Final Scientific/Technical Report

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IV. Project Title: Protic Salt Polymer Membranes: High-Temperature Water-Free Proton-Conducting Membranes

V. Principal Investigator: D. Gervasio, University of Arizona; Tucson, AZ
Team members: C.A. Angell, R. Marzke, J. Yarger, Arizona State University; Tempe, AZ
W. Youngs, University of Akron, Akron, OH

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VII. Executive summary

This research on proton-containing (protic) salts directly addresses proton conduction at high and low temperatures. This research is unique, because no water is used for proton ionization nor conduction, so the properties of water do not limit proton fuel cells. A protic salt is all that is needed to give rise to ionized proton and to support proton mobility. A protic salt forms when proton transfers from an acid to a base. Protic salts were found to have proton conductivities that are as high as or higher than the best aqueous electrolytes at ambient pressures and comparable temperatures without or with water present. Proton conductivity of the protic salts occurs providing two conditions exist: i) the energy difference is about 0.8 eV between the protic-salt state versus the state in which the acid and base are separated and 2) the chemical constituents rotate freely. The physical state of these proton-conducting salts can be liquid, plastic crystal as well as solid organic and inorganic polymer membranes and their mixtures. Many acids and bases can be used to make a protic salt which allows tailoring of proton conductivity, as well as other properties that affect their use as electrolytes in fuel cells, such as, stability, adsorption on catalysts, environmental impact, etc. During this project, highly proton conducting (~ 0.1S/cm) protic salts were made that are stable under fuel-cell operating conditions and that gave highly efficient fuel cells. The high efficiency is attributed to an improved oxygen electroreduction process on Pt which was found to be virtually reversible in a number of liquid protic salts with low water activity (< 1% water). Solid flexible non-porous composite membranes, made from inorganic polymer (e.g., 10%indium 90%tin pyrophosphate, ITP) and organic polymer (e.g., polyvinyl pyridinium phosphate, PVPP), were found that give conductivity and fuel cell performances similar to phosphoric acid electrolyte with no need for hydration at ambient pressures. Synthesis and processing of these protic salts into proton-conducting membrane is far from optimized. This protic salt approach has great promise for more improvements in proton conducting membranes for making practical compact, lightweight and inexpensive fuel cells with uses ranging from small electronics (Power = 1 to 100 Watts) to transportation (kiloWatts) to stationary applications ($\geq$100 kiloWatts).

VIII. Comparison of the actual accomplishments with the goals and objectives of the project.

VIII.1. The project objective was to make new proton-conducting solid polymer electrolyte membrane (PEM) materials with the following properties:

- High proton conductance at high temperature (-40 to up to 120°C),
- Effectively no co-transport of molecular species with proton,
- Reduction of fuel cell overvoltage,
- Durable, good mechanical strength and chemical stability.

This program developed the concept of proton transfer in protic salts and made new liquid, solid and polymer membrane proton-conducting salts. This program showed how stable protic salt electrolytes could be formed. This program showed how high cathode activity results when there is practically no bulk water or electrolyte adsorption on Pt. The best new protic salt membranes were similar to 90%ITP-10%PVPP, whose conductivity, shown in Fig. 1, is on the order of 0.1 S/cm at 120°C with no hydration and ambient pressure.

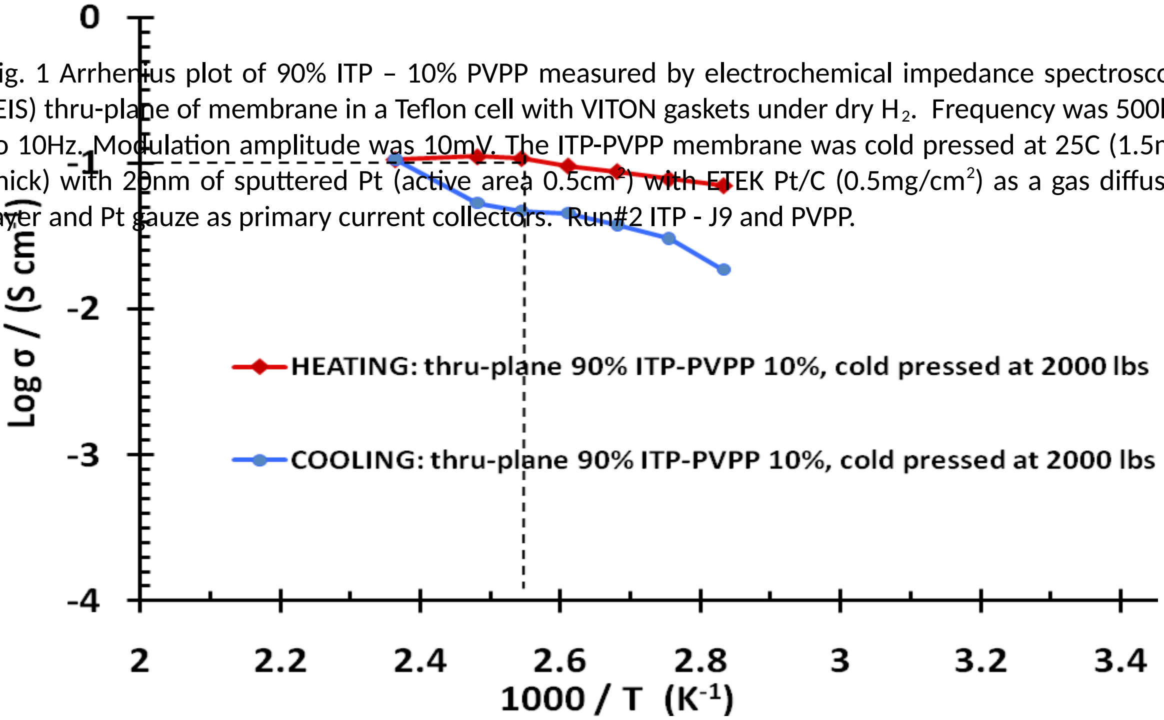


Fig. 1 Arrhenius plot of 90% ITP – 10% PVPP measured by electrochemical impedance spectroscopy (EIS) thru-plane of membrane in a Teflon cell with VITON gaskets under dry H_2. Frequency was 500kHz to 10Hz. Modulation amplitude was 10mV. The ITP-PVPP membrane was cold pressed at 25C (1.5mm thick) with 20nm of sputtered Pt (active area 0.5cm^2) with ETEK Pt/C (0.5mg/cm^2) as a gas diffusion layer and Pt gauze as primary current collectors. Run#2 ITP - J9 and PVPP.

There were difficulties consistently making these new composite membrane materials. But with further optimization of the processing, this approach should be reproducible and overcome all barriers to making membranes for practical efficient high power-density HT PEM fuel cells.

VIII.2. Summarize project activities for the entire period of funding, including

- VIII.2.a. original hypotheses,

This project involved synthesis of neat proton-containing salts, a new class of proton conductors. The approach to making high-temperature proton-conducting membranes was based on protic ionic liquids (pILs) concepts. Protic ionic liquids (pILs) are solvent-free proton-conducting electrolytes that form when a proton is transferred from a Bronsted acid to a Bronsted base. The pILs can function at very high temperatures. pILs can be tailored by choosing base and acid. The conductivity depends on the pK difference of the acid and base (Fig. 2), because this sets the energetics of proton transfer (Fig.3.).

The first proof of the validity of this concept was the correlation between the open circuit voltage in a hydrogen anode and air cathode fuel cell with the difference in pK of the base and acid for various pIL electrolytes (Fig.4.). Next, simple liquid electrolyte fuel cells were made to develop pILs (Fig.5.).

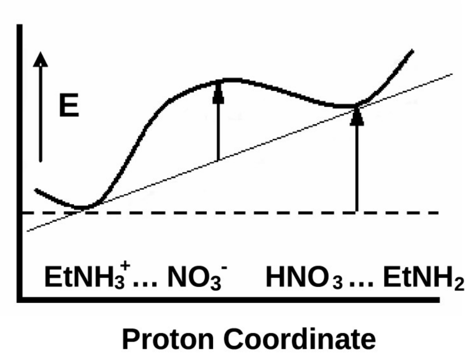


Fig.3. Energetics of proton transfer for the EAN (ethyl ammonium nitrate) pIL with: proton transferred (Left) not transferred (Right).

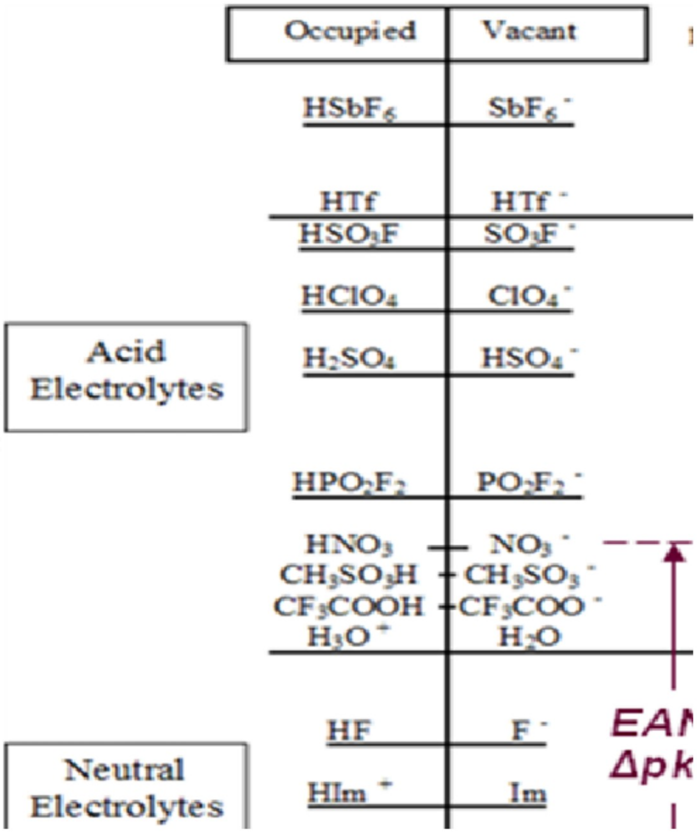


Fig. 2. Gurney diagram ordering according to pK Bronsted bases (large positive pK) from bottom to Bronsted acids (large negative pK) to top.

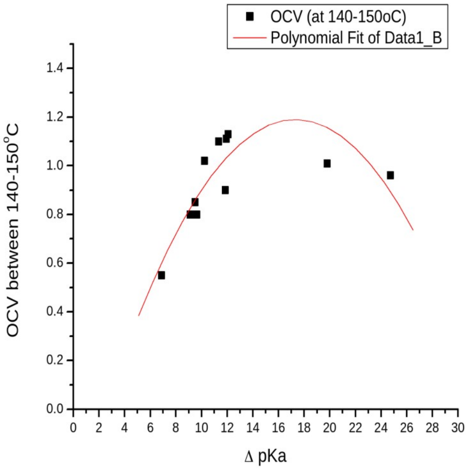


Fig.4. Correlation between open circuit voltage (OCV) and difference in log of proton dissociation constant (ΔpKa) for constituents in protic ionic liquids.

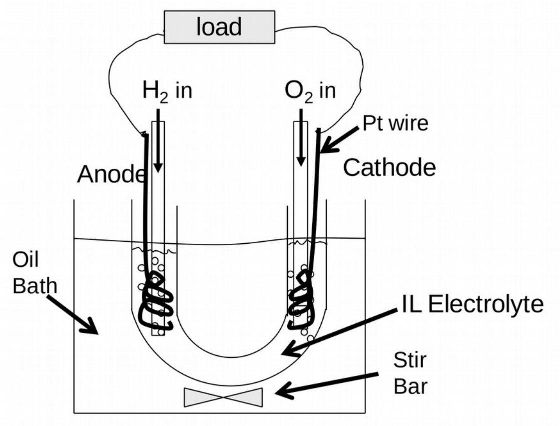


Fig. 5. Schematic diagram of a gas-fed liquid electrolyte fuel cell with Pt wire electrodes.

Results (Fig.6.) indicated that pILs were as good as if not better than the only naturally occurring high-temperature fuel-cell electrolyte, phosphoric acid.

Making a new electrolyte is no simple task. There are many requirements for proton-conducting fuel-cell electrolytes. In general, the electrolyte needs to be a conductor for protons, with conductivity for $H^+ > 10^{-2}$ Siemen/cm, and an insulator for electrons. Electron conductivity needs to be $< 10^{-9}$ Siemen/cm. Fuel cells need to operate at temperatures from - 50 to + 230°C to be practical. The electrolyte needs to be stable to the local acidity and reducing potentials in presence of Pt at the anode and alkalinity and oxidizing environments in presence of Pt catalysts at the cathode up to 230°. Extra considerations with membrane electrolytes include: low permeability to H_2 and O_2 gas, no electro-osmosis (transfer of water, or other molecules with proton), dimensionally stability with changing water content and temperature, good adhesion to electrodes, and cohesion for avoiding pinholes (no shorting of electrodes). One has to bear in mind all of these factors when making changes to develop a useful electrolyte.

Water is used as an ionizing solvent with acid or base for conducting proton in conventional electrolytes. To date, there has been some success using water based electrolytes to make fuel cells. However, problems include: need for humidification of electrolytes (or else conductivity drops as ionizing solvent water is lost) and the formation of Pt-oxides at high electrode (cathode) potentials, which limits fuel-cell voltage and limits efficiency to 60% instead of 90%.

Fig.6. Total polarization plots for a liquid-electrolyte fuel cell with simple gas bubbler on spiral Pt wire electrodes for three electrolytes, namely: 1)phosphoric acid (96%) at 100°C (solid black circle, dashed line), versus 2)ethyl ammonium nitrate at 100°C (red star, solid line), and 3)ethylammonium-bifluoride, at 25°C (open triangle, dotted line).

Concentrated phosphoric acid is one of the few naturally occurring substances for conducting proton without water. Phosphoric acid has drawn much attention as a fuel cell electrolyte as it conducts proton at temperatures as high as 190C, which allows for compact radiation of heat to ambient.

Phosphoric acid can ionize itself, that is, a proton can be transferred between two molecules of phosphoric acid (H_3PO_4) to form a salt ($H_4PO_4^+$: $H_2PO_4^-$). One molecule of phosphoric acid acts as an acid and the other as a base. The salt that forms is a protic ion liquid (pIL) which behaves quite similarly to the pILs and solid protic salts as high-temperature proton conductors that were synthesized during this program. There has been some success using phosphoric acid to make fuel cells. However, there have been problems, because phosphoric acid is a liquid which can leak, leading to ionic shorts (voltage loss), and because adsorption of phosphoric acid on Pt limits cell voltage and efficiency.

Figure 7. Proton hopping in phosphoric acid.

