Fluoroalkylphosphonic-acid-based proton conductors

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May 16, 2006

FCP 15

This presentation does not contain any proprietary or confidential information

DE-FG36-06GO16031

Overview

Timeline

- Start: April 2006
- Finish: March 2011
- Zero percent complete

Budget

- Total project funding
  - DOE $1,500,000
  - Contractor $381,000
- Funding received in FY05
  - None
- Funding for FY06
  - $150,000 from DOE for period from April – Oct 2006

Barriers

- Barriers
  - Thermal, air and water management.
- Targets
  - Membrane ionic conductivity > 0.10 S/cm at < 120 ^{o}C and water partial pressure of 1.5 kPa for transportation
  - Membrane ionic conductivity > 0.10 S/cm at > 120 ^{o}C for stationary

Partners

- Dr. Alex Kitaygorodskiy, Clemson
- Dr. Ashok Krishnaswami, JEOL
- Professor Klaus D. Kreuer, Max Planck Institute, Stuttgart, GE

(all these will help with NMR studies of proton transport rates

Objectives

Overall project objective	• Provide new electrolyte materials for use in next-generation hydrogen-fuel-cell power sources, especially for automotive transportation applications.
Specific project objectives	(1) Synthesize and characterize new proton-conducting electrolytes based on the fluoroalkylphosphonic acid functional group; and (2) Create and apply new computer models to study protonic conduction in fluoroalkylphosphonic acid-based electrolytes.
Year 1 Milestones (April 2006 – March 2007)	• Synthesize and/or purify at least 10 g each of one or more small-molecule fluoroalkylphosphonic acid electrolytes. • Fabricate and validate an apparatus for measuring ionic conductivity of electrolytes at temperatures between ambient and 120 ^{o}C and relative humidities between 25 and 100 percent. • Develop classical force fields for and perform MD simulations of low molecular weight fluoroalkylphosphonic acid electrolytes using developed force field. • Develop first generation of the multi state empirical valence bond model (MS-EVB) for proton transport in fluorophosphonic acid.

Approach

Task 1.0 Synthesize new fluoroalkyl-phosphonic-acid-based electrolytes. – Small-molecule acids, trifluorovinylether monomers, TFE copolymer ionomer membranes	**Task 5.0** Perform computer simulations of fluoroalkylphosphonic-acid electrolytes. – Develop and validate force fields including multi-state empirical valence bond model for explicit treatment of proton transport in MD simulations. Predict proton and water transport rates.
Task 2.0 Characterize new fluoroalkyl-phosphonic-acid-based electrolytes. – Structure, purity, ion (proton) transport rates (diffusivity, conductivity)	**Task 6.0** Perform computer simulations of fluoroalkylphosphonic acid electrolyte / heterocycle/water mixtures. – As in Task 5.
Task 3.0 Demonstrate conductivity of at least 0.07 S/cm at 80% RH at ambient temperature.	**Task 7.0** Project Management and Reporting. – Deliver membrane(s) to Topic 2 awardee; periodic reports; annual reviews
Task 4.0 Demonstrate conductivity of at least 0.10 S/cm at 50% RH at 120 ^{o}C.	

Fluoroalkyl-phosphonic-acid-based proton conductors

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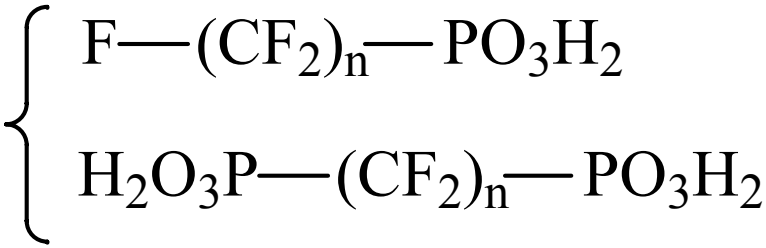
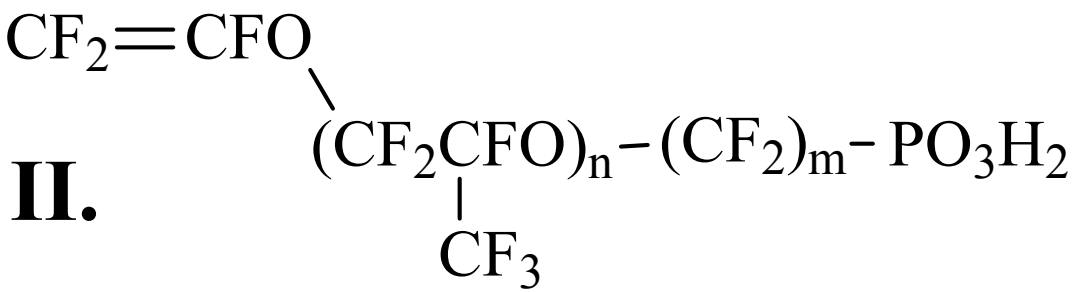
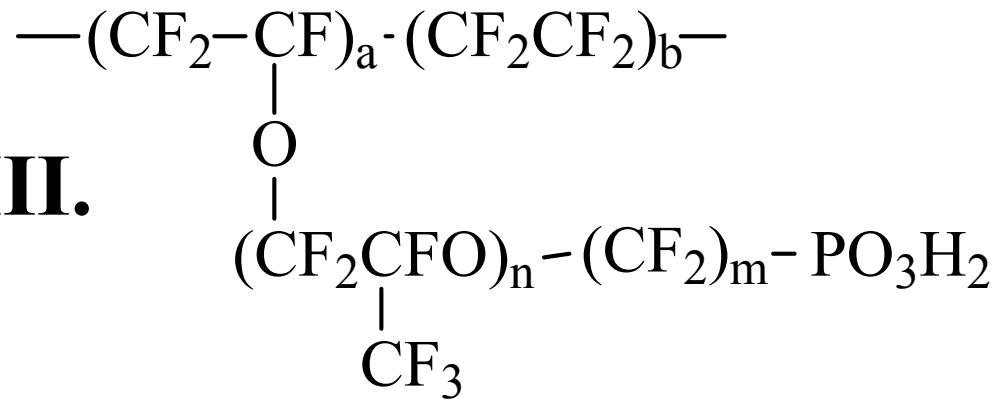
Electrolyte Structures

I. 	Small molecules
II. 	Trifluorovinylether monomers
III. 	Ionomers

Why fluoroalkyl-phosphonic acids?

