Electrochemistry in Ionic Liquid Electrolytes

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Outline

A. Motivation

B. Learn about Electrochemistry in Non-Traditional Electrolytes
Ionic Liquids (ILs)

C. Show that:

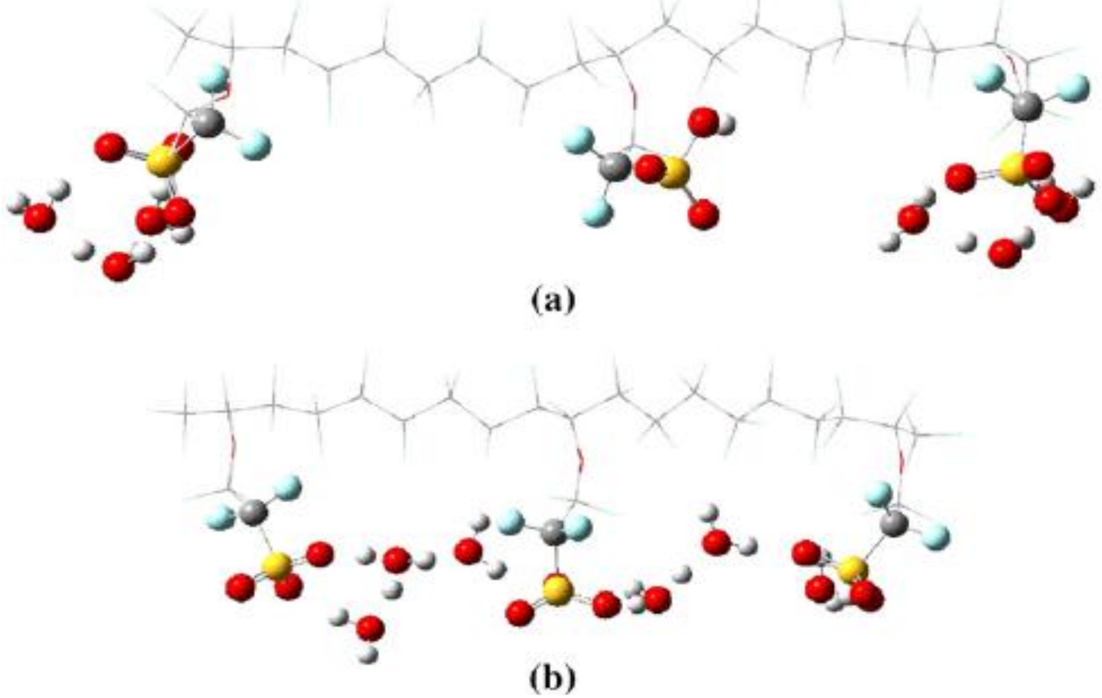
i. using protic salt IL electrolytes avoids problems with aqueous electrolytes
  a. allows more efficient devices:
    i. Fuel cells
    ii. Electrolyzers
    iii. Hydrogen purification and compression

Relevance and Motivation

OBJECTIVE:

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

- o *DURABILITY* by virtue of having
  - proton conductivity that surpasses the 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
- o *ELECTRODE PERFORMANCE*
  - by assisting catalyst to promote reduced activation overvoltage



(a) Non-conducting Low water form

(b) Proton conducting High water form

The water solvated acid membrane only conducts H^+ when in the “high water” form (b) when all pendant acid and water units are in contact with adjacent units

Approach

SYNTHESIS OF “DRY” PROTON ELECTROLYTE MEMBRANEs (PEMs)

- ☐ PEMs are being made based on “solvent free” liquid salts, called ***protic ionic liquids (pILs).***

- ☐ A pIL is the salt that forms when an ***acid transfers its proton to a base***.

- ☐ ***pILs*** are being optimized ***by varying acid and base moieties*** to optimize electrolyte properties (stability, conductivity, etc.).

- ☐ ***pIL electrolytes*** are ***used to model salt PEMs***.

- ☐ ***Salt PEMs*** are optimized
  - for proton conductivity by making a polymer with a high density (low Equivalent Weight) of covalently bound acid (base) and electrostatically bound base (acid) so ions are not leachable from membranes and
  - for membrane solubility by using polymers that are not water soluble.

How do we do all of this ??

It’s a long road… so let’s get going !!

Not so fast …

Q. Why are we using a solvent free salt for an electrolyte?

A. To avoid water and water transport

Q. What's the big deal? Why are we avoiding water and water transport?

A. Water transport during proton conduction requires a heavy humidifier (humidifier that is bigger than the fuel cell "engine") … and water itself poisons electrode catalysts.

Q. Oh really? How does water "poison" the catalysts?

A. Take a lesson from Metallurgy. *See next slides !!*

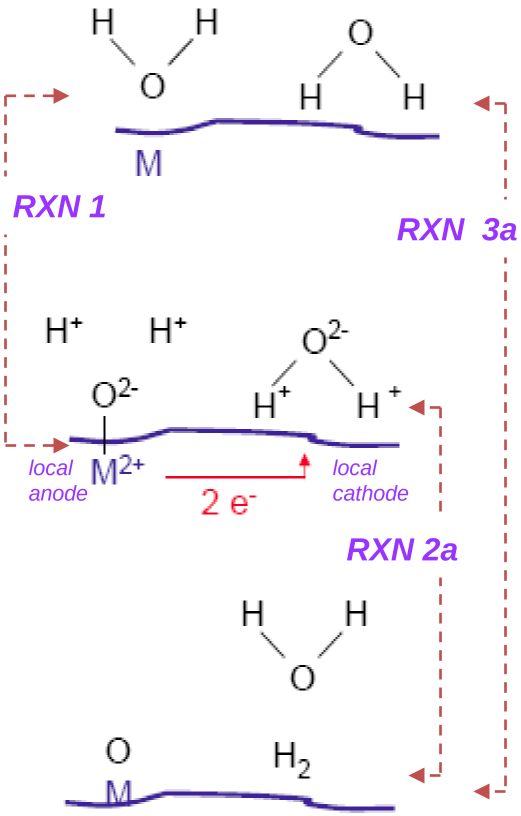
Metallurgists know that making Metals that react with Water *requires avoiding Water to avoid forming the Metal’s oxide*

- **Driving Force to form a Metal-oxide in the presence of water is the spontaneous liberation of energy (ΔH^f) when forming a metal oxide**

	Metal Oxide	$\Delta H^{formation}$ (calories/gram)	
reactive metals	aluminum oxide (Al_2O_3)	- 4000	(= -1675.7 kJ/mole)
	silicon dioxide (SiO_2)	- 3418	
un-reactive metals	copper oxide (Cu_2O)	- 278	
	gold oxide (Au_2O)	> 0	(Au oxide unstable)

Surface Oxide Formation

by “Local Cell” Process



- **Rapid surface oxide formation by Local Cell process prevents Al smelting in air**

  - **Water (H_2O) reacts with a metal (M), like aluminum or silicon, forming undesirable metal oxide (MO) as is schematically shown below.**

$$M + H_2O \rightarrow MO + 2\,e^- + 2\,H^+ \qquad \text{(Reaction 1)}$$

  - **The liberated electrons are consumed by proton to form hydrogen (reaction 2a) or by oxygen reduction to form water (reaction 2b).**

$$2\,e^- + 2\,H^+ \rightarrow H_2 \qquad \text{(Reaction 2a)}$$

$$2\,e^- + \tfrac{1}{2}\,O_2 + H_2O \rightarrow 2\,OH^- \qquad \text{(Reaction 2b)}$$

  - **Adding reaction 1 with reaction 2a or reaction 2b gives the net undesirable metal oxide formation reaction (reaction 3a or reaction 3b) .**

$$M + H_2O \rightarrow MO + H_2 + \text{heat} \qquad \text{(Reaction 3a)}$$

$$M + \tfrac{1}{2}\,O_2 \rightarrow MO + \text{heat} \qquad \text{(Reaction 3b)}$$

Undesirable METAL OXIDE FORMATION (reactions 3a and 3b) OCCURS IN the presence of WATER because e^- is more stable on H^+ or O_2 than on the metal

What metallurgist knew this first?

Charles Martin Hall

(1863-1914)

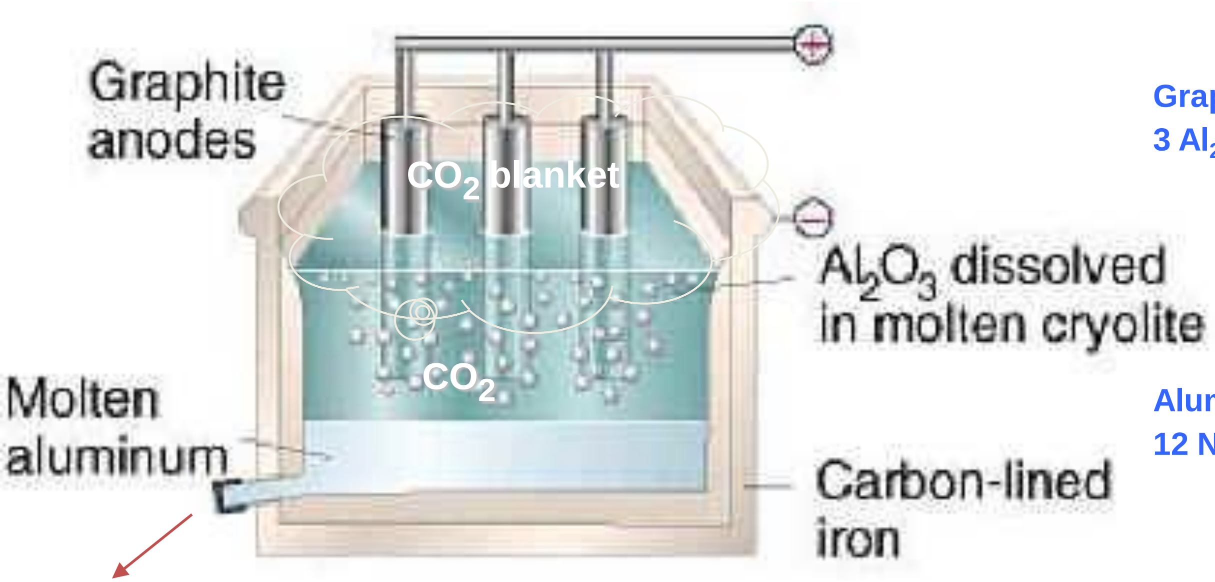
High-Temperature Molten-Salt Electrochemistry

Inventor who brought aluminum to America in 1886
US Patent number 400,655, granted to Hall in 1889
Founder of “Pittsburgh Reduction Company” renamed
Aluminum Company of America (**ALCOA**) in 1907

In 1886, aluminum (like silver) cost ***$8*** per pound.
By 1914, the cost of aluminum was down to ***18 cents***.
Today cost is < $1 for Al *versus* > $200 for Ag

Electroplating of a Metal that is Reactive with Water

- ❑ **Hall Process: water-free Aluminum electroplating**
  - o **Al metal electroplated from Al-oxide in molten salt**
    - ▪ **Molten salt composition: Cryolite (Na_3 AlF_6), AlF_3, Al_2O_7**
    - ▪ **Large voltage window achievable in cryolite salt electrolyte**
      - **Al electroplates on a cathode at 900°C and a potential of -1.662 volt vs. S.H.E.**



Pour metallic aluminum ingot

Graphite Anode reaction

$3\ Al_2O_2F_4^{2-} + 3C + 24\ F- \longrightarrow 3\ CO_2 + 6\ AlF_6^{3-} + 12\ e^-$

Aluminum Cathode reaction

$12\ Na^+ + 4\ AlF_6^{3-} + 12\ e^- \longrightarrow 12\ Na^+F^- + 4\ Al + 12\ F^-$

Net reaction:

$2\ Al_2O_3 + C \longrightarrow 4\ Al + CO_2$

Q. What did Charles Hall teach us?

A. Undesirable spontaneous reactions 3a and 3b are avoided by using Water-Free Processing

- **Water (H_2O) reacts with a reactive metal (M), like aluminum or silicon, forming undesirable metal oxide (MO), shown below.**

$M + H_2O \rightarrow MO + 2\,e^- + 2\,H^+$ (Reaction 1)

- **The liberated electrons are consumed by proton to form hydrogen (reaction 2a) or by oxygen reduction to form water (reaction 2b).**

$2\,e^- + 2\,H_2O \rightarrow 2\,OH^- + H_2$ (Reaction 2a)

$2\,e^- + \frac{1}{2}\,O_2 + H_2O \rightarrow 2\,OH^-$ (Reaction 2b)

- **Adding reaction 1 with reaction 2a or reaction 2b gives the net undesirable metal oxide formation reaction (reaction 3a or reaction 3b).**

$M + H_2O \rightarrow MO + H_2$ (Reaction 3a)

$M + \frac{1}{2}\,O_2 \rightarrow MO$ (Reaction 3b)

An aside…The History of Metals vs. ΔH_f of their Metal-oxides

Metals with a great heat of oxide formation came later in history !!

- ***Coinage and noble (Cu, Ag, Au) metal making***
  - Low or no negative heat of formation
    - **Au oxide (ΔHf > 0 cal/g)** ***First metal known (prehistoric times)***
    - **Ag oxide (-32 ca/g)** ***As old as gold (mentioned in Genesis)***
    - **Cu oxide (-278 cal/g)** ***First made circa 9000 BC***
  - Can plate and smelt in presence of water, air

- ***Base (Fe, Steel) metal making***
  - Moderate heat of formation
    - **Fe oxide (-1230 cal/g)** ***First iron made 1200 BC***
  - Can smelt & plate in water, air

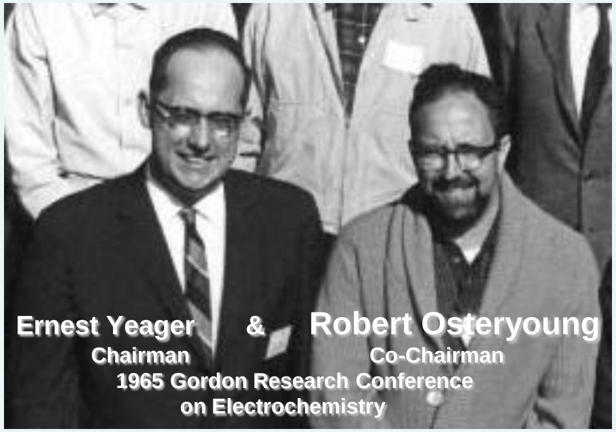
- ***Active (Al, Si) metal making***
  - High negative heat of formation
    - **Al oxide (-4000 cal/g)** ***First Al metal made 1886***
    - **Si oxide (-3418 cal/g)** ***First Si semiconductors made 1950's***
  - **Can't plate Al metal from salts in water nor readily smelt Al metal from ore**
    - **until *1886* aluminum was scarce as silver**
      - then Hall plated Al in *water-free* salt
      - Al dropped in price 200x
      - abundant alumina became an abundant structural metal
      - ***Hall achieved a great success by electroplating Al metal from a F^- salt melt at 900ºC.***

This is how molten salt electroplating was for many years! …until…

… 90 years later.

Room Temperature Ionic Liquids (RTILs) in Electrochemistry

Sailor who explored the salty sea of low-temperature water-free electrochemistry



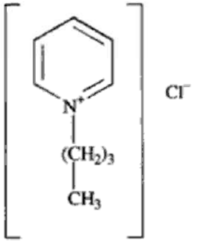
Ernest Yeager & **Robert Osteryoung**
Chairman Co-Chairman
1965 Gordon Research Conference
on Electrochemistry

Robert A. Osteryoung

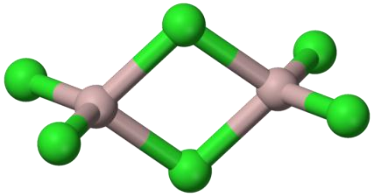
January 20, 1927- August 10, 2004

Pioneer of
Low-temperature molten salts
aka "Ionic Liquids" (ILs)

In the mid 1970's, R. Osteryoung showed a mixture of **1-butylpyridinium chloride** and **2 $AlCl_3$** melts at 35°C



1-butylpyridinium chloride



aluminum trichloride dimer, 2 $AlCl_3$

forming a low temperature **molten salt,**
[1-butyl pyridinium]$^+$ [heptachloro aluminate]$^-$.
$[pyr\text{-}(CH_2)_3CH_3]^+$ $[Al_2Cl_7]^-$

The reduction the **heptachloroaluminate anion $[Al_2Cl_7]^-$** in this "ionic liquid" is the limiting cathode process, forming aluminum metal at the low temperature of 35°C.

Today these low-temperature liquid salts (ionic liquids) are being studied and developed at an ever-quickening pace.

Low Temp. Aluminum Electroplating in Ionic Liquids

Electrodeposition of Al from Low Temperature Ionic Liquids pioneered by ***Robert Osteryoung***

Osteryoung, R.A., Welch, B.J., "Electrochemical Studies in Low Temperature Molten Salt Systems Containing Aluminum Chloride". J. Electrochem. Soc., 118 (1981), 455.

- **Conditions**
  - **for an $AlCl_3$ and n-butylpyridinium chloride (RCl) salt electrolyte the melting temperature is 30ºC and the plating potential is -2.1V vs. Ag/AgCl**
  - for an $AlCl_3$ and NaCl (RCl) salt electrolyte the melting temperature is 175ºC and the plating potential is -1.9V vs. Ag/AgCl

$$2R^+Cl^- + Al_2Cl_6 \xleftrightarrow{k_1} 2R^+AlCl_4^-$$

  - **Electrolyte forming reactions:**
    - **At *low Al concentrations*, the Al species in the melt forms as:**

$$2R^+AlCl_4^- + Al_2Cl_6 \xleftrightarrow{k_2} 2R^+Al_2Cl_7^-$$

    - **At *high Al concentrations*, the Al species forms as:**
  - **Plating reactions:**
    - **Cathode reaction:**

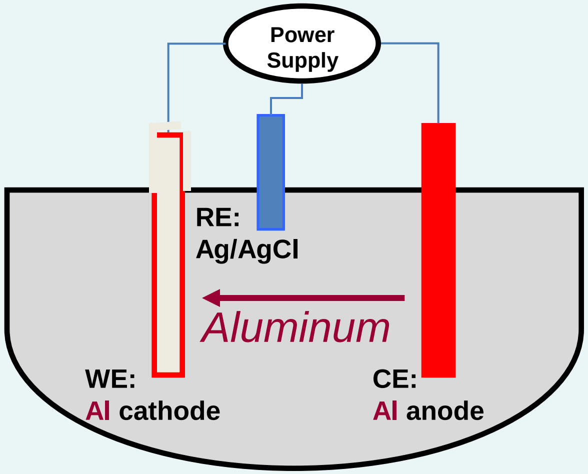
$$2\,R^+AlCl_4^- + 6\,e^- \rightarrow 2\,Al + 2\,R^+Cl^- + 6\,Cl^-$$

    - **Al Anode reaction:**

$$2\,Al \rightarrow 2\,Al^{3+} + 6\,e^-$$

    - **Net reaction:**

Transfer Al from anode to cathode

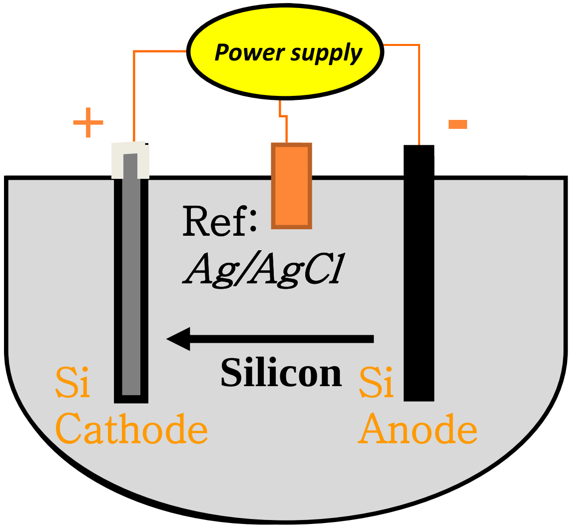


Example 2. cont.

Silicon Plating from Room Temperature Ionic Liquid (RTIL)

like Osteryoung's Al plating process

- Ionic liquid electroylte: RCl (n-butylpyridinium chloride) and silicon ($SiCl_4$, $NaSiF_6$, $SiHCl_3$, or Si_2Cl_6).
- Reactions
  - **IL Rxn with Si:** $2\,R^+Cl^- + Si_2Cl_6 \rightarrow 2\,R^+SiCl_4^-$
  - **Cathode Rxn:** $R^+SiCl_4^- + 3\,e^- \rightarrow Si + R^+Cl^- + 3\,Cl^-$
  - **Anode Rxn:** $Si + R^+Cl^- + 3\,Cl^- \rightarrow R^+SiCl_4^- + 3\,e^-$
  - **Net Rxn:** *Transfer of Si from anode to cathode*
- 3 electrode cell
  - Cathode, reference (Ag/AgCl), anode
  - RT to 120^{o}C operating temp (avoid water)
  - CV & Chronoamperometry
  - Inert gas purge



N. Borisenko et al., “In Situ STM Investigation of Gold Reconstruction and of Silicon Electrodeposition on Au(111) in the Room Temperature Ionic Liquid 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide”, J. Phys. Chem. B 2006, 110, 6250-6256

Abedin, S. Z. et al., **“Electrodeposition of Metals and Semiconductors in Air- and Water-Stable Ionic Liquids”**, Chemphyschem [2006] **7** , 58-61

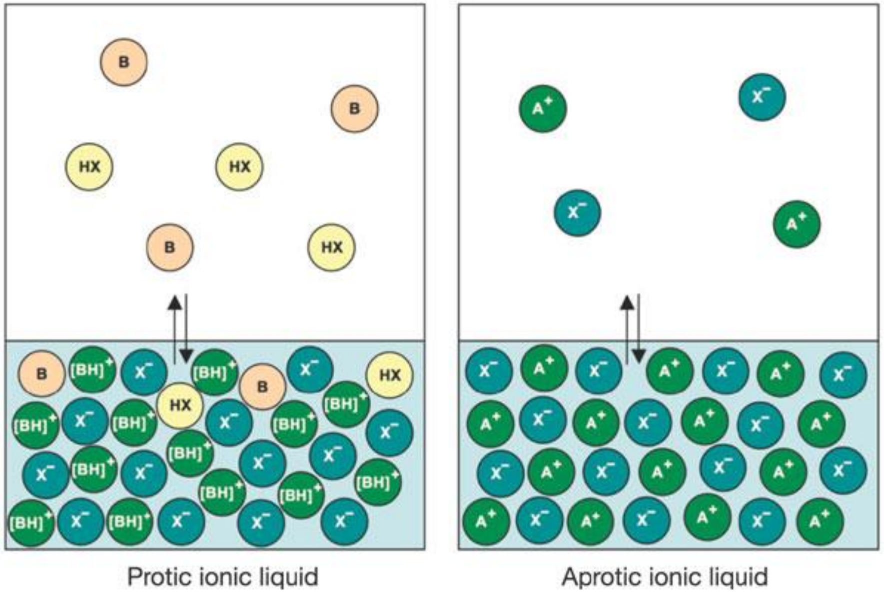
Now we are getting somewhere !

