2006 DOE Hydrogen Program Review

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

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**Arizona State University**

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This presentation does not contain any proprietary or confidential information

Project ID #
FCP 6

# Overview

## Timeline

- January 15, 2006
- January 14, 2011
  - go/no go end of year 3
- 5% completed

## Budget

- Total project funding
  $1,500K
  - DOE: 80%
  - Contractor: 20%
- Funding received in FY05
  - None (new project)
- Funding for FY06
  - $300,000

## Barriers

- Barriers addressed
  - Stability of electrolyte
  - Timely syntheses
  - Understanding mechanism of proton conduction

## Partners

- Arizona State University
- University of Akron
- Boeing

# Objectives

**Overall**

**To make new proton-conducting solid polymer electrolyte membrane (PEM) materials that have:**

- **high proton conductance at high temperature (up to and greater than 120oC),**
- **effectively no-cotransport of molecular species, like water, with the proton**
- **the reduction of oxygen electrode overpotential**
- **good mechanical strength and chemical stability.**

**2006**

**Protic ionic liquid (PIL) electrolyte with high conductivity at high temperatures operating stably in a fuel cell with low polarization.**

**2007**

**A PIL filled solid membrane (protic ionic liquid electrolyte filled in a porous solid support or/and in a solid polymer support) with high conductivity at high temperatures operating stably in a fuel cell with low polarization.**

**2008**

**Explain the mechanism of proton conductivity of PIL and PSM electrolytes based on experimental data from pulse gradient NMR and imaging eNMR and eNMR with multiple pulse sequences.**

# Approach

**Synthesis of Proton Conductors**

Two types of PEM will be developed based on protic salt electrolyte concepts. Protic ionic liquids (PILs) will be used to model membranes. Acid and base moieties as well as polymer properties will be systematically varied to optimize properties of a protic salt membrane (PSM).

i. protic ionic liquid (PIL) filled PEMs consisting of:

ia. bi-phasic porous matrices filled with water immiscible ionic liquids immobilized by capillary forces

ib. ionic liquids sorbed in polymers

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. (Year 1) Synthesis of two types of polymer systems having base moieties in the side groups.

iib. (Year 2) Mixed polymer systems of the two types of polymers from the first year will be synthesized. Work will begin on polymer systems containing acid side chains.

iic. (Year 3) Blends of polymers containing acid side chains and basic side chains will be formed and their properties explored.

**Characterization of Proton Conduction**

The mechanism of proton conduction will be determined to guide membrane optimization.

Proton conduction will be characterized by:

i. Electrochemical impedance spectroscopy (EIS)

ii. Three NMR methods:

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

iib. eNMR to measure the distribution of species during proton conduction and

iic. eNMR for determining molecular motions during proton conduction.

# Approach #2

**Task 1: Synthesis, and characterization of two types of polymer systems having base moieties in the side groups will be a major goal of the first year.**

**Task 2: Optimization of polymer length will also be studied along with a concern for processability of the resulting polymers.**

**Task 3: Electrostatic Binding of acid moieties in the polymer matrix will be examined.**

**Task 4: Mixed polymer systems of the two types of polymers from the first year will be synthesized. Mixed polymer systems will have less crystallinity and greater side chain flexibility which should give greater proton mobility.**

**Task 5: Work will begin on polymer systems containing acid side chains.**

**Task 6: Blends of polymers containing acid side chains and basic side chains will be formed and their properties explored.**

**Task 7: The synthesis of mixed polymer systems that contain both acid and basic sites will be explored.**

**Task 8: New polymer materials will be evaluated at ASU for stability and proton conductivity using EIS and eNMR.**

# Approach #3

## 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 m2/s.

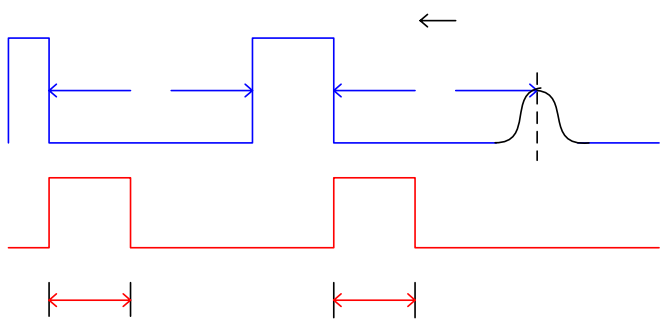
**Details: effect of a magnetic field gradient upon NMR signal amplitude**