Still much can be learned about designing proton conductors by closer consideration of what is known about proton transfer in phosphoric acid. [“D. Gervasio, “Fuel Cells with Neat Proton-conducting Salt Electrolytes”, Ch. 20 in Fuel Cell Science: Theory, Fundamentals and Bio-Catalysis, Jens Norskov, Andrzej Wieckowski, EDs. John Wiley & Sons (2010)]. Protons in phosphoric acid move through electrolytes via translations, rotations and vibrations as dictated by Statistical Mechanics. There are 2 modes of ion transport: i) a slower translational diffusion of protons and anions; and ii) a faster “proton hopping”, i.e., a coordinated rotational and vibrational transport. Liquid concentrated phosphoric acid can conduct proton with no co-transport of other species, via a proton hopping mechanism, illustrated in Figure 7. This mechanism for proton conduction in phosphoric acid suggests how to make a synthetic electrolyte that conducts proton with no water. Namely proton is passed from species i) which have suitable energy difference between the protonated and non-protonated forms (i.e., have suitable pK) and ii) which have suitable symmetry (i.e., are free to rotate). This becomes clear when looking closely at how protons are conducted in phosphoric acid.

Ortho-phosphoric acid (H_3PO_4) auto-ionizes into different proton states, e.g., hydronium phosphate ($H_4PO_4^+$) and dihydrogen phosphate ($H_2PO_4^-$). The energy of these proton states can be quantified by their dissociation constant (K). The difference in the logarithm of the dissociation constant ($-\log_{10} K_a$) for two dissociation reactions (see Table 1) is directly proportion to the free energy difference ($\Delta G^o = - 2.3\ RT \log K_a$) for those two proton occupancies.

Table 1: Acid dissociation constants (K_a) for different proton states of phosphoric acid

Dissociation Reaction	**K_a**	**$- \log_{10} K_a$**
$H_4PO_4^+ + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_3PO_{4(aq)}$	$K_{a0} = \sim 10^2$	$pK_{a0} = -2$
$H_3PO_4 + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)}$	$K_{a1} = 7.5\times10^{-3}$	$pK_{a1} = 3$
$H_2PO_4^- + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)}$	$K_{a2} = 6.2\times10^{-8}$	$pK_{a2} = 7$
$HPO_4^{2-} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)}$	$K_{a3} = 2.14\times10^{-13}$	$pK_{a3} = 12.7$

The difference in the dissociation constants (ΔpK's) for these states is on the order of thermal energy. Since the proton transfer is accessible by thermal excitation, the proton can readily reside on phosphoric acid and be removed. All that is needed is a bonding path. Figure 7 shows the bonding path, in which proton transport occurs by rotational and vibrational transfer of proton between such species (proton states), phosphoric acid (H_3PO_4) and phosphonium ion ($H_4PO_4^+$). The proton is passed by rotational and vibration motions, because phosphoric acid and its various ionic forms form tetrahedra, and any 2 species have both the suitable energy separation (proper ΔpK) for proton transfer and symmetry required for the vibrations and rotations allowing proton transfer.

This study of phosphoric acid leads to a general rule. Proton conduction can occur when 2 conditions are met:

i. there is an energy separation (ΔpK) between proton acceptor and donor species on the order of thermal energy and
ii. these species have high symmetry so that the required rotational and vibrational motions are not impeded during proton transfer.

When a proton-containing salt is made to satisfy these 2 conditions, this rule predicts the protic salt will be useful as a proton-conducting electrolyte.

VIII.2.b. approaches used

To develop solid proton-conducting membranes that do not need to be hydrated to operate even at temperatures above the boiling point of water, a number of liquid, solid and solid polymeric electrolytes were made. The liquids guided making of solid polymer electrolyte membranes (PEMs).

VIII.2.b.1. Synthesis of Proton Conductors

Two types of PEM were developed based on protic salt electrolyte concepts. Liquid protic salts or protic ionic liquids (PILs) are easier to make than polymers but can be reliably be used to model many membrane properties, like stability and adsorption. Eventually the polymer properties are systematically varied as well as the acid and base moieties in order to optimize properties of a protic salt membrane (PSM). The first big question is "how can a highly proton conducting ionic liquid be made?" Next, "how can an electrolyte promote good fuel cell performance (high efficiency and power)?" and finally "how can an electrolyte be conductive, promote good fuel cell performance and be stable?” We start with conductivity and by making a variety of pILs and comparing to phosphoric acid.

Fig. 8 Arrhenius plot of conductivity of protics compared to phosphoric acid.

EAN is fairly conductive (nearly 0.1 S/cm at 100C) and showed decent activity in a simple fuel cell (Fig.6) so next the effect of EAN electrolyte on fuel cell polarization was examined on a real fuel cell electrode. Results with EAN were compared to phosphoric acid as shown in Fig. 9.

At low current densities EAN electrolyte promotes much faster kinetics for the hydrogen and oxygen fuel cell as evidenced by the over 0.2 volt higher open circuit potential. Unfortunately EAN wets the Teflon bonded electrode, so mass transport limits power generation for pure EAN. Adding 1% ethyl ammonium phosphate (EAP) to 99% EAN alters the wetting properties so the high efficiency of 99% EAN 1% EAP was observed for 2 or 3 decades of current. However, even the good performance at low current densities lasts only short time, apparently, because EAN decomposes and poison Pt catalyst. This is consistent with the voltammetry of Pt in EAN equilibrated with pure oxygen as shown in Figure 10. Each time the Pt is cycled from ~0 to ~1 volt, the oxygen reduction current decreased. There was even a suspicion that EAN might be promoting good kinetics via an outer sphere mechanism from radicals because of nitrate oxidation. To test if radicals were responsible for the high fuel cell performance, more stable pILs (based on tertiary amines and fluorinated electrolytes) were examined.

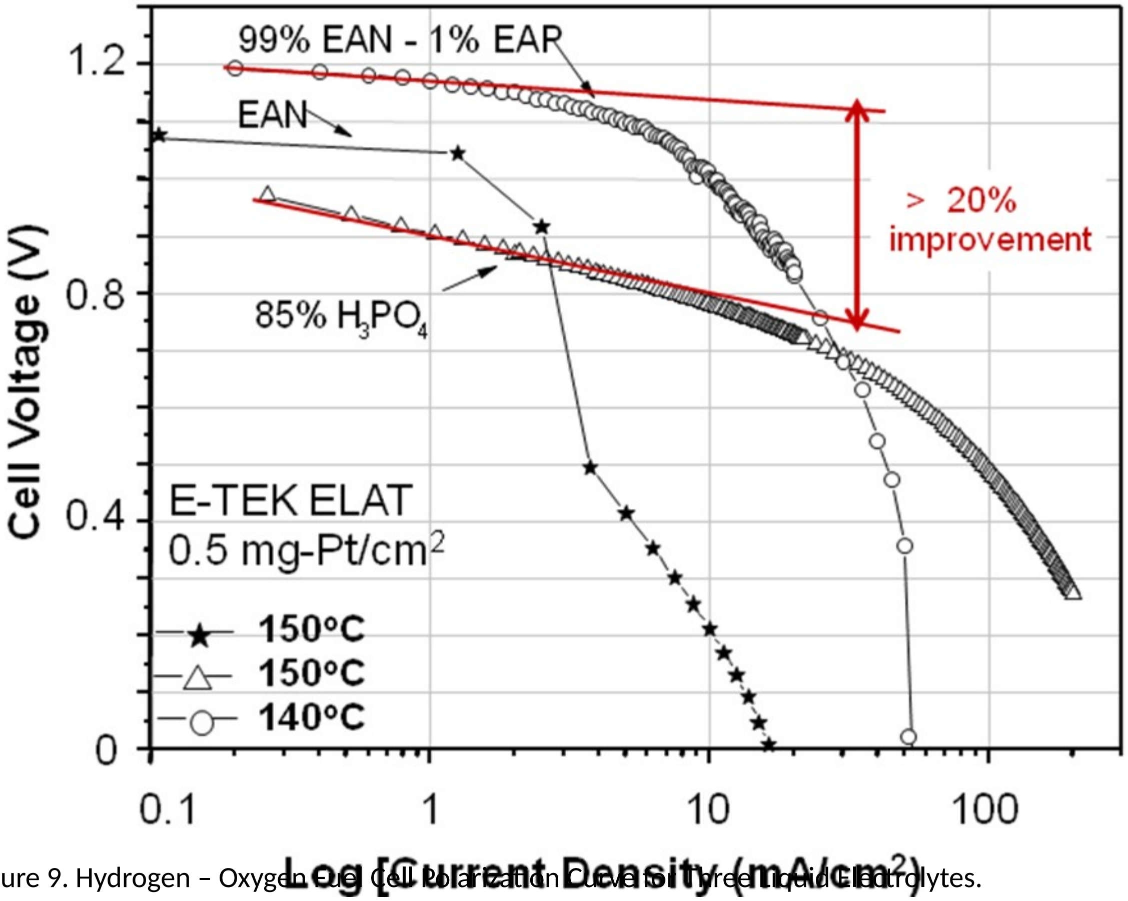


Figure 9. Hydrogen – Oxygen Fuel Cell Polarization Curve for Three Liquid Electrolytes.

Figure 10. Cyclic Voltammogram of Pt in ethyl ammonium nitrate equilibrated with 1 atmosphere of pure oxygen gas.

EAN is a primary amine which is not stable to oxidation because the CH bond is prone to oxidative attack. To enhanced electrolyte stability a tertiary ammine was tried, namely triethyl ammonium sulfonate (TEAMS). Whereas EAN decomposes and poisons platinum catalyst on the electrode, TEAMS is fairly stable however the activity is low at higher potentials (as seen in Fig 11). This is apparently due to adsorption of TEAMS on Pt, in a similar way that phosphoric acid adsorption limits activity in aqueous electrolytes.

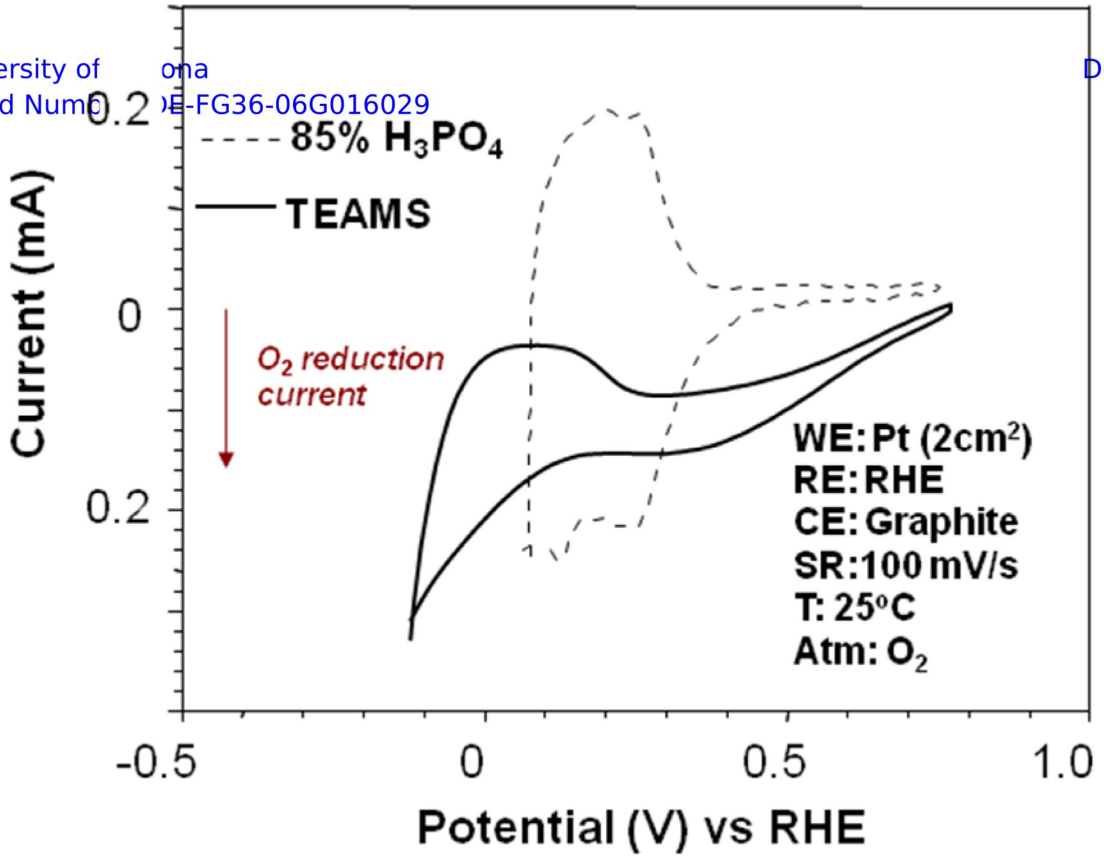


Figure 11. Cyclic Voltammogram of Pt in., triethylammonium sulfate (TEAMS), a more stable ionic liquid than ethylammonium nitrate (EAN), equilibrated with 1 atmosphere of oxygen gas.

Next, 2 pyridine salts were tried. These two pyridine pILS were pyridinium phosphate (PP) and 2 fluoropyridinium triflate (2 FPTf). These two pILs are similar in that they are organic pyridine bases reacted with oxy acids have similar differences in pK for their respective acid and bases. These 2 pILs differ in acid strength and adsorption properties. The fluorinated electrolyte, 2-FPTf, is expected to be a more acidic salt and more weakly binding because electron density is strongly attracted to the fluorine moieties. Consistent with these considerations are the 2 Figures 12 for the 2 voltammetries of Pt and the 2 Figs. 13 for the 2 fuel cell performances in these 2 electrolytes. The pyridinum phosphate (PP) limits oxygen electrode kinetics on Pt as seen by the low current densities and onset potential (0.9V vs RHE as seen in Figure 12), whereas the kintics in 2 FPTf are very good as seen by the large current densities and onset of oxygen reduction occurring at nearly the reversible potential (1.2V vs RHE in Fig 12). Fuel cell performances seen in the 2 Figure 13 are consistent with voltammetry results of Fig 12. In Fig 13, the fuel cell performance is much higher (higher power, voltage and efficiency) with 2-FPTf than with PP electrolyte.