But wait …

What are these ionic liquids?

General characteristics of Ionic Liquids

- “Ionic Liquids” are molten salts with melting points below 100°C.
- Composed of over 99.99% ions
- Low vapor pressures
- Highly conductive
- Excellent solvating properties
- Thermally stable, for both high and low temperature uses.
- Large window for electrochemical reactions (5V)
- Protic Ionic Liquids (PILs) have mobile protons.



http://www.nature.com/nature/journal/v439/n7078/images/nature04451-f2.2.jpg

Typical room temperature ionic liquids (RTILs)

- ❑ Room temperature ionic liquids (RTILs) consist of:
  - ❖ Bulky and asymmetric organic positive ions (cations), such as:
    - 1-alkyl-3-methylimidazolium,
    - 1-alkylpyridinium,
    - N-methyl-N-alkylpyrrolidinium
    - ammonium ions.
  - ❖ Negative ions (anions) include:
    - halides (Cl^-, F^-, Br^-, I^-) which generally give high melting sals,
    - Inorganic anions such
    - tetrafluoroborate
    - hexafluorophosphate
    - large organic anions
    - bistriflimide
    - triflate
    - tosylate
    - formate
    - alkylsulfate
    - alkylphosphate
    - glycolate

Tailorable

Properties, such as: melting point, viscosity, and solubility and stability are determined by the identity and geometry of substituents on the cation and anion.

Simple preparation of pILs

Amine + Acid

↓

Stirring in acetone/dry-ice bath

↓

Solution

↓

Heated at 120°C in Silicon bath

↓

H_2O Removal

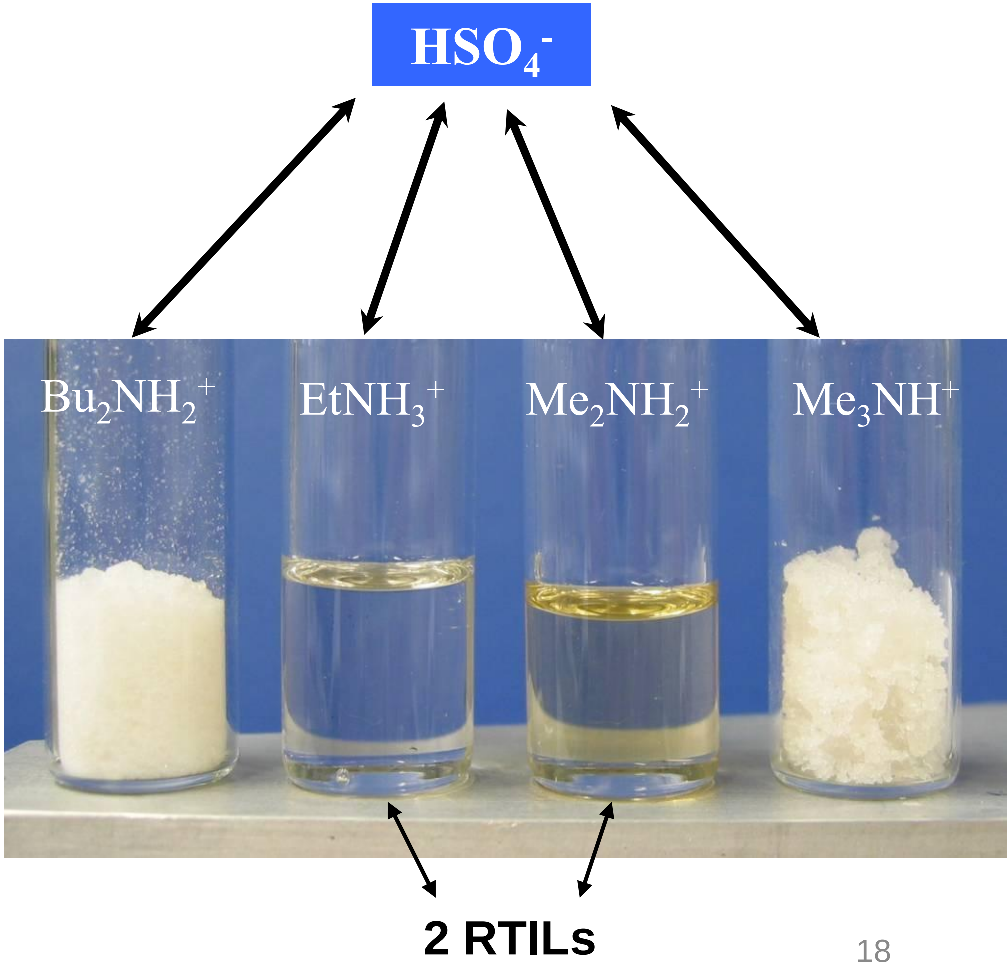
↓

Dried in Vacuum Oven at 90°C

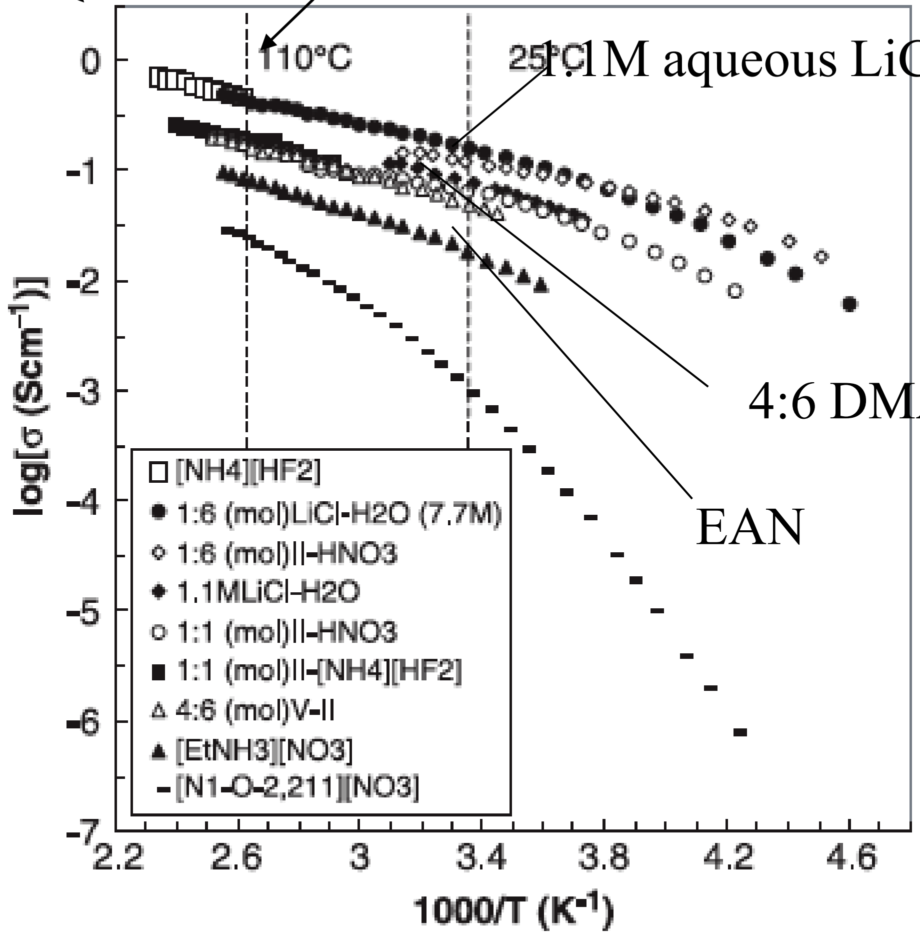
Mass analysis, Karl-Fischer titration

Samples : $H_2O = 100 : <1$ (mol%)

Example: hydrogen sulfates



Ionic-conductivity of ILs



$[NH_4]^+[HF_2]^-$

7.7M aqueous LiCl solution

1.1M aqueous LiCl

4:6 DMAN-MAN

EAN

IL electrolytes can have high ionic conductivities, rivaling aqueous solutions

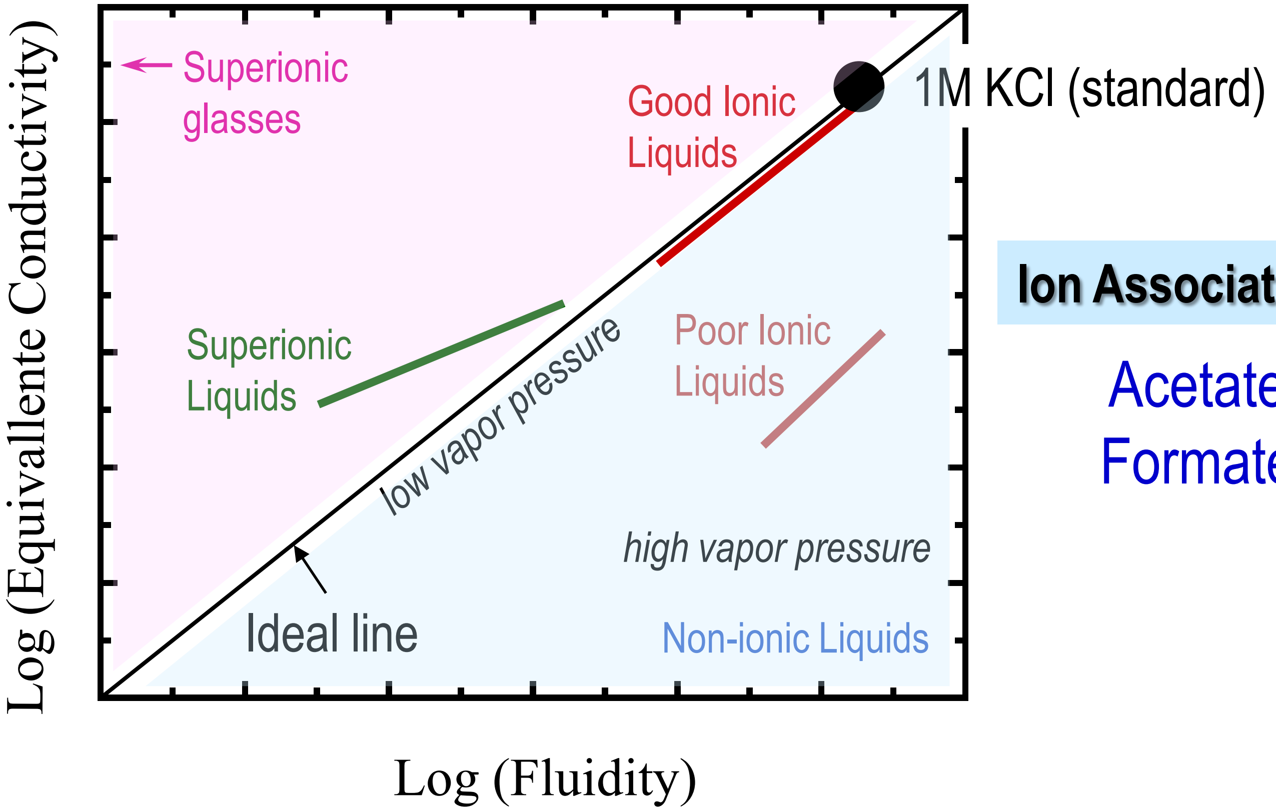
IR losses should be minimal

From: Xu and Angell, Science, (302), 422, 2003

Conduction mechanism: the Walden Plot

Decoupling

$LiAlCl_4$



Ion Association

Acetate
Formate

Summary: ion conduction mechanisms

- **on *Ideal line* is by *translation***
- **in *Poor Ionic Liquid* region is due to *frictional drag***
- **in *Superionic Liquid* region is by *hopping* !!**

Ionic Liquids and Fuel Cells

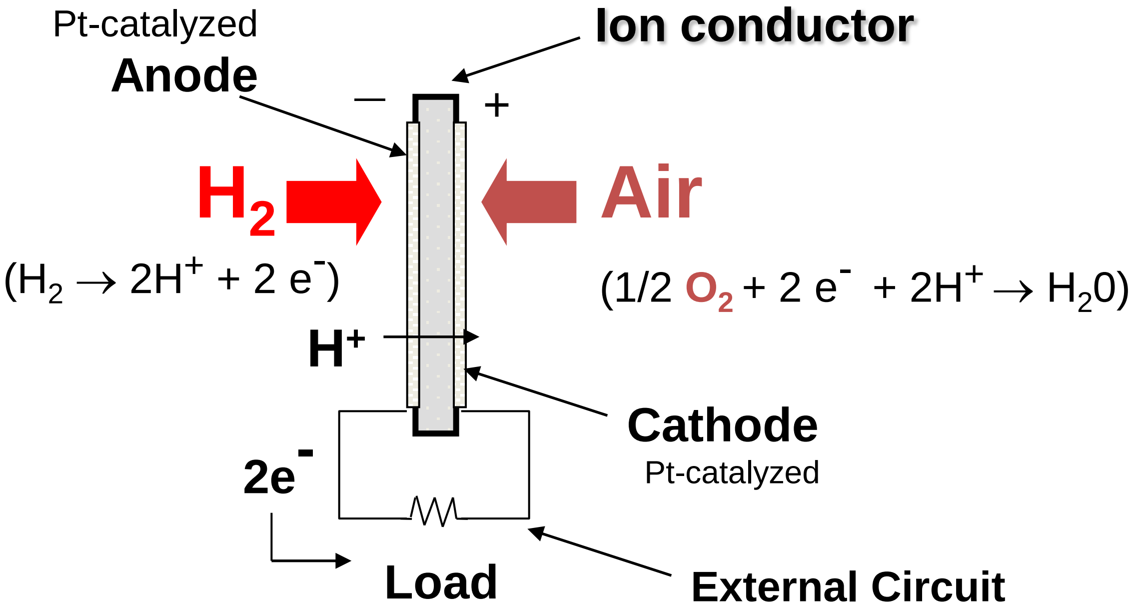
OK, now we are ready to talk about …

Proton Transfer Salts:

a New Class of Solvent-free Fuel Cell Electrolytes
based on
Proton-Conducting Ionic Liquid (pIL) Concepts

Hydrogen – Oxygen Fuel Cell

- proton conductor surrounded by two electrodes
- dissimilar feeds at the identical electrodes (hydrogen at anode, oxygen at cathode) generate dissimilar electrode potentials whose difference E_C^0 - E_A^0 is the fuel cell voltage V_{FC}^0



Pt-catalyzed **Anode**

Ion conductor

Cathode Pt-catalyzed

External Circuit

Load

Anode Reaction: $H_2 \rightarrow 2\ H^+ + 2\ e^-$ $\qquad E_A^0 = 0$ V

Cathode Reaction: $\frac{1}{2}\ O_2 + 2\ e^- + 2\ H^+ \rightarrow H_2O$ $\qquad E_C^0 = 1.23$ V

Fuel Cell Reaction: $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O + \Delta\ G^0$ $\qquad V_{FC}^0 = Ec^0 - Ea^0 = 1.23$ V

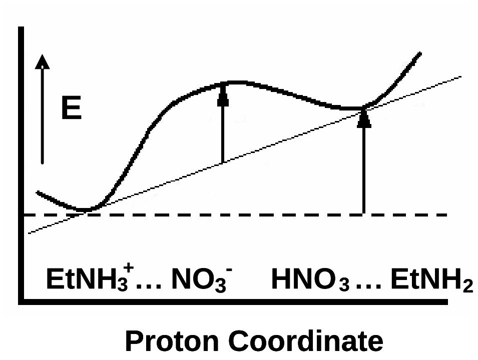
$\Delta G^0 = -nFV_{FC}^0 = -230$ kJ

*Fuel cell conducts proton, so we need a proton conducting ionic liquid, or pIL

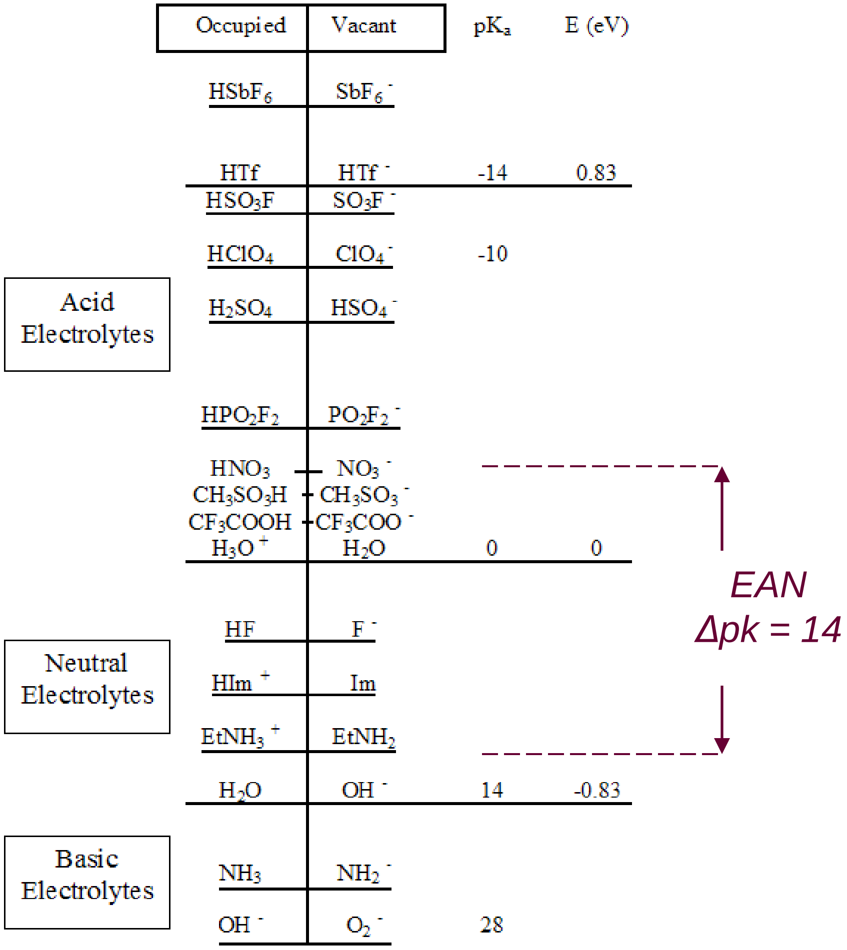
PROTIC IONIC LIQUID (pIL) CONCEPTS

- ***pILs belong to a new class of solvent-free proton-conducting low temperature molten salt electrolyte that can function at very high temperatures***

- ***A protic ionic liquid (pIL) is a salt made by transferring a proton from an acid to a base AND that retains a proton in the salt.***



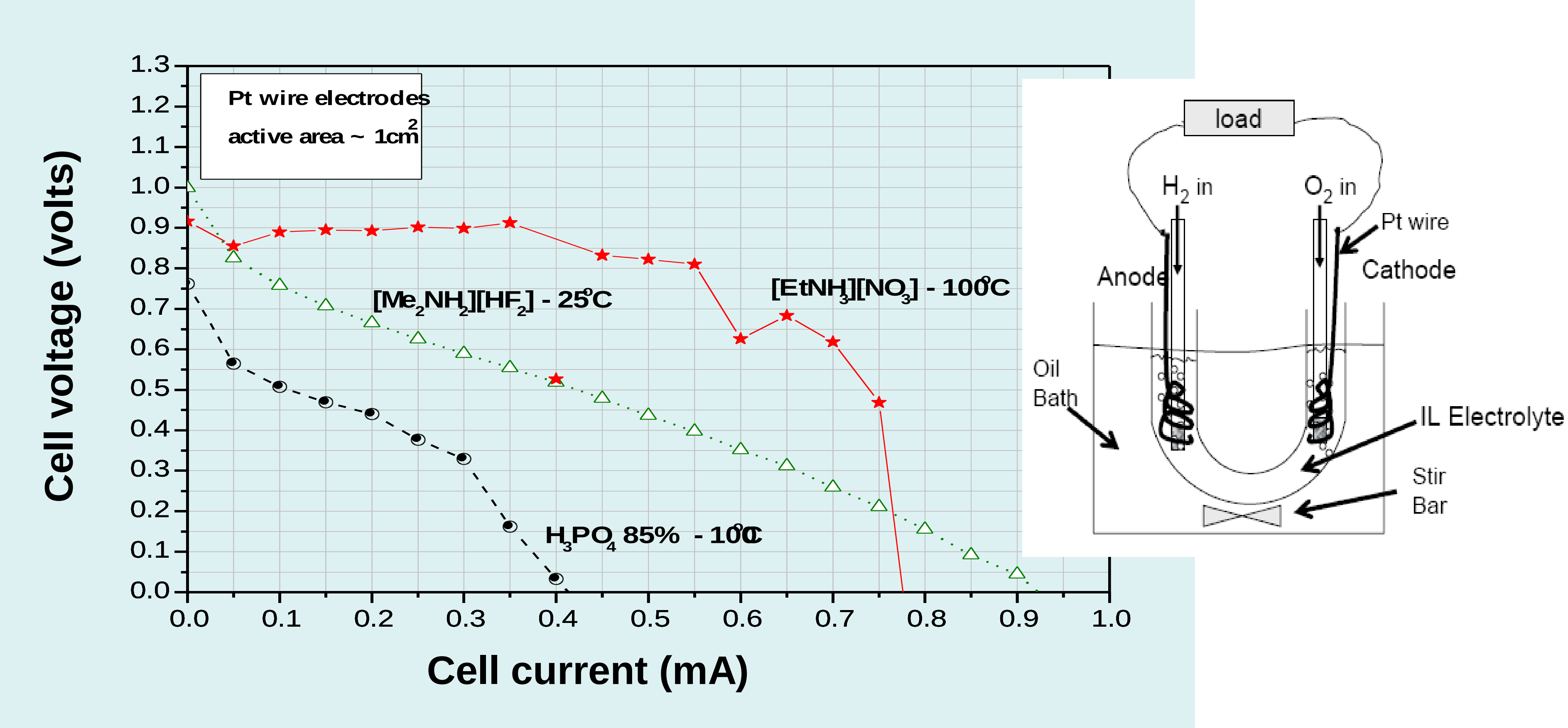
- ***Energy Diagram for the EAN (ethyl ammonium nitrate) pIL with:***
  - ***- proton transferred (Left)***
  - ***- not transferred (Right),***