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

**Effect of diffusion (E.L. Hahn)**

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

**Pulsed gradient spin echo technique:**



**Linear plot fit:**

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

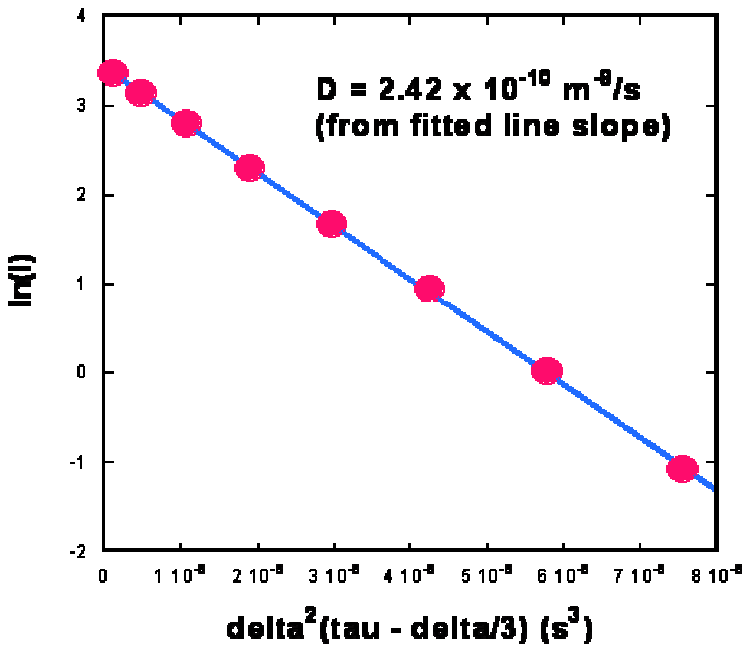
**Plot $S(t)/S_0$ vs. ($\delta^2$ ($\tau$-$\delta$/3)) to get slope** $Dg^2\gamma^2$

(Stejskal and Tanner, 1965)

