Pt

Technical Result: NMR of protic salt membranes

NMR probe of molecular structure and dynamics for In^{3+} -doped SnP_2O_7 samples with different phosphate levels



Phosphorus-31 MAS NMR spectra of (a) no (b) trace, and (c) excess free phosphoric acid. The spectra were collected with direct detection and 10 kHz MAS. Spinning sidebands are asterisks.



Phosphorus-31 static NMR spectra of (a) trace and (b) free phosphoric acid

Multi-nuclear solid-state phosphorus-31 magic angle spinning (MAS) NMR

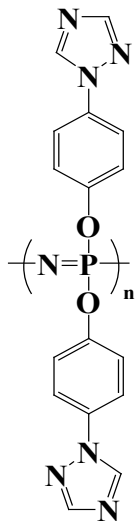
- Broad ^{31}P resonance centered near -36 ppm is observed that spans nearly 20 ppm is like with SnP_2O_7 * however, the resonance observed here is broader than previous ^{31}P MAS NMR spectra for SnP_2O_7 [*Fayon, F.; King, I. J.; Harris, R. K.; Gover, R. K. B.; Evans, J. S. O.; Massiot, D., Characterization of the Room-Temperature Structure of SnP_2O_7 ..., *Chem. Mater.* **2003**, 15, 2234-2239].
- Broad signal reflects lower degree of crystallinity and/or a high degree of structural disorder for the In^{3+} -doped samples studied here.
- Resonance at ~0 ppm can be assigned to unreacted phosphoric acid.

^{31}P static NMR

- Phosphoric acid site is not completely isotropic and therefore not just liquid residing on the surface of the material, but rather “trapped” in the structure which can greatly impact membrane conductivity by bridging grains of ITP minimizing inter-granular resistance for proton conduction.
- **This bridging is the role a polymer is expected to play in an inorganic (ITP)/organic polymer membrane** (e.g., polyvinyl pyridinium phosphate or polyphosphazine azole phosphate with ITP).

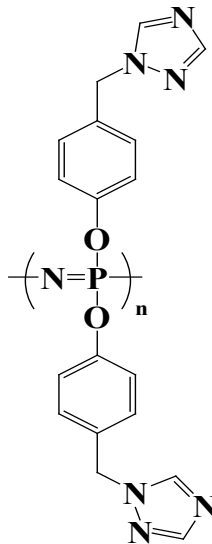
Technical Result: Polyphosphazene protic salt membrane

The goal is to make a polymer that can be formed alone or with ITP into a membrane that is flexible yet still has a high conductivity from low (sub 25°C) to high (above 120°C) temperatures and with no (0% RH) to high (100% RH) humidification.



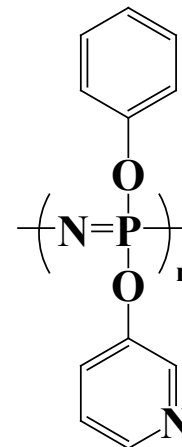
(1)

Polybis[triazolylphenoxy]phosphazene



(2)

Polybis[triazolylmethylphenoxy]phosphazene

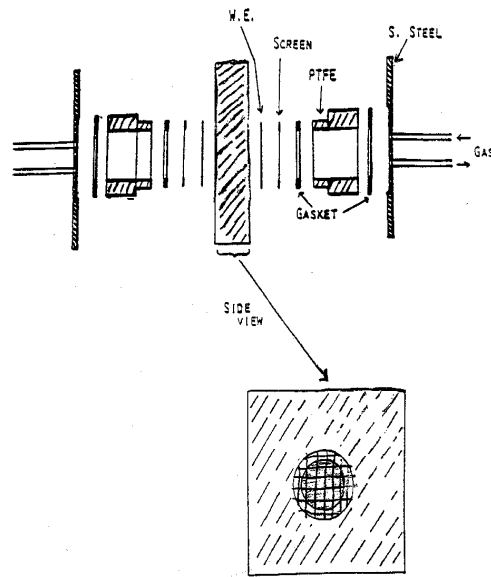


(3)