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

Fuel Cell with Pt wire, liquid electrolyte and gas bubble feed

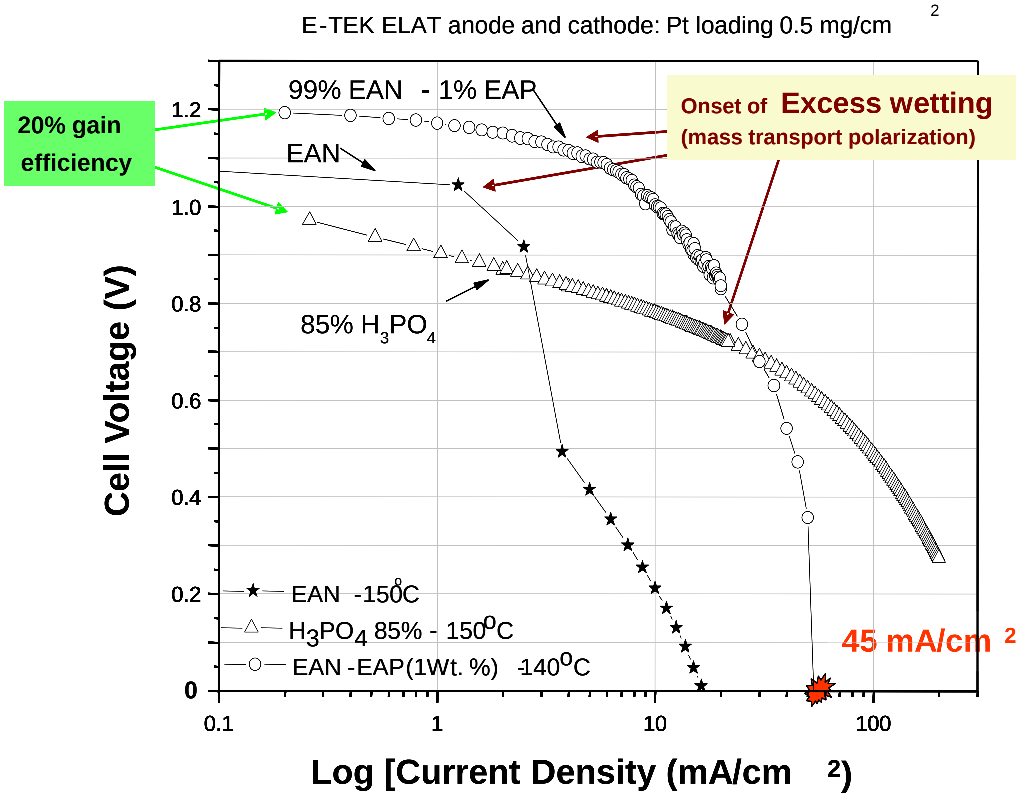
JP Belieres



Fuel cells with protic salts show better relative performance than with 85% H_3PO_4

Fuel Cell with pIL and gas fed Porous Electrode

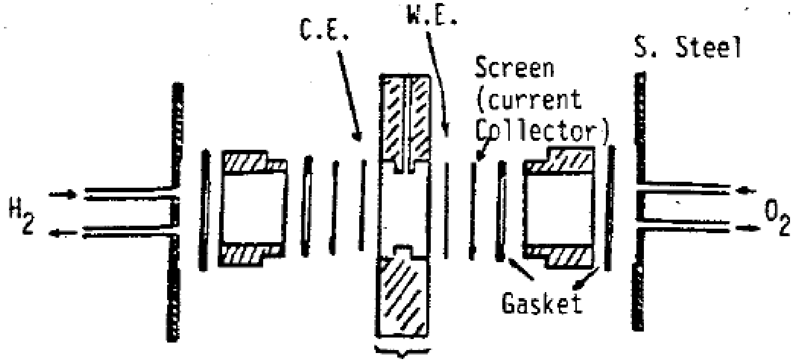
JP Belieres


E-TEK ELAT anode and cathode: Pt loading 0.5 mg/cm²

20% gain efficiency

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

45 mA/cm²



Liquid Electrolyte Cell

- ***Fuel cells with protic salts still show better performance than with 85% H_3PO_4***

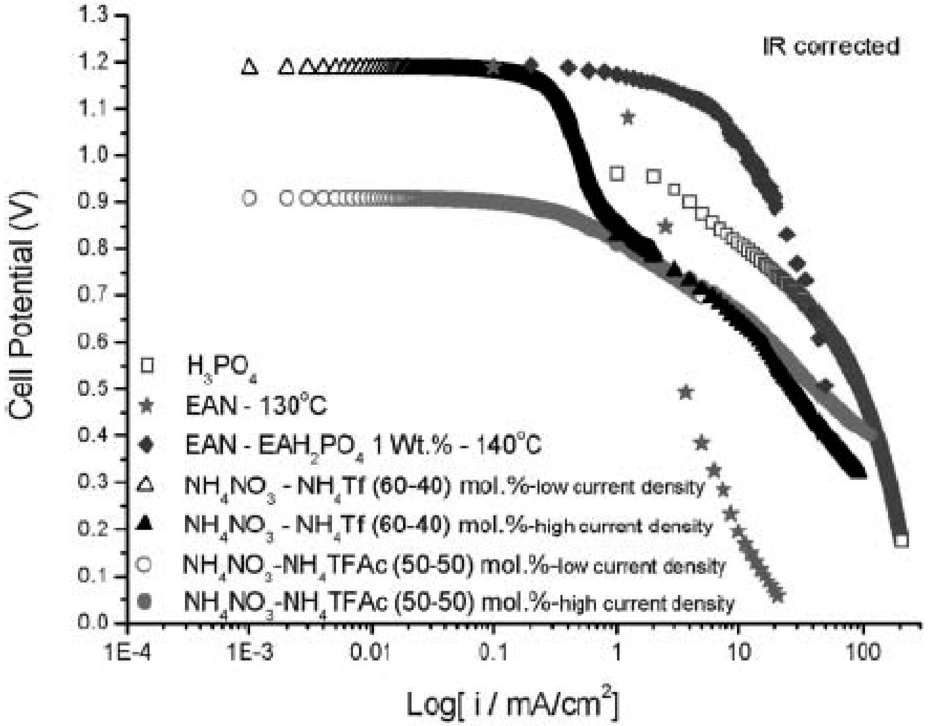
•***But electrolyte wetted gas-fed electrode (TEFLON) !!***

- ***New material goal, a more stable electolyte that does not wet electrode***

Fuel Cells with 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.

Jean-Philippe Belieres, Don Gervasio and Austen Angell, *Chem. Commun.*, 2006, 4799.

*** New stable electrolyte found**

*** Tafel plots indicate barrier free O_2 reduction at low currents probably due to the low water activity of the salts.**

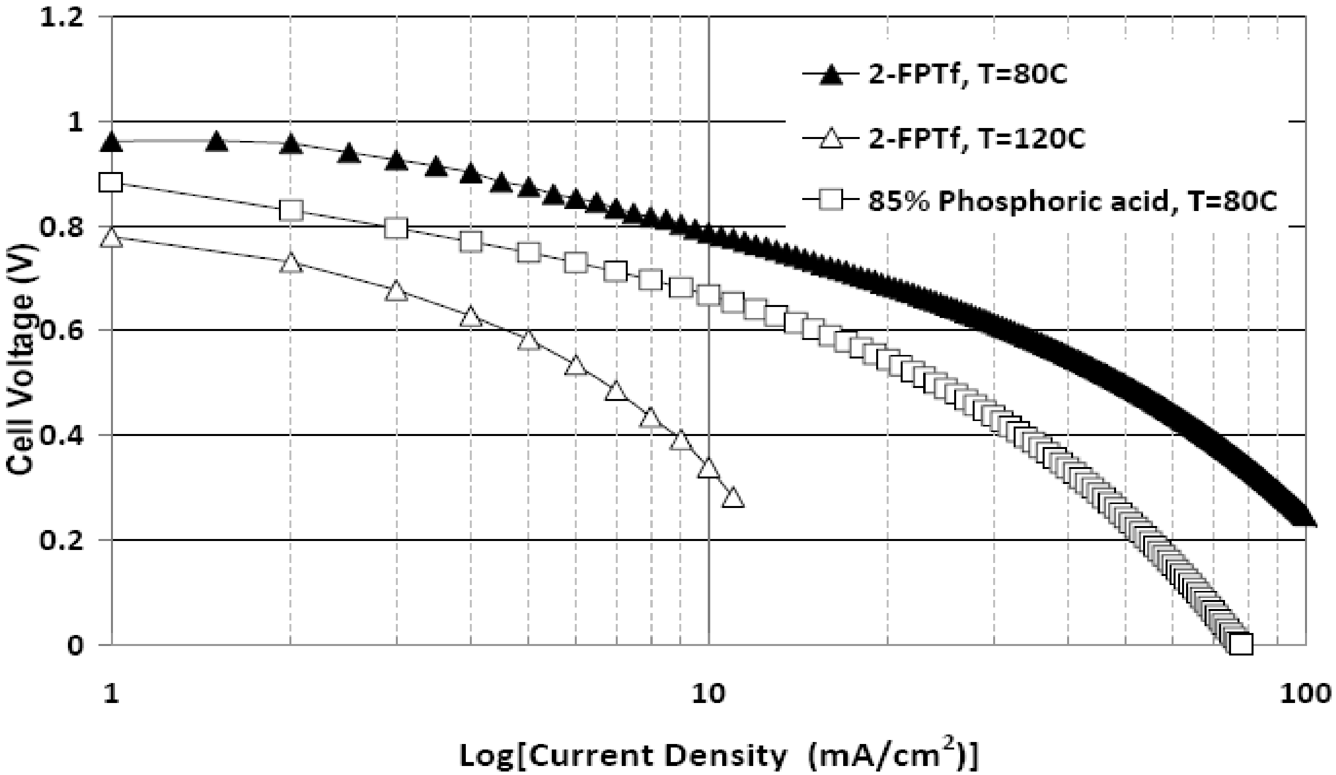
*** at intermediate loads, sudden drop, probably due to adsorption but remain stable through higher cell loads.**

What's next?

- **stop adsorption of electrolyte, by:**
  1. **Further tailoring mixtures with non – adsorbing components for higher performance**
  2. **Making polymeric forms of salt electrolytes**

More Efficient and Stable Fuel Cell

with an Electrochemically and Physically stable pIL, 2-FPTf

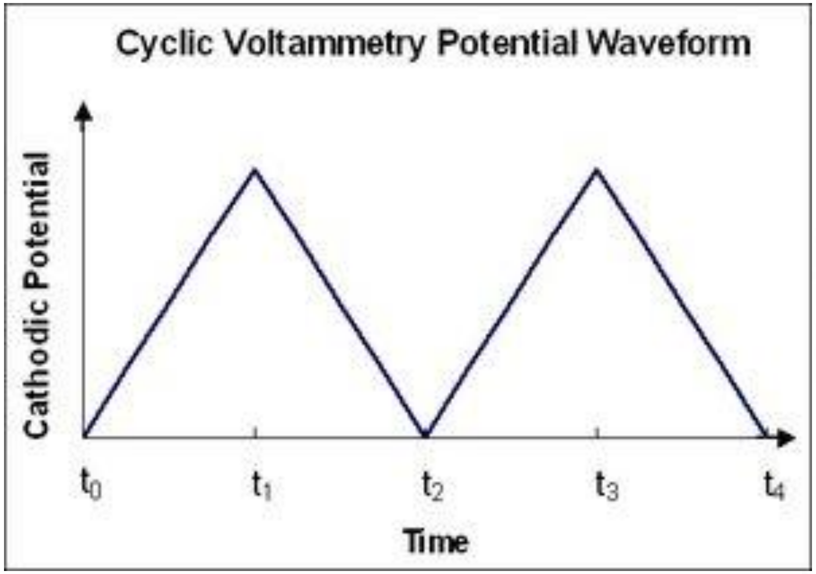


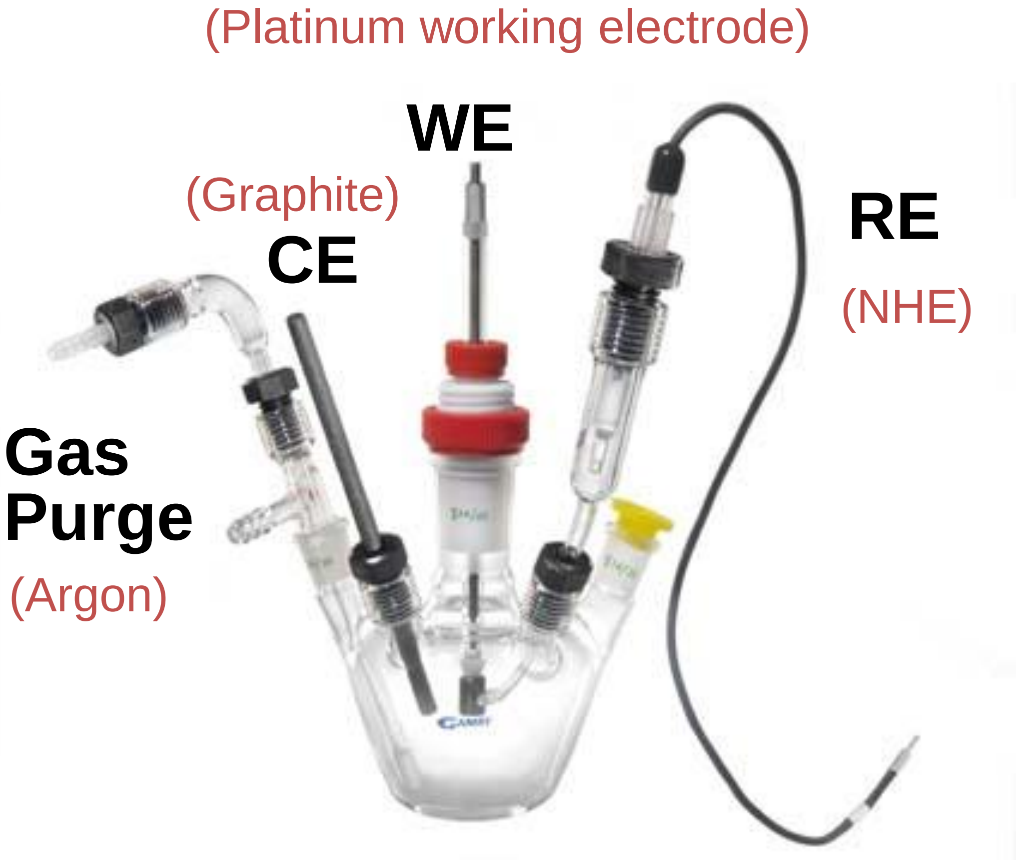
STEADY STATE I/V curves for H_2 and O_2 fed to Pt-catalyzed porous electrodes in 2-FPTf electrolyte at 80C and 120C and 85% phosphoric acid electrolyte at 80C. σ(2-FPTf) = 4×10^{-3} Scm^{-1} A = 0.5 cm^2, $t^{electrolyte}$ = 0.3 cm.

Why is a fuel cell better with this particular salt electrolyte ?

Its water-free, stable and weakly-adsorbing … all 3 needed !

Voltammetry … a tool to understand Fuel Cell I/V curves

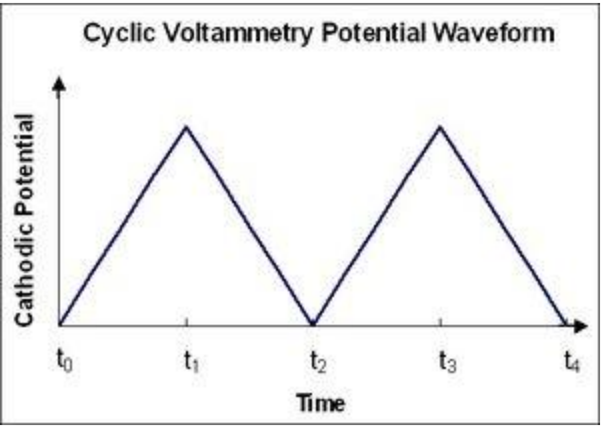




Sweep Potential of working electrode versus the reference electrode.

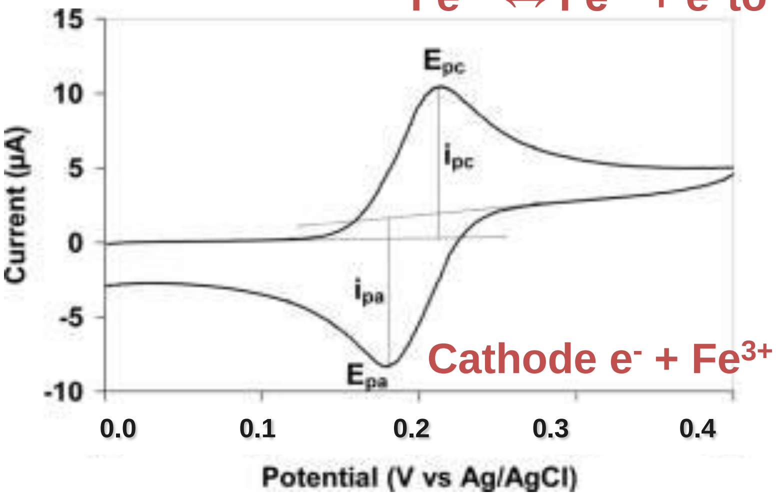
Measure resulting current between working and counter electrode.

Cyclic Voltammetry: non-steady state I/V curve



Sweep Potential vs. Reference Electrode

Fe^{2+} ↔ Fe^{3+} + e^- to anode



Cathode e^- + Fe^{3+} ↔ Fe^{2+}

Plot Working Electrode (WE) Current on the y vs. WE potential versus a Reference on x axis.

http://content.answers.com/main/content/wp/en/thumb/d/dc/300px-Cyclicvoltammetrywaveform.jpghttp://chemeducator.org/sbibs/s0005005/spapers/550231sp_gifs/550231sp_image002.jpg

Current Response on WE can be:

- **due to electron transfer to a species in solution**
  - **Fe in solution has top & bottom wave (reversible)**
  - **oxygen in solution has only bottom response (irreversible)**
- **due to electron transfer from a reaction of electrode surface-confined species *(next slide)***

Voltammetry of a Pt surface in:

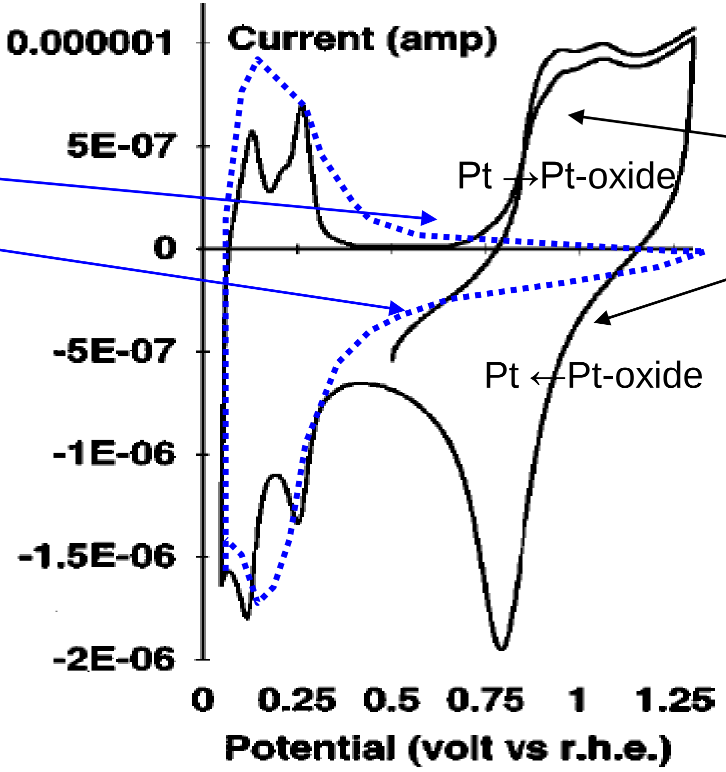
- **aqueous sulfuric acid electrolyte (solid black line)**
- **versus protic salt (dotted blue line).**

With protic salt electrolyte

There is
- no Pt-oxide formation
- nor reduction

to impede O_2 reduction.

Water-free



With aqueous electrolyte

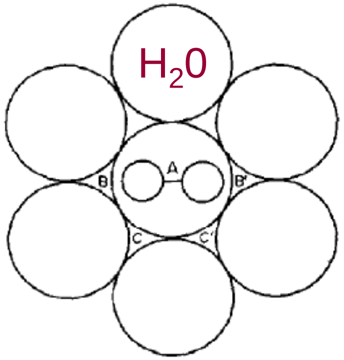
Pt-oxide formation

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

Pt-oxide reduction

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

Pt-oxide impedes O_2 reduction.



Does low water activity make Pt a better <u>cathode</u> electrocatalyst ?

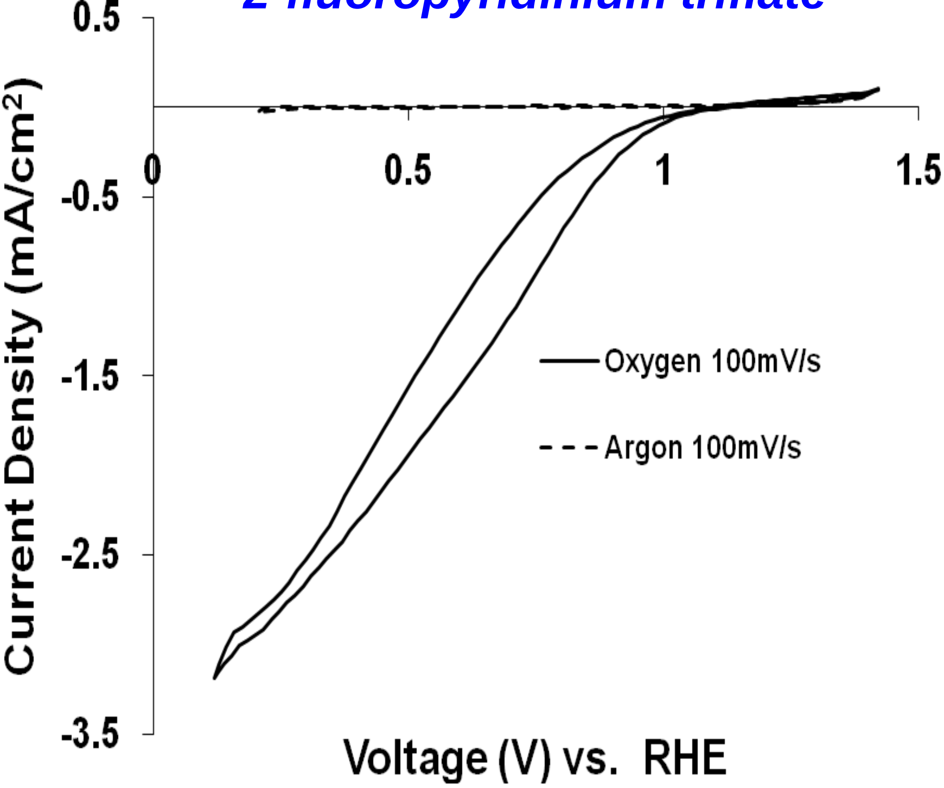
How do you know if Pt catalysis of oxygen reduction is better??