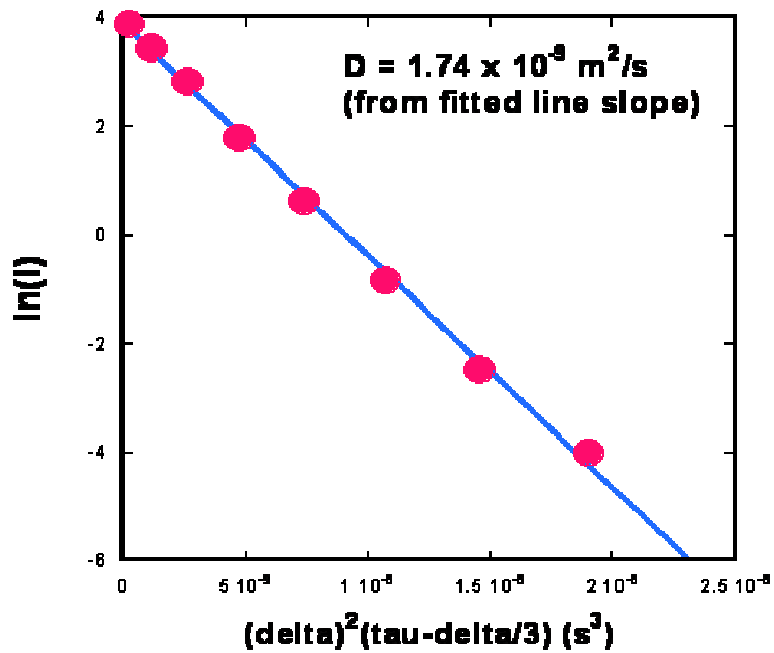
# Approach #3

## Proton mobility (diffusivity)

Plot yielding room temperature diffusivity of protons in neat TFMSA




Plot yielding room temperature diffusivity of protons in 6M TFMSA




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

In 6M TFMSA D is substantially increased over neat TFMSA

# Approach #4

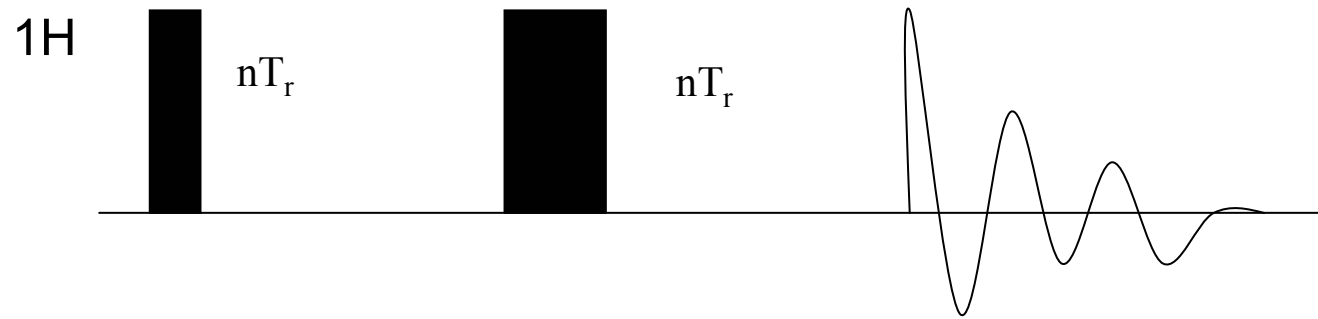
## High-Speed 1H MAS NMR to Investigate Proton Conductivity in PEM

Solid-state 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 will establish H+ structure and dynamics in PEM.

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



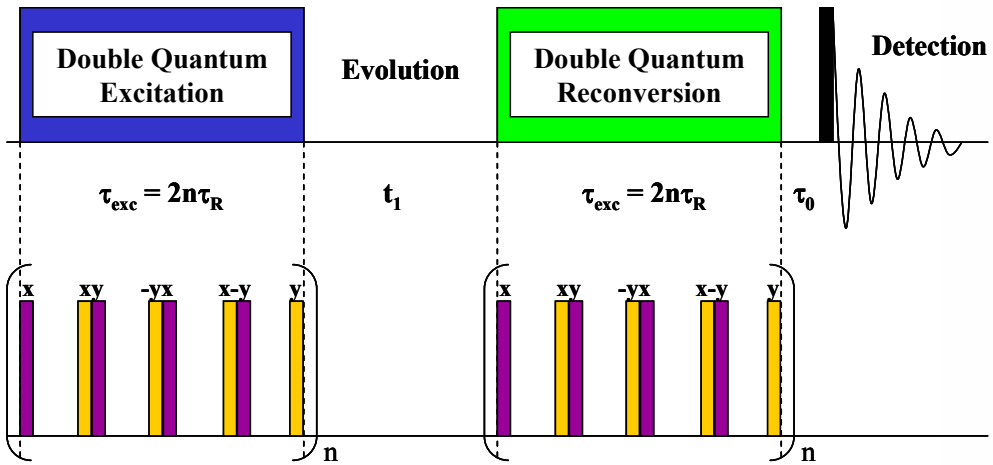

- Complimentary to the DQ-filter is the conventional spin-echo pulse sequence
- This sequence can be used to filter out the rigid component of the NMR spectra
- The spin-echo technique will be implemented to investigate highly mobile $^1$H species in PEM
- Measurements will be made as a function of temperature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

