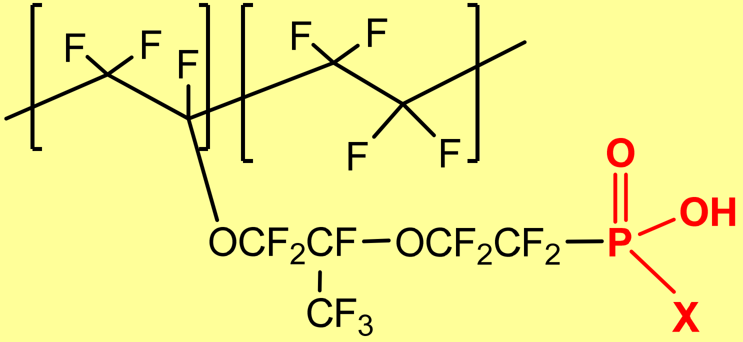
Fluoroalkyl-phosphonic-acid-based proton conductors



$X = OH; C_4F_9; CF_3; \boxed{OCH_2CF_3}$

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and

Oleg Borodin, Grant Smith, and Gregory Voth, University of Utah

Annual DOE Merit Review, Hydrogen Program

Washington DC, May 19, 2009

fc_07_creager

DE-FG36-06GO16031

Overview

Timeline

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

Budget

- Total funding over 5-yr project term
  - DOE $1,500,000
  - Contractor $381,390
- Total funding received from DOE to date
  - $800,000
- Funding received from DOE for FY08
  - $350,000
- Funding anticipated from DOE FY09
  - $300,000
- Cost-share to date from contractor
  - $91,000 expended (approximate)

Barriers

- Barriers
  - A,B,C; Durability / Cost / Performance.
- Targets
  - Membrane conductivity > 0.07 S/cm at 20 °C and water partial pressure of 1.5 kPa
  - Membrane conductivity > 0.10 S/cm at operating temp (120 °C) and water partial pressure of 1.5 kPa

Partners

- Dr. Alex Kitaygorodskiy, Clemson
- Dr. Ashok Krishnaswami, JEOL
- Professor Klaus D. Kreuer, Max Planck Institute, Stuttgart, GE
- Dr. Cortney Middlesteadt, Giner Inc
- Dr. John Kerr, LBLN

Relevance; Project 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 (FPA) functional group; and (2) Create and apply new computer models to study proton conduction in fluoroalkylphosphonic acid (FPA)-based electrolytes.

Timeline and Milestones

Year 1; (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 model for proton transport in fluoroalkylphosphonic acid.

Year 2; (April 2007 – March 2008)

- Synthesize and/or purify at least 5 g each of one or more trifluorovinyl-ether (TFVE) fluoroalkylphosphonic acid monomers.
- Demonstrate electrolyte conductivity of at least 0.07 S/cm at 80% RH at ambient temperature
- Implement explicit proton shuttling methodology in the framework on classical MD simulations.
- Perform classical MD simulations several low-molecular-weight and a few high-molecular-weight fluorophosphonic acid-based electrolytes under anhydrous and low-water-uptake conditions.
- Compare electrolyte conductivities and self-diffusion coefficients of ^{1}H, ^{19}F, ^{31}P predicted by MD simulations with experimentally measured values.
- Deliver a membrane for evaluation by the Topic 2 contractor at the end of year 2.

Year 3; (April 2008 – March 2009)

- Synthesize and purify at least three samples of fluoropolymer ionomers by co-polymerization of TFVE fluoroalkylphosphonic acid monomers with tetrafluoroethylene (TFE).
- Demonstrate electrolyte conductivity of at least 0.10 S/cm at 50% RH at 120 ^{o}C.
- Perform an initio MD simulations of small molecules
- Predict proton transport in fluoroalkylphosphonic acids as a function of chain length, the nature of acid groups and water hydration.
- Prepare membranes consisting of polybenzimidazole (PBI) doped with small-molecule fluoroalkylphosphonic acids. (Not being pursued.)

Approach

Task 1.0 Synthesize new fluoroalkyl-phosphonic-acid-based electrolytes. – Small-molecule acid model compounds – Trifluorovinylether (TFVE) monomers – Copolymers of TFVE monomers with tetrafluoroethylene (TFE) to give ionomer membranes	**Task 5.0** Perform computer simulations of fluoroalkylphosphonic-acid electrolytes. – Perform classical and DFT-based Born Oppenheimer Molecular Dynamics (BOMD) of various of fluoroalkyl-phosphonic acids
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/water mixtures using MD with Q-HOP. – As in Task 5.
Task 3.0 Demonstrate conductivity of at least 0.07 S/cm at 80% RH at ambient temperature (30 °C).	**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 °C.	

Relevance: Why fluoroalkyl-phosphonic acids?