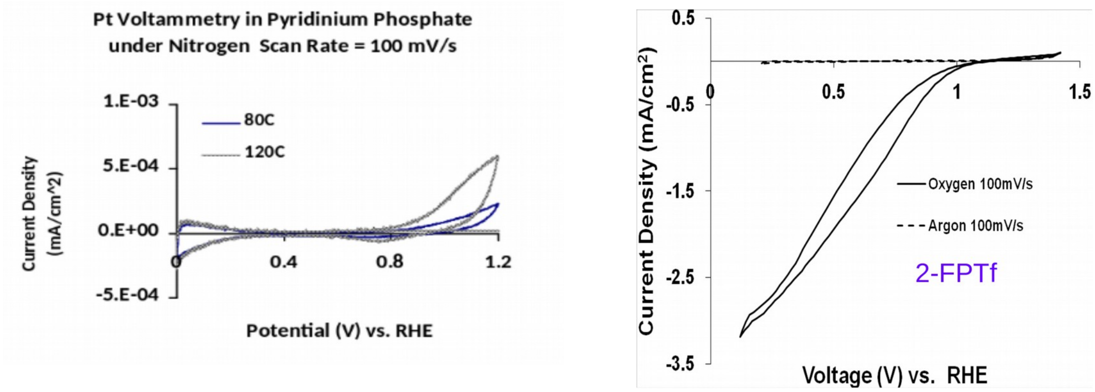
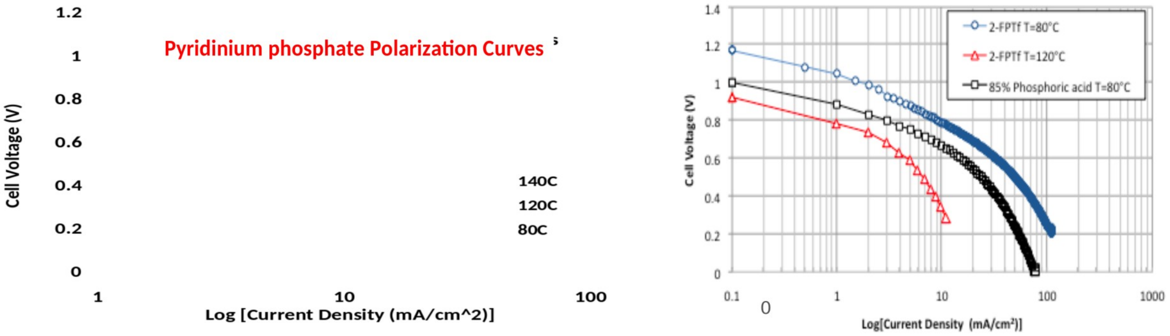


Fig. 12 Voltammetry of Pt in fluorinated pIL (2-FPTf, on right) and non-fluorinated pIL (PP, on

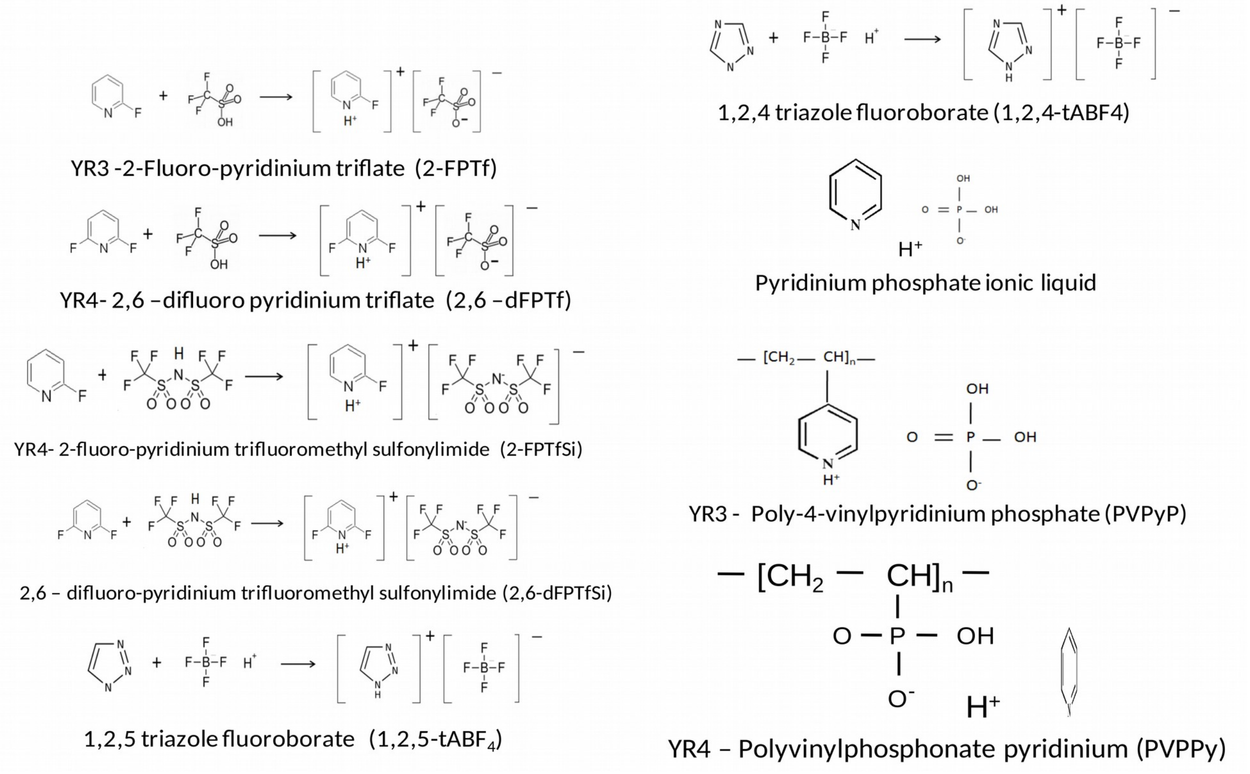
Fig. 13 Fuel cells with hydrogen anode and oxygen cathode using a non-fluorinated pyridinium salt (PP, left) and fluorinated salt (2-FPTf, right) as electrolytes.



The work with ionic liquids served to establish principles and properties of this new class of electrolyte. Ion conduction occurs according to the two rules formulated earlier concerning pK and rotational symmetry. A conductive protic salt used in a fuel cell will give a high efficiency cell provided the electrolyte is stable, has low water activity (low amount of bulk like water) and the salt does not strongly adsorb on platinum.

Although this evolution of results from EAN to 2-FPTf is quite spectacular, these results are a means to an end, not the end itself, because long ago it was concluded that liquid electrolytes are not acceptable in fuel cells. Liquid electrolytes, like phosphoric acid, promote shortened cell life due to softening of mechanical structures and catastrophic failure due to liquid migration leading loss of cell voltage due to ionic shorts of cells in series in a fuel cell stack. A solid electrolyte membrane is considered the only acceptable electrolyte for a fuel cell. So the next goal was to extend the pIL concepts to solid proton-conducting polymer electrolyte membranes (PEMs).

A number of stable and fairly active pIL electrolytes were made during the course of this project and these are listed in Scheme II, below.



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-tABF$_4$)

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

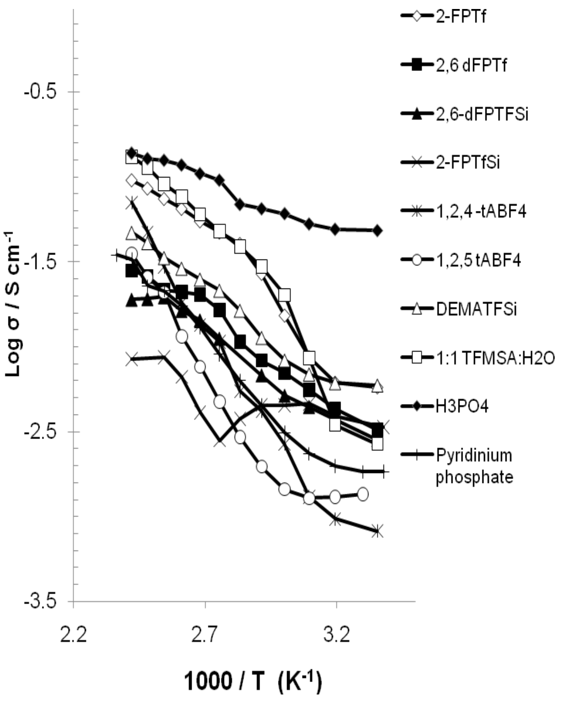
Pyridinium phosphate ionic liquid

YR3 - Poly-4-vinylpyridinium phosphate (PVPyP)

YR4 – Polyvinylphosphonate pyridinium (PVPPy)

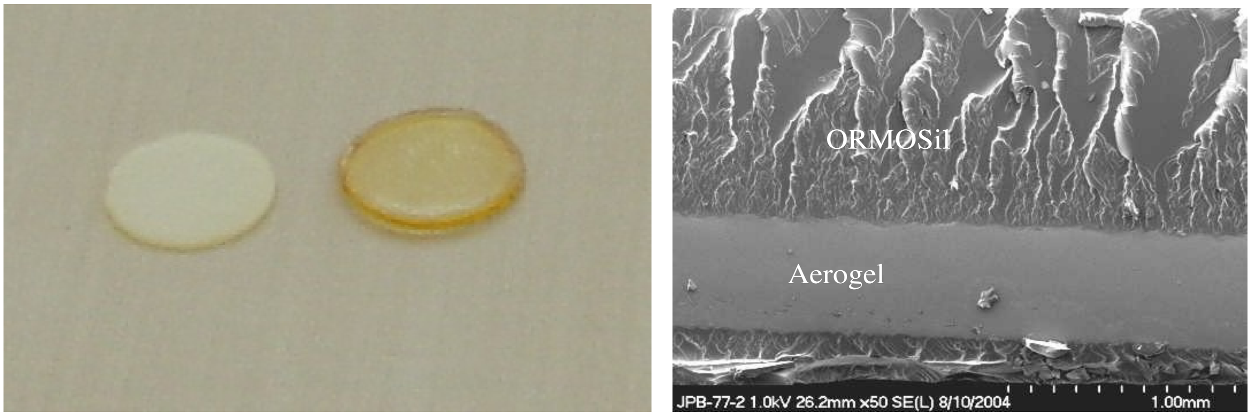
Scheme II

Although these electrolyte are fairly conductive (as can be seen from the insert on the left) and stable liquid electrolytes, it is worth repeating that a solid electrolyte membrane is considered the only acceptable electrolyte for a fuel cell. So the next goal was to extend the pIL concepts to solid proton-conducting polymer electrolyte membranes (PEMs).



Solid protic-salt polymer membranes

The first type of PEM using protic salt electrolyte concepts was a protic ionic liquid (PIL) filled polymer membrane in which the ionic liquid was absorbed into a solid polymer membrane. About 40 wt% of EAN was added to a cross-linked polymer, e.g., an aerogel. The aerogel coated with the ORMOSil polymer. Conductivity was measured over three temperature cycles from room temperature to 180 °C.



(a) (b)

Fig. 14 (a) Polymer without and with ionic liquid fill (b) SEM of polymeric support for ionic liquid.

Advantage of the ionic liquid filled polymer is that it gives a solid membrane with high conductivities (>10^{-1} Scm^{-1}) to > 160°C (see Fig 14) in which no humidification is needed so water management is simplified. Disadvantages of the ionic liquid filled polymer is this material contains a liquid which can leach out of the fuel cell to cause loss of conductivity (Fig 15) and performance as well as form ionic form shorts.

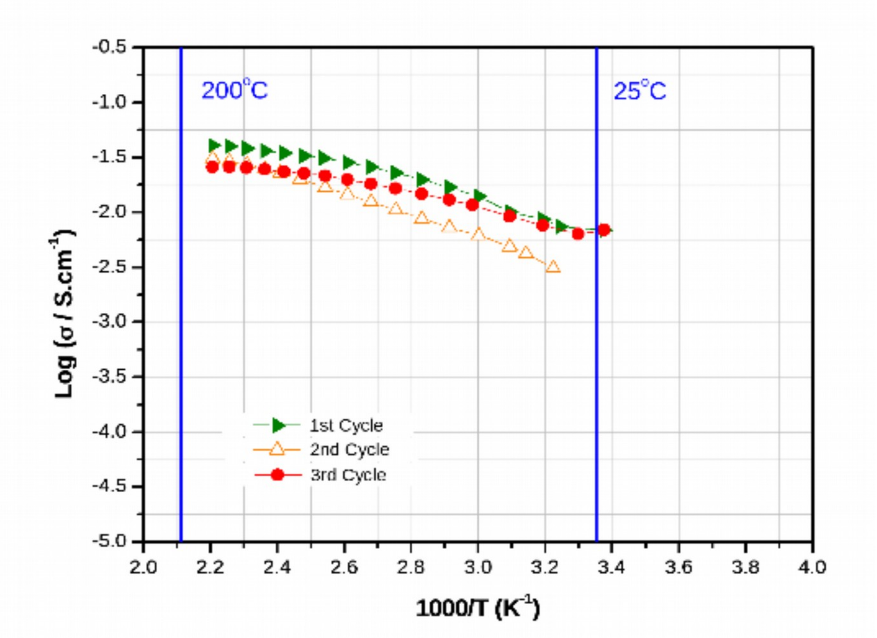
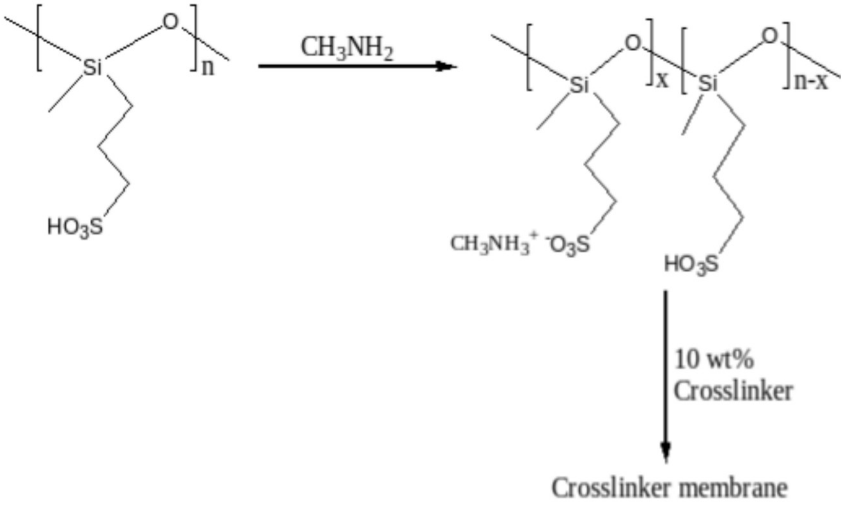


Fig. 15 Conductivity of 40% ethyl ammonium nitrate in polymer.

ii. non-leachable PEMs consisting of novel polymers in which allow all acid and base moieties to be immobilized by covalent and electrostatic binding.

iia. synthesis of two types of polymer systems having base moieties in the side groups.



Scheme I

The polymer electrolyte membrane fuel cell (PEM FC) has attracted considerable interest because of it conducts proton but other ionic species are immobile (non-leachable). In addition, the PEM FC can be highly efficient, generate good power and give zero harmful emissions. So far only Nafion® or Dow membranes, which possess both high proton conductivity and excellent chemical stability, have proven acceptable in practice. However, the operating temperatures of Nafion® and Dow membranes are limited to below 100°C due to the hydration requirement. Fuel cells operating at such low temperatures can be easily poisoned by trace CO present in the feed gas. To overcome the catalyst poisoning problem and gain better water management, fuel cells need to operate at higher temperatures (>120°C). Thus, development of high temperature proton-transporting membranes is an urgent need.