# Approach #4

## 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).

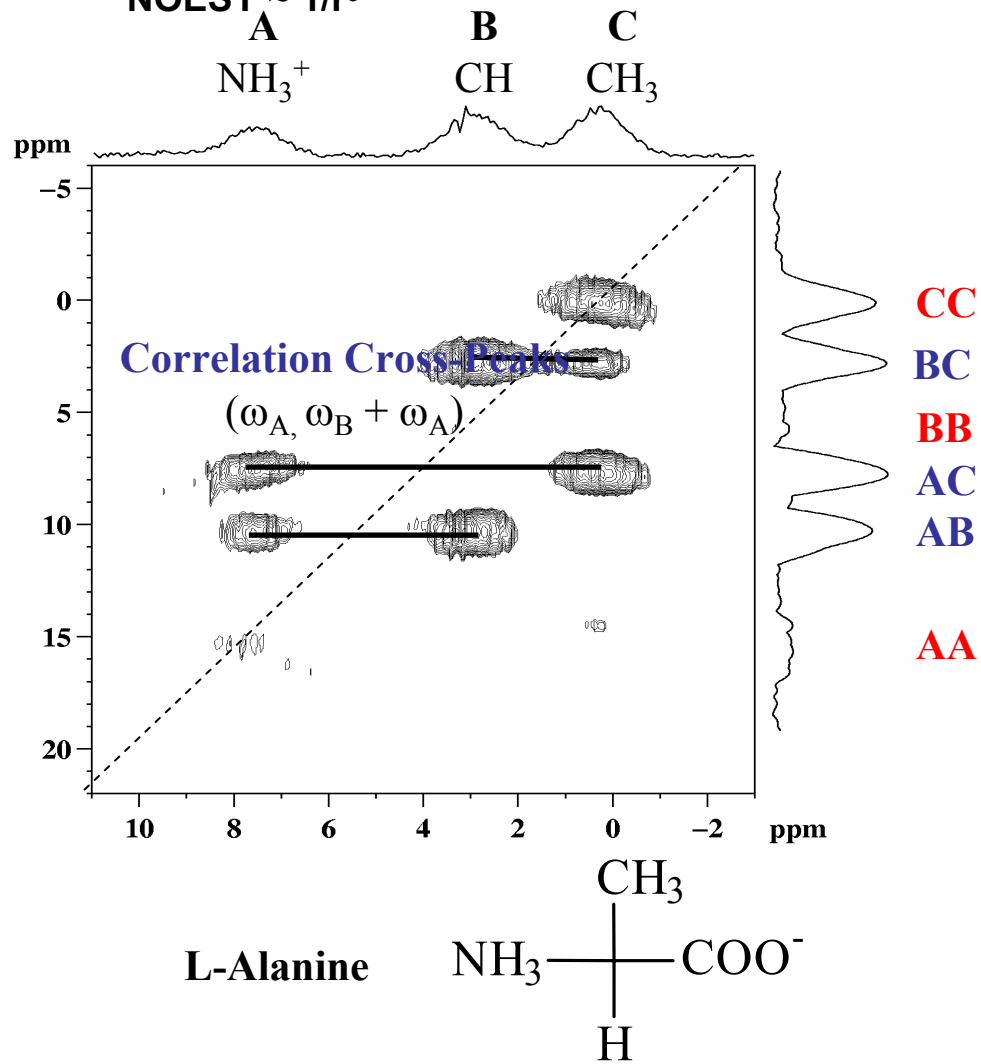
### 2D Double Quantum




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

## BABA 2Q-1Q Correlation

**Through Space Dipolar Connectivities! ~1/r³**
**NOESY ~ 1/r⁶**



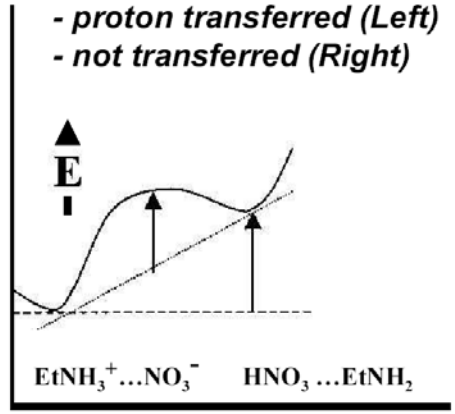
# Accomplishment

## *Proton Ionic Liquids (PILs)*

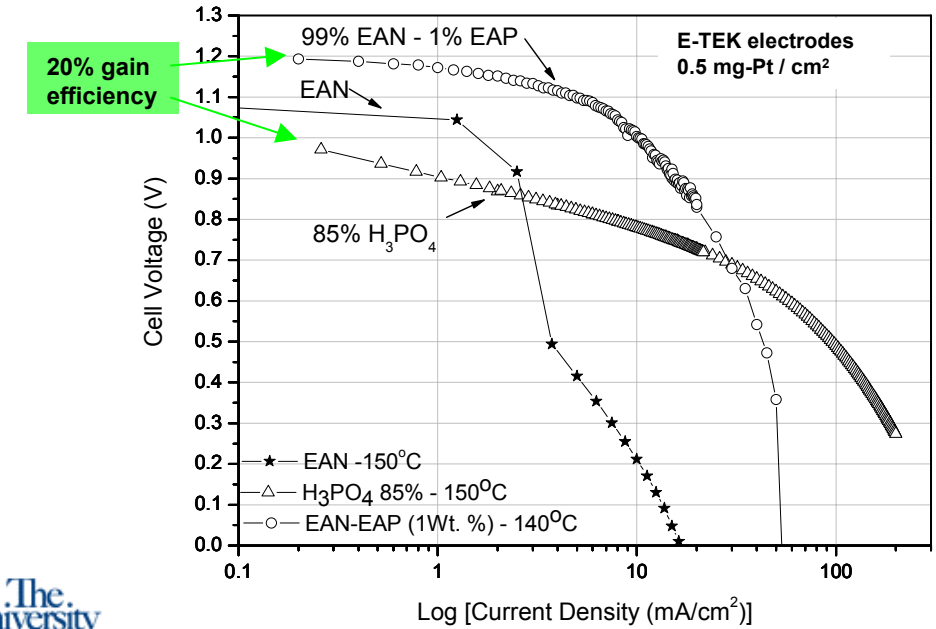
***a New Class of Solvent-free, Involatile, Fuel Cell Electrolytes***