Thermodynamic Limit of Oxygen Cathode

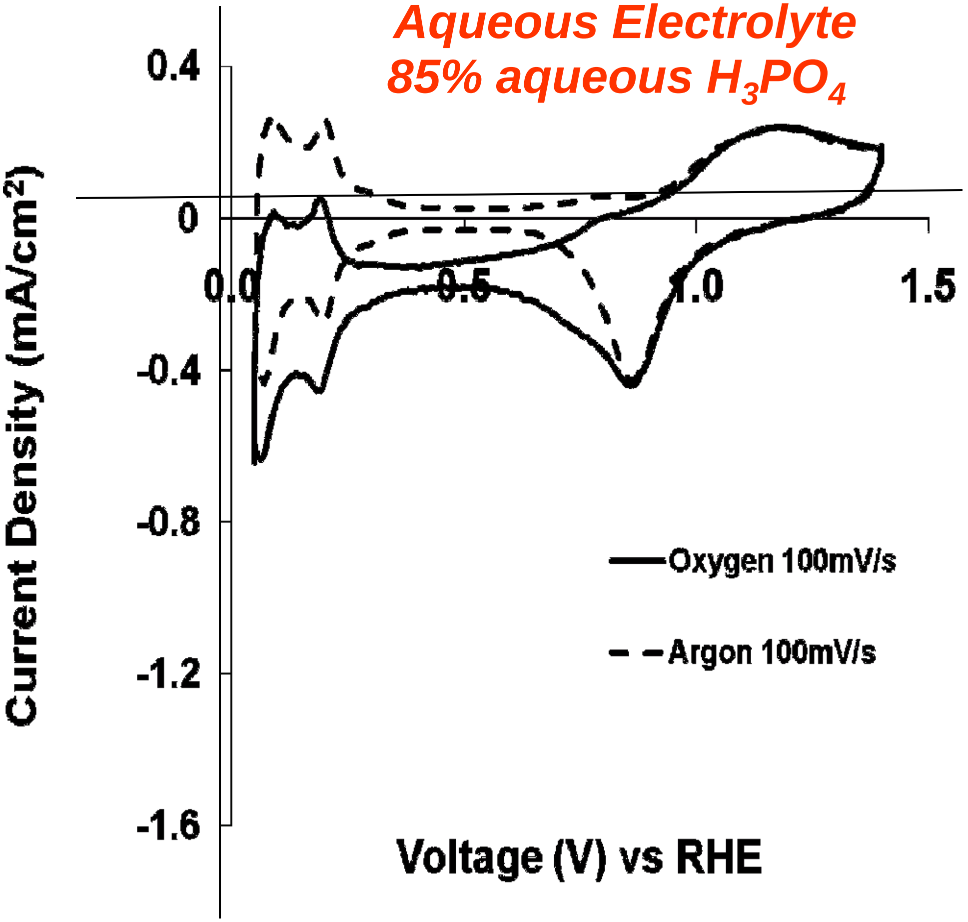
$O_2 + 4\,e^- \xrightarrow{\text{Pt, H}^+} H_2O$ $\quad$ $E^o = 1.2$ V versus NHE

Voltammetry of Pt with Oxygen in:

Salt Electrolyte
2-fluoropyridinium triflate



Aqueous Electrolyte
85% aqueous H_3PO_4



Water-free

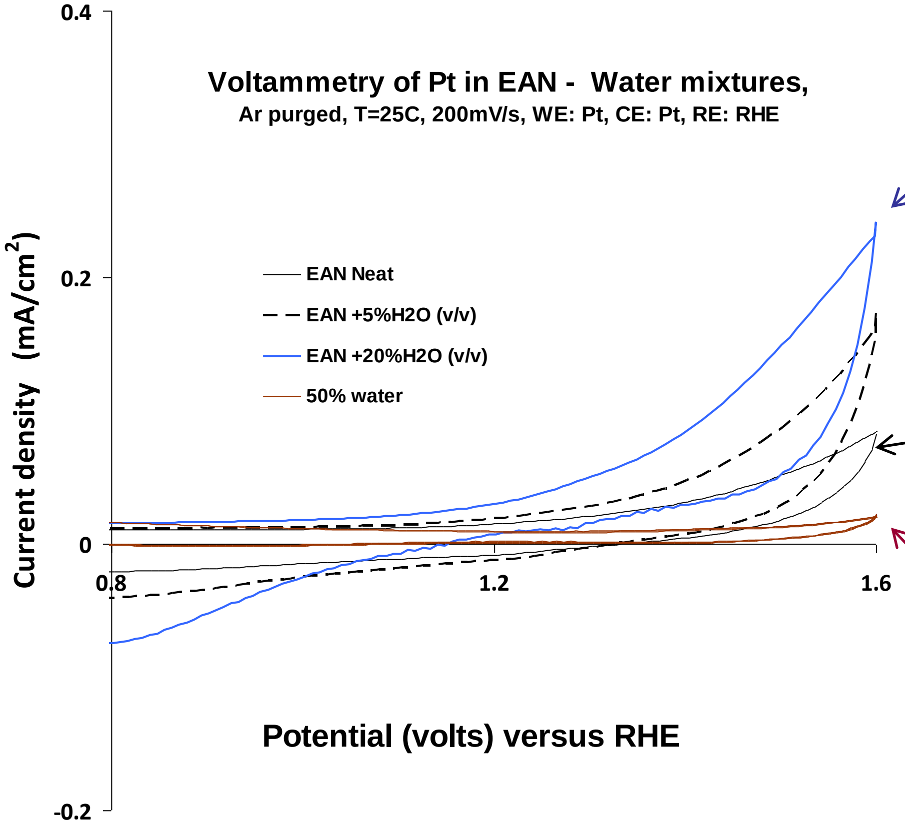
Voltammetry of Pt in 2-fluorpyridium triflate shows:

- 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*

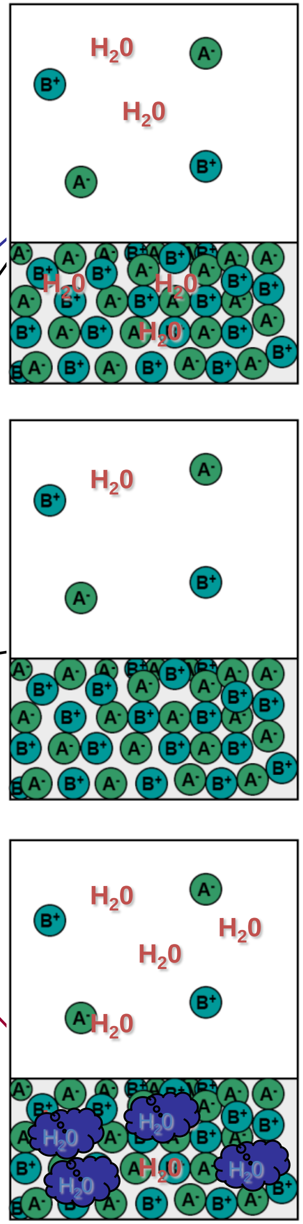
Effects of Dispersed and Bulk Water

H_20 = dispersed water

H_20 = bulk water



Stable



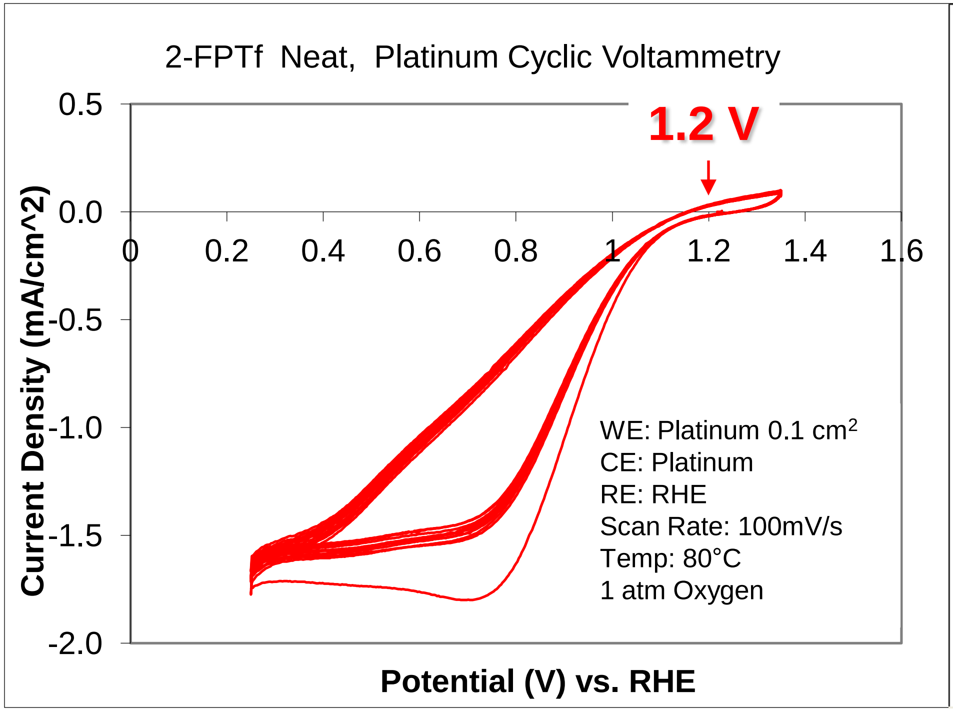
5 to 20% Dispersed H_20 in IL

Trace H_2O in Neat IL

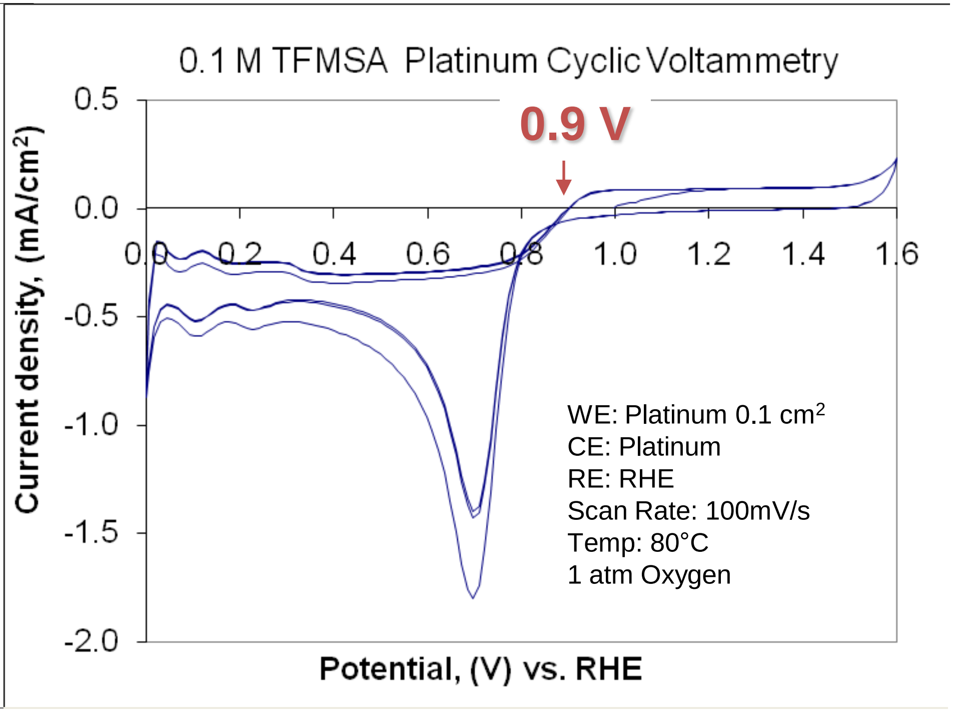
50% Dispersed and Bulk H_20 in 50% IL

Voltammetry of Pt in Fluorinated Ionic Liquid vs Aqueous Electrolyte

without bulk water



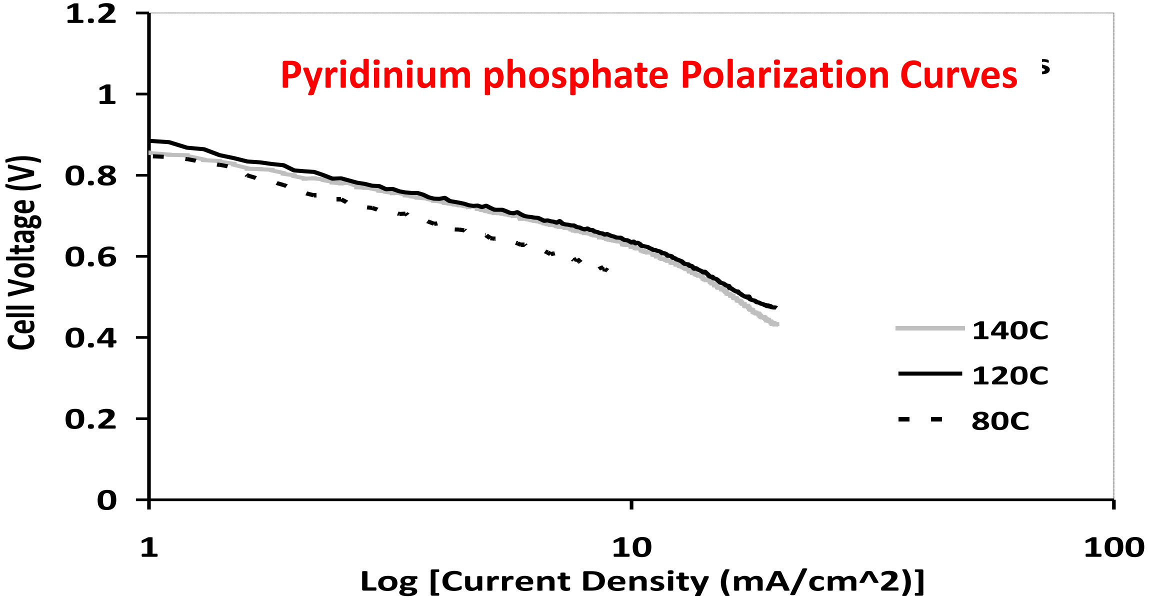
with bulk water



- **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]**

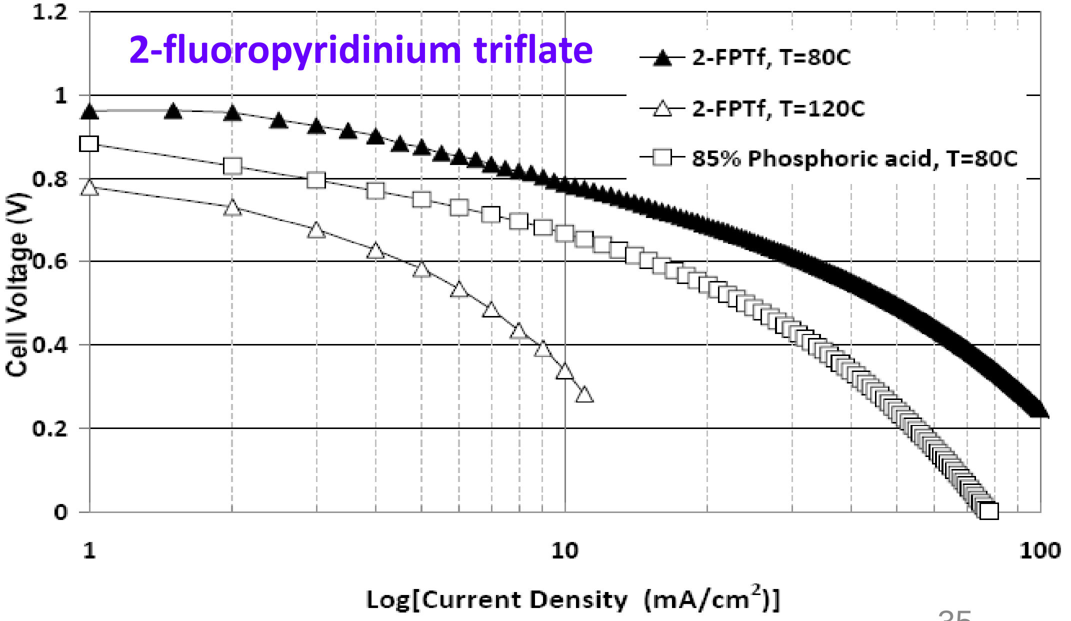
Water free

Hydrocarbon pIL (PP) vs fluorocarbon pIL (2-FPTf)



Hydro-carbon (PP)
- Stronger adsorbing
- *Lower* power

Fluoro-carbon (2-FPTf)
- Weaker adsorbing
- *Higher* power



Voltammetry of hydrocarbon and fluorocarbon Ionic Liquid Electrolytes

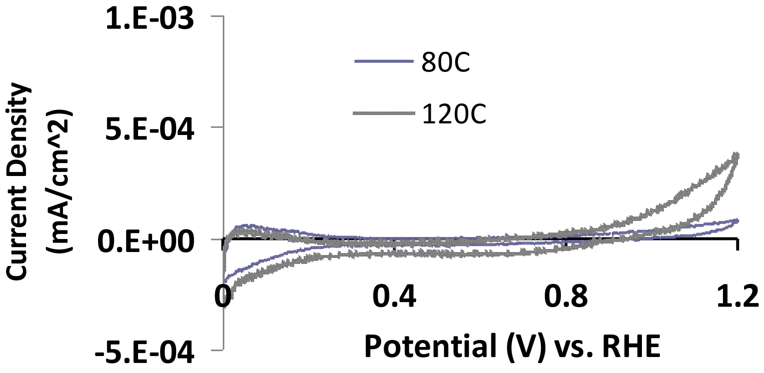
Voltammetry of Pt in pyridinium phosphate shows:

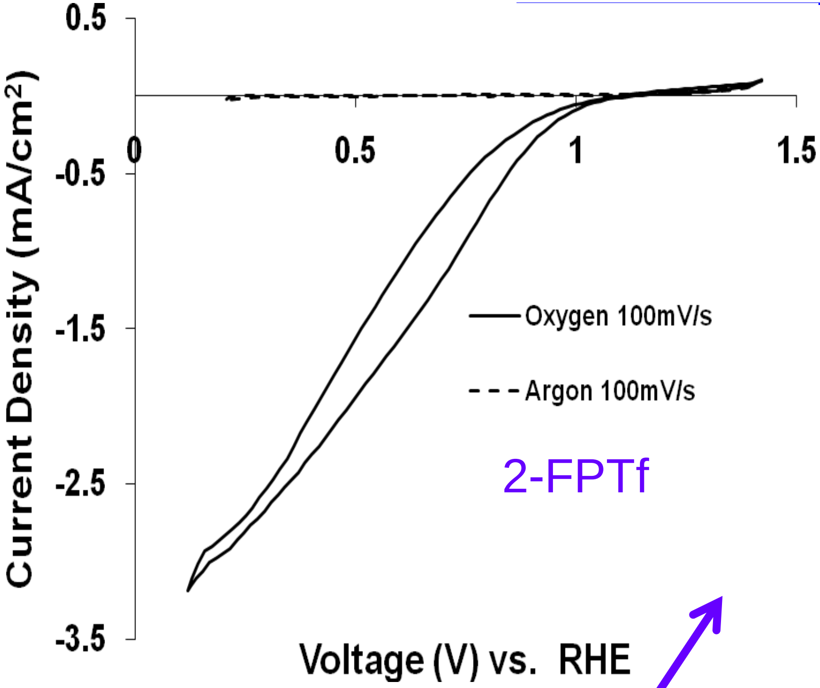
- **Oxidatively unstable**
- **Lower O2 reduction current**

Voltammetry of Pt in 2-fluorpyridium triflate shows:

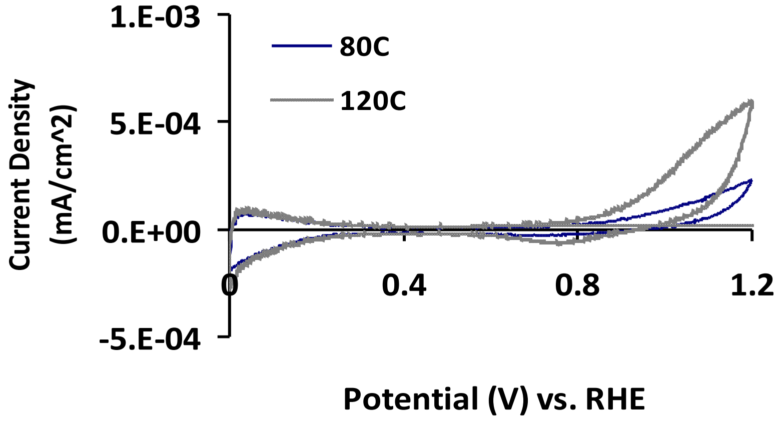
- Stable after 100 cycles in presence of O_2
- O_2 reduction starts near thermodynamic limit [1.18V at 80ºC
- Oxidation current at E>1.18V *is for water oxidation to O_2*

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

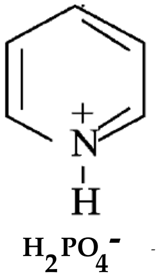




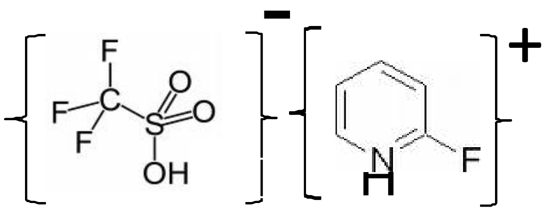
Pt Voltammetry in Pyridinium Phosphate under Nitrogen Scan Rate = 100 mV/s