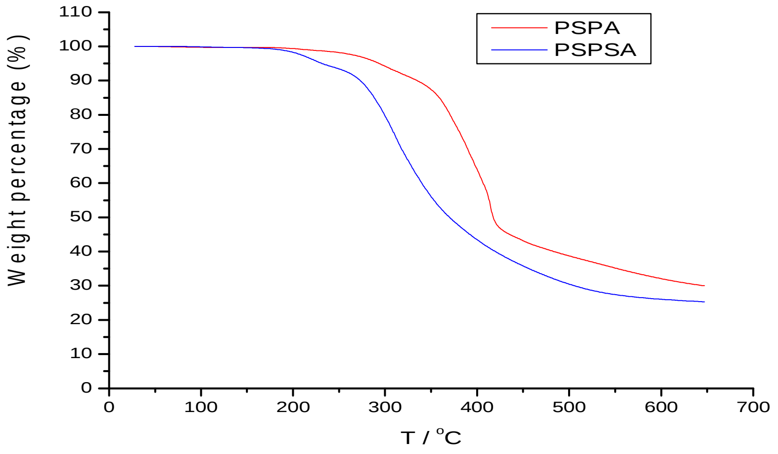


Fig. 16. TGA plot for fully neutralized and crosslinked polysiloxane membranes. Heating rate: 10°C / min under air atmosphere.

Polysiloxane has been proposed by many researchers as a matrix for fuel cell applications due to the ease of introduction of organic functional groups, and also inorganic nano-particles, through sol-gel processes [1-9]. Unfortunately, most of the published literature has been focused on materials characterization and proton conductivities. Few fuel cell tests with these membranes have appeared. We reported the first such tests on membranes, which are based on “dry” (i.e. unplasticized by pILs) ionic poly siloxanes. The ionic groups are pendant functional groups (amine or acid). Scheme I shows a covalently attached acid that has been reacted with methyl amine base. The same ionic polysiloxanes plasticized with protic ionic liquids (organic or inorganic) have been developed and described in our lab [10, 11], including their performance in fuel cells [11]).

Fig. 16 shows the TGA results for crosslinked poly siloxane membrane in air atmosphere (Note: PSPA is for poly siloxane in which pendant propyl amine is neutralized with methanesulfonic acid and PSPSA is for poly siloxane with pendant propylsulfonic acid neutralized with methylamine).It is clearly shown that these membranes are stable enough for applications in high temperature fuel cells (120-160°C).

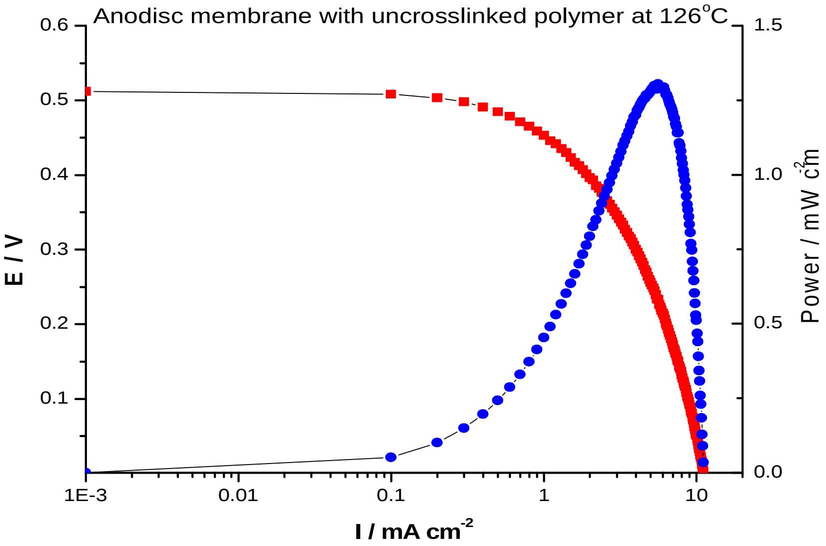


Fig. 17. I/V and power curves at 126°C of the fuel cell based on Anodisc membrane containing un-crosslinked PSPA ($N:CH_3SO_3H = 4:1$).

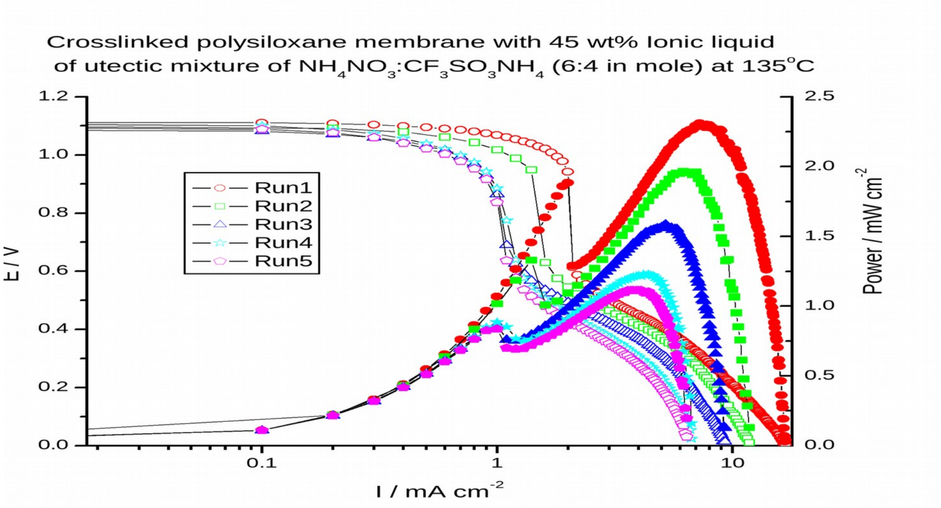


Fig. 18. I/V and power curves at 135°C of the fuel cell based on crosslinked polysiloxane membrane with 45 wt% of eutectic mixture of NH_4NO_3: $CF_3SO_3NH_4$ (6:4)

Fig. 17 shows the fuel cell test result using un-cross-linked, *25% neutralized*, PSPA absorbed into anodisc (to provide the rigidity needed to avoid short-circuits) at 126°C. The open cell voltage is around 0.5V and the highest current density is 11mA cm^{-2}. *Note that there is no vehicular mechanism for proton transport available in this membrane.* When the same polysiloxane is crosslinked and loaded with 45wt% of eutectic mixture of NH_4NO_3: $CF_3SO_3NH_4$ (6:4 mol ratio) the open cell voltage of the fuel cell at 135°C goes up to 1.1V (see Fig. 18), which is mainly due to the effect of the ionic salt as reported in the previous publication [11]. However, the highest current density is only 18mA cm^{-2}. The impedance of the fuel cell at different temperatures shows that with continued cycling the impedance of the fuel cell increases, which suggests that the ionic liquid leaches out of the membrane under test conditions.

All the fuel cell tests were made using commercially available ETEK electrodes, which are optimized for acidic PEMFCs. These preliminary tests suggest that more elaborate work needs to be done to optimize the fuel cell performance. Alternative electrodes might be preferable for these neutral proton-transfer salt- based PEMFCs which use carbon nanotubes to gel the pILs and that do not use noble metal catalysts.

1. G. Scharfenber et al, *Fuel Cells*, 06, 237 (2006).
2. S. Y. Lee et al, *Advanced Materials*, 17, 626 (2005).
3. W. F. Chen, P. L. Kuo, *Macromol.*, 40, 1987 (2007).
4. M. Jeske et al, *Fuel Cells*, 7, 40 (2007).
5. W. J. Liang, C. P. Wu, C. Y. Hsu, P. L. Kuo, *J. Polymer Science A. Polym. Chem.*, 44, 3444 (2006).
6. U. L. Stangar et al, *J. Solid State Electrochemistry*, 9, 106 (2005).
7. R.C.T.Slade et al, *Solid State Ionics*, 145, 127 (2001).
8. V.D.Noto et al, *Electrochimica Acta*,50, 3998 (2005).
9. V.D.Noto et al, *Electrochimica Acta*,50, 4007 (2005).
10. W. Xu and C. A. Angell, *Science*, **302**, 422 (2003).
11. J. P. Belieres, D. Gervasio, C. A. Angell, *Chemical Communications*, 46, 4799 (2006).

Temperature Dependence of the Liquid and Polymer Membrane Electrolytes

Conductivity of the membranes were determined experimentally using electrochemical impedance spectroscopy (EIS see discussion in section **VIII.2.b.2.i.** below) at 120°C, 100°C, 80°C, 20°C. TGA and DSC show all of the materials are thermally stable to at least 300°C in all cases. The conductivity results as a function of temperature for the variations of siloxane membranes are given in Figures 19 to 24.

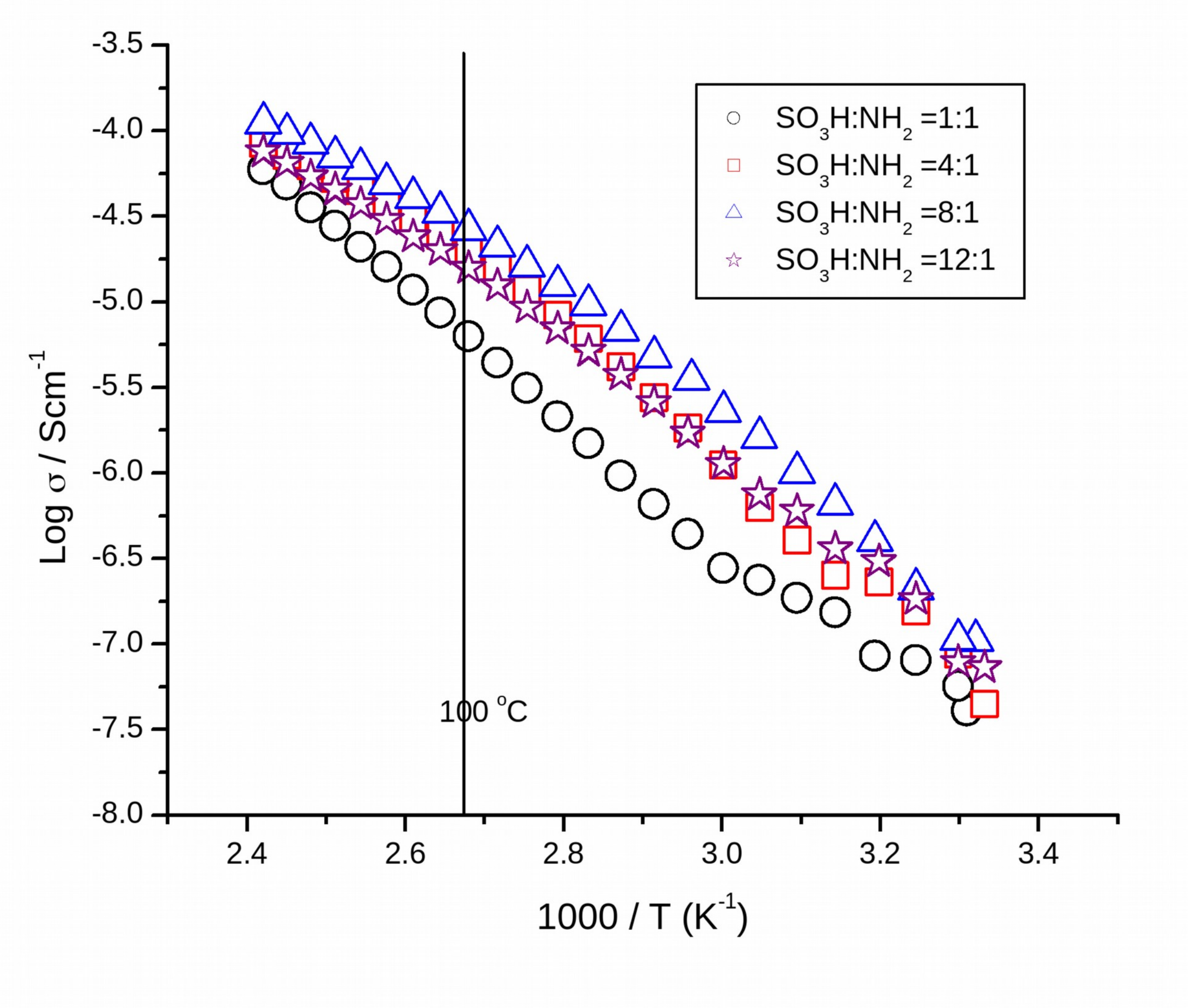


Figure 19. Ionic Conductivities of non-Leachable Polysiloxane

Protic Ionic Membrane (PIM) made of dry polysiloxane with pendant propyl sulfonic acid groups neutralized with methylamine. All samples are self -standing films. The maximum conductivity of $10^{-4.28}$ S cm^{-1} at 100°C is reached when 1 in every 8 acids is neutralized.