1. Fluoroalkylphosphonic acids are **stronger acids** than phosphoric and alkylphosphonic acids which should promote proton hopping and transport;
2. Fluoroalkylphosphonic acids should have **weaker adsorption** onto Pt which should help prevent electrocatalyst poisoning and promote higher oxygen reduction activity;
3. Fluoroalkylphosphonic-acid-based electrolytes should provide **higher oxygen solubility** than other phosphorous-acid-based electrolytes which should also promote higher oxygen reduction activity; and
4. Fluoroalkylphosphonic acids should be highly **robust** which will provide durability in PEM fuel-cell power sources

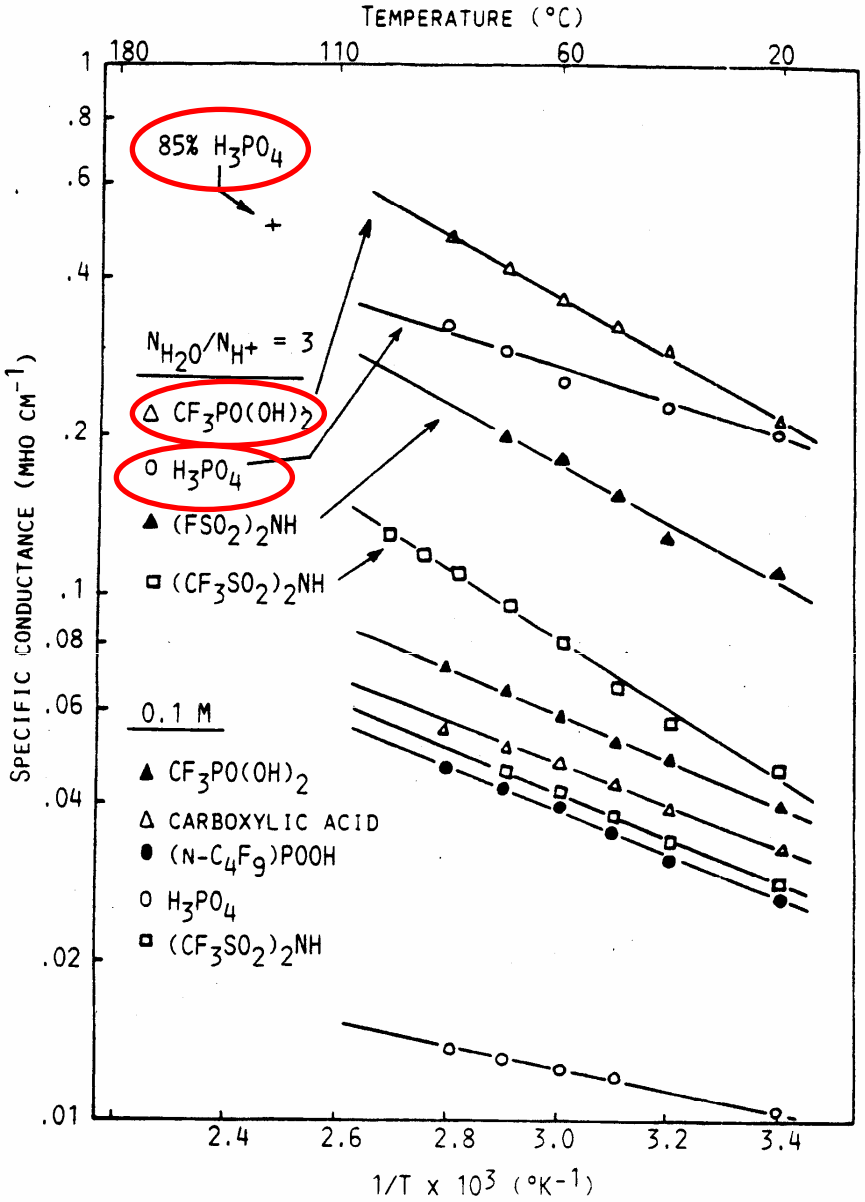


FIG. 51. SPECIFIC CONDUCTANCE OF VARIOUS ACIDS AS A FUNCTION OF TEMPERATURE.

Specific conductance of some phosphonic-acid-based electroltyes

- Trifluoromethylphosphonic acid has the highest ionic conductivity of all the common phosphorous acids for comparable water content and temperature.

Razaq, M., A. Razaq, and E. Yeager, Electrochemical characteristics of acid electrolytes for fuel cells. 1989, Case Western Reserve University: Cleveland, OH. 214 pp. NTIS No. PB89178768

Oxygen reduction in H_2O_3P-CF_2CF_2-PO_3H_2 electrolyte

Kanamura, K.; Tanaka, A.; Gervasio, D.; Kennedy, V.; Adzic, R.; Yeager, E. B.; Burton, D.; Guneratne, R., Perfluoro-ethylene-1,2-bis-phosphonic acid fuel cell electrolyte. Journal of the Electrochemical Society 1996, 143, 2765-2770.