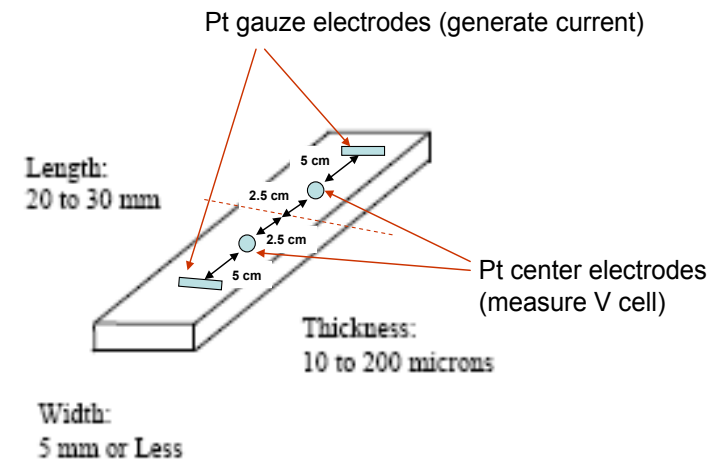
Polybis[(3-hydroxypyridinoxy)phenoxy]phosphazene

3 new polymers cast into membranes and treated with phosphoric acid to form salt membranes. Testing of proton conductivity of neat polyphosphazenes and their blends with ITP are currently under way at ASU.

Technical Result: In-plane and thru plane conductivity geometries

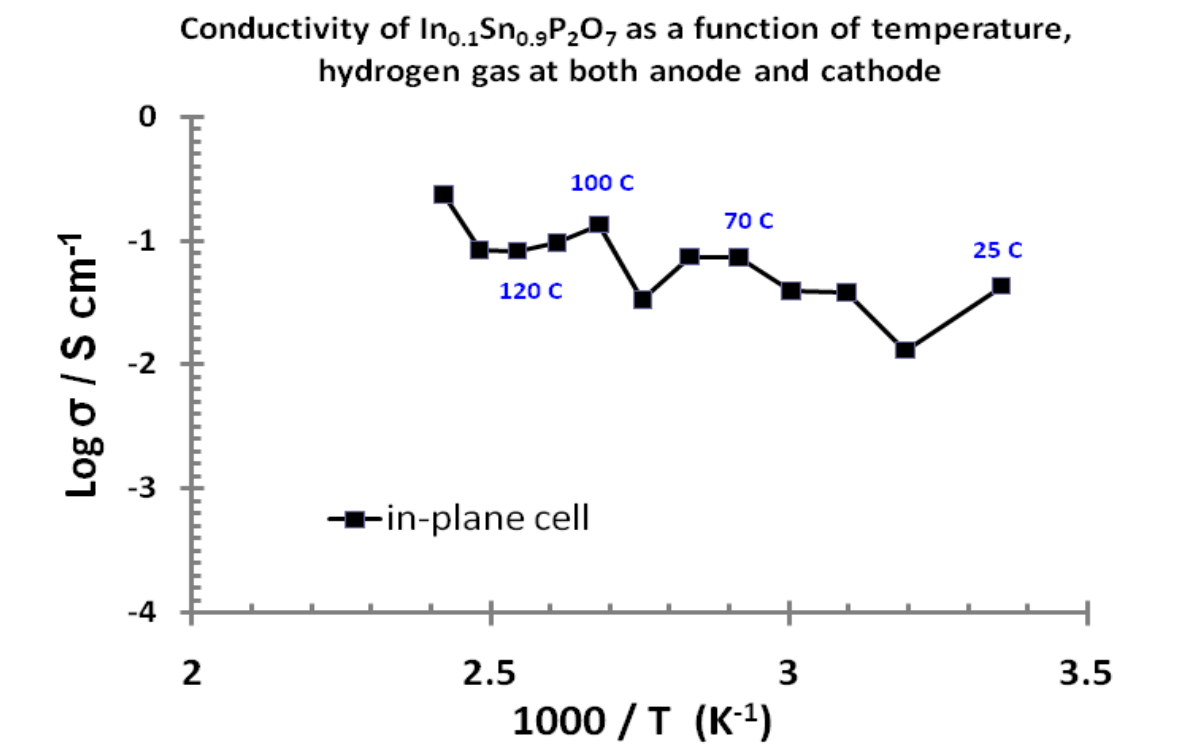


Membrane proton-conductivity characterization using *through-plane geometry* with hydrogen fed to the anode and cathode. Temperature controlled with cell in an oven.