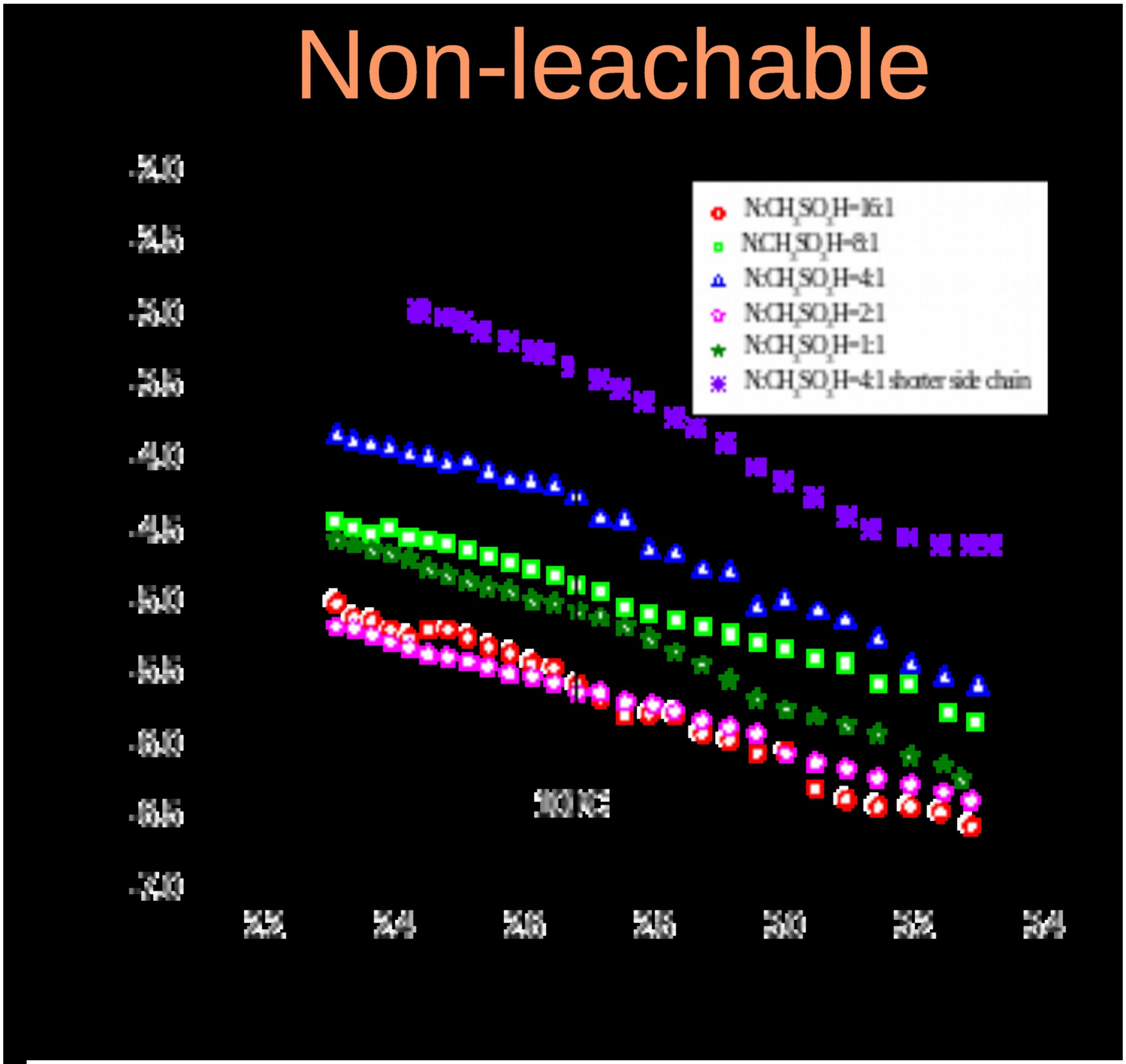


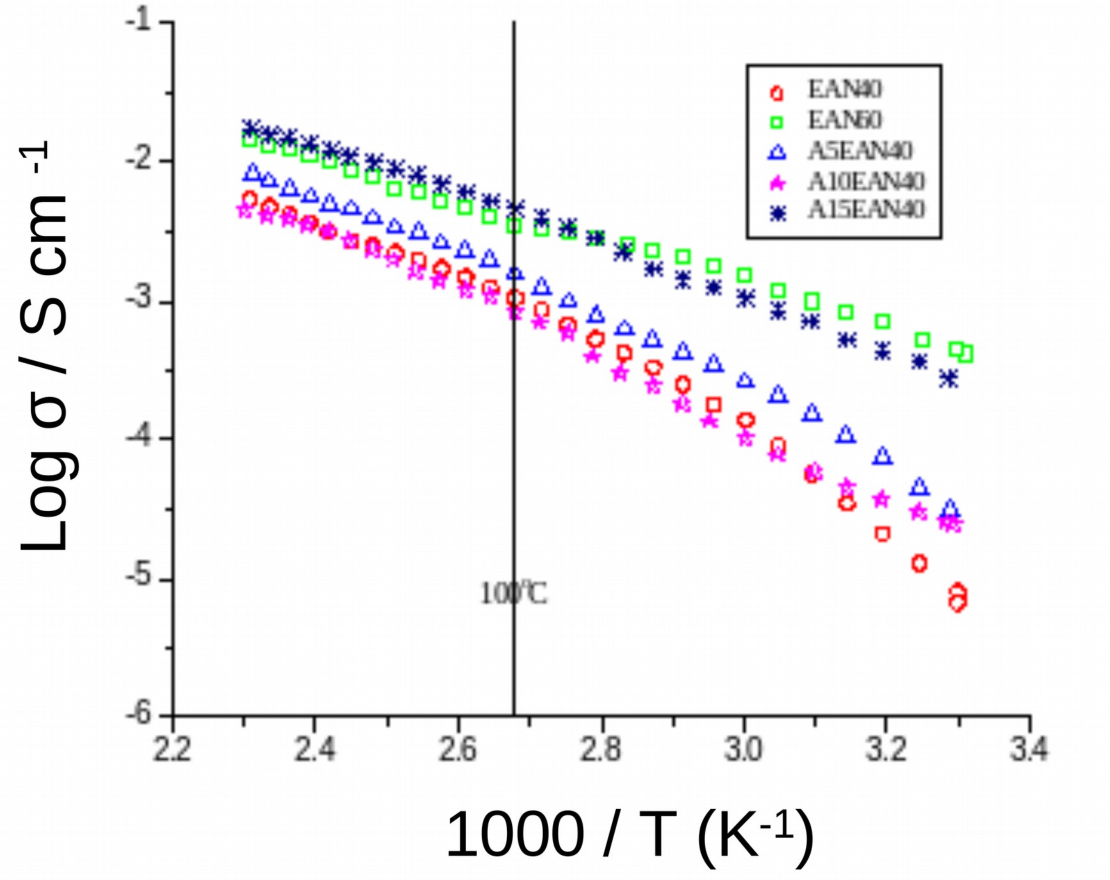
Figure 20. Non-leachable Polysiloxane Protic Ionic Membrane (PIM)

Cond

groups to varying extents. Maximum conductivity is reached when 1 in every 4 amines (25%) is neutralized. When shorter sidechains are used the conductivity increases by almost one order of magnitude, *an unexpected effect which must be further investigated.*

Leachable

Figure 21. Leachable Polysiloxane Protic Membrane



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

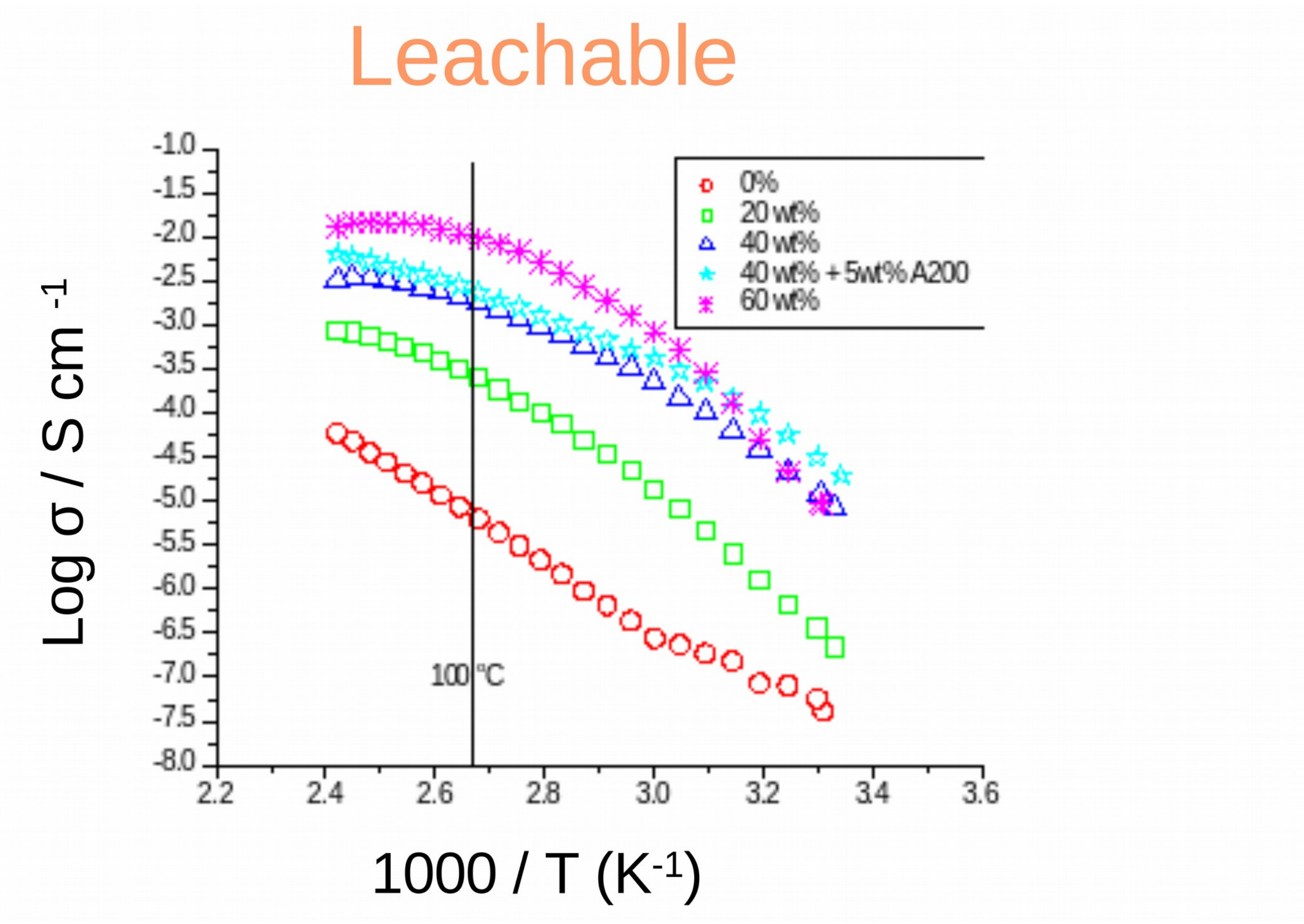
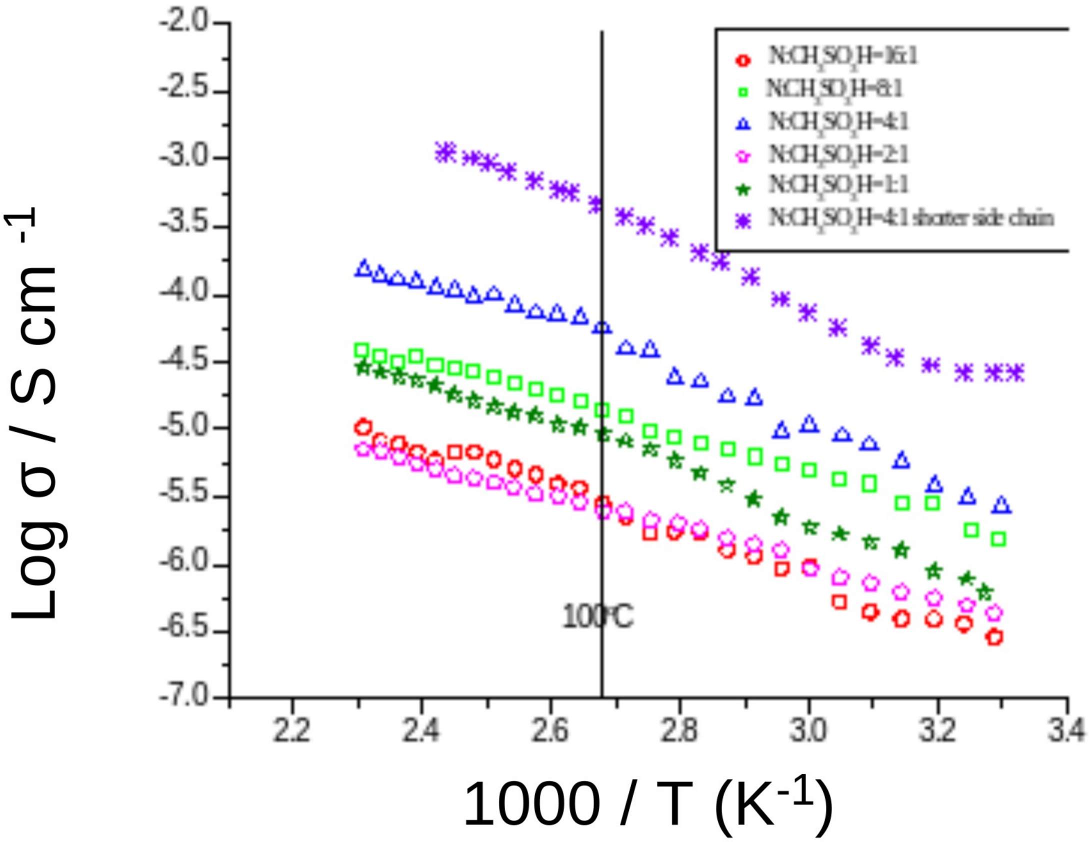


Figure 22. Leachable Polysiloxane Protic Membrane

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

Non-leachable

Figure 23. Non-leachable Polysiloxane Protic Ionic Membrane (PIM)



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

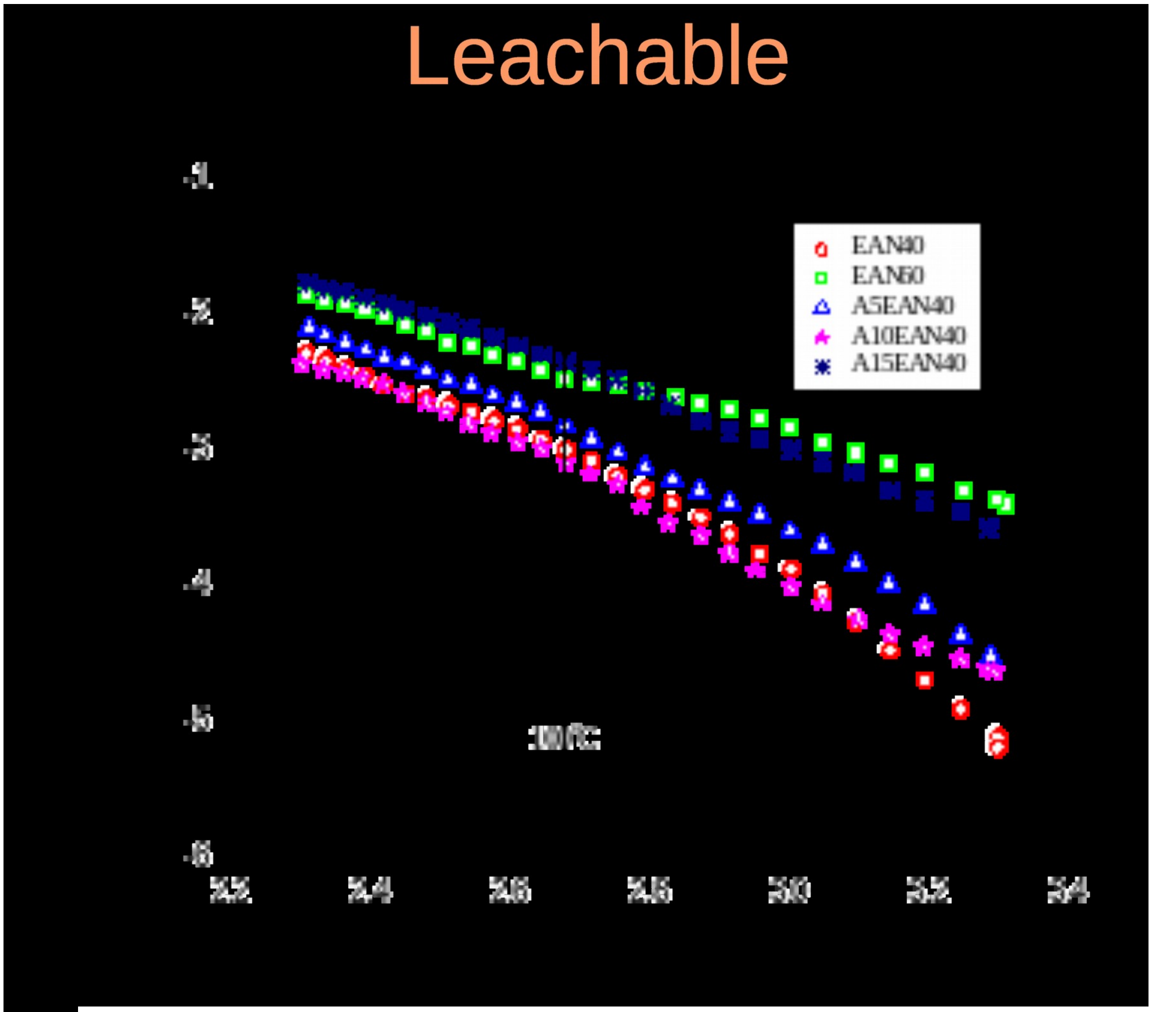


Figure 24. Leachable Polysiloxane Protic Membrane

Ionic co

methanesulfonic acid at the ratio N:CH_3SO_3H =4:1 and containing different percentages of EAN and fumed silica A200. EAN40 stands for crosslinked film containing **40wt% EAN**; etc. A5EAN40 stands for crosslinked film containing 40wt% EAN and 5wt% A200 silica spheres; Likewise for A10 and A15.