Weakly adsorbing



Pyridinium Phosphate



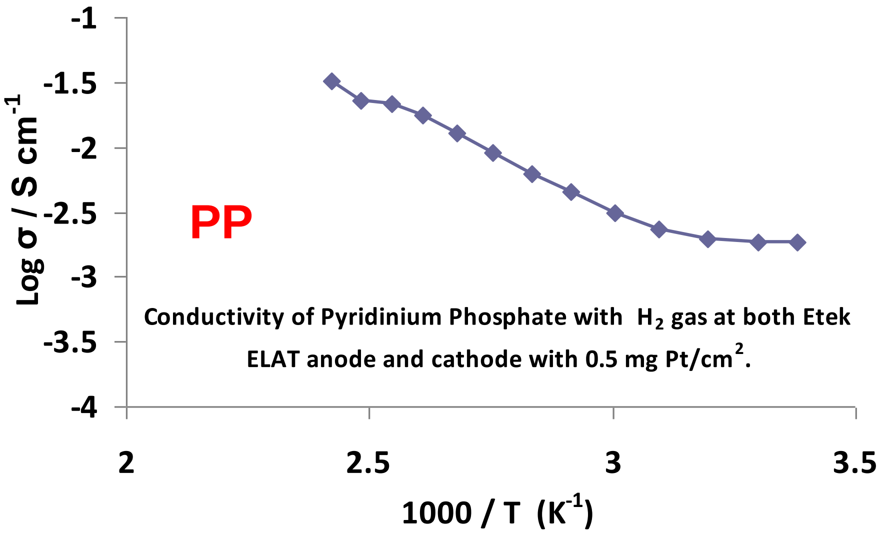
2-Fluoropyridiniumtriflate

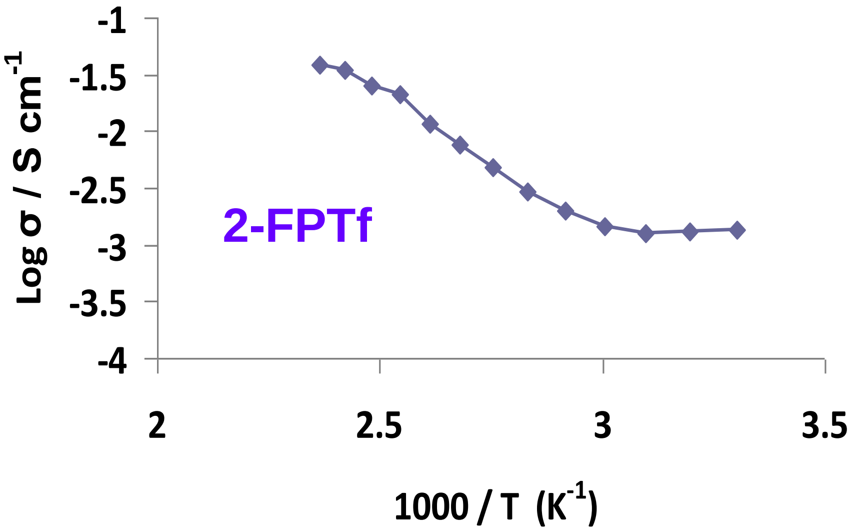
Proton Conductivity of Liquid hydrocarbon vs fluorcarbon pIL

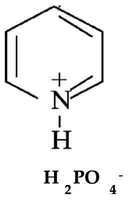
as a function of temperature, dry H2 gas fed to ETEK ELAT Pt anode and cathode

Liquid hydrocarbon pIL
pyridinium phosphate (PP)

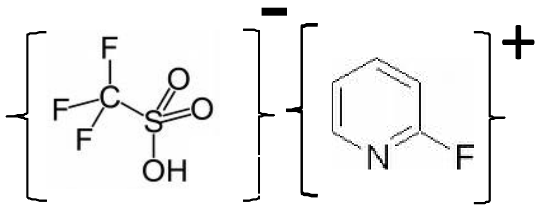
Liquid fluorocarbond
Fluoropyridinium triflate2-FPTf





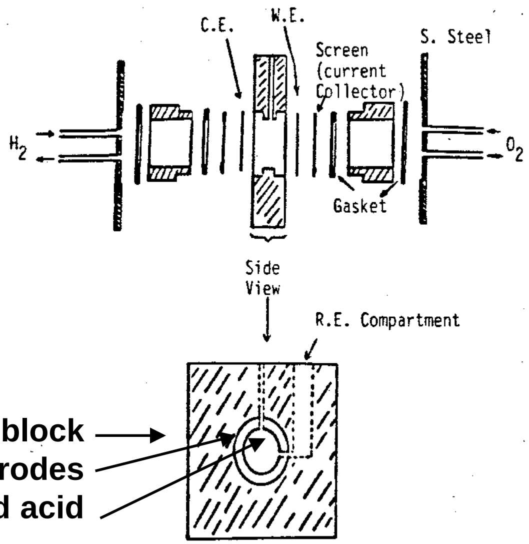


H$^+$ conductivities for
hydrocarbon pIL
and
fluorocarbon pIL
are about the same !

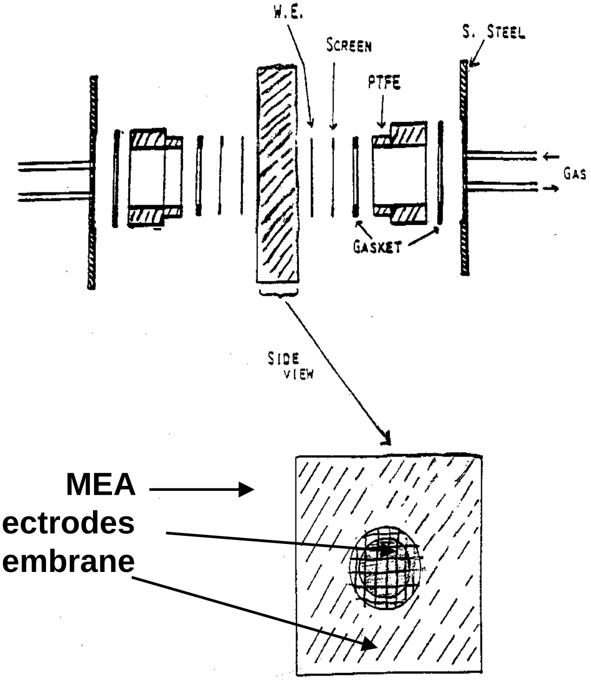


Liquid versus Solid Membrane as Proton Electrolyte

Schematic Diagram of Liquid vs Solid PEM Fuel Cell



Teflon block
Holds electrodes
Contains liquid acid



MEA
With electrodes on membrane

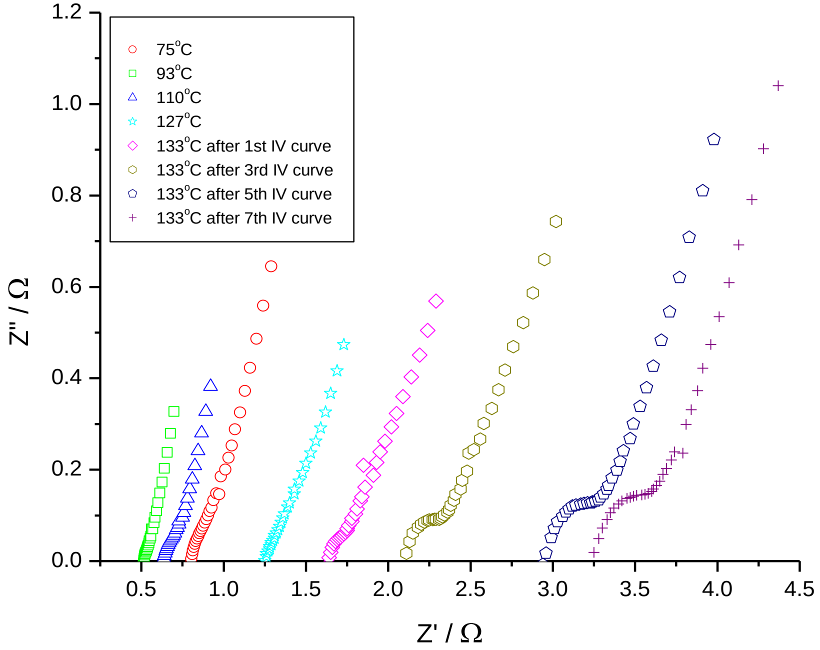
micro fuel cell with liquid electrolyte, like phosphoric acid.

micro fuel cell with PEM electrolyte, like Nafion.

Can you really make a proton "hop" through a pIL ?? !!

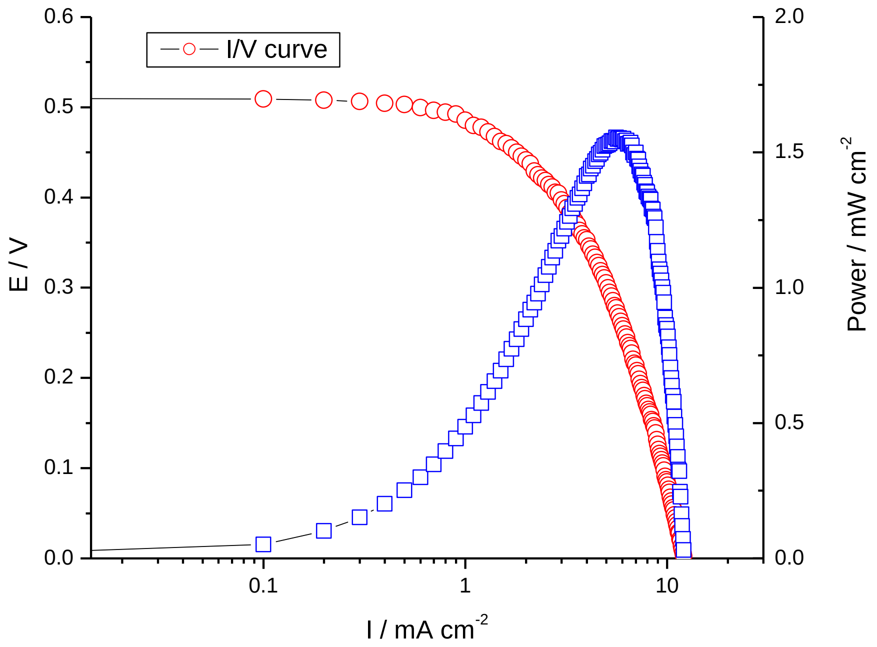
Non-leachable PEM 1:siloxane protic salt membrane

EIS for H^+ conductivity



Fuel Cell I/V Curve

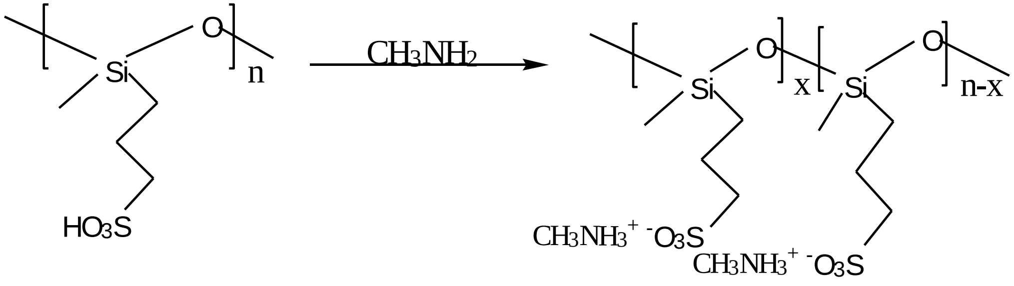
I/V curve and power for the fuel cell based on anodisc imbibed with polysiloxane with pendant sulfonic acid that neutralized by methylamine. Fuel cell runs at 127°C



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

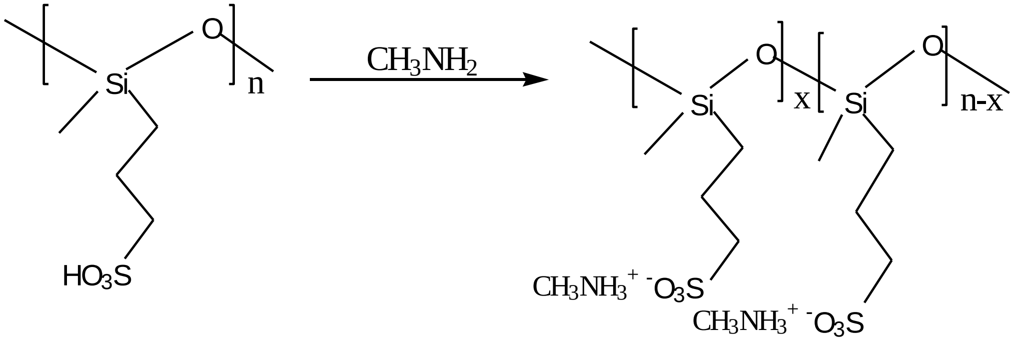
Non-leachable

Pendant sulfonic acid polymer fully neutralized with methyl amine

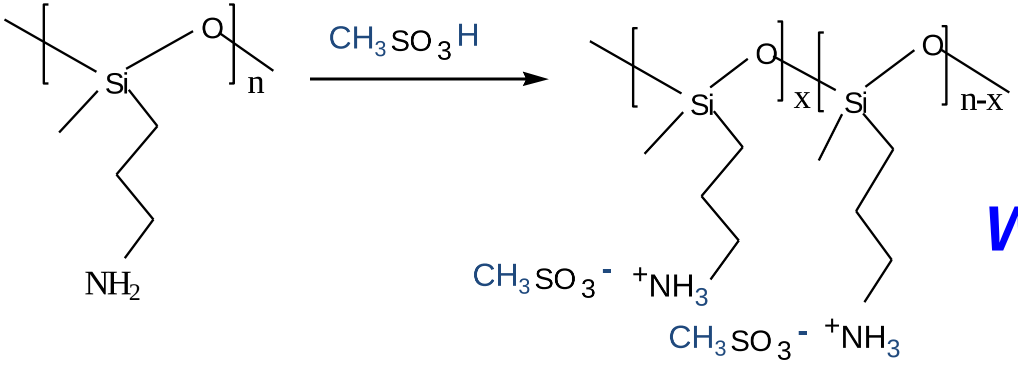


Summary on non-leachable Siloxane-based PEMs

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* appear as a “dry” proton-conductor in a fuel cell membrane.

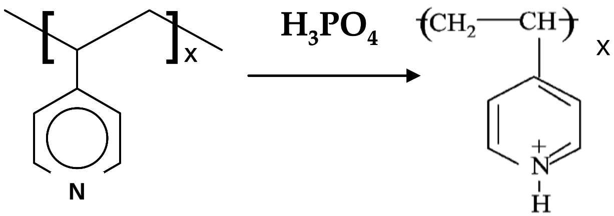
Con: siloxane membranes have limited physical stability (soft and water soluble) resulting in low performance (low open circuit voltage OCV, 0.45V, and low power, 2mW/cm^2) in a fuel cell due to reactant crossover in this PEM.

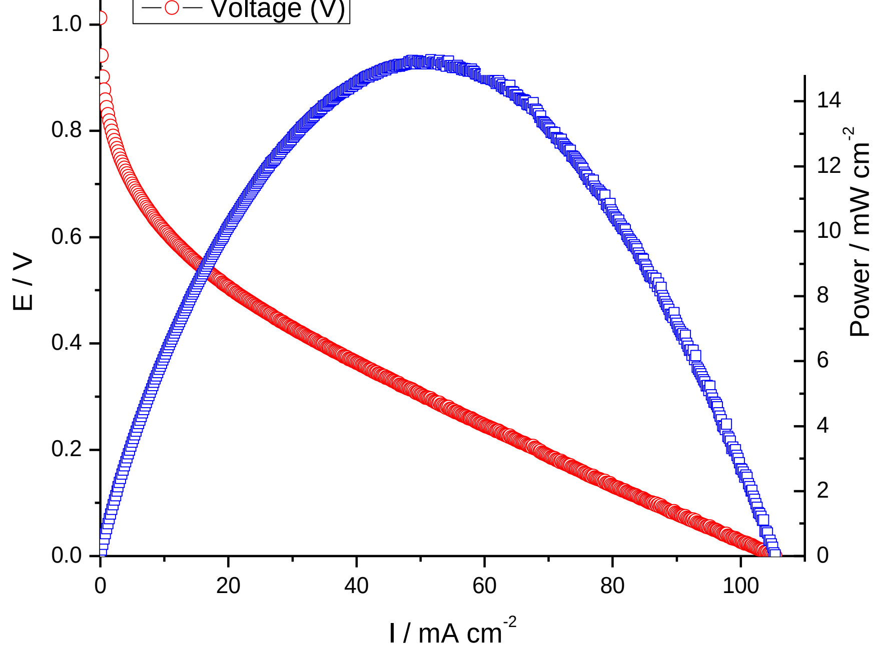
Was the H+ really hopping?

What’s next?

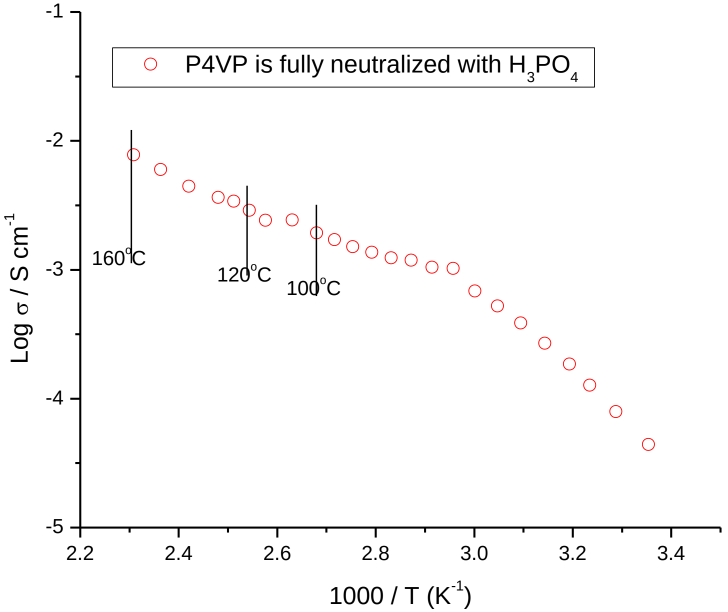
Another non-leachable PEM

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/cm^2 E-Tek ELAT electrodes. σ =0.005 S/cm. Temp. = 162^{o}C;

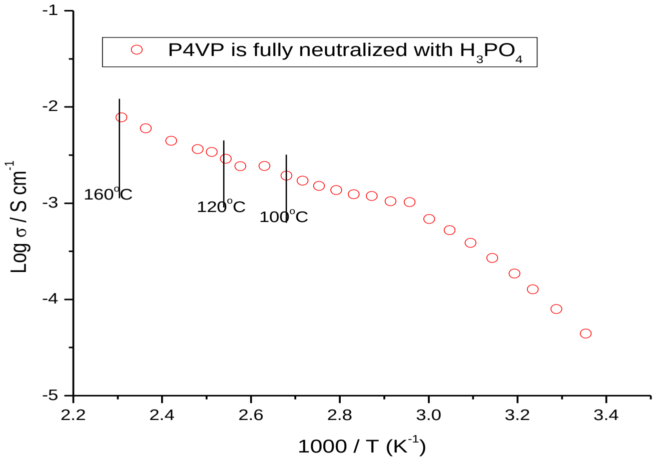


Conductivity of poly vinyl pyridine with 1 H3PO4 per 1 pyridine as a function of temperature.

Solid Membrane of Polyvinyl Pyridinium Phosphate vs Liquid Pyridinium Phosphate

Poly vinyl pyridine with 1 H_3PO_4 per 1 pyridine

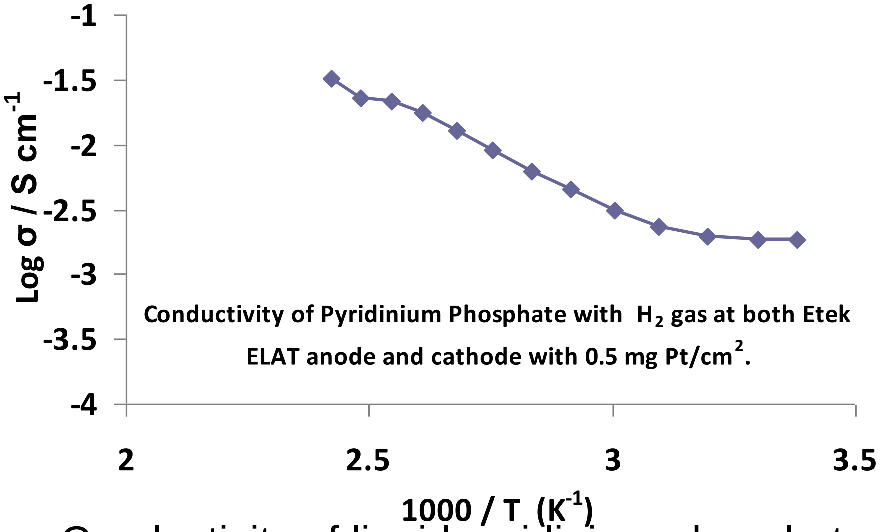
Solid Non-Leachable
Membrane Electrolyte



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

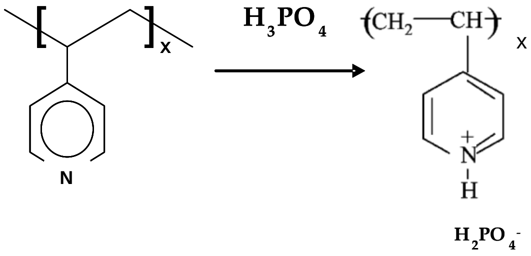
Liquid pyridinium phosphate

Analogous
Liquid Electrolyte



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

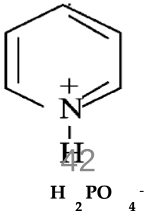
Conductivity of liquid pyridinium phosphate as a function of temperature, H_2 gas fed to both anode and cathode. Electrodes are E-tek ELAT with 0.5 mg Pt/cm^2.