Membrane proton-conductivity characterization using the Bekktech *in-plane geometry* with hydrogen fed to the anode and cathode. Temperature controlled with cell in an oven.

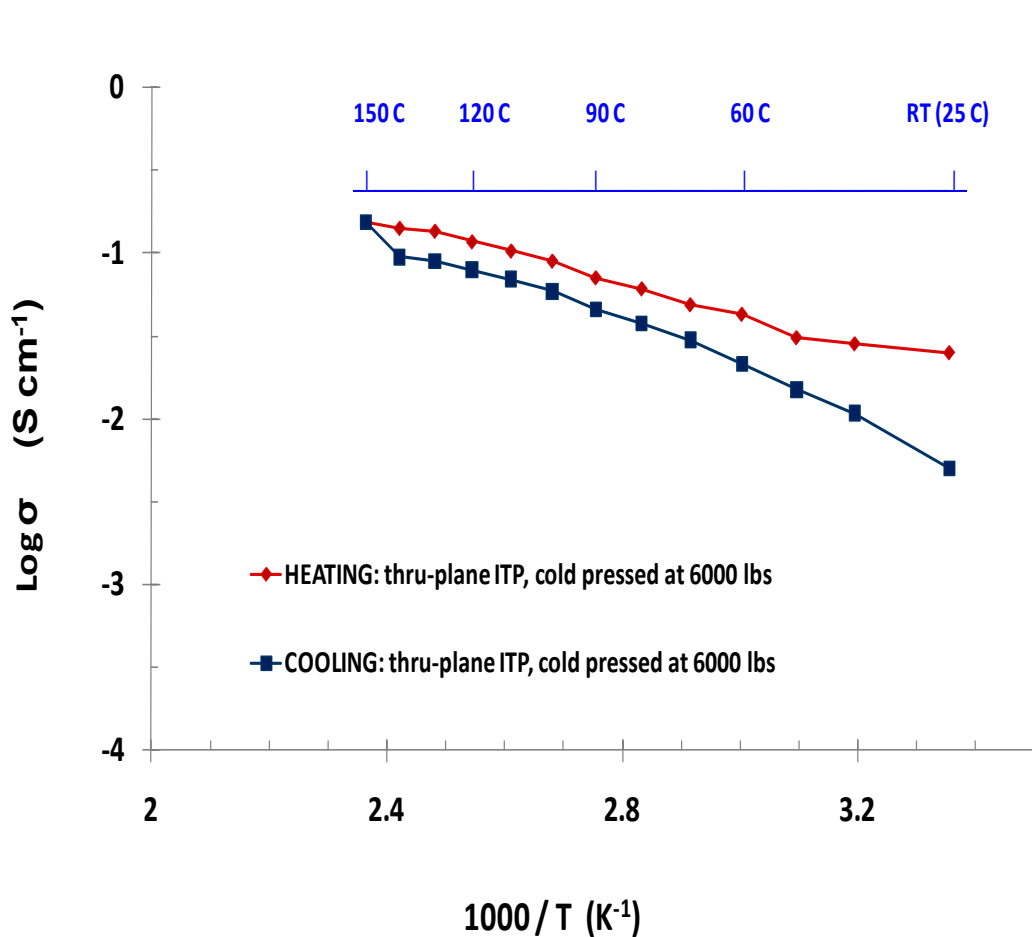
Technical Result: In-plane conductivity of ITP



Arrhenius plot of conductivity of an ITP membrane using in-plane geometry under dry H_2 gas.
Electrodes: 40nm Pt sputtered on ITP (active area $W=0.55\text{cm}^2$, $T=0.4\text{cm}^2$, $L=5\text{mm}$ apart) $0.5\text{mg}/\text{cm}^2$ of Pt on C ETEK and Pt current collectors. 30January2010

New ITP powder was pressed at RT with a carbide/tungsten die at 12kpsi.
New pellet seems to be coming apart with heating leading to inter granular contact resistance.
Samples hot pressed remain intact.