These polysiloxane membranes qualitatively illustrated that a “dry” proton conductor can be made with i) immobilized pendant acid (base) reacted with ii) free base (acid) to immobilize the second (ii) to the first (i) electrostatically. Polysiloxanes were somewhat soluble so not very mechanically stable and therefore abandoned. Polyphosphazene can be doped with acid and bases as easily as polysiloxanes and can be processed into insoluble films. However, no useful polyphosphazene were available during the project.

iib. blends of polymers including composite membrane of inorganic and organic polymers

An organic polymer poly vinyl pyridinium phosphate (PVPP) and an inorganic polymer 10mol% indium 90% tin phosphate ($In_{0.1}$ $Sn_{0.9}$ P_2O_7 or ITP for short) were blended to make the first composite proton-conducting membrane in which the organic and inorganic phases were both “dry” proton conductors.

First a pure ceramic indium tin phosphate (ITP) powder was prepared in our lab, and processed into pure ITP membranes. If found highly conductive, then the pure ITP material is blended with an organic polymer, polyvinyl pyridinium phosphate (PVPP), to form a ITP/PVPP composite. This was found to have proton conductivities just in excess of 0.1 S/cm when properly prepared.

Preparation of pure ceramic indium tin phosphate.

A mass of indium oxide, 0.5027g, tin oxide, 4.8933g and aqueous phosphoric acid (85wt%) 12.1685g reagents were mixed by hand in a ceramic crucible with a stirring rod at 300C for approximately 1hr to form a ceramic “dope”. This dope was then calcined in the crucible (uncovered) at 650C for 2.5hrs. The calcined material was hand ground in a mortar and pestle and then cold pressed at 6000 lbs for 1 minute to form a ~ 1 cm2 pellet membrane. The pellet was heated at 200C for 1 hour. Figure 25 shows an Arrhenius plot for the conductivity of a solid pure ITP membrane from 25 to 150°C.

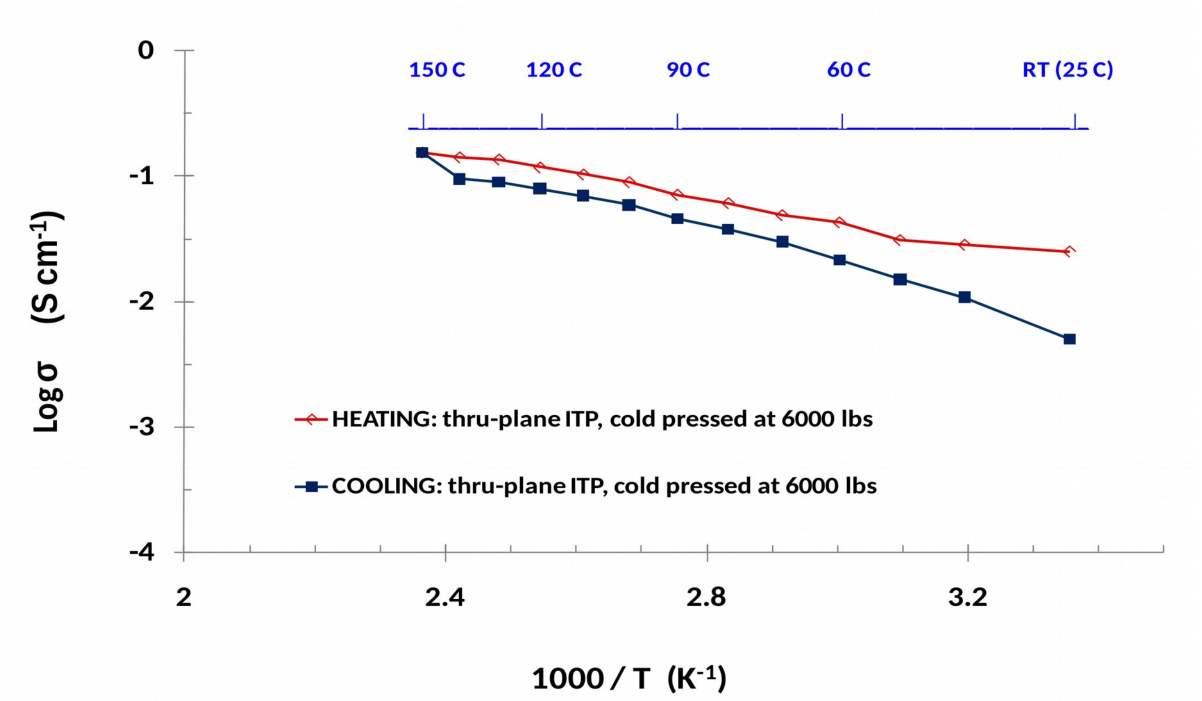
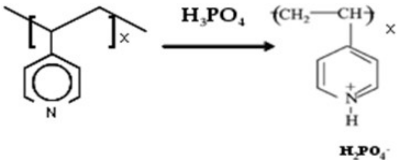


Figure 25. Arrhenius plot of the through-plane conductivity of a pure ITP membrane with electrodes under dry hydrogen atmosphere. Membrane thickness = 1.65mm, and area = 0.484 cm^2. Frequency range: 50 kHz to 10 Hz. AC amplitude: 50mV. Thickness of sputtered Pt el= 20nm. ETEK electrodes (0.5 mg of Pt per cm^2) used as gas diffusion layer. Pt screen current collectors. J4 ITP membrane.

Each side of the ITP membrane pellet surfaces was coated with a 20nm thick Pt layer by dc sputtering. The ITP membrane was characterized for proton conductivity by electrochemical impedance spectroscopy under a hydrogen atmosphere (Randles circuit method) where the highest frequency intercept is the areal resistance. The Arrhenius plot of this ITP membrane (designated J4) in Figure 25 is for the through-plane conductivity between 2 sputtered Pt electrodes. This particular J4 sample was well behaved and did not need water for conductivity nor was it affected by exposure to liquid water. However, almost 20 supposedly identical ITP samples were made by 3 people, but only 2 or 3 samples exhibited the qualities of sample J4 in Figure 25. The variability in samples is attributed to inconsistencies during the hand processing of the ceramic ITP component. ITP does not melt so the reactants must be carefully and thoroughly mixed during heating of the reactants for uniform ceramic formation.

Next an organic protic salt polymer, solid poly vinyl pyridinium phosphate was formed by mixing poly vinyl pyridine with 1 H3PO4 per 1 pyridine. There was a slight molar excess of phosphoric acid to form the protic salt polymer as shown in Scheme III.



Scheme III

The excess phosphoric acid was washed with water and methanol until the pH of the rinse was 7. The conductivity of this PVPP organic salt polymer is shown in Figure 26along with the monomeric pyridinium phosphate and 2 fluoropyridinium triflate. Interesting the polymer is about 5 times less conductive than the monomer which is expected due to more restricted motion in the polymer than the monomer. The PVPP membrane was used also for “pumping hydrogen” and electrolyzing water and performed steadily for fairly long times (hours) with no added pIL or other ionic constituents. The steady fuel cell, hydrogen pump and electrolysis results area all sign of proton hopping is the mechanism of proton conduction in the PVPP membrane.

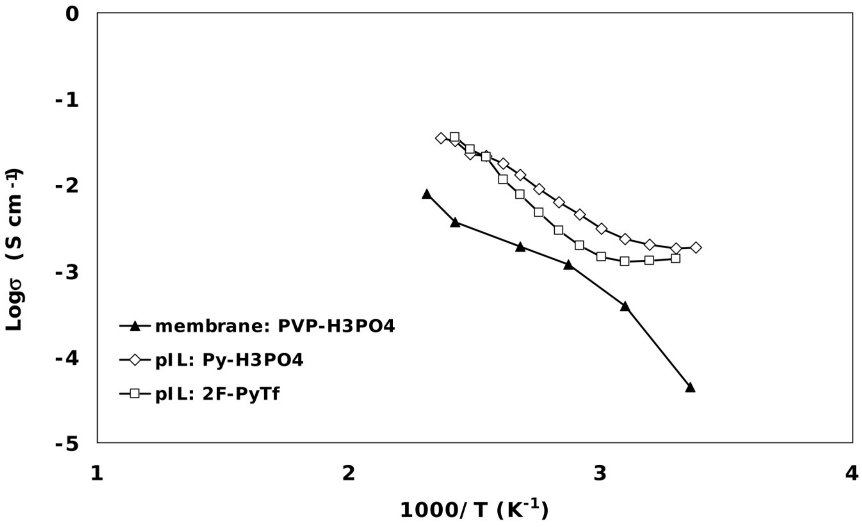
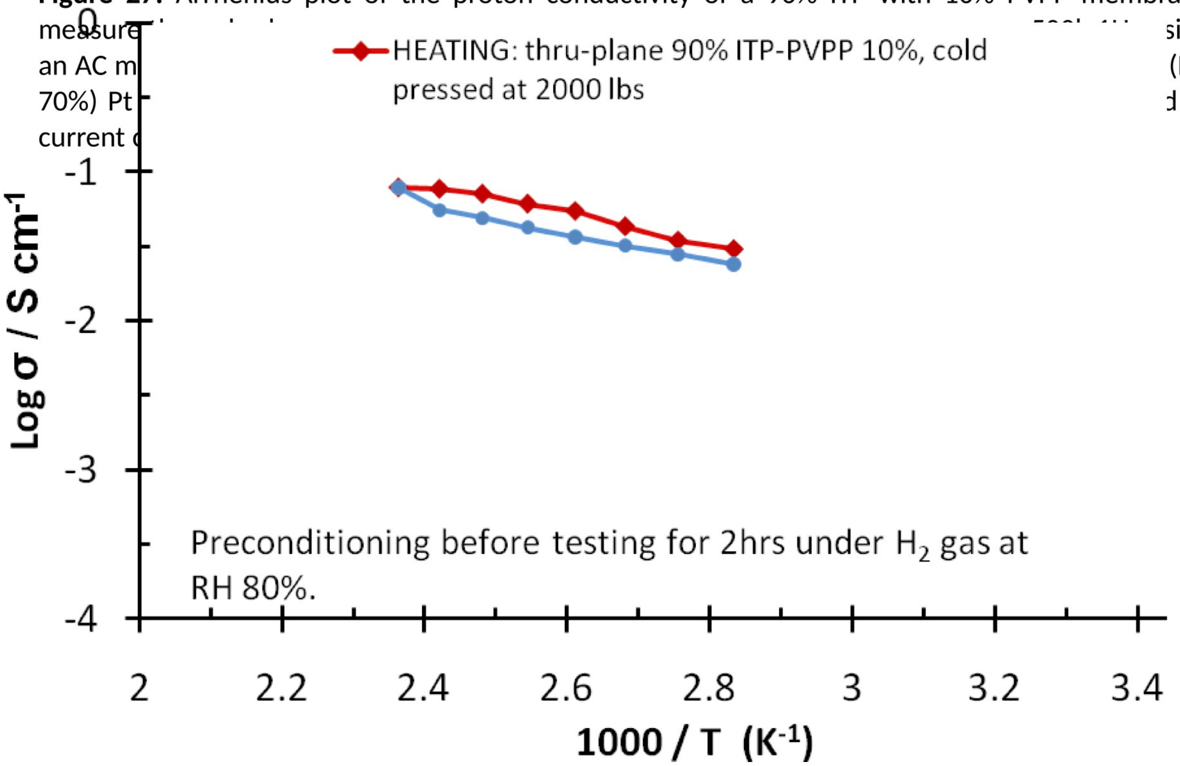


Fig 26. Conductivity for 3 electrolyte samples as a function of temperature. Solid triangle: Solid poly vinyl pyridinium phosphate (PVP-H3PO4) membrane, Open diamond: Liquid vinyl pyridinium phosphate pIL (P-H3PO4), Open square: Liquid 2-fluoro pyridinium triflate (2-FPyTf). Electrodes E-Tek Pt/C (0.5mg/cm^2) fed dry: H_2 gas. T=25 to 150°C

Comparison of ITP in Figures 25 and PVPP in Fig 26 4 shows that the conductivity of PVPP is about an order of magnitude lower than the conductivity ITP.

An inorganic / organic composite membrane was made from 90 wt% ITP with 10 wt% of the organic poly vinyl pyridinium phosphate as a binder. The conductivity is shown in Figure 27 below.

Figure 27. Arrhenius plot of the proton conductivity of a 90% ITP with 10% PVPP membrane measure sing
an AC m (RH
70%) Pt d Pt
current



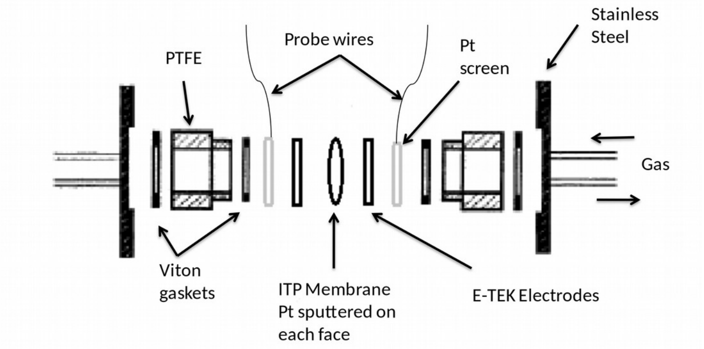
This conductivity of this composite membrane of 90% ITP and 10% PVPP blend (Fig 27) is comparable to pure ITP (fig 25), because there is so little PVPP is present and also possibly because there may be a synergistic effect between the ITP and thin layer of PVPP in which the PVPP can bridge ITP grains.

This 90% ITP and 10% PVPP composite showed over an order of magnitude greater conductivity than 70% ITP and 30% PVPP composite (not shown). The performance of these inorganic/organic composite membranes is quite sensitive to preparation and processing.

C. 2. 2. Fuel cell performance

C.2.2. (a) conventional cell

To assess the practical performance of the membrane in a fuel cell, a housing was made from Teflon to accept the solid electrolyte membrane so the polarization (I/V) curve could be obtained with this membrane between 2 Pt electrodes sputtered onto the membrane and with ETEK gas diffusion layers fed hydrogen on one side and oxygen the other. The schematic of the cell and the actual cell are shown in Figure 28.