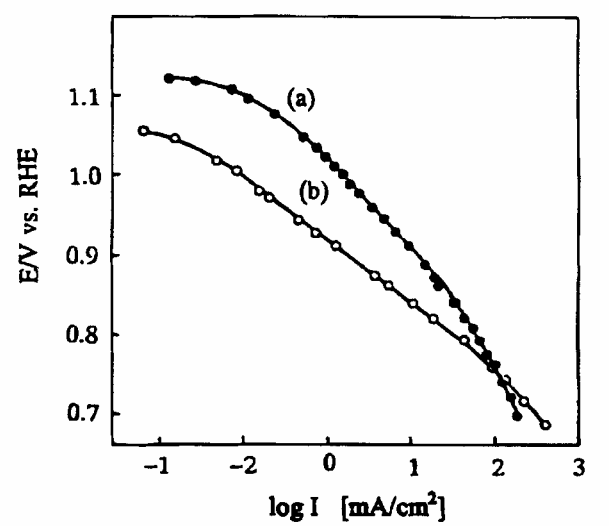


Fig. 5. Polarization curves for O_2 reduction on Pt-catalyzed Teflon-bonded gas-fed electrode (Standard Prototech electrode, Pt loading = 0.3 mg/cm²) in (a) 85% bis-phosphonic acid and (b) 85% phosphoric acid for 1 atm pure O_2. T = 100°C. A = 1 cm².

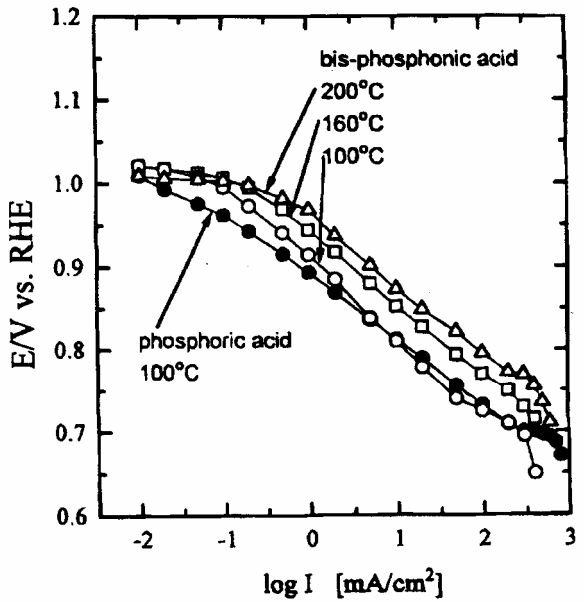


Fig. 6. Polarization curves for O_2 reduction on a Pt-catalyzed Teflon-bonded gas-fed electrode (Standard Prototech electrode, Pt loading = 0.3 mg/cm²) in 85% phosphoric acid (filled circles) in 85% bis-phosphonic acid at 100°C (open circles), 160°C (open squares), and 200°C (open triangles) equilibrated with 1 atm pure O_2 over solution. Superficial electrode area = 1 cm².

- Oxygen reduction occurs with lower overpotential at Pt in contact with fluoroalkylphosphonic acid electrolyte relative to phosphoric acid

Project Tasks

1. Synthesize new fluoroalkylphosphonic-acid-based electrolytes
   - Small-molecules, TFVE monomers, Ionomer membranes
2. Characterize new fluoroalkylphosphonic-acid-based electrolytes
   - Structure / purity, conductivity, ion self-diffusion
3. Demonstrate conductivity of at least 0.07 S/cm at 80% RH at ambient temperature.
4. Demonstrate conductivity of at least 0.10 S/cm at 50% RH at 120 C.
5. Simulations of fluoroalkylphosphonic-acid-based electrolytes
   - Classical force fields, multi-state empirical valence bond (MS-EVB) models
6. Simulations of fluoroalkylphosphonic acid electrolyte / heterocycle/water mixtures
7. Project Management and Reporting

Synthesis

- Trifluoromethylphosphonic acid and pentafluoroethylphosphonic acid are commercially available and are being acquired.
- Difunctional acids and trifluorovinylether acids will be prepared using known methods.
- Ionomer synthesis via TFE co-polymerization will proceed following methods known to us.