Technical Result: Through-plane conductivity of ITP



Temperature (°C)	HEATING Conductivity (S/cm)	COOLING Conductivity (S/cm)	AVERAGE Conductivity (S/cm)
25	0.025	0.005	0.015
40	0.028	0.011	0.019
50	0.031	0.015	0.023
60	0.043	0.022	0.032
70	0.049	0.030	0.039
80	0.061	0.038	0.049
90	0.071	0.046	0.059
100	0.090	0.059	0.074
110	0.103	0.070	0.086
120	0.118	0.079	0.098
130	0.136	0.090	0.113
140	0.142	0.095	0.118
150	0.155	0.155	0.155

Prep of ITP sample: J4 (4/29/10)

- Mass Indium Oxide 0.5027g
- Mass Tin Oxide 4.8933g
- Mass Phosphoric Acid (85%) 12.1685g
- reagents were mixed in a ceramic crucible while stirring at 300C for approx. 1hr
- calcined in the crucible (uncovered) at 650C for 2.5hrs.
- cold pressed at 6000lbs for 1 minute
- the pellet was reheated at 200C for 1 hour. The pellet was then platinized by sputtering a 20nm thick Pt layer on each side of the membrane.

Arrhenius plot of ITP membrane measured thru-plane by EIS from 50 kHz to 10 Hz. AC modulation amplitude: 50mV. Membrane thickness = 1.65mm, Active area = 0.484 cm², thickness sputtered Pt = 20nm. ETEK electrodes (0.5 mg of Pt per cm²) gas diffusion layer. Pt screen current collectors.

Summary

- FY09: Protic Liquid and Solid Salt Electrolytes give “dry” proton-conducting membranes
- FY10: More stable fluorinated liquid electrolytes show lower polarization for oxygen electro-reduction reaction
- FY10: Non-aqueous electrolytes could enable use of non-Pt catalysts
- FY09 – FY10: 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).

Supplemental Slides

Plans for Future Work

- Make and test proton conductivity and fuel cell behavior for membranes based on:
 - i. ITP and
 - ii. blends of ITP and organic polymers
 - iii. send to Bekktech for confirmation of conductivity found at ASU
 - iv. Correlate NMR and Conductivity measurements
- Study voltammetry of Pt on a solid salt (ITP) membrane electrolyte to find electrochemical active area of Pt in an 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 2 systems.
- Interpret voltammetry of Pt on ITP for Pt-oxide. If Pt-oxide free consider inspection by X-irradiation to confirm if Pt stays metallic at high potential (1.2V) or not. This X-ray work would be done with Dr. Deborah Meyers at the Advanced Light Source.
- Optimize membranes from inorganic (ITP) and organic polymer blends:
 - i. Synthesis of ceramic membranes of ITP organic polymers (such as polyphosphazene triazoles with various acids)
 - ii. Process ITP/polymer blend membranes for higher conductivity, flexibility and toughness in analogy to the ITP/polymer blends of Nagao et al., i.e., “Sn_{0.9}In_{0.1}P₂O₇ based Organic/Inorganic Composite Membranes”, P. Heo, M. Nagao, T. Kamiya, M. Samo, A. Tomita, T. Hibino, J. Electrochem. Soc, 154 B63-B67 (2007).
 - iii. Test the ITP membrane conductivity as a function of humidification of gases and test samples after exposed to water (to probe for conductivity changes if any free phosphate are removed).

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**
- Collaborations with PI to commercialize salt membrane technology**
 - Boeing Company, developing HTPEM FC stacks APU**
 - MER Corp., developing high power density stacks with HTPEM**