1. They should be similar to phosphoric acid in allowing for **structure-diffusion-based proton hopping** without the need for excess liquid water;

2. They are **stronger acids** than phosphoric and alkylphosphonic acids which should promote proton dissociation, hopping and transport;

3. They should have **weaker adsorption** onto Pt than other phosphorous-acid-based electrolytes which should help prevent electrocatalyst poisoning and promote higher oxygen reduction activity;

4. They should provide **higher oxygen solubility** than other phosphorous-acid-based electrolytes which should also promote higher oxygen reduction activity; and

5. They should be quite **chemically and thermally stable** which will provide durability in PEM fuel-cell power sources

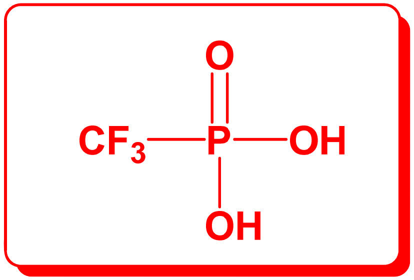
Technical Accomplishments

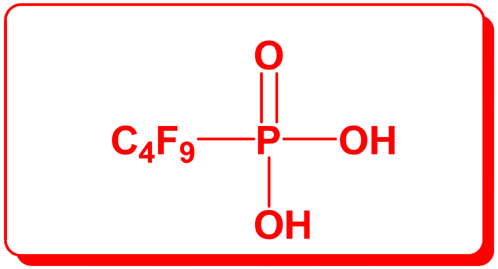
1A. Small molecule studies; experiments

- *(New) Anhydrous conductivity; phosphonic / phosphinic / sulfonic / carboxylic*
- *(New) Viscosity correlations*
- *(New) Proton hopping by PFG-NMR*
- *(New) Role of pyrophosphates*
- *(New) Acid strength effects*
- *Fluoroalkyl group chain length effects*
- *Added water effects*