Characterization

Variable temperature / humidity membrane ionic conductivity

A. Vacuum / gas inlet / outlet.

B. Impedance analyzer

C. Pressure transducer

D. Water injection port and syringe

E. Thermocouple

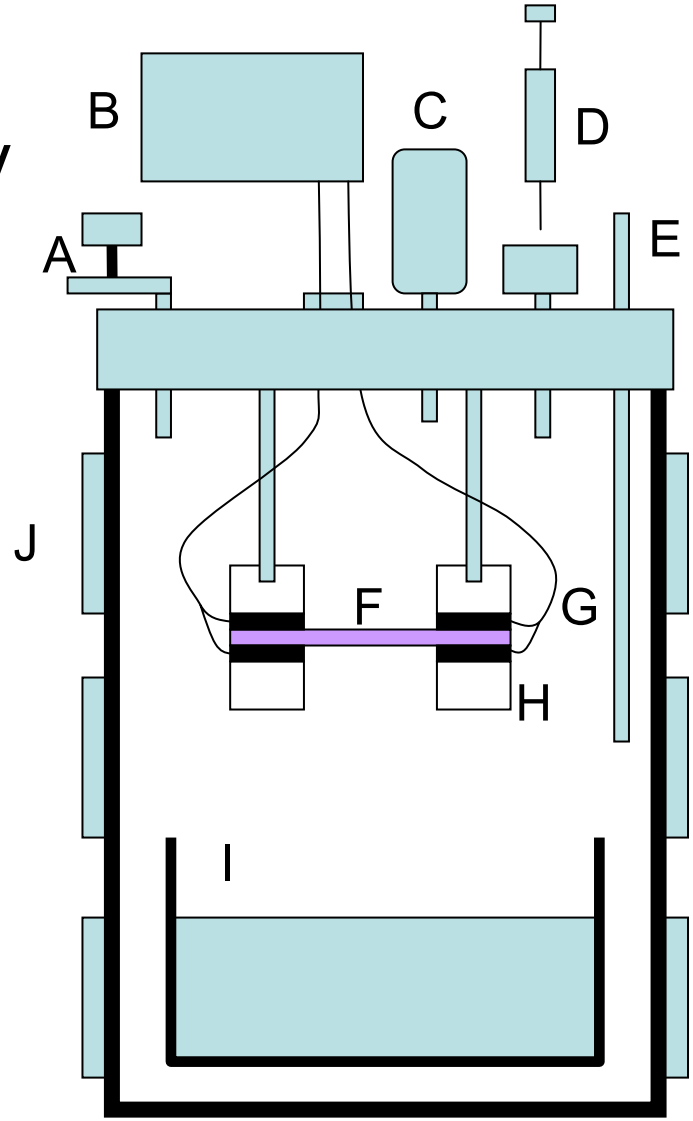
F. Electrolyte membrane

G. Dual platinized platinum foil contacts

H. PEEK open-faced conductivity cell

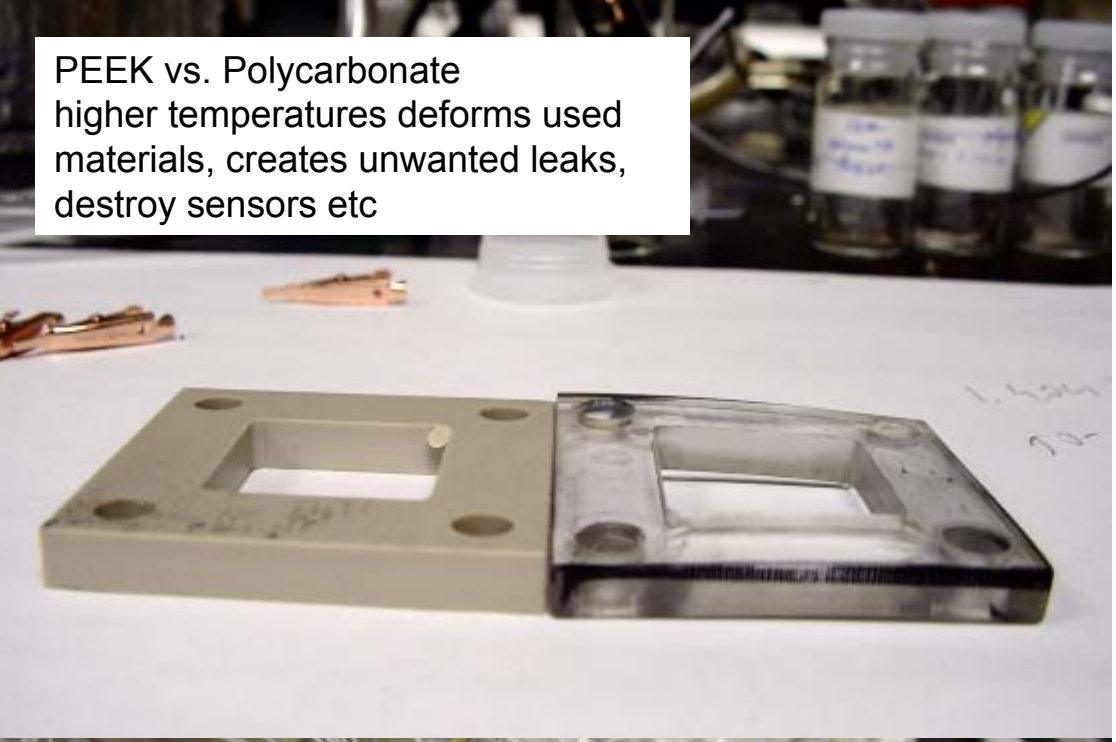
I. Saturated salt solution for humidity control (optional)