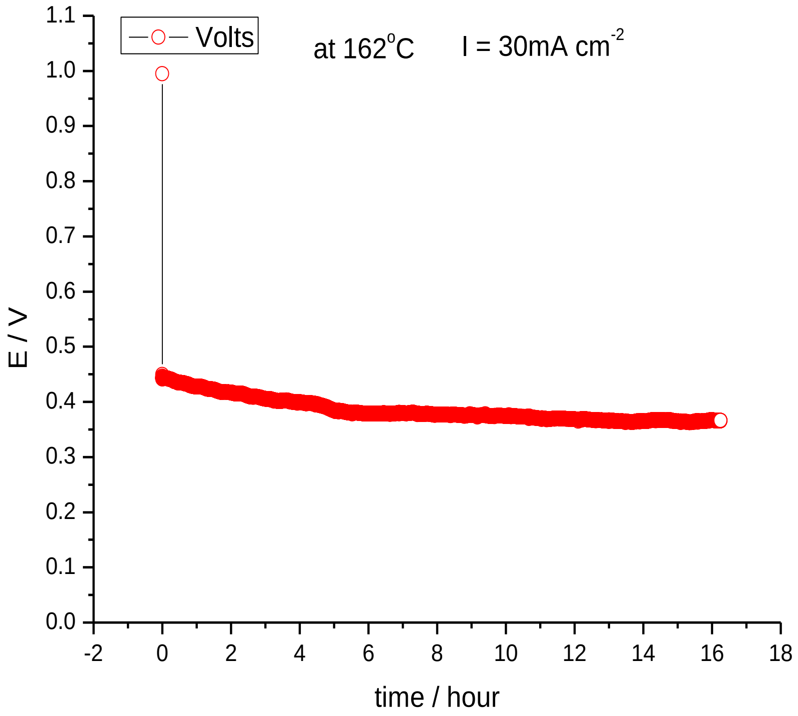
Solid

H+ conductivity for
solid salt
and
liquid salt
are SIMILAR !

Liquid



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



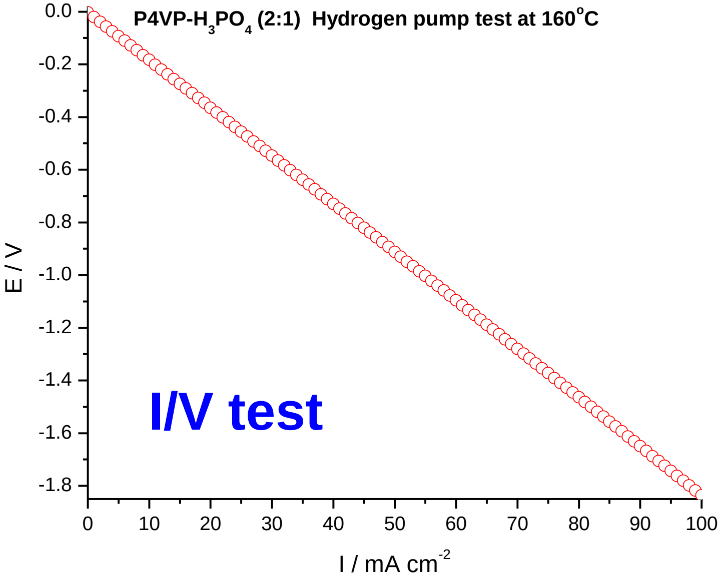
Cell voltage in time at constant load for a H_2/O_2 fuel-cell with a membrane made of polyvinylpyridine in which each pyridine is reacted with phosphoric acid. Pt loading =0.5 mg/cm^2 E-Tek ELAT electrodes. Load is 30 mA/cm^2. Temperature = 162°C.

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.

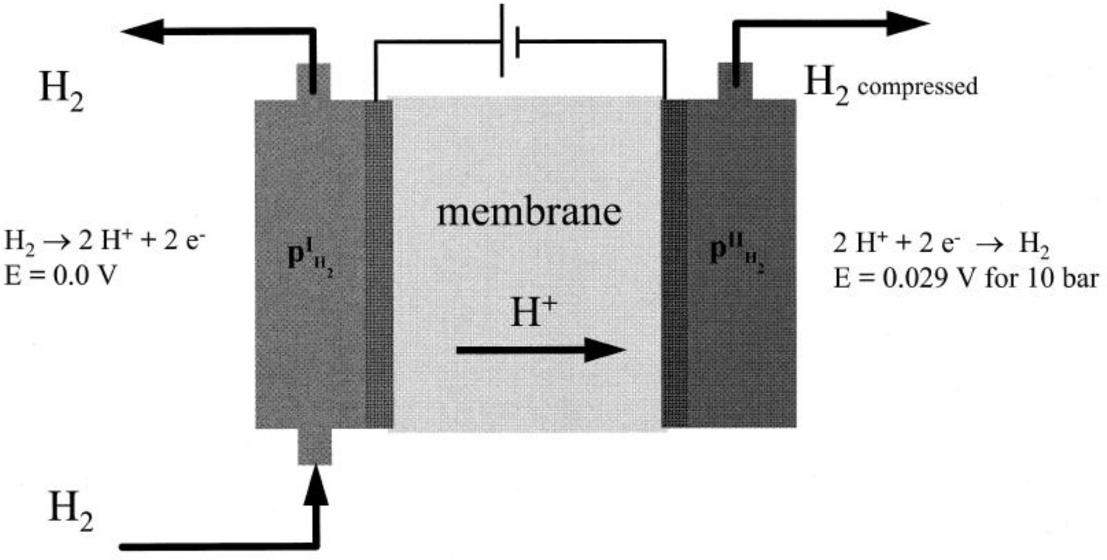
Overnight fuel cell stability while passing H^+ current

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

Electro-chemical Hydrogen Pump with PVPP membrane



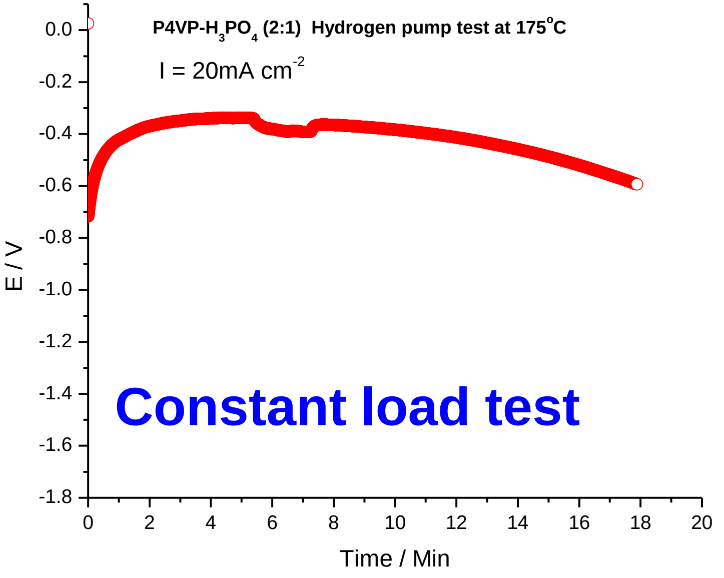
I/V test



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

Electrochemical H_2 pressurization

Pt loading =0.5 mg/cm² E-Tek ELAT electrodes.



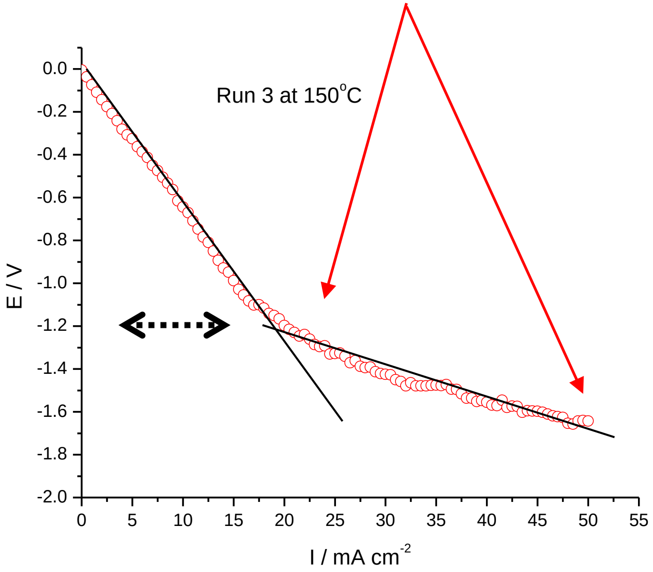
Constant load test

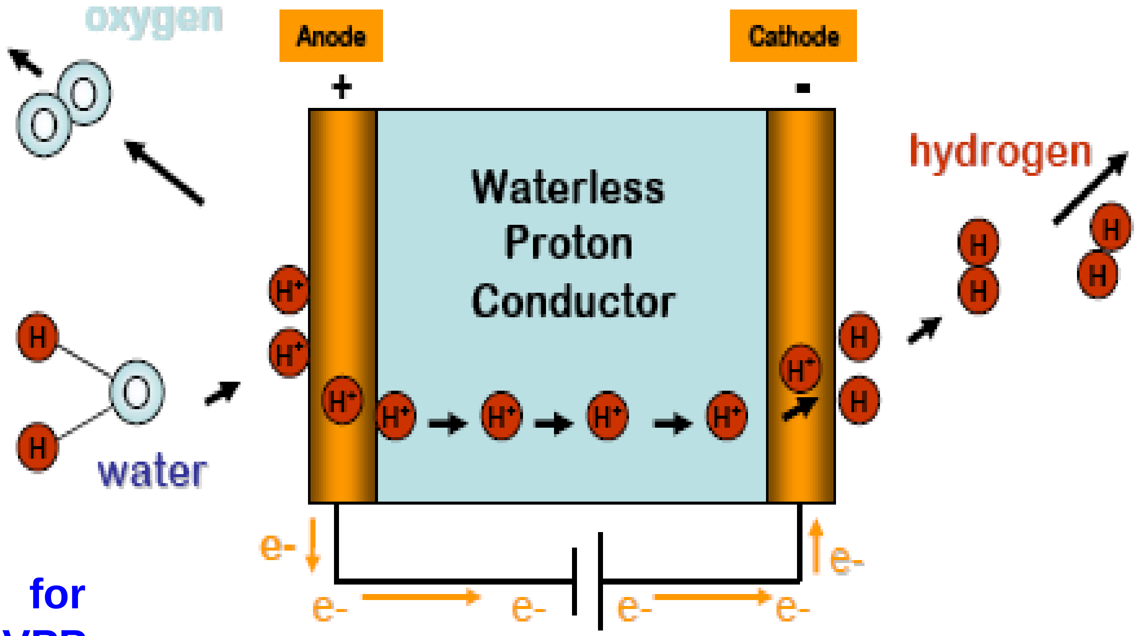
Proton is the only ion being conducted

Schematic diagram of the PEM electrolysis cell

using a membrane that requires no water for H^+ conduction

Is this really water electrolysis?

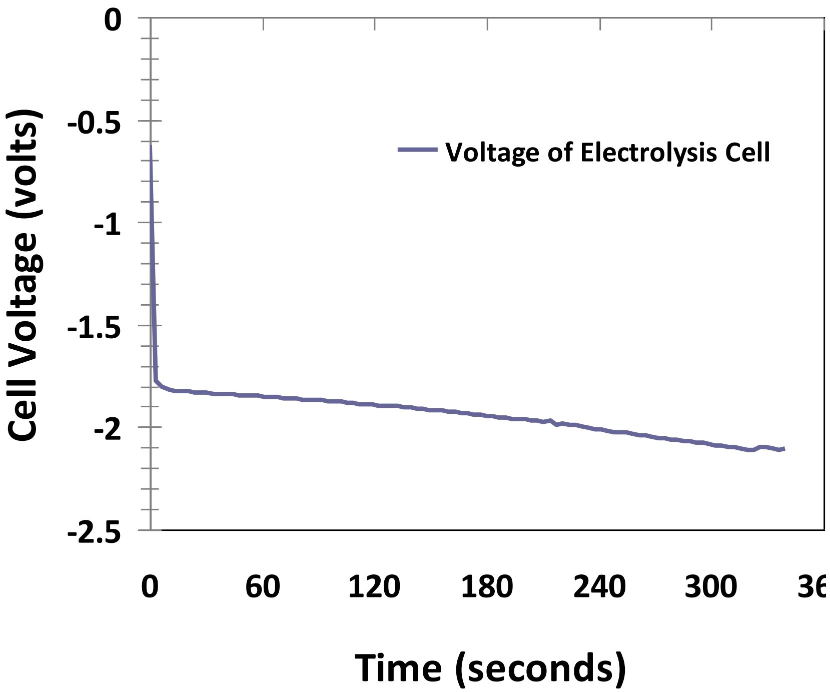


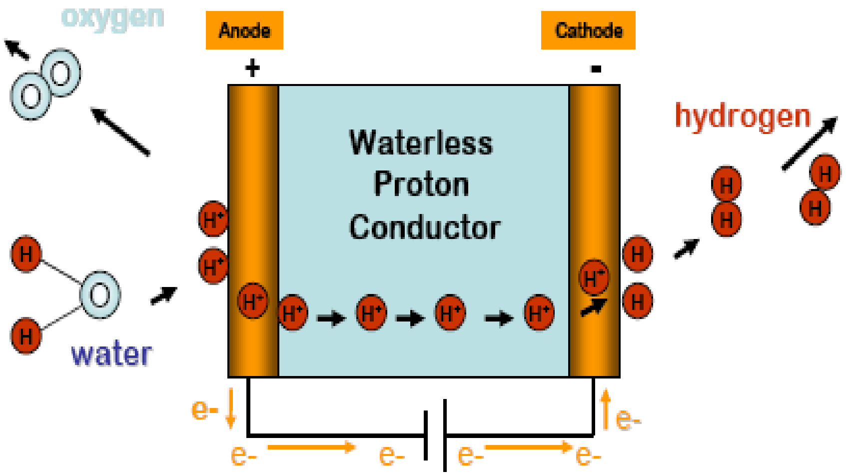


Preliminary experiment testing for water electrolysis on Pt using a PVPP membrane. Temperature of cell, 150°C. Water vapor temperature, 90°C.

Galvanostatic electrolysis of water on Pt in PVPP PEM cell

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





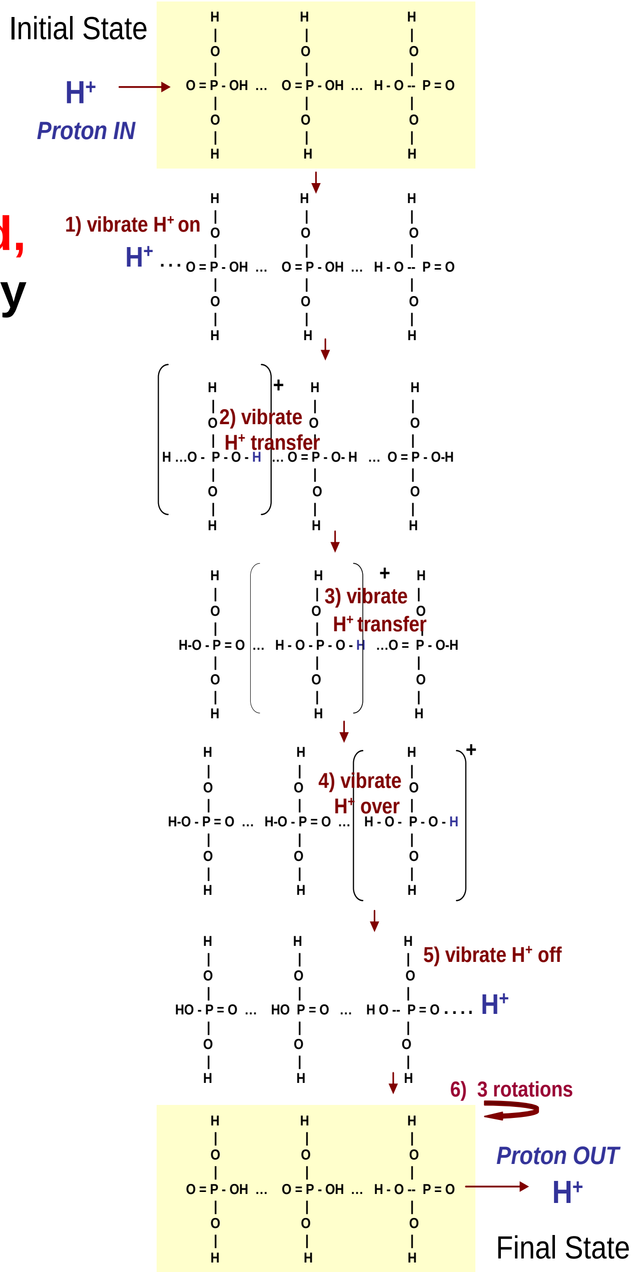
Cell voltage in time for the galvanostatic electrolysis of water on E-tek ELAT electrode with Pt loading of 0.5 mg/cm^2 used for anode and cathode with a solid electrolyte membrane (t=35 mil) of polyvinyl pyridinium phosphate (PV P^+ : $H_2PO_4^-$; 1:1). Constant cell load current = 11 mA/cm^2, Cell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

Yes, it really is water electrolysis and only Proton is conducted in the membrane !!

Ceramic Salts

Ions of In and Sn stabilize
“solid salts of phosphoric acid”

Proton hopping



Proton can transfer between phosphoric acid, H_3PO_4, and phosphonium ion, $H_4PO_4^+$, by rotational and vibration motions, because …

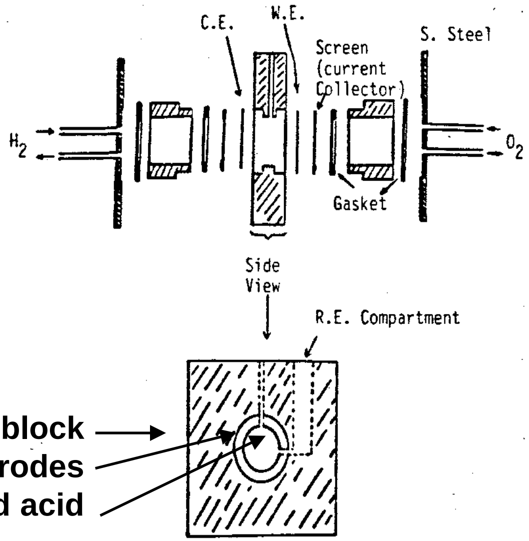
these 2 species

- **are high symmetrical (rotators)**
- **have suitable energy separation (proper ΔpK)**

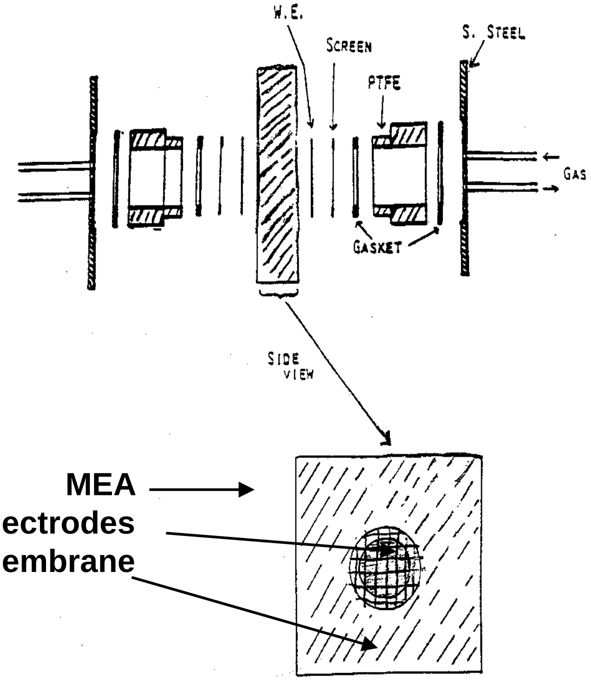
$$H_4PO_4^+ + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_3PO_{4(aq)} \qquad K_{a0} = \sim 10^2$$
$$H_3PO_4 + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)} \qquad K_{a1} = 7.5\times10^{-3}$$
$$H_2PO_4^- + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)} \qquad K_{a2} = 6.2\times10^{-8}$$
$$HPO_4^{2-} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)} \qquad K_{a3} = 2.14\times10^{-13}$$

$$pK_{a0} = -2$$
$$pK_{a1} = 3$$
$$pK_{a2} = 7$$
$$pK_{a3} = 12.7$$

Schematic Diagram of Liquid vs Solid PEM Fuel Cell



Teflon block
Holds electrodes
Contains liquid acid



MEA
With electrodes on membrane

Schematic representation of PTFE micro fuel cell with Gas Fed Electrodes and liquid electrolyte, like phosphoric acid.

Schematic representation of a micro fuel cell with Gas Fed Electrodes and PEM electrolyte, like Nafion.

Liquid Electrolyte vs Solid PEM Fuel Cell

Issues making *liquid fuel cells unacceptable*

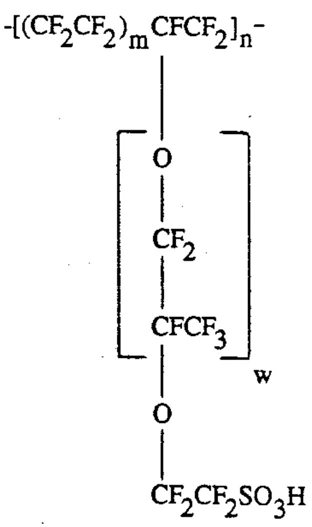
- liquids leak
- liquid can have ionic shorts
- liquids accelerate mechanical failure

All issues eliminated by using solid electrolytes

Solid electrolyte fuel cell is preferred !

Nafion Proton-Conducting Polymer Membranes

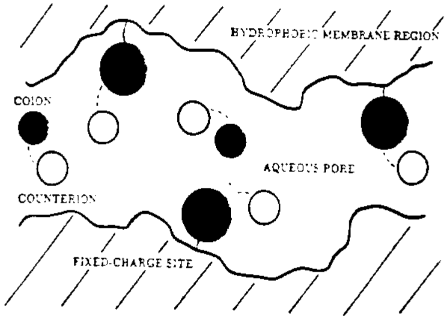
Nafion 117



Perfluorocarbon cation exchange polymer, shown here in the H^+ form.

Model of a channel

in a cation exchange polymer membrane
Where ion conduction is believed to occur.