**Benefits of Elevated Temperature (> 140 to 200°C) Fuel Cells**
- simplified system with all gas fluidics (water is vapor)
- allows use of impure hydrogen (crude reformate) anode feed

**Continuing Research**
- improve electrolyte stability
- form solid polymer membrane form of PIL




**Polarization Curves for $H_2$ / $O_2$ Fuel cell**




## Why use Protic Ionic Liquids in fuel cells ?

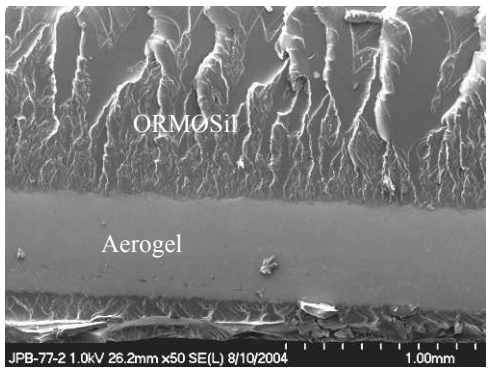
- **Tailorable: PILs are formed from combinations of common Brönsted acids and bases and give new opportunity for tailoring of physical and chemical electrolyte properties, such as:**
  **chemical stability, proton conductivity,**
  **$O_2$ solubility, adsorption, electrode kinetics, etc.**
- **Low vapor pressure, high thermal stability and boiling point enabling high temperature use**
- **High proton conductivity with no need for water**
- ***Higher efficiency alternative electrolytes***