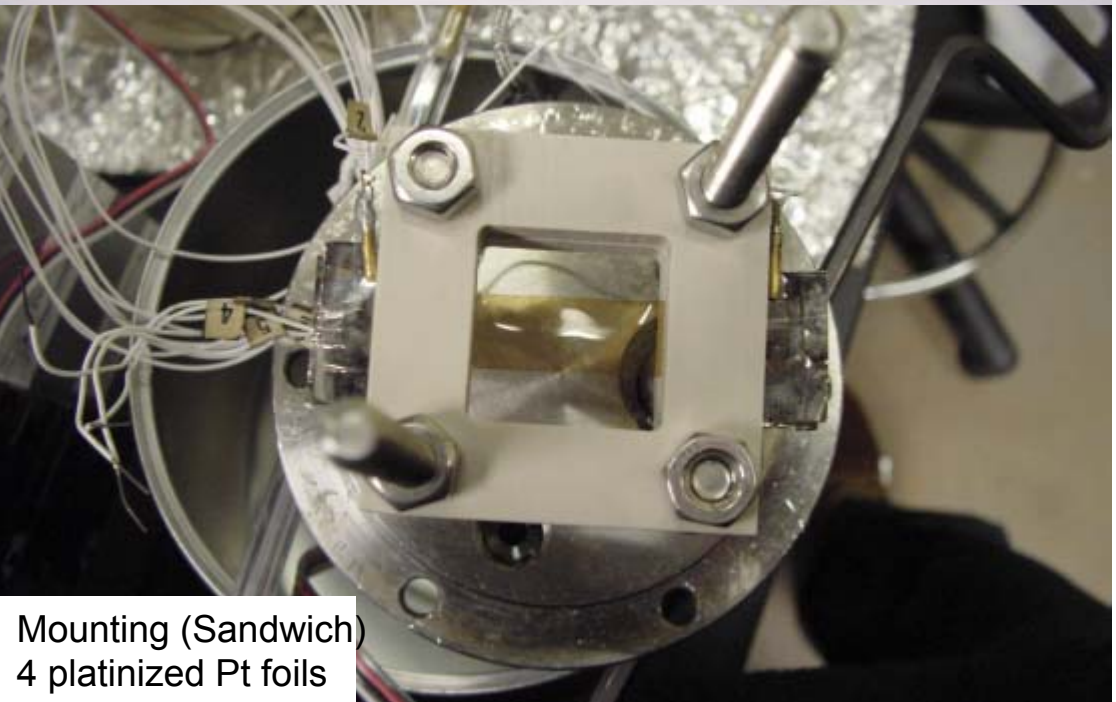
J. Heating tape for temperature control



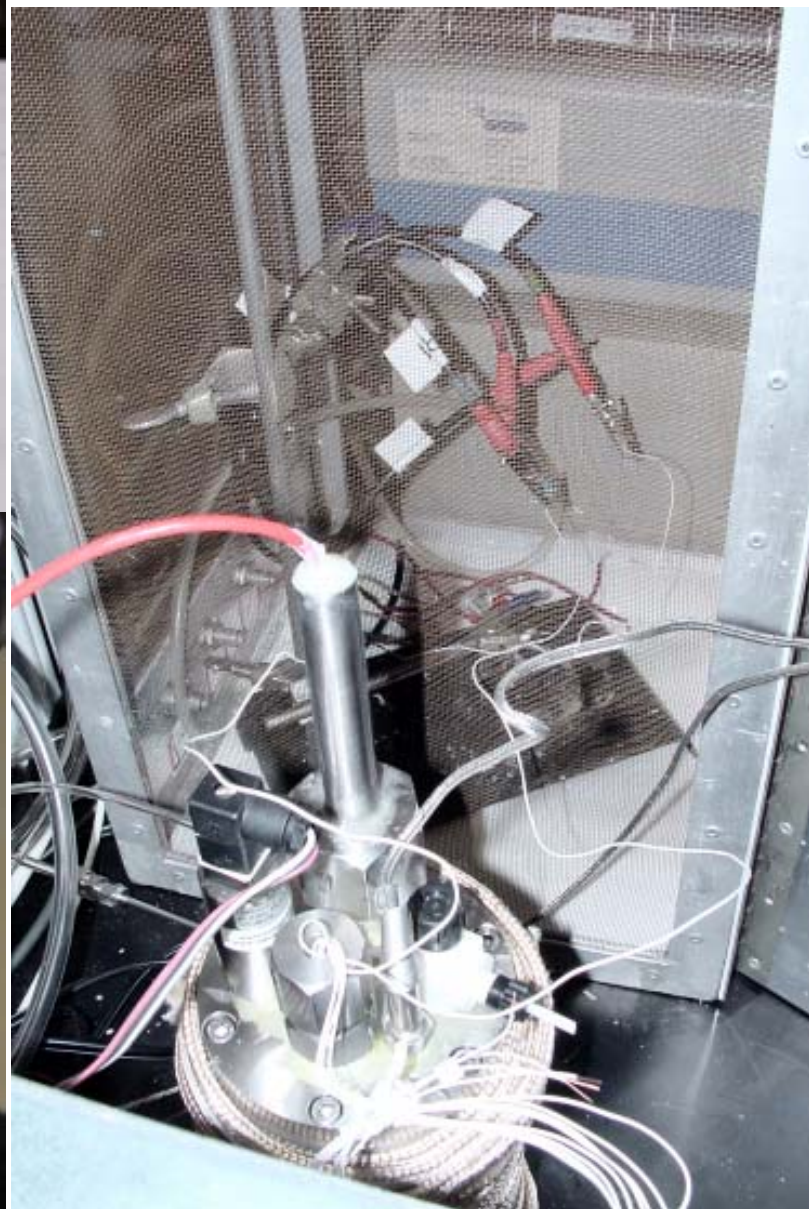
Conductivity measurement

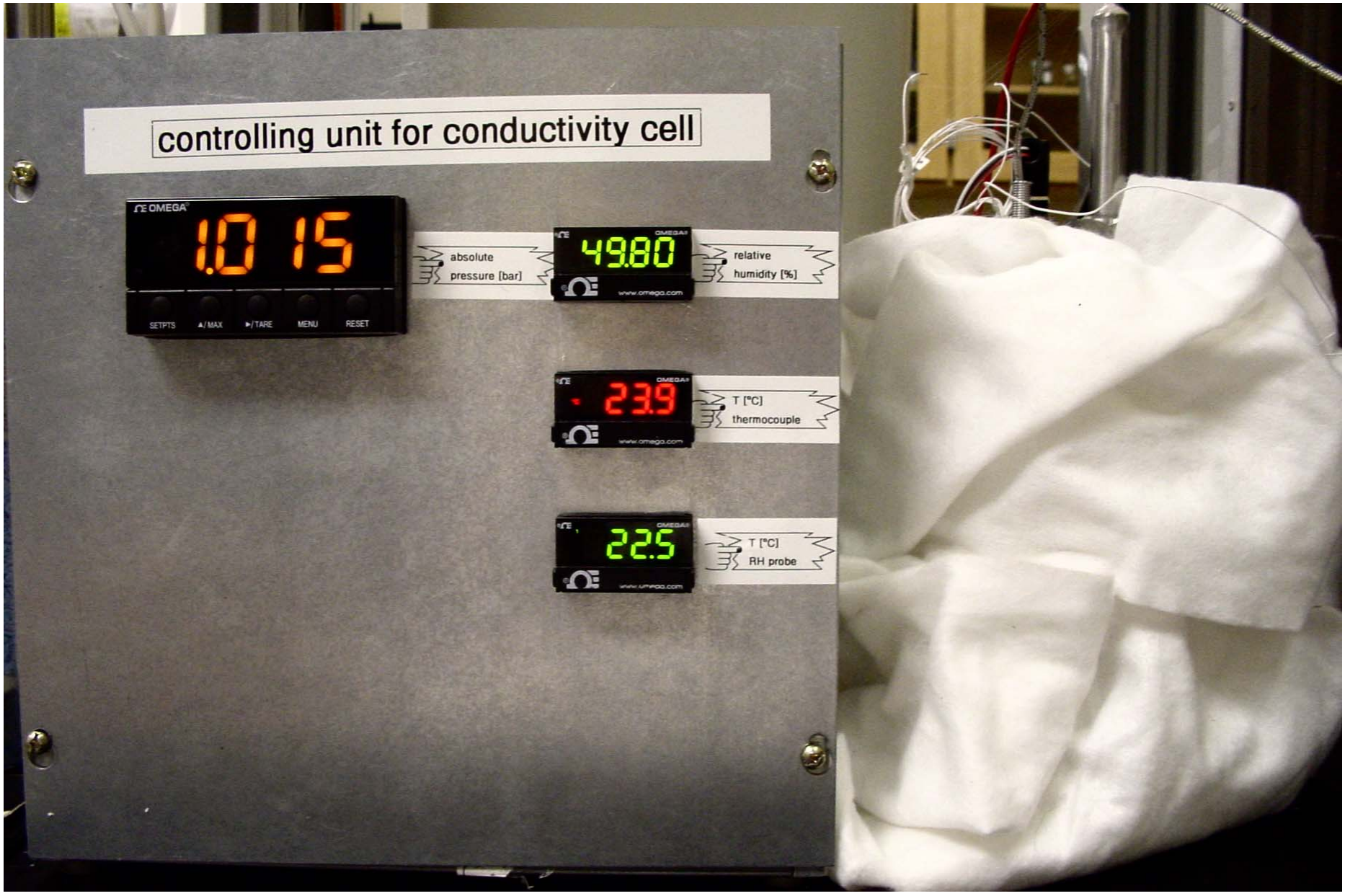
PEEK vs. Polycarbonate
higher temperatures deforms used materials, creates unwanted leaks, destroy sensors etc





Mounting (Sandwich)
4 platinized Pt foils




