Fluoroalkyl-phosphonic-acid-based proton conductors

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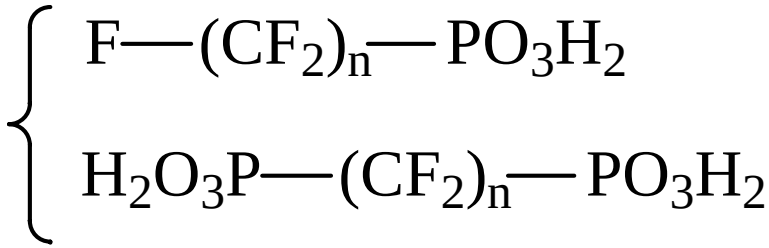
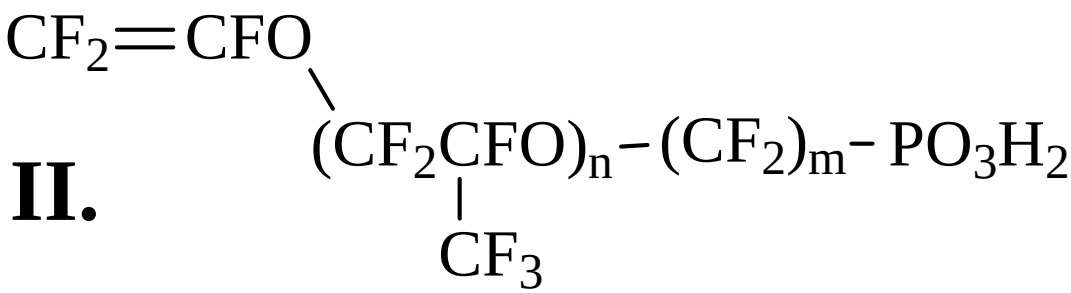
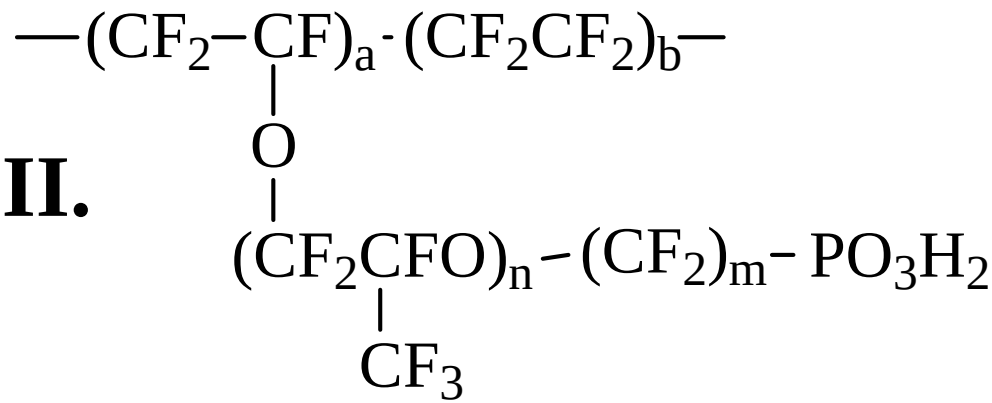
This presentation does not contain any proprietary or confidential information