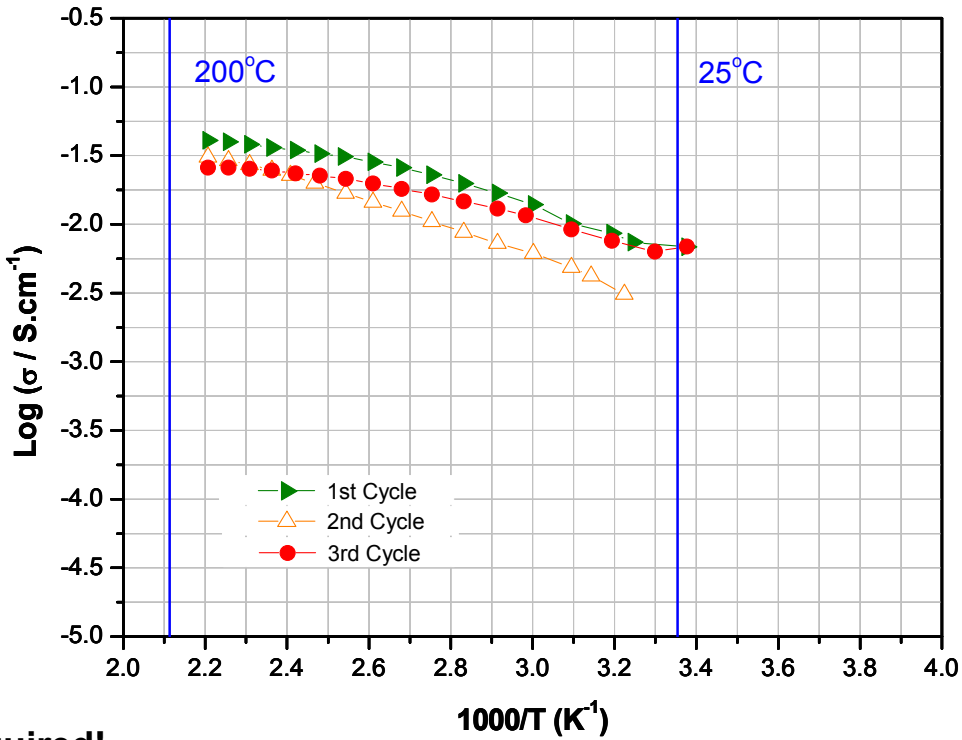
***Don Gervasio , C. Austen Angell***

# Accomplishment

## ORMOSil/Cross-linked Aerogel Membranes

EAN was added to a cross-linked aerogel. The aerogel was coated with the ORMOSil polymer. Conductivity was measured over three temperature cycles from room temperature to 180 °C.




**Advantages: No Humidification required!**

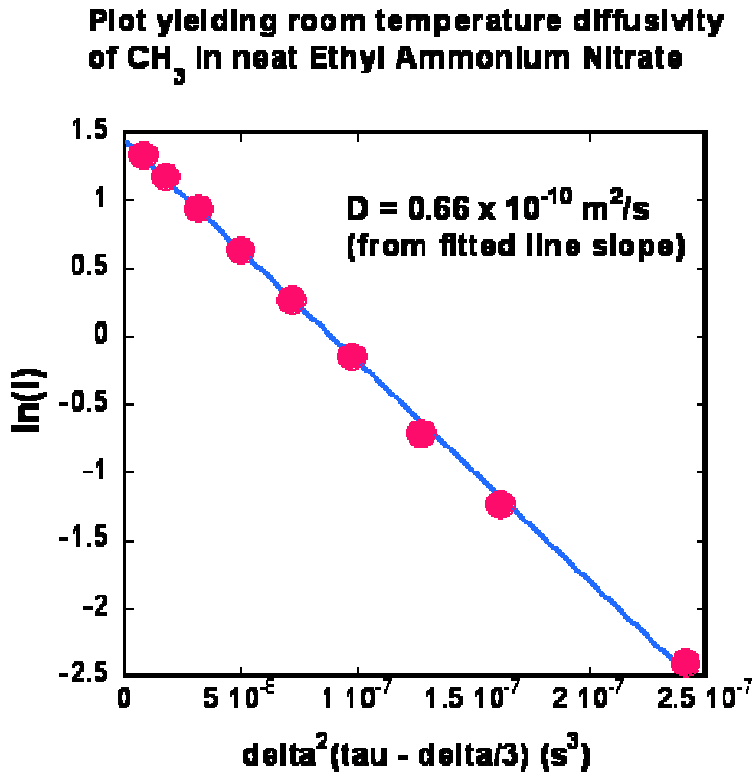
**- Simplifies water management. High Ionic Conductivities (>10-1 Scm-1) to >160 °C.**

**Disadvantages: Material is a liquid**

**- Leaching out of the liquid in a fuel cell can cause loss of conductivity, performance and shorts.**

# Accomplishment

**Proton diffusivity in ethyl ammonium nitrate (EAN).**




**Surprise:**

this liquid's proton diffusion takes place via motion of methyl groups.

# Future Work

- Make highly stable ionic liquid electrolytes
- New Polymer and New Aerogel Systems
- Cross-linkers/ Coating Optimization
- Fill IL in solid hosts for proton conducting membrane
- Make polymers with all ions immobilized
- Conductivity testing (EIS)
- NMR characterization (diffusivity and eNMR)

# Summary

- Protic salt electrolytes are non aqueous proton conductors
- No bulk water means little or no Pt-OH on surface, expect:
  - Lower overpotential for oxygen reduction and higher cell efficiency possible with protic salt electrolytes
  - Lower corrosion and Pt particle growth
- Other Benefits:

  Increasing the PEM fuel cell operating temperature from 80°C to 120°C or higher at zero or low relative humidity
  - Increases fuel cell power output
  - Greatly simplifies the system design (water management, parasitic losses from compressors and humidifiers).

# Critical Assumptions and Issues

- **Assumption: Results in liquids electrolytes translate to solid polymer electrolyte membranes.**

- **Assumption: non-leachable PEMs with tethered acid and/or base groups are more desirable than PEMs of the same acid and/or base groups that are not tethered but use surface tension for immobilizing moieties in solid host.**

- **Issue: It is not certain if the tethering approach can be made to give conductivity equal to or nearly equal to the high conductivity found with an ionic liquid immobilized in a solid support.**