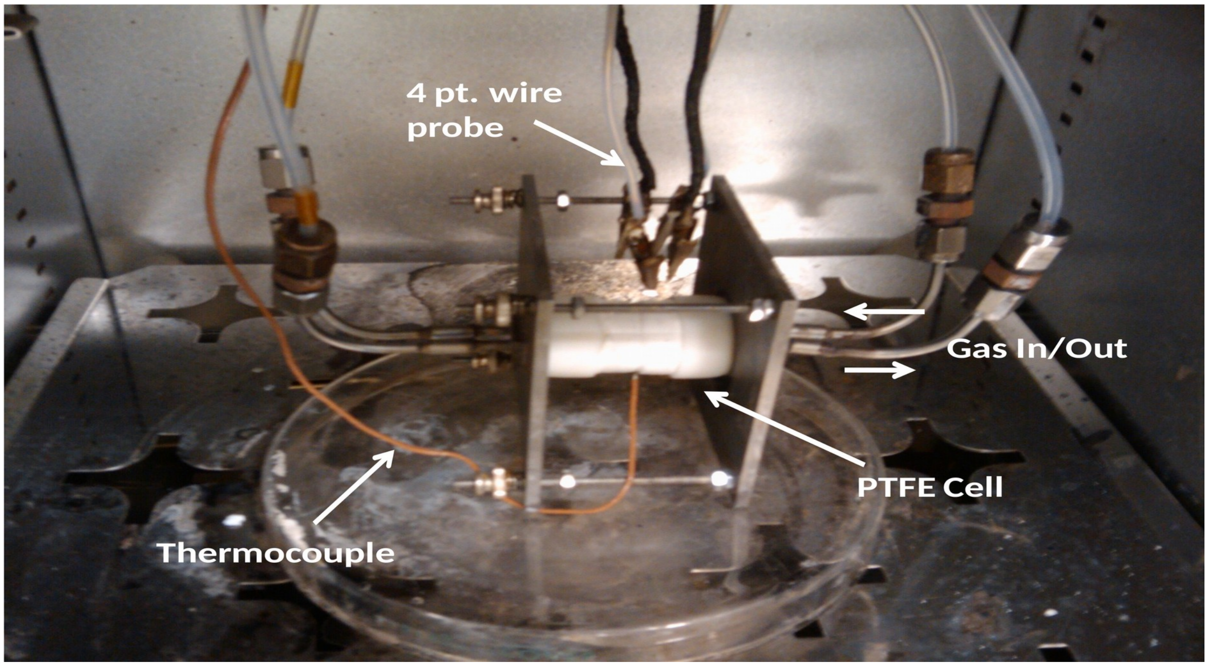


Figure 28. Schematic diagram (top) and real hardware (bottom) for accepting solid electrolyte membrane electrode assembly and feeding oxygen to one side and hydrogen to the other to produce fuel cell measurements.

Figure 29 shows preliminary fuel cell performance for two membranes a pure solid ceramic membranes of non-stoichiometric ITP ($In_{0.1}Sn_{0.9}P_2O_7$) alone as well as the ITP ceramic blended with a non-leachable organic salt PVPP in a 70wt% ITP and 30wt% PVPP ratio. The highest power is with pure ITP but the highest efficiency is with the ITP blended with PVPP polymer. This later improvement is most likely due to decreasing of gas crossover when the pores of the porous ITP membrane are filled by PVPP polymer.

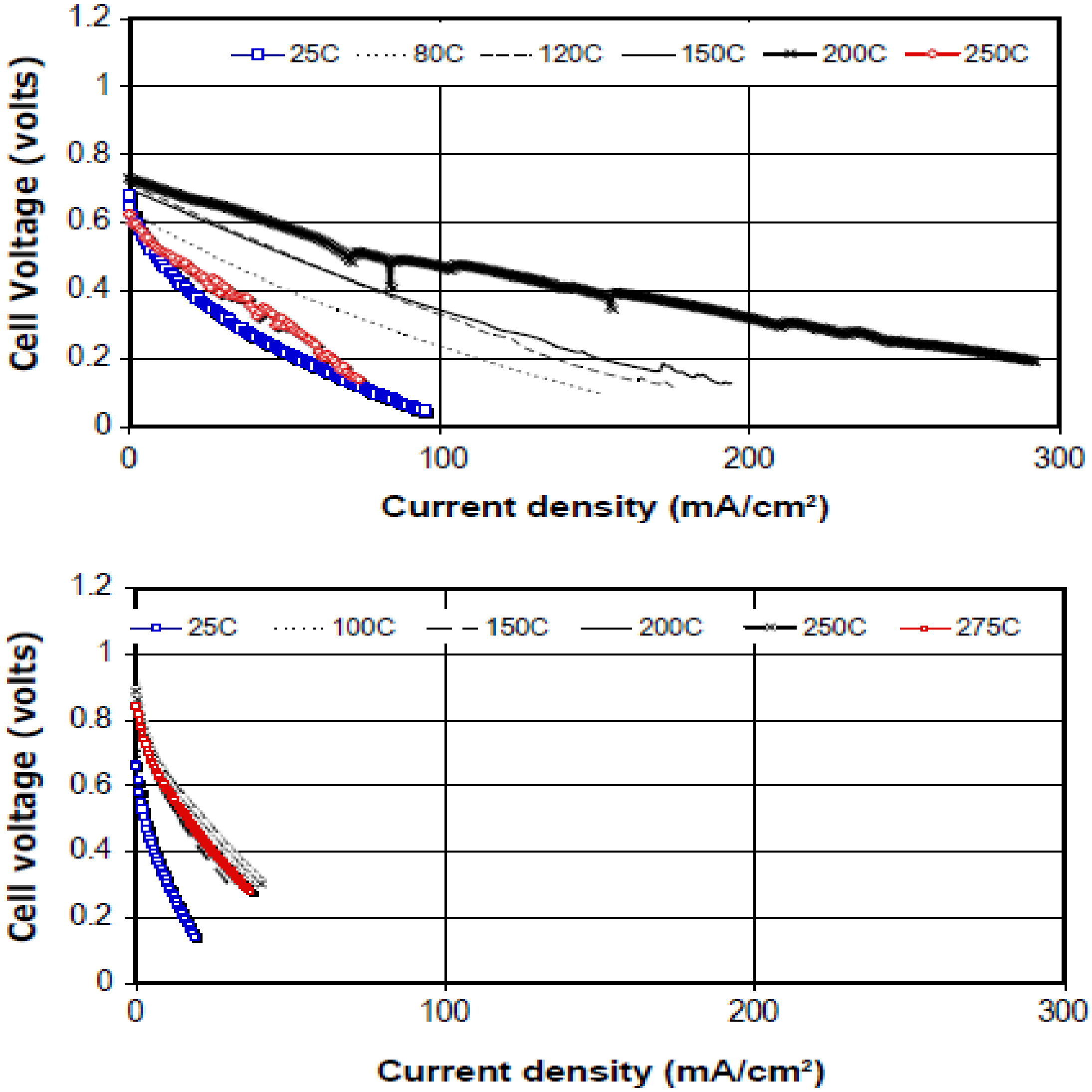


Figure 29. Fuel cells made with a pure ITP membrane (top) and a membrane with an ITP/PVPP blend (bottom).

The results to date have been encouraging but there is clearly room for improvement and many unanswered questions go begging for answers.

VIII.2.b.2. Characterization of Proton Conduction

The mechanism of proton conduction was determined to guide membrane optimization. Proton conduction was characterized by:

i. Electrochemical impedance spectroscopy (EIS)
ii. NMR methods:

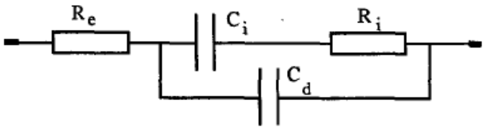
i. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) can be done by either the blocking electrode or Randles method.

Blocking electrode model

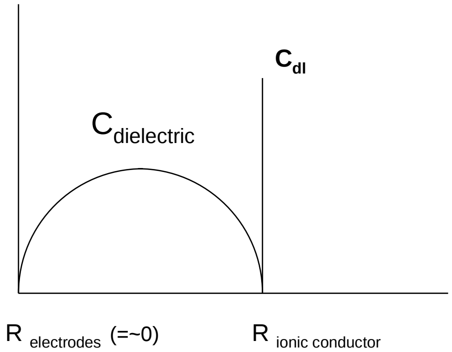
When there is no electrode depolarization, frequency dependent impedance data can be used to determine the dielectric membrane conductance and the capacitance of the electrodes as modeled by the "blocking electrode circuit".

Simplified Blocking Electrode Circuit



R_i = bulk ionic resistance
C_i = interfacial capacitance (C_{dl})
C_d = dielectric capacity,
R_e = resistance of electrodes (negligible)

"ideal cell" for perfectly symmetrical blocking electrodes



Nyquist Plot for Blocking Electrode

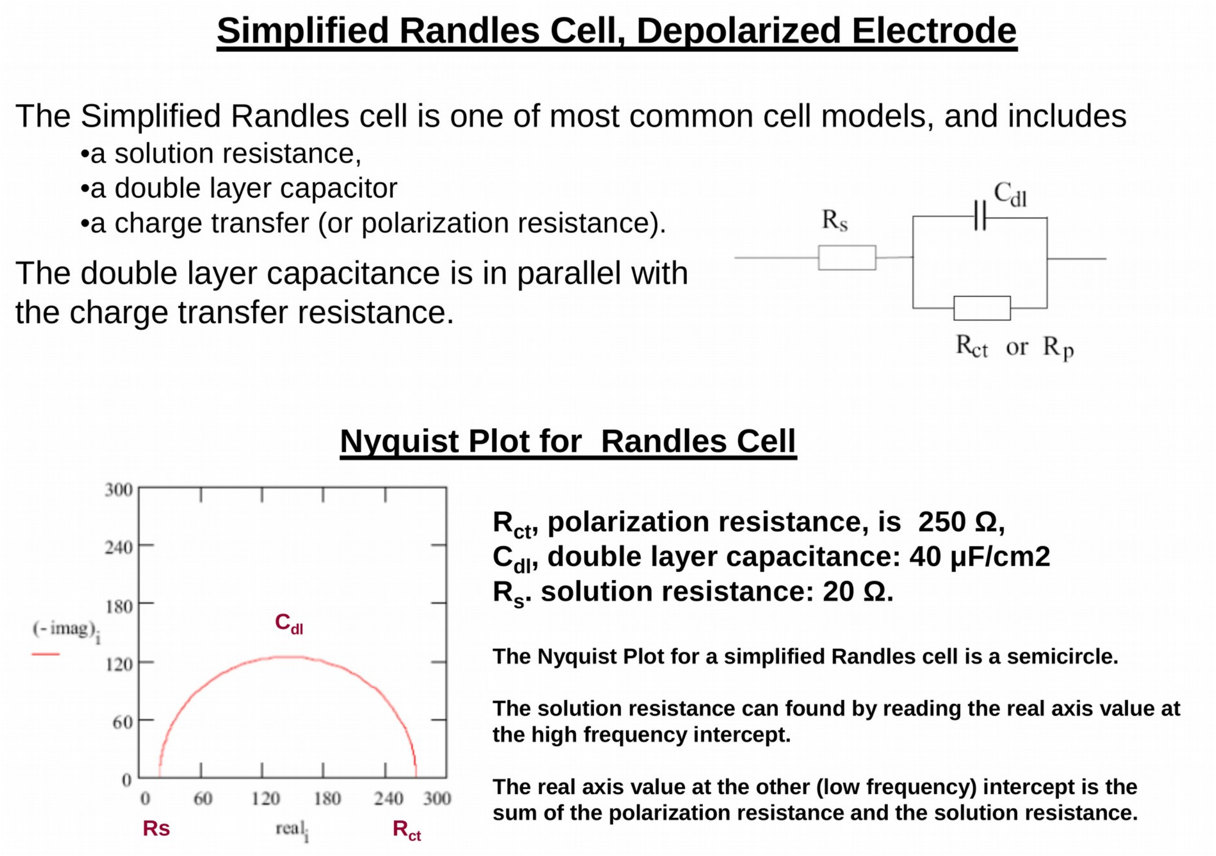
- Circuit for ac treatment of a traditional "dip cell"
- Simple method to measure ionic conductance

Problem: if electrodes "polarize" then an interfacial resistance develops and circuit is no longer valid

Some measurements of some membranes were made using the "blocking electrode" method (mainly by Xiaoguang Sun).

Randles Circuit model

When a charge transfer of a species, like hydrogen, occurs on the electrode, the membrane conductance and the electrode capacitance can be obtained by impedance measurements using the +



Simplified Randles Cell, Depolarized Electrode

The Simplified Randles cell is one of most common cell models, and includes
- a solution resistance,
- a double layer capacitor
- a charge transfer (or polarization resistance).

The double layer capacitance is in parallel with the charge transfer resistance.

Nyquist Plot for Randles Cell

R_{ct}, polarization resistance, is 250 Ω,
C_{dl}, double layer capacitance: 40 μF/cm2
R_s. solution resistance: 20 Ω.

The Nyquist Plot for a simplified Randles cell is a semicircle.

The solution resistance can found by reading the real axis value at the high frequency intercept.

The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance.

Most measurements in this project were done by the Randles method.

iia. Pulse field gradient NMR to determine the diffusivity of ions

Magnetic field gradient NMR to measure proton mobility (diffusivity) in protic liquids

Physical effect: destruction of NMR signal from moving nuclear moments in a magnetic field gradient.

Measurement of this effect: apply strong, pulsed magnetic field gradients during time intervals between two radio-frequency pulses used to generate a spin “echo” NMR signal. Measure attenuation of signal vs. duration or strength of gradient pulses.

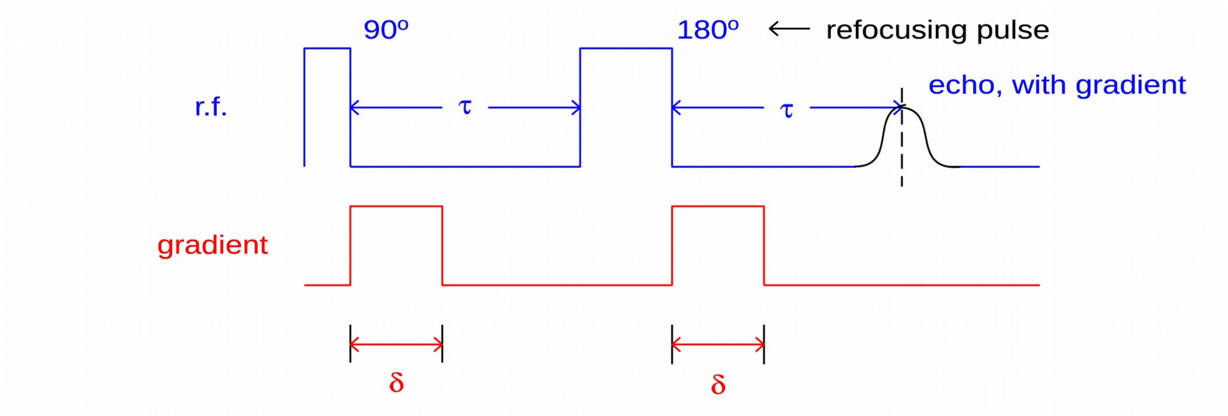
Apply diffusion equation to extract values of proton diffusivity, referenced to a standard value for water of 2.30 x 10-9 m^2/s.