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

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

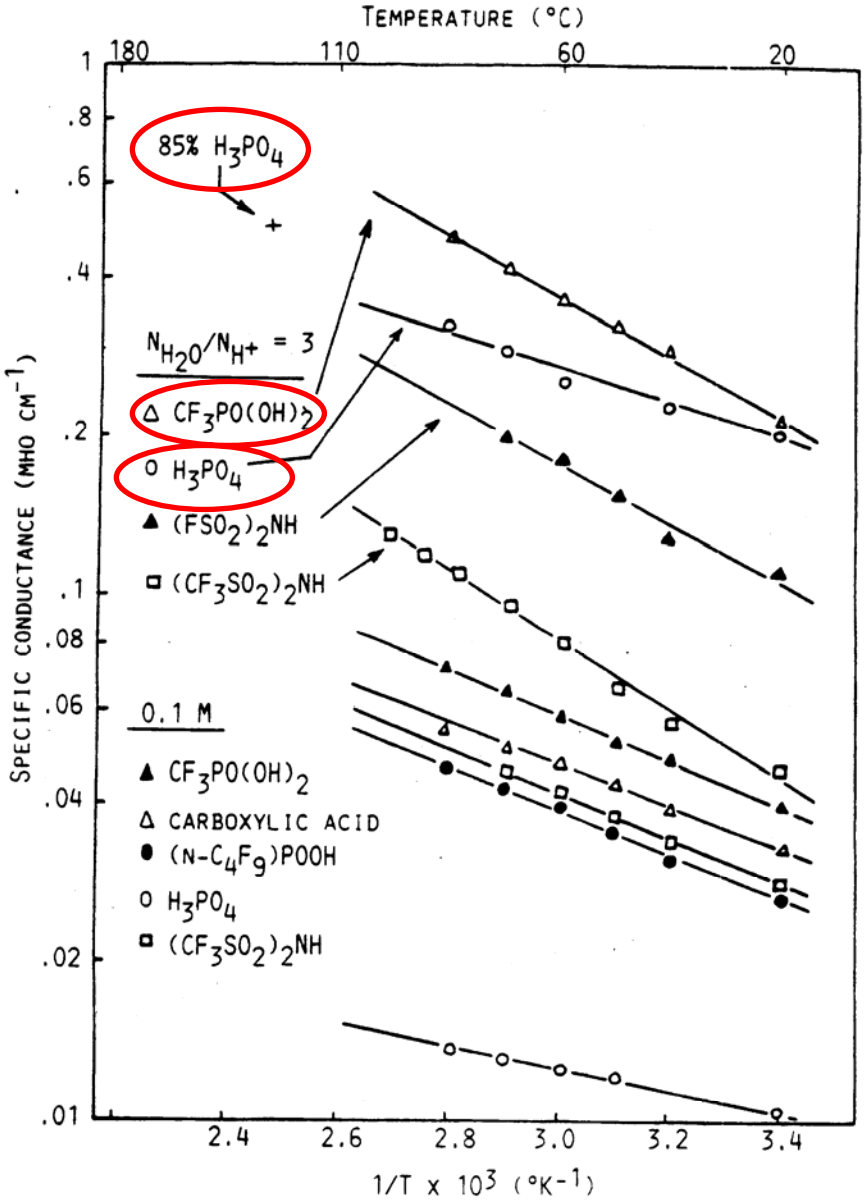


FIG. 51. SPECIFIC CONDUCTANCE OF VARIOUS ACIDS AS A FUNCTION OF TEMPERATURE.

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.

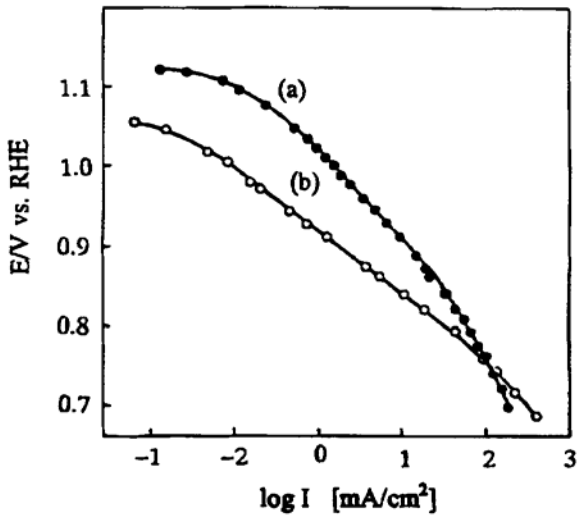


Fig. 5. Polarization curves for O_2 reduction on Pt-catalyzed Teflon-bonded gas-fed electrode (Standard Prototech electrode, Pt loading = 0.3 mg/cm²) in (a) 85% bis-phosphonic acid and (b) 85% phosphoric acid for 1 atm pure O_2. T = 100°C. A = 1 cm².

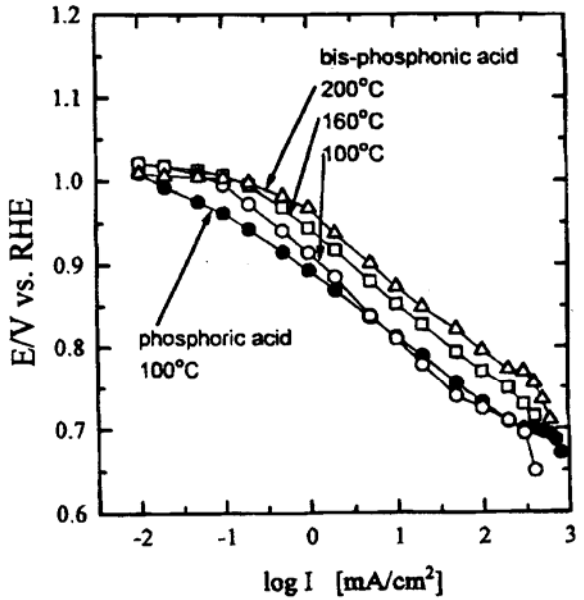


Fig. 6. Polarization curves for O_2 reduction on a Pt-catalyzed Teflon-bonded gas-fed electrode (Standard Prototech electrode, Pt loading = 0.3 mg/cm²) in 85% phosphoric acid (filled circles) in 85% bis-phosphonic acid at 100°C (open circles), 160°C (open squares), and 200°C (open triangles) equilibrated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

Multiscale Simulation Methodology

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

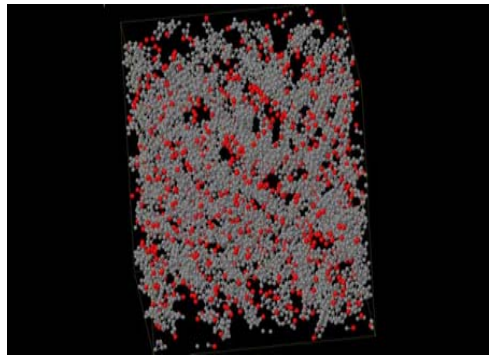
Classical force field and MS-EVB model development

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

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

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