controlling unit for conductivity cell
OMEGA
1.015
SETPTS
▲/MAX
►/TARE
MENU
RESET
absolute
pressure [bar]
49.80
relative
humidity [%]
23.9
T [°C]
thermocouple
22.5
T [°C]
RH probe

Saturated salt solutions for humidity control

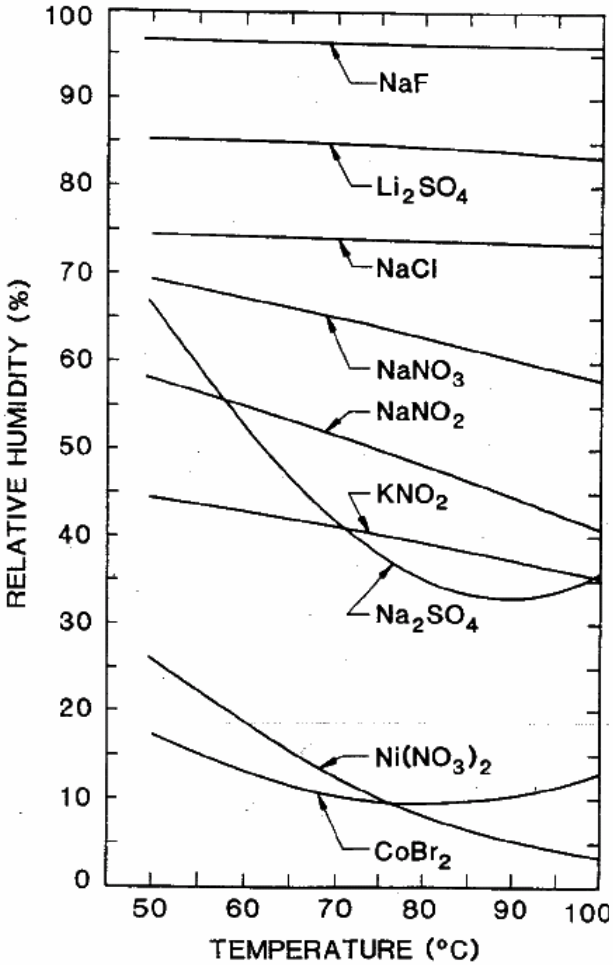


Fig. 4. Equilibrium Relative Humidity Values vs. Temperature for Various Saturated Salt Solutions