● **Fixed charge sites (-SO3$^-$)**

● **Co-ions from H_3PO_4 ($H_2PO_4^-$, $H_4PO_4^+$)**

○ **Counter-ions to fixed charge (H^+)**

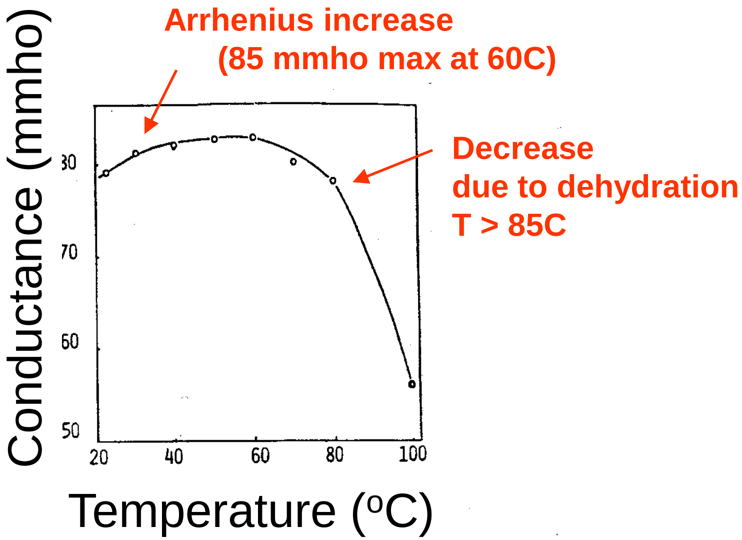
Note:

● **For Room temp represents water (H_2O)**

○ **For RT represents hydronium ion (H_3O^+).**

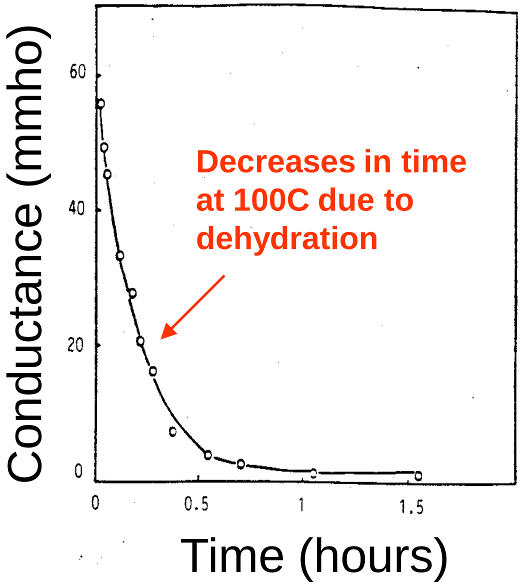
Low Temp Proton Conductance of Nafion 117 membrane

Pre-equilibrated with water



Arrhenius increase
(85 mmho max at 60C)

Decrease
due to dehydration
T > 85C



Decreases in time
at 100C due to
dehydration

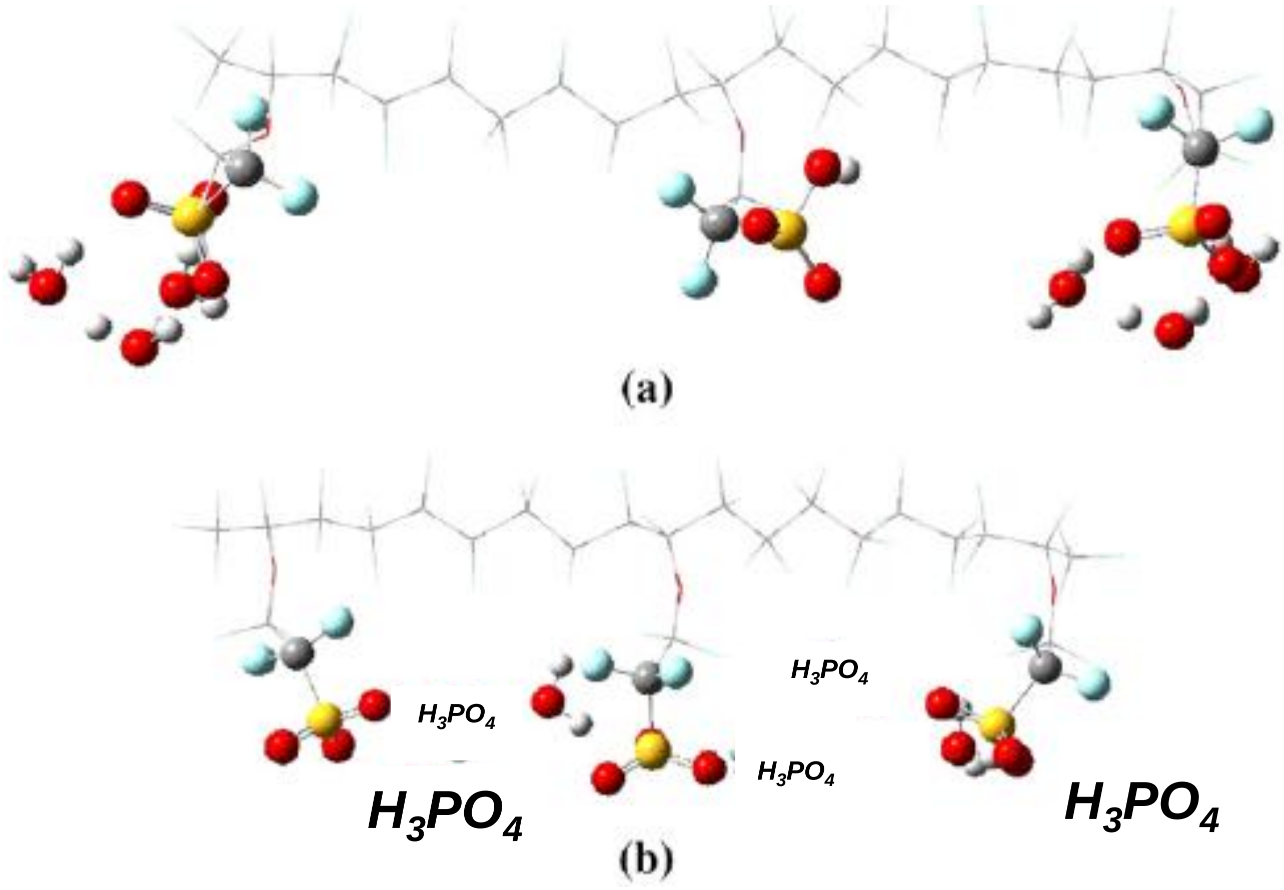
Conductance versus temperature
Geometrical Area = 2cm^2, t = 0.018 cm.

Conductance versus time at 100°C
Geometrical Area = 2cm^2, t = 0.018 cm.

From: "Oxygen Reduction in Various Acid Electrolytes",
E. Yeager, M. Razaq, D. Gervasio, A. Razaq, D. Tryk,
J. Serb. Chem. Soc., 57, 819-833 (1992).

As water goes away
so does the proton conductivity

To maintain Proton Conduction solvate Nafion with H_3PO_4 instead of H_2O



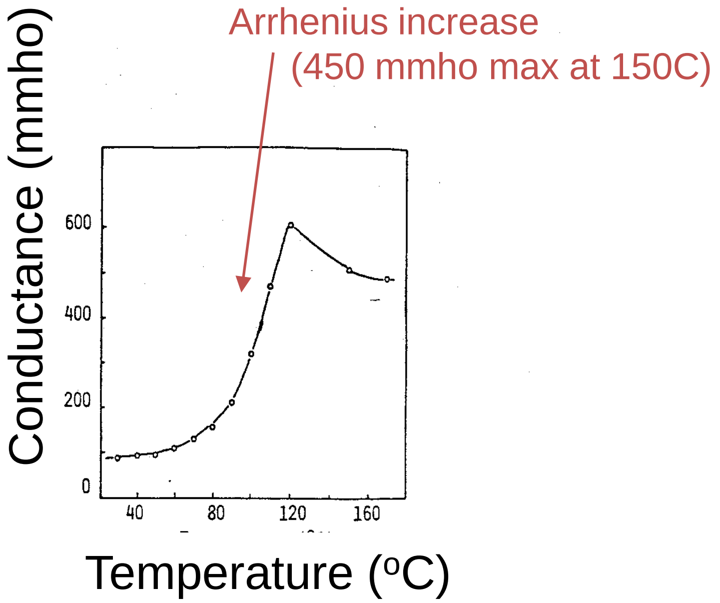
a) Non-conducting
Low ***H_3PO_4*** form

b) Conducting
High ***H_3PO_4*** form

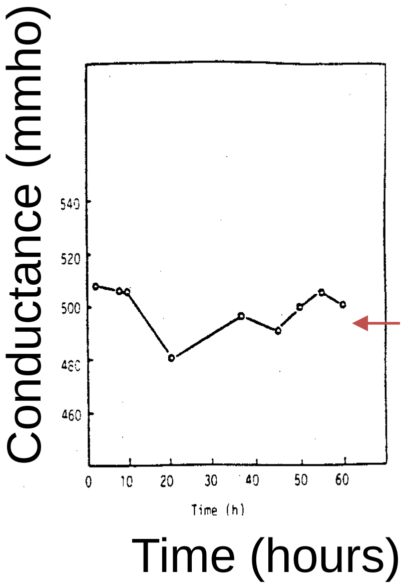
The *H_3PO_4* solvated Nafion membrane will conduct proton when the pendant acid and *H_3PO_4* units are in contact with adjacent units

High Temp: Conductance of Nafion 117 Membrane

Pre-equilibrated with ortho-phosphoric acid



Arrhenius increase
(450 mmho max at 150C)



Steady at 500 mmho
in time,
No dehydration !

Conductance versus temperature
Pre-equilibrated at 150°C for 12h.
Geometrical Area = 2cm^2, t = 0.018 cm.

Conductance versus time at 175°C
Pre-equilibrated at 150°C for 12h.
A = 2cm^2, t = 0.018 cm.

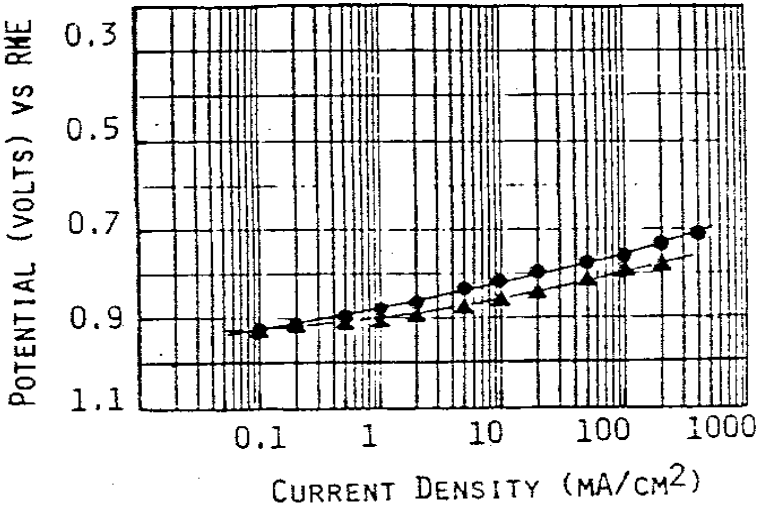
From: "Oxygen Reduction in Various Acid Electrolytes",
E. Yeager, M. Razaq, D. Gervasio, A. Razaq, D. Tryk,
J. Serb. Chem. Soc., 57, 819-833 (1992).

Phosphoric acid stays
so proton conductivity stays

Phosphoric acid loaded Nafion 117 MEA

H_2 / O_2 PEM *Fuel Cell Performance at 150 °C*

From: "Nafion 117 Membrane with Concentrated Phosphoric Acid as the Proton Solvating Agent for Use in a Solid Polymer Electrolyte (SPE) Fuel Cell",
D. Gervasio, M. Razaq, A. Razaq, E. Yeager
Electrochem. Soc. (1991), Washington, D.C., Ex. Abs., 91-1, 13.



~~First High Temperature PEM Fuel Cell~~

- **Good initial performance at ambient P and high T**
- **Dimensional instability**

IR-free Polarization Curve of a Prototech standard gas fed cathode (0.3 mg-Pt/cm^2) on a Nafion 117 membrane at 150°C at ambient pressure.

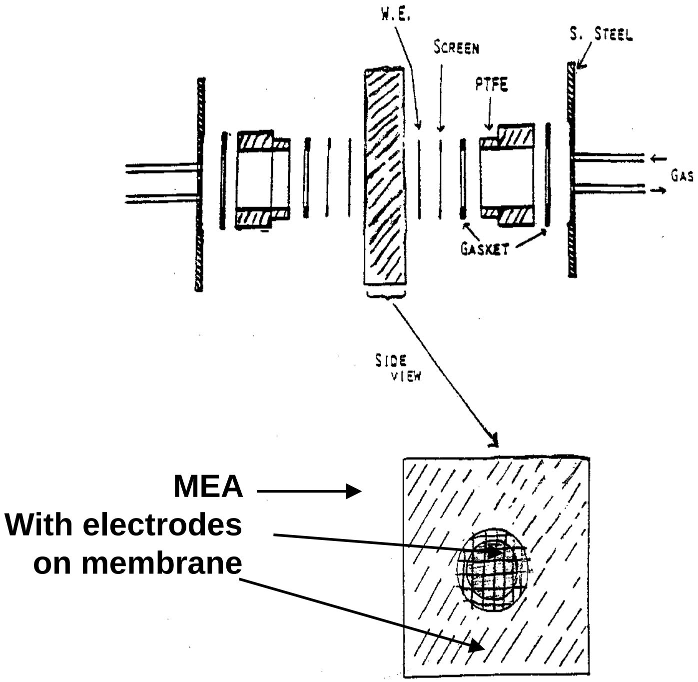
Membrane pre-equilibrated by soaking in H_3PO_4 for 12h at 150°C.
Pure O_2 cathode. Pure H_2 anode.

But H_3PO_4 comes out if soaked in water !!
What can you do to stop H_3PO_4 leaking out?

Indium tin phosphate (ITP = $In_{0.1}Sn_{0.9}P_2O_7$)

ITP Ceramic Membrane Synthesis

- Mix 3 reactants in Pt crucible
- Ramp temperature slowly to 650°C
- Press into membrane



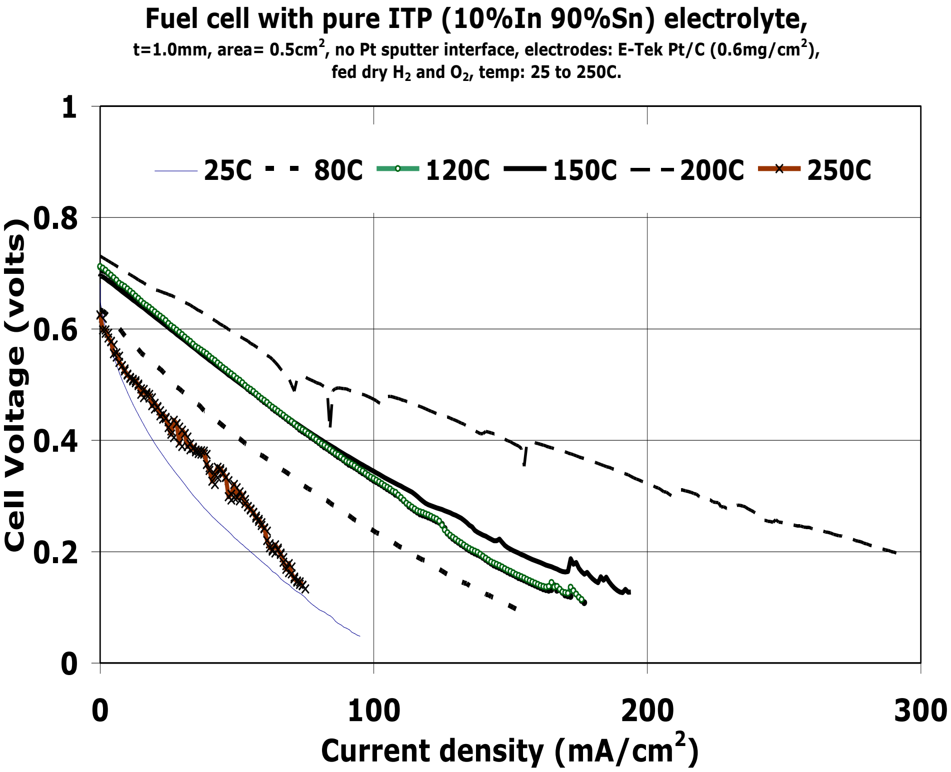
MEA

With electrodes on membrane

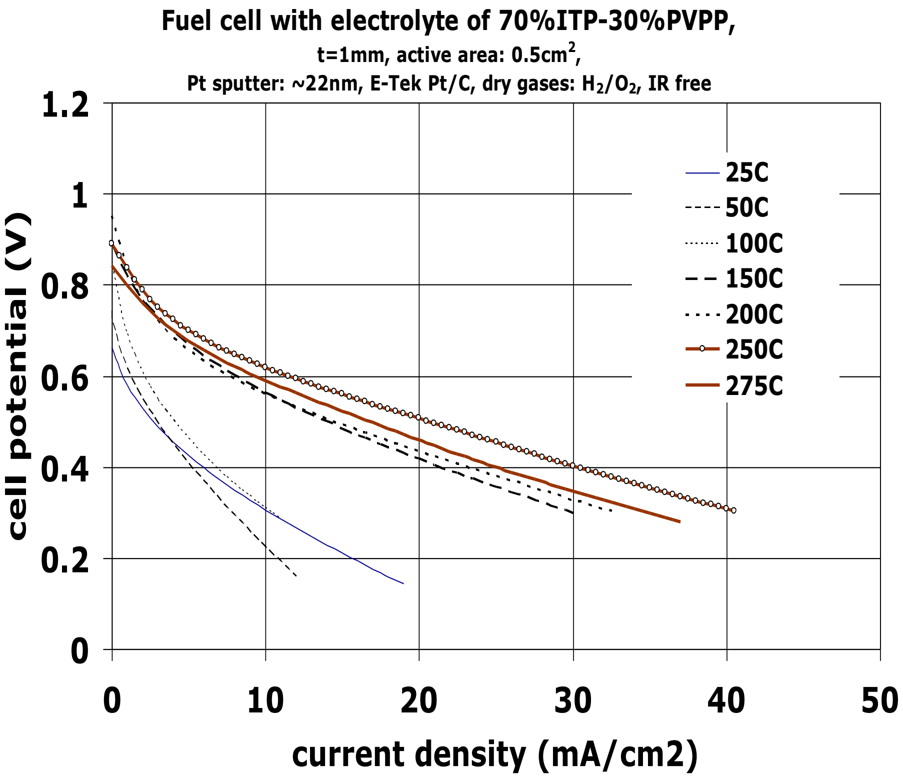
5 mol% In + 45 mol% Sn + 50 mol% $H_3PO_4 \rightarrow$ **$In_{0.1}Sn_{0.9}P_2O_7$**

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.

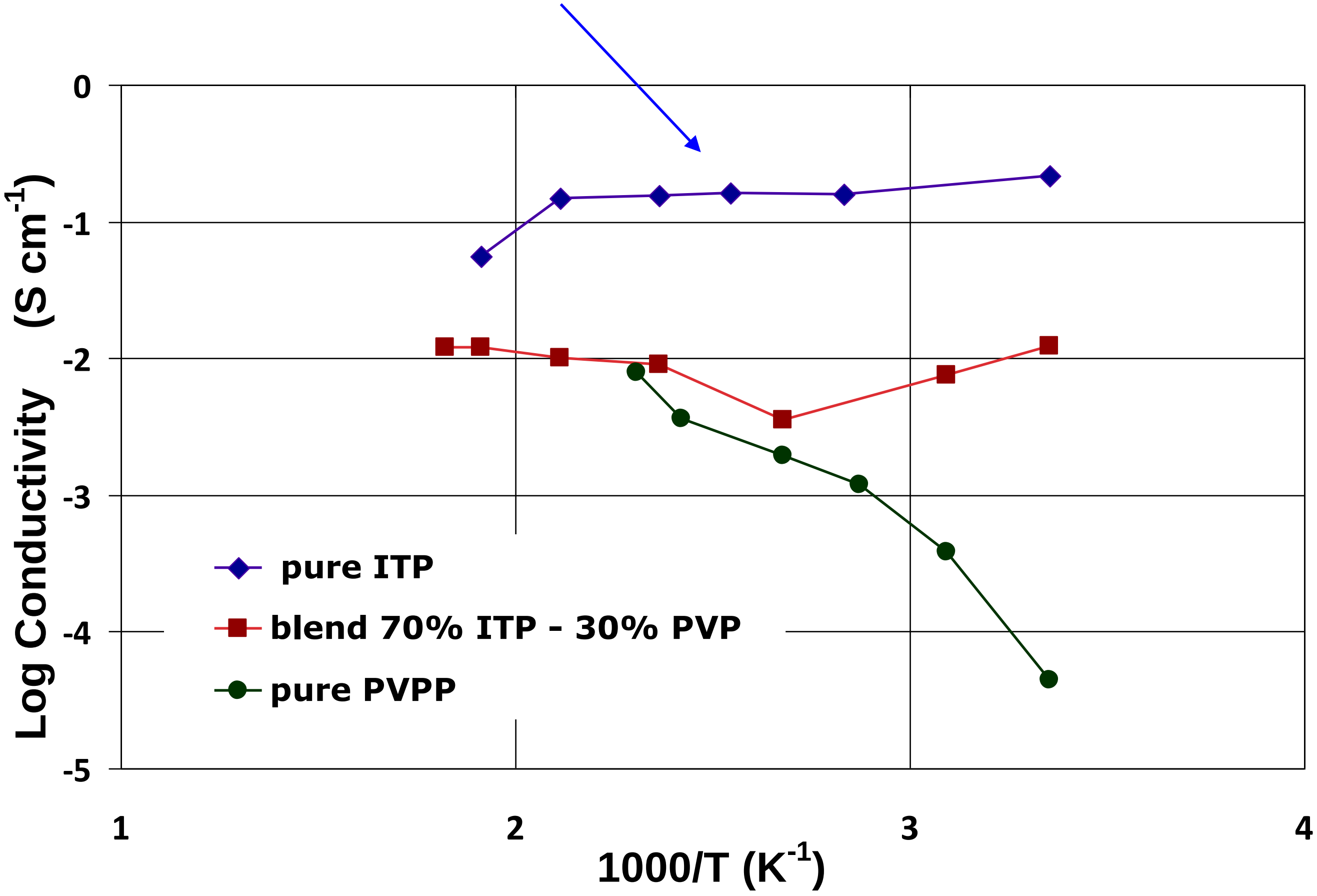
Blend 70% ITP 30% PVPP


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

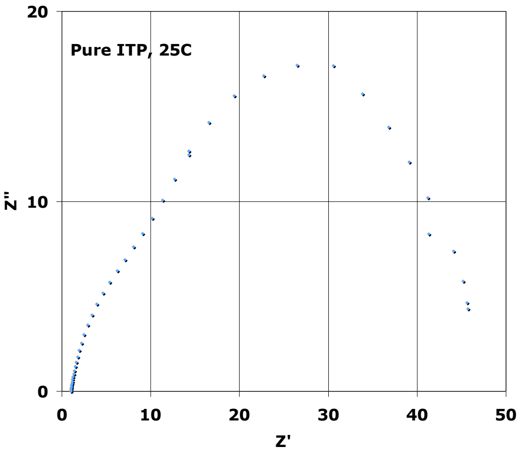
Membrane thickness=1mm, membrane area= 0.5cm^2
Electrode of ~22nm sputtered Pt with E-Tek GDL
Fed dry H_2/O_2 gases at Room Temperature to 250^{o}C