Details: effect of a magnetic field gradient upon NMR signal amplitude

$$S(t) = S_0 e^{(-\tau/T_2 - KDg^2t^3)}$$

Measure attenuation S(t)/S0 to determine D in a known g

<u>Pulsed gradient spin echo technique:</u>



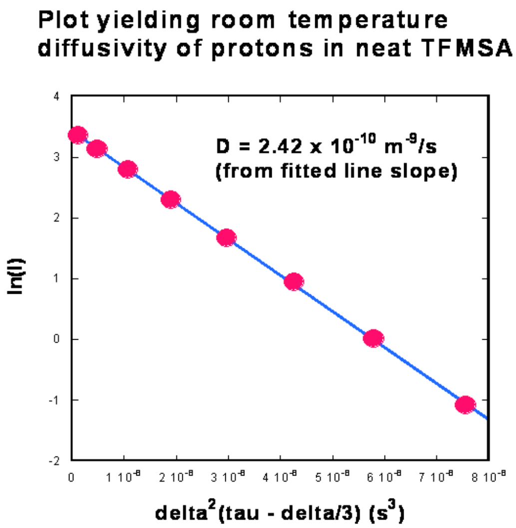
Linear plot fit:

$$\log\left(\frac{S(\tau,\delta)}{S(\tau,0)}\right) = -Dg^2\gamma^2\delta^2(\tau - \delta/3)$$

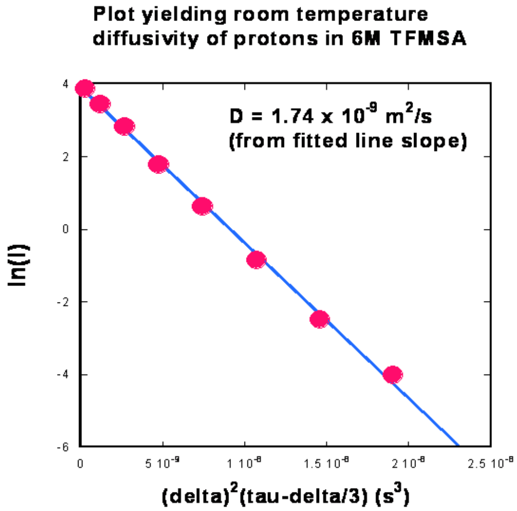
Plot $S(t)/S_0$ vs. (δ^2 (τ-δ/3)) to get slope $Dg^2\gamma^2$

This method is widely accepted and has been used since originally developed by Stejskal and Tanner in 1965.

Model system: neat TFMSA versus aqueous 6M TFMSA



D of H$^+$ for neat TFMSA ~ 10% that of water

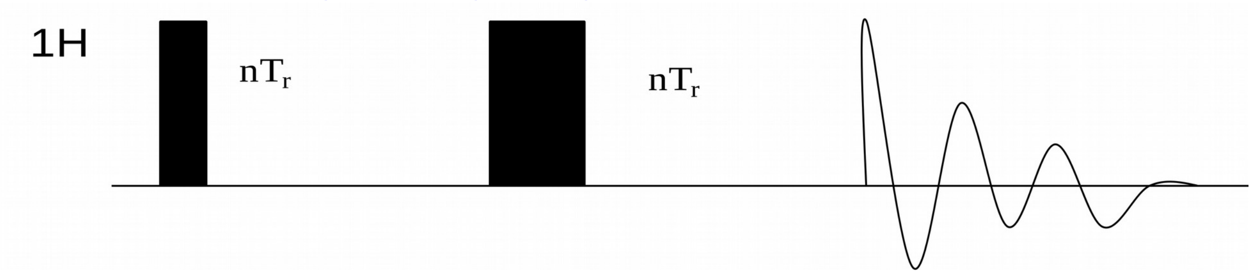


In 6M TFMSA D is substantially increased over neat TFMSA

iib. 2D NMR

2D NMR was done but not extensively with solid-state magic angle spinning (MAS) probes that exceed speeds of 35 kHz available to study PEM. Coupling high-speed MAS with high-field NMR (800 MHz) yields high-resolution 1H NMR spectra in solids combined with multiple pulse sequences can establish H+ structure and dynamics in proton conducting polymer electrolyte membranes (PEMs).

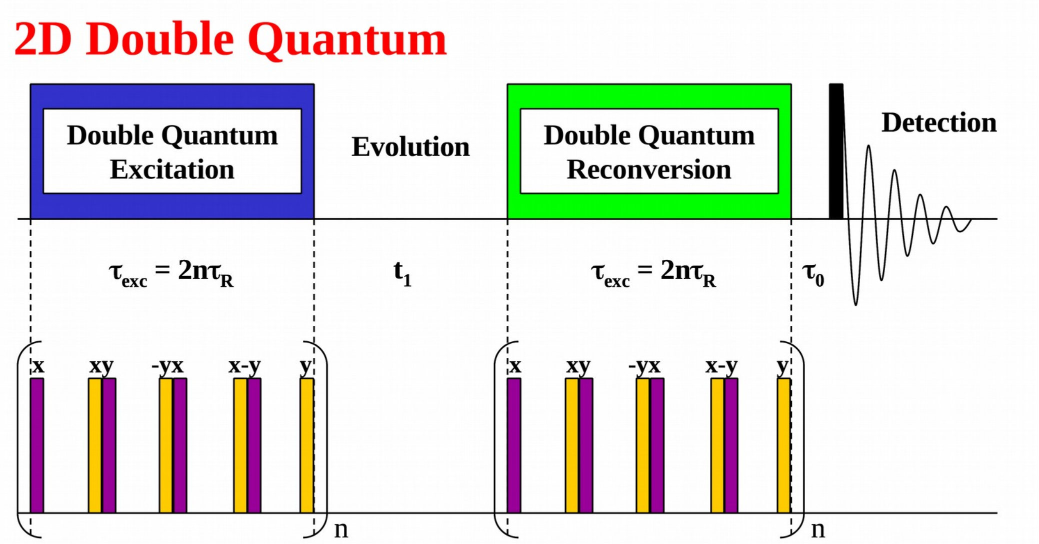
Spin-echo is to Filter out Rigid Proton Signal in High-speed 1H MAS NMR



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

Back-to-Back (BABA) Pulse Sequence

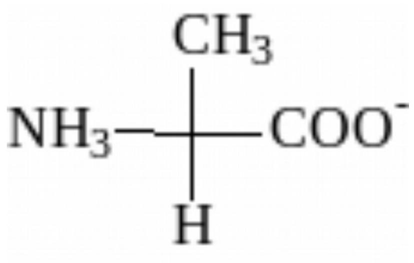
Schnell H. W. Spiess, “ High resolution 1H NMR Spectroscopy in the Solid State: Very Fast Sample Rotation and Multiple Quantum Coherence”, J. Magn. Reson. **151**, 153-227 (2001).

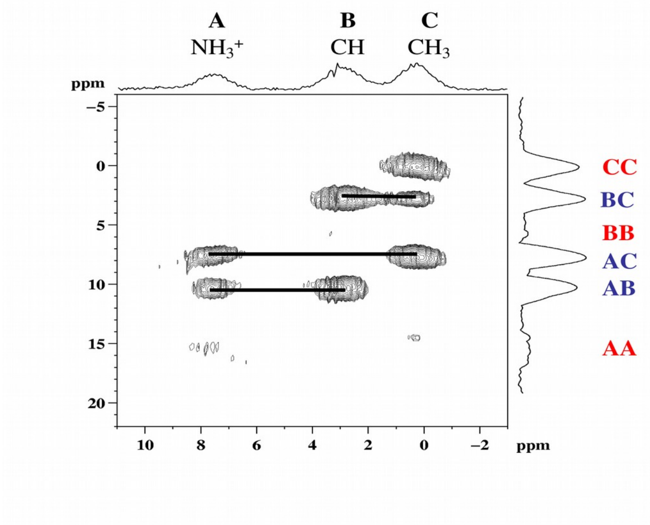


This sequence (DQ-Filter) was used as a mobility filter to select only rigid proton components in PEM (low mobility) and also be implemented in a two-dimensional fashion to obtain correlation spectra that establishes spatial connectivity.

BABA 2Q-1Q Correlation

An example of the through space dipolar connectivities by ~$1/r^3$; NOESY by ~ $1/r^6$ is L-alanine.





This dipolar NMR technique was developed by G. Holland at ASU but not used extensively.

iic. eNMR - MRI for determining molecular motions and distributions during proton conduction.

e NMR involves passing current along the gradient line in an NMR spectrometer. By following the response in time, one can measure changes in the distribution of species along this line during proton conduction. Imaging by NMR (magnetic resonance imaging, or MRI) is a powerful tool for following ions, water, and other molecules that can be transported as proton is transported by the electrolyte. This can be used to distinguish whether the “vehicle” or the “hopping” mechanism or both are operative. Hardware was set up for this measurement but was not finished in time to be used to characterize membranes.

VIII.3. Problems encountered and departure from planned methodology, and an assessment of their impact on the project results.

Because the ITP does not melt, the processing of a uniform ceramic ITP powder and pressing of ITP with PVPP organic polymer into an organic inorganic composite membrane was a challenge to do reproducibly by hand and led to inconsistencies which affected the solubility of the membranes and consequently their performance. Processing appears to be a key issue for making a practical proton-conducting composite ITP/PVPP and similar membrane materials.

IX. Identify products developed under the award and technology transfer activities, such as:

a. Publications (list journal name, volume, issue), conference papers, or other public releases of results

1. "Inorganic salts as high conductivity electrolytes for >150°C fuel cells", Jean-Philippe Belieres, Don Gervasio and C. Austen Angell, accepted in Chem. Commun., DOI: 10.1039/b611150e (2006).
2. "Proton transfer salts: A new class of solvent-free, involatile, fuel cell electrolytes", D. F. Gervasio, J-P Belieres, and C. Austen Angell, American Chemical Society, Division of Fuel Chemistry, Fuel Cell Chemistry and Operation, San Francisco, CA, September 2006, Paper No. 171.
3. "Binary inorganic salt mixtures as high conductivity liquid electrolytes for high temperature fuel cells", J.-P. Belieres, N. Byrne, X.-G. Sun, L. Holmes, G. Tucker, D. Gervasio, J. Yarger and C. A. Angell, 211th Electrochemical Society Meeting - Chicago, Illinois, May 2006, Ex. Abs. No. 321.
4. "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.
5. "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.
6. "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.
7. "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.
8. "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.
9. "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
10. "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.
11. Study of Transport Properties of Trifluoromethanesulfonic acid monohydrate: Diffusivity, Conductivity and Viscosity, Mohammed Abdullah, M. S. Thesis, Physics Department, Arizona State University, April, 2008.
12. "Characterization of ... protic ionic liquids: NH chemical shift", J.-P.Belieres in the I&EC division, Paper #82, ACS, Philadelphia, PA (2008).
13. "Fuel Cells with Neat Proton-conducting Salt Electrolytes", Dominic Gervasio, Chapter 20 in Fuel Cell Science: Theory, Fundamentals and Bio-Catalysis, Jens Norskov, Andrzej Wieckowski, Eds., John Wiley & Sons (2010).
14. "Catalysis of Electrode Reductions in Salt Electrolytes with Low-Water-Activity", D. Gervasio, University of Arizona, Tucson AZ, 85721, Ex. abs. 1757, Spring 2010 ECS meeting Vancouver, Canada.
15. Electrochemical Reduction in Ionic Liquids, Jeffery Thomson, Materials Science, ASU Ph. D. Thesis, D. Gervasio advisor, 12 March 2010.
16. "Protic ionic liquids as probes for acidity of superacids", *in preparation.*

b. Web site or other Internet sites that reflect the results of this project

Individual faculty websites of C. A. Angell, R. Marzke, J. Yarger, D. Gervasio, W. Youngs.

c. Networks or collaborations fostered

Teaming was developed at ASU between C. Angell, J. Yarger (Chemistry), R, Marzke (Physics) and D. Gervasio (Materials) and W. Youngs (Chemistry at U Akron).

Jason Simmons of NIST and D. Gervasio established a collaboration on the characterization of proton conduction by neutron scattering.

Potential teaming is being considered to establish collaboration between D. Gervasio and D. Meyers of Argonne National Lab on *in situ* structural characterization of electro-catalyst surfaces in anhydrous salt electrolytes.

d. Technologies/Techniques

1. Jason Simmons of NIST and D. Gervasio established a collaboration to characterize proton conduction in solid protic salts using neutron scattering.
2. Discussed using in situ XAFS and XANES of Pt surface in salt electrolytes with D. Meyers of Argonne National Lab to detect presence or absence of oxide on Pt at various potentials.
3. D. Gervasio and C. Angell demonstrated water electrolysis in protic salt electrolytes including salt membranes.
4. D. Gervasio demonstrated “hydrogen pumping” in protic salt electrolytes including salt membranes.

e. Inventions/Patent Applications, licensing agreements

1. “Neutral Protic Salt Electrolytes and Protic Salt Imbibed Polymer Membranes for High Temperature Fuel Cell Applications”, US 7,833,643, Nov. 16, 2010.
2. “Alkaline FuelCell Membranes”, C. A. Angell, X. G. Sun, J. P. Belieres, D. F. Gervasio, U.S. Pat. Appl. Publ. (2007), US 2007122675 A1 20070531 AN 2007:593919.
3. “Fluorinated Protic Salt Electrolyte for High Temperature PEM Fuel Cells” D. Gervasio, C. A. Angell, D. Gervasio, disclosure July 2006.
4. “Inorganic Salt Mixtures as Electrolyte Media in Fuel Cells”, J.P. Belieres,D. Gervasio, C. A. Angell, Attorney Docket No. FR 22193-020WO1 / M7-050
5. “Binary Inorganic Salt Mixtures as High Conductivity Liquid Electrolytes for >100°C Fuel Cells”, J.P. Belieres, C. A. Angel, D. Gervasio, Provisional Application Ser. No. 60/863,760, filed on October 31, 2006.

Conclusion and Recommendations for future research

This work clearly showed that proton can be conducted without water using protoic ionic liquids which are Bronsted salts which contain a proton and whose acid and base moieties have pK separated by more than 4 units and less than 14. A key finding is that the base used should be significantly different than the basicity of water or else water displaces the base and an ordinary acid membrane is left behind. This is the case where the acid moiety is sulfonic acid found on perfluorinated polymeric membranes. This PI suggests that a fruitful route for attaining highly proton-conductive stable protic salt membranes is to use the STABLE poly-phosphazene (-P=N-) polymer backbone with electrochemically STABLE pendant acid or base units on the phosphorous of poly-phosphazene and with suitable pK so the base is NOT the same pK as water. From this work this should give stable water-free proton conductors which should allow for stable fuel cells with Pt catalysts and possible with non-platinum catalyst for the hydrogen anode and oxygen cathode.