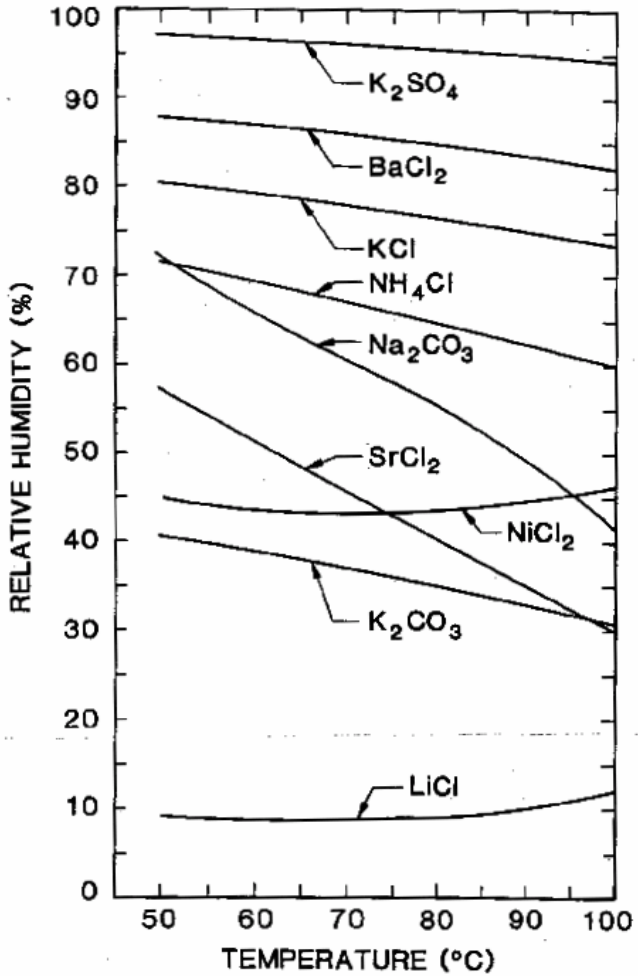


Fig. 3. Equilibrium Relative Humidity Values vs. Temperature for Various Saturated Salt Solutions

Salt	T [°C]	RH [%]	Max error [%]
Ni(NO3)2	80	8.44	2.50
LiCl	**80**	**9.35**	**0.98**
CoBr2	80	9.96	1.40
MgCl2	**80**	**26.05**	**+/- 0.34**
Na2SO4	80	35.14	0.43
K2CO3	**80**	**35.42**	**0.23**
KNO2	80	39.41	0.70
SrCl2	80	40.66	2.20
NiCl2	80	43.82	0.17
NaNO2	80	48.54	0.22
Na2CO3	**80**	**55.68**	**0.33**
NaNO3	80	62.98	0.77
NH4Cl	**80**	**64.99**	**0.63**
NaCl	80	73.94	0.95
KCl	**80**	**76.61**	**0.19**
Li2SO4	80	84.68	2.20
BaCl2	80	85.14	0.10
K2SO4	**80**	**95.79**	**0.14**
NaF	80	96.43	0.07

Variable temperature ionic conductivity cell for liquid electroltyes

A. Vacuum / gas inlet / outlet.

B. Impedance analyzer

C. Pressure transducer

D. Thermocouple

E. Cell holder

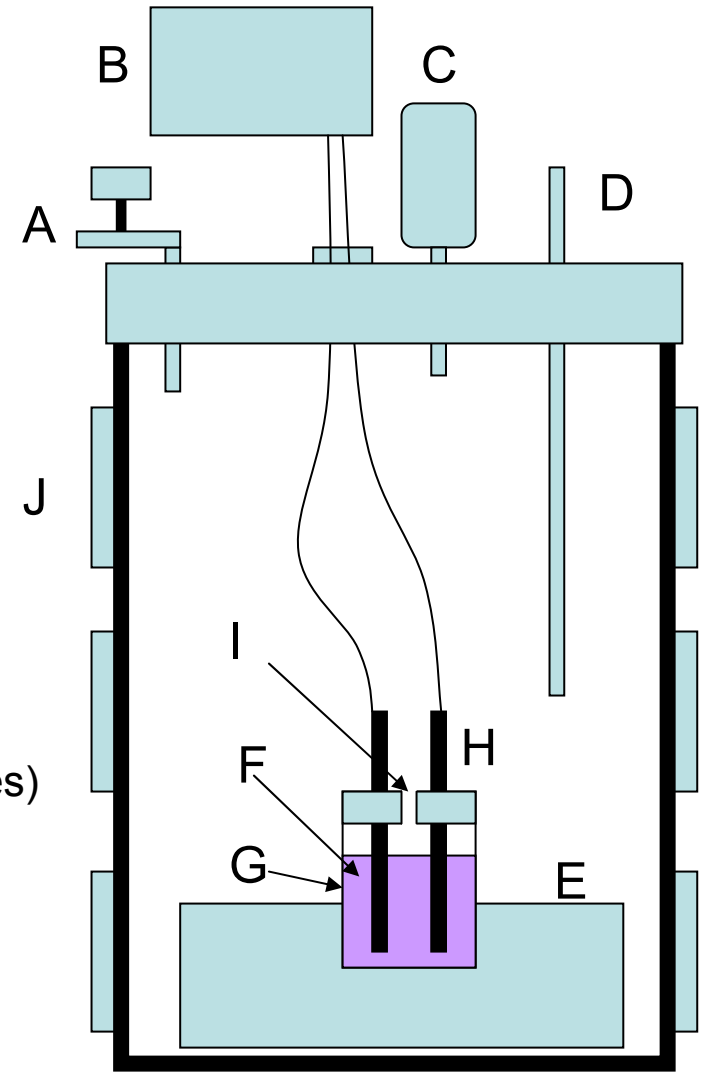
F. Liquid electrolyte (acid plus water plus additives)

G. PEEK cell body

H. Platinized platinum rod electrodes

I. Pressure equalization hole (very narrow)

J. Heating tape for temperature control



Multiscale Simulation Methodology

QC calculations on representative fluoroalkylphosphonic-acids fragments interacting with water and heterocycles