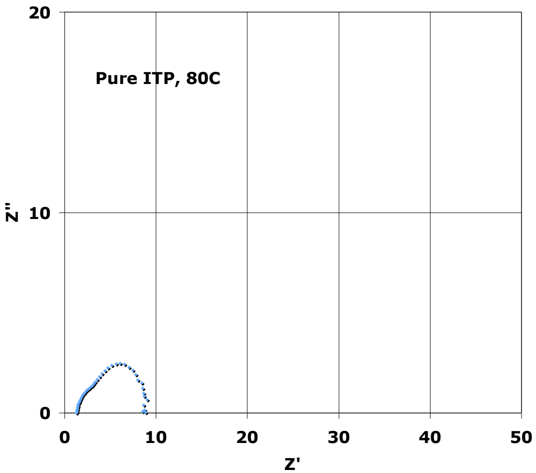
Proton Conducting Membranes of a Ceramic, a Polymer & a Ceramic-Organic Polymer Blend

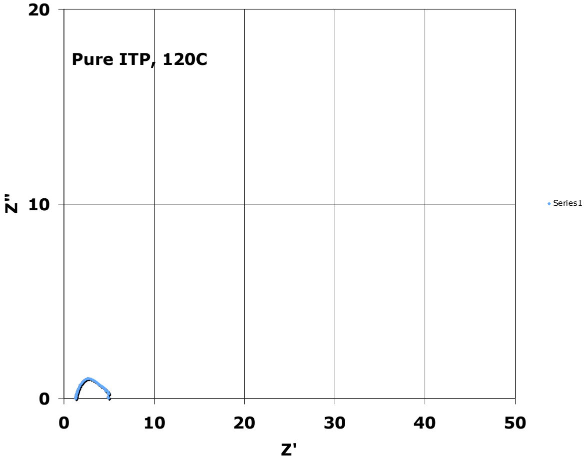
Conductivity of neat ITP ceramic membrane
> 0.1 S/cm* from 25C to 200C

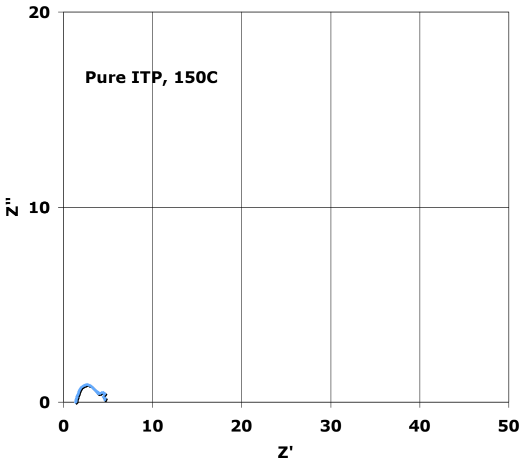


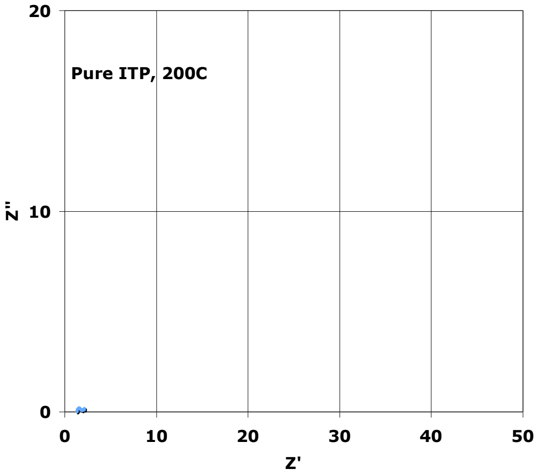
EIS of a dry non-leachable proton-conducting pure ITP (= $In_{0.1}Sn_{0.9}P_2O_7$) membrane

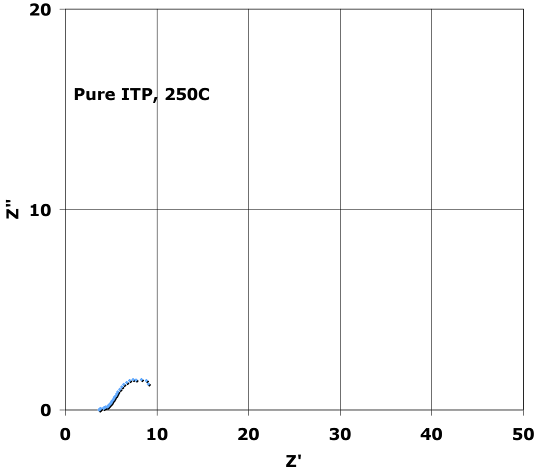






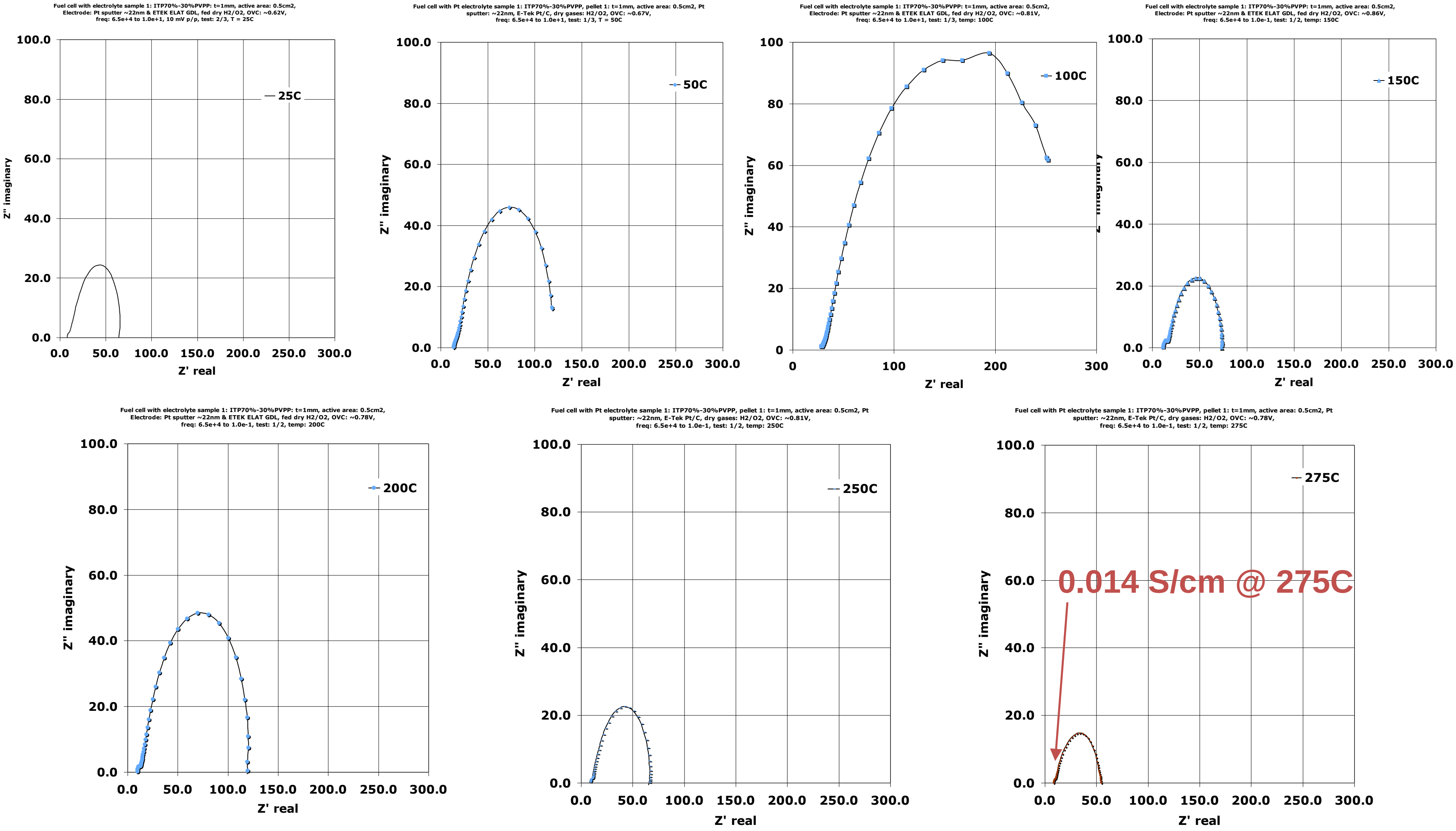






temp C	temp K	1000/T	Log G (S/cm)	G (S/cm)
25.0	298.2	3.35	-0.66	0.22
80.0	353.2	2.83	-0.80	0.16
120.0	393.2	2.54	-0.80	0.16
150.0	423.2	2.36	-0.82	0.15
200.0	473.2	2.11	-0.83	0.15
250.0	523.2	1.91	-1.26	0.06

EIS of a dry non-leachable proton-conducting 70% ITP-30% PVPP membrane



Fuel cell with electrolyte sample 1: ITP70%-30%PVPP: t=1mm, active area: 0.5cm2, Electrode: Pt sputter ~22nm & ETEK ELAT GDL, fed dry H2/O2, OVC: ~0.62V, freq: 6.5e+4 to 1.0e+1, 10 mV p/p, test: 2/3, T = 25C

Fuel cell with Pt electrolyte sample 1: ITP70%-30%PVPP, pellet 1: t=1mm, active area: 0.5cm2, Pt sputter: ~22nm, E-Tek Pt/C, dry gases: H2/O2, OVC: ~0.67V, freq: 6.5e+4 to 1.0e+1, test: 1/3, T = 50C

Fuel cell with electrolyte sample 1: ITP70%-30%PVPP: t=1mm, active area: 0.5cm2, Electrode: Pt sputter ~22nm & ETEK ELAT GDL, fed dry H2/O2, OVC: ~0.81V, freq: 6.5e+4 to 1.0e+1, test: 1/3, temp: 100C

Fuel cell with electrolyte sample 1: ITP70%-30%PVPP: t=1mm, active area: 0.5cm2, Electrode: Pt sputter ~22nm & ETEK ELAT GDL, fed dry H2/O2, OVC: ~0.86V, freq: 6.5e+4 to 1.0e-1, test: 1/2, temp: 150C

Fuel cell with electrolyte sample 1: ITP70%-30%PVPP: t=1mm, active area: 0.5cm2, Electrode: Pt sputter ~22nm & ETEK ELAT GDL, fed dry H2/O2, OVC: ~0.78V, freq: 6.5e+4 to 1.0e-1, test: 1/2, temp: 200C

Fuel cell with Pt electrolyte sample 1: ITP70%-30%PVPP, pellet 1: t=1mm, active area: 0.5cm2, Pt sputter: ~22nm, E-Tek Pt/C, dry gases: H2/O2, OVC: ~0.81V, freq: 6.5e+4 to 1.0e-1, test: 1/2, temp: 250C

Fuel cell with Pt electrolyte sample 1: ITP70%-30%PVPP, pellet 1: t=1mm, active area: 0.5cm2, Pt sputter: ~22nm, E-Tek Pt/C, dry gases: H2/O2, OVC: ~0.78V, freq: 6.5e+4 to 1.0e-1, test: 1/2, temp: 275C

0.014 S/cm @ 275C

Electrochemical Impedance Spectroscopy of a fuel cell with 70% ITP-30% PVPP solid electrolyte at T = 25, 50 100, 150, 200. 250, 275^{o}C, **(ITP = $In_{0.1}Sn_{0.9}P_2O_7$)**
Electrode: Pt sputter ~22nm & ETEK ELAT GDL, fed dry H_2/O_2,
EIS freq: 6.5e^{+4} to 1.0e^{+1}, amplitude:10 mV, electrolyte t=1mm, area: 0.5cm^2.

Conclusions about Membranes with pure ITP and ITP-PVPP Blend

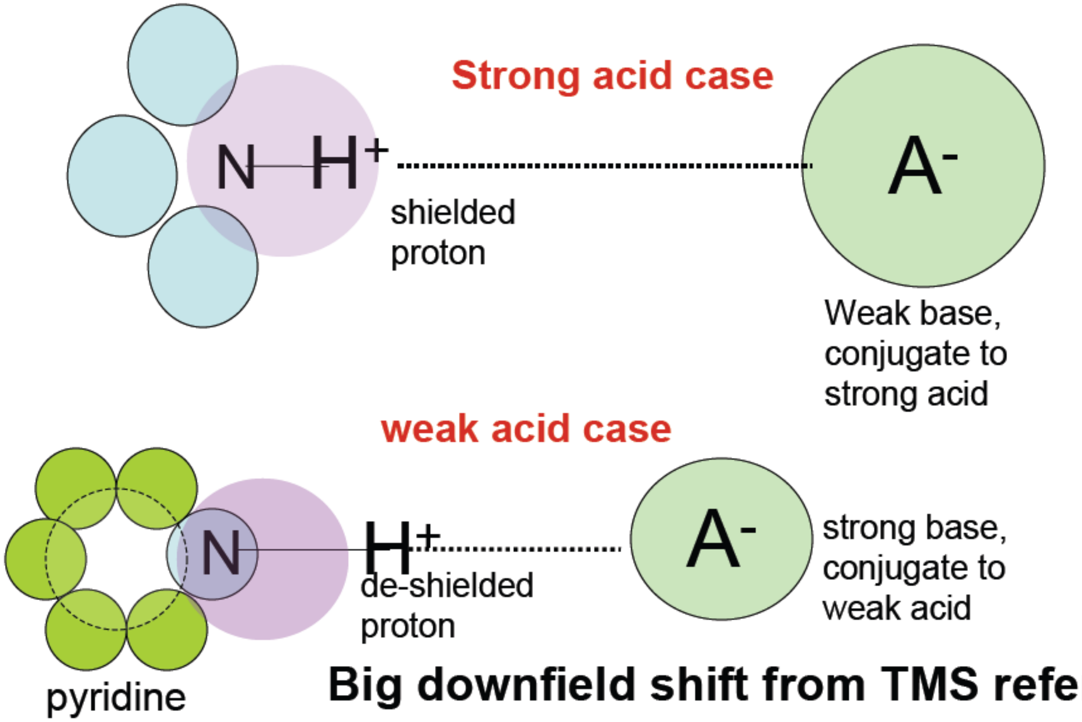
PURE ITP

- A neat indium tin phosphate (ITP) membrane was made that has conductivity 0.16 S/cm from 25°C to temperatures greater than 200°C and 0% RH which is better conductivity than PVVP and the blend of ITP & PVPP over all temperatures from 25C to 250C .
- Crossover eliminated by blending 70 wt% ITP with 30 wt% of a proton conducting organic polymer, PVPP, but at a cost of reduced conductivity.
- Pure ITP showed lower OCV but higher power than blend of ITP & PVPP over all temperatures
- Finding a suitable ITP-polymer blend is desirable to stop crossover in pure ceramic ITP

BLEND of ITP-PVPP

- 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 from 25 to 275C with an unexpected slight drop in conductivity between 25C and 100C.

Characterization of protic salt by following the NMR chemical shift of the N-H proton



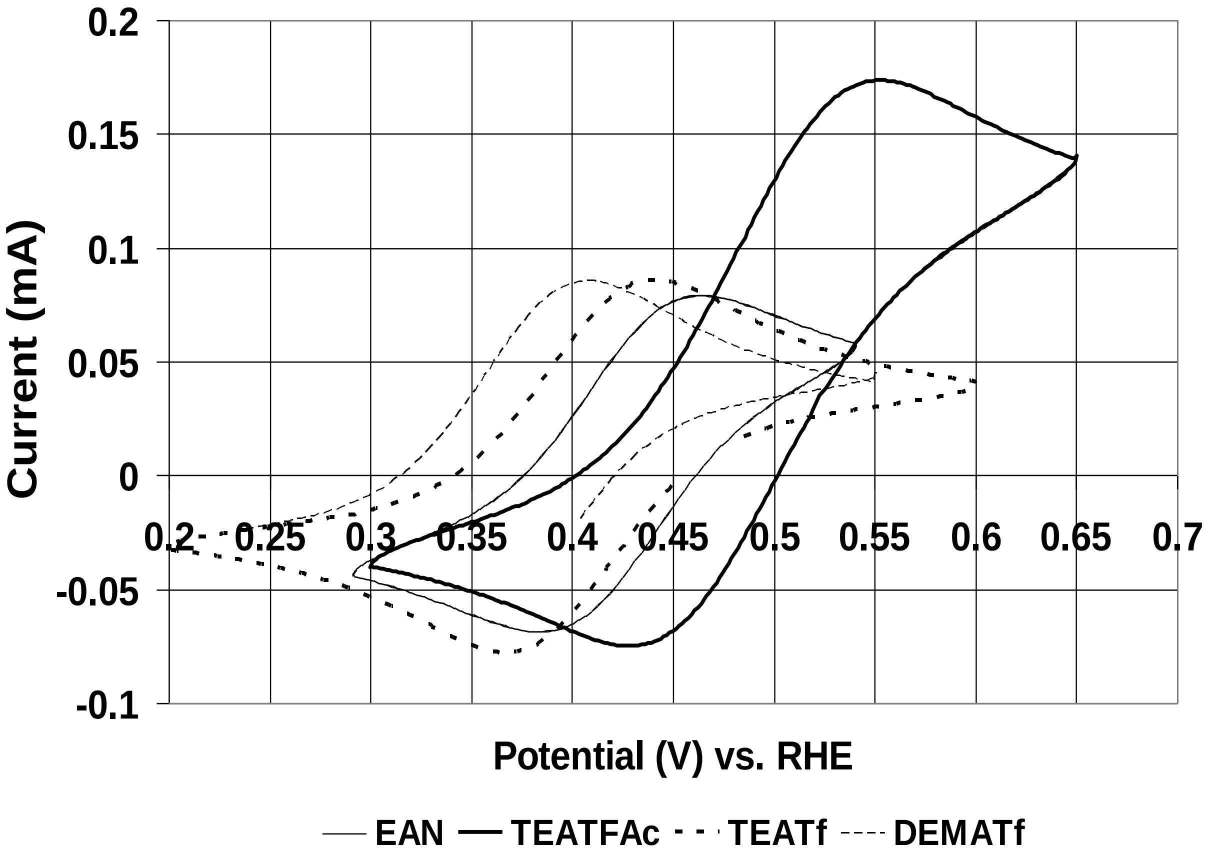
Big downfield shift from TMS reference

Acid strength from the voltammetry of ferrocene in solution

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

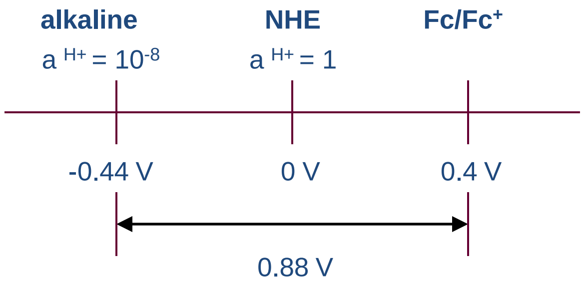


The acidity function H can be defined by

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

- 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).

Conclusions

Evidence is presented showing that new protic salt membrane electrolytes conduct only proton with no water

With no bulk water activity, salt electrolytes allow for higher performance Pt electro catalysis.

Recent advances in new protic salt electrolytes show promise for higher efficiency and more robust

- **Fuel cells**
- **Hydrogen generation by water electrolysis**
- **Hydrogen compressors**

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

❑ Status of Protic Ionic Liquids (pILs)

- Found stable pILs with high proton conductivity and fuel cell performance
- Demonstrated proton conductivity and fuel cell performance in non-leachable protic salt polymer and ceramic membranes
- 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 blendsof ITP with salt and inert polymers, like VITON
- Continue NMR characterization of relative proton and counterion mobilities.
- Chemical NMR imaging of membranes as a function of proton current.

Acknowledgements

U. S. Army Research Office
U. S. Department of Energy
for supporting this work

Thank you for your attention

Additional Slides

Publications

1. **“Protic Salt Polymer Membranes: Water-Free Proton-Conducting Membranes”**, D. Gervasio, invited talk to the Southeast Regional Meeting American Chemical Society (SERMACS), Greenville, SC, October 26, 2007.
2. **“High temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFCs) for Portable Power in Large-Scale Energy Storage Devices”,** D. Gervasio, Paper Number 195, 212th Meeting of the Electrochemical Society, Washington DC, October 11, 2007.
3. **“High Temperature Fuel Cells using Ionic Polysiloxane Membranes”,** With and Without Ionic Plasticizers, X. Sun, D. Gervasio and C. Angell (Arizona State University) Paper Number 442, 213rd Meeting of the ECS, May 18-22, 2008 Phoenix, AZ.
4. **“On the State of the Proton in Protic Ionic Liquids”**, J. Belieres, N. Byrne, D. Gervasio and C. Angell (Arizona State University) Paper Number 464, 213rd Meeting of the ECS, May 18-22, 2008 Phoenix, AZ.
5. **“Stable Protic Ionic Liquid (PIL) Fuel Cell Electrolytes”**, J. Thomson, R. Marzke and D. Gervasio (Arizona State University) Paper Number 466, 213rd Meeting of the ECS, May 18-22, 2008 Phoenix, AZ.
6. **“Binary inorganic salt mixtures as high conductivity liquid electrolytes for high temperature fuel cells”,** J.-P. Belieres, N. Byrne, X. Sun, D. Gervasio, J. Yarger and C. A. Angell, Paper number 321, The Electrochemical Society, Chicago, IL, May 6-10, 2007.
7. **“Characterization of Poly(dichlorophosphazene)s and their reactions to Poly(organophosphazene)s”,** Alyison Leigh; Sujeewani Ekanayake; Supat Moolsin; Matthew Panzer; Wiley Youngs; Claire Tessier; Chrys Wesdemiotis, The University of Akron, Akron, OH, Mass Spectroscopy Society Meeting, Session: Materials and Polymers - Poster Hall Code: WPJ Time Slot/Poster Number: 217 June 2008
8. **“Proton activity in ionic liquids: The ILPA index and its application in optimizing fuel cell efficiency, protein stability, and large molecule solubility”.** C.A. Angell, N. Byrne, J-P. Belieres, COIL II 2007(plenary lecture), Yokohama , Japan.
9. **“Protic ionic liquids as probes for acidity of superacids”,** *in preparation.*
10. **Study of Transport Properties of Trifluoromethanesulfonic acid monohydrate: Diffusivity, Conductivity and Viscosity,** Mohammed Abdullah, M. S. Thesis, Physics Department, Arizona State University, April, 2008.
11. **“Characterization of … protic ionic liquids: NH chemical shift”,** J.-P.Belieres in the I&EC division, Paper #82, ACS, Philadelphia, PA (2008).