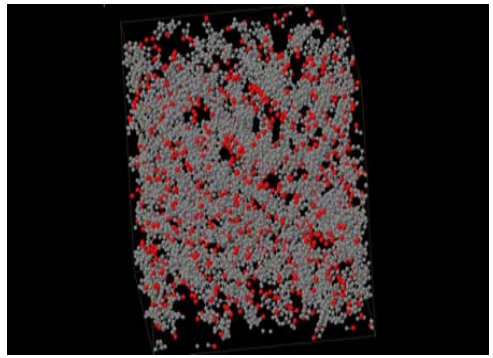
Classical force field and MS-EVB model development

Atomistic MD Simulations of small-molecule fluoroalkylphosphonic-acids-based Electrolytes
Validate ability simulations to accurately predict D_i, λ measured at Clemson, MPI

Atomistic MD Simulations of polymeric fluoroalkylphosphonic-acids-based polymeric electrolytes

$$-(CF_2CF)_a-(CF_2CF_2)_b-$$
$$\quad\quad|$$
$$\quad\quad O-R_f-PO_3H_2$$

Validate against experimental data (D_i, λ) at selected points, understand transport mechanism and membrane morphology



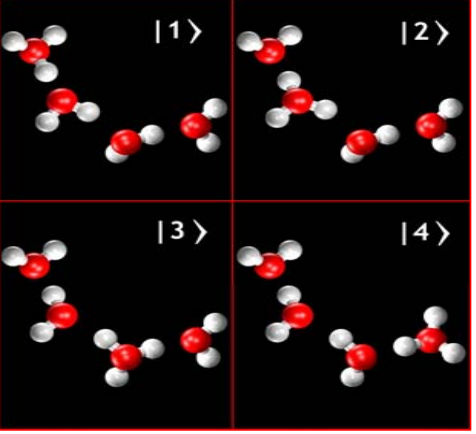
Snapshot from preliminary simulations of the fluoropolymer membrane using IS-CG model

Develop implicit solvent coarse-grained (IS-CG) model for fluoroalkylphosphonic-acids-based electrolytes.
Perform simulations using IS-CG model.

Predict transport (D_i, λ) via MPM simulations using membrane morphology from IS-CG simulations for low temperature and high RH

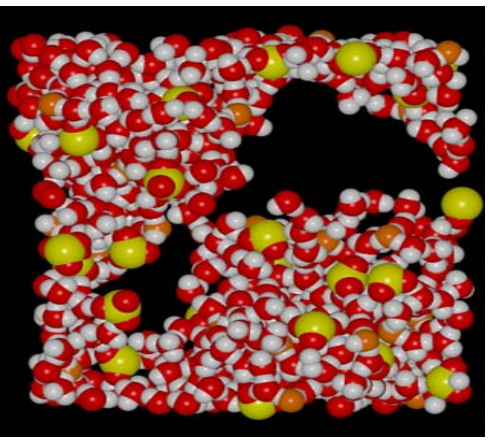
Optimize membrane structure to improve proton transport at RH=20%, 120 ^oC and low temperature high RH

Proton Transport Model



EVB states in water

- Goal: Accurately predict proton shuttling via Grotthuss mechanism in fluoroalkylphosphonic-acids-based small molecule and polymeric electrolytes
- Approach: Extend Multistate Empirical Valence Bond (MS-EVB) model for simulating proton transport in fluoroalkylphosphonic-acids-based electrolytes within a framework of classical molecular dynamics simulations



On a left: A representative configuration illustrating the distribution of hydrophilic/hydrophobic domains in the Nafion simulation.

- Advantages of the proposed approach:
  - MS-EVB model allows long (nanosecond) simulations with explicit proton hopping via Grotthuss mechanism
  - Accurate MS-EVB model has been developed and validated in Voth's group for water and Nafion™
  - The MS-EVB approach has been recently extended to treatment of multiple protons with the computational costs scaling linearly with the number of protons

MS-EVB references:
Schmitt and Voth, J. Phys. Chem. B 102, 5547 (1998)
Wang and Voth, J. Chem. Phys. 122, 144105 (2005)
Petersen et al, J. Phys. Chem. B 109, 3727 (2005)

Future Work

- Electrolyte synthesis and characterization work will begin in earnest in spring / summer 2006.
- Gen 1 ionic conductivity measurement apparatus for membranes is constructed; Gen 2 for liquids is being fabricated.
- Simulation work will progress with special focus on ion transport in target electrolytes

Summary

- Fluoroalkylphosphonic acid electrolytes offer excellent prospects for achieving high proton conductivity at both low and high temperature under both wet and dry conditions.
- A combined experimental (synthesis and characterization) and modeling approach is ideal for providing insight into transport mechanisms and guiding development of superior materials for technological applications.

Responses to Previous Year Reviewers' Comments

- This project began in April 2006. It has not yet been reviewed.

Publications and Presentations

- This project began in April 2006. No publications or official presentations have yet been made that derive from project funding.

Critical Assumptions and Issues

- Synthesis. Methods for successfully synthesizing high-quality fluoroalkylphosphonic-acid ionomer electrolytes suitable for making robust membranes are needed. Much prior work indicates that this can be done but the proof will lie in creating materials that meet the technical milestones.
- Conductivity. No electrolyte material to date has shown the combination of high ionic conductivity at high and low temperature under both wet and dry conditions that is desired for transportation fuel-cell applications.
- Durability. Fluoropolymer electrolytes in general are quite robust however little is known about how durable the target fluoroalkylphosphonic acids are likely to be.