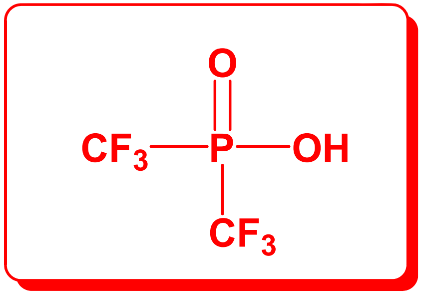
Model Compound Structures

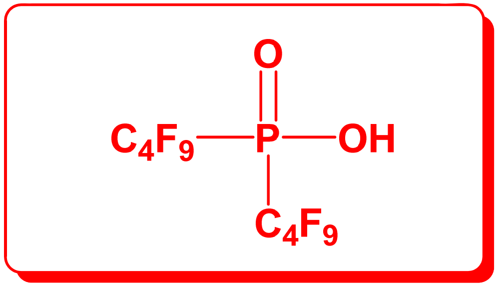
Phosphonic acids


$CF_3-P(=O)(OH)-OH$

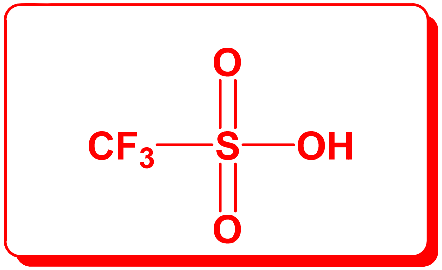

$C_4F_9-P(=O)(OH)-OH$

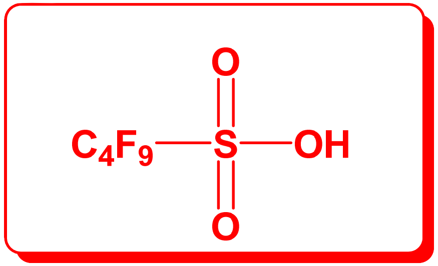
Phosphinic acids

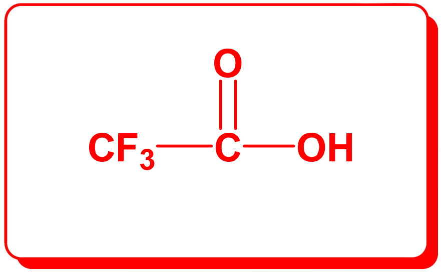

$CF_3-P(=O)(CF_3)-OH$


$C_4F_9-P(=O)(C_4F_9)-OH$

Sulfonic / carboxylic acids

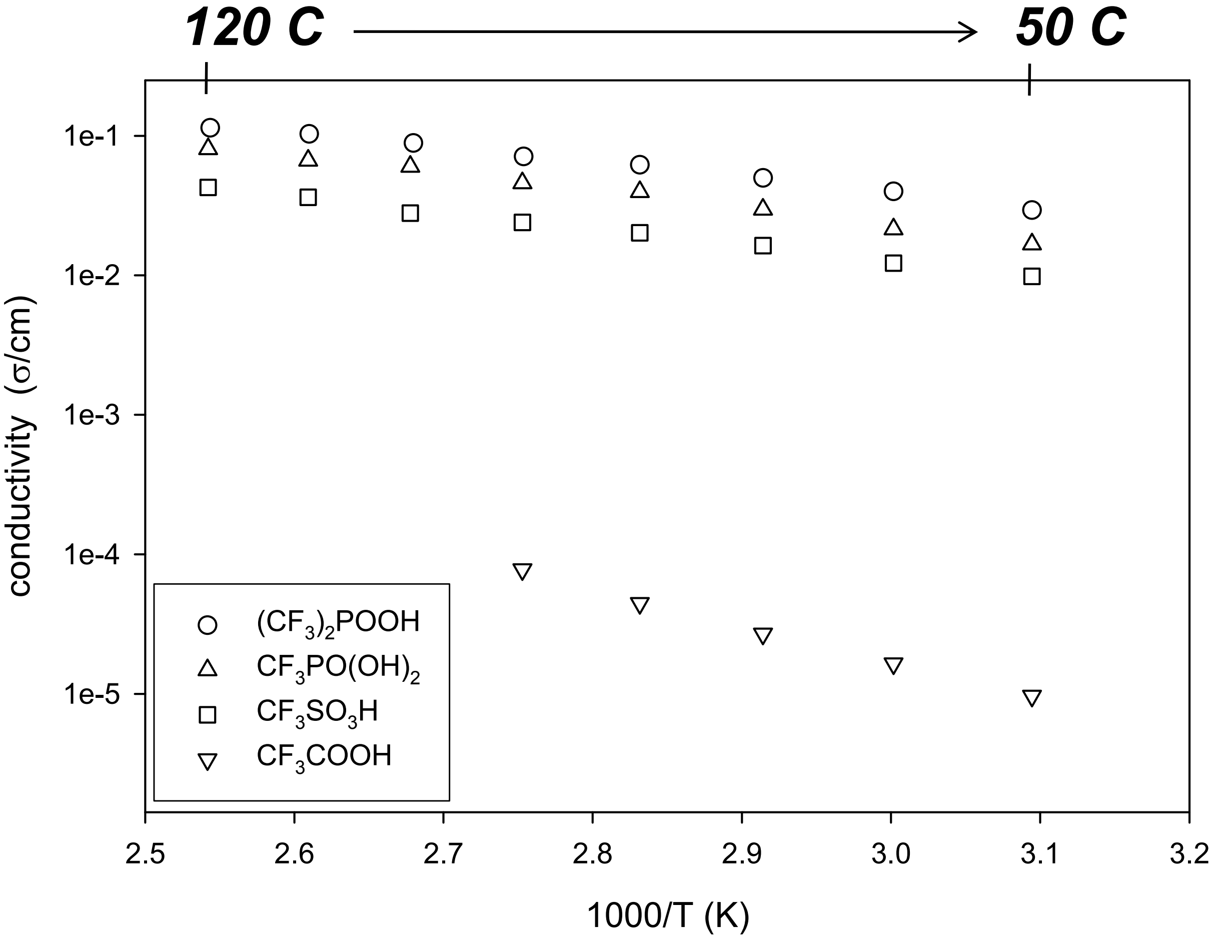

$CF_3-S(=O)_2-OH$


$C_4F_9-S(=O)_2-OH$


$CF_3-C(=O)-OH$

Anhydrous conductivity

- ***Fluoroalkyl phosphonic / phosphinic acids have the highest anhydrous conductivity of all model acids tested.***



Viscosities of anhydrous acid samples at ambient temperature

- ***High conductivity is achieved despite a relatively high viscosity. Suggests a role for proton hopping.***

Substance	**Viscosity (cP)**	**Temperature (^{o}C)**
$(CF_3)_2PO_2H$	22	ambient
$(CF_3)PO_3H_2$	Very high (super-cooled liquid)	n/a
CF_3SO_3H	2.9	ambient
CF_3COOH	0.96	20 C

Proton hopping; PFG-NMR 85 C

- ***A higher diffusion coefficient for ^{1}H than for ^{19}F as measured by PFG-NMR provides clear evidence for proton hopping in all FPA acids!!***
- ***Sulfonic and carboxylic acids show NO evidence of proton hopping in the absence of water at this temperature.***

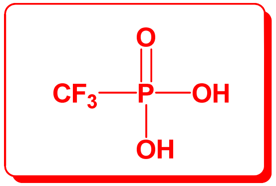
Table 1. Diffusion Coefficients for select nuclei in the model compounds (m^2/s) at 85 ^{o}C.

	At 85 ^{o}C		
Compound	$10^{10}D(H_{OH})$	$10^{10}D(F_{Rf})$	$D(H_{OH})/D(F_{Rf})$
$CF_3PO(OH)_2$	1.12	0.50	2.25
$(CF_3)_2POOH$	9.47	5.99	1.58
CF_3SO_3H	10.8	10.7	1.00
CF_3COOH	33.0	33.0	1.00
$C_4F_9PO(OH)_2$	0.26	0.14	1.94
$C_4F_9SO_3H$	4.87	4.87	1.00
$(C_4F_9)_2PO(OH)$	0.14	0.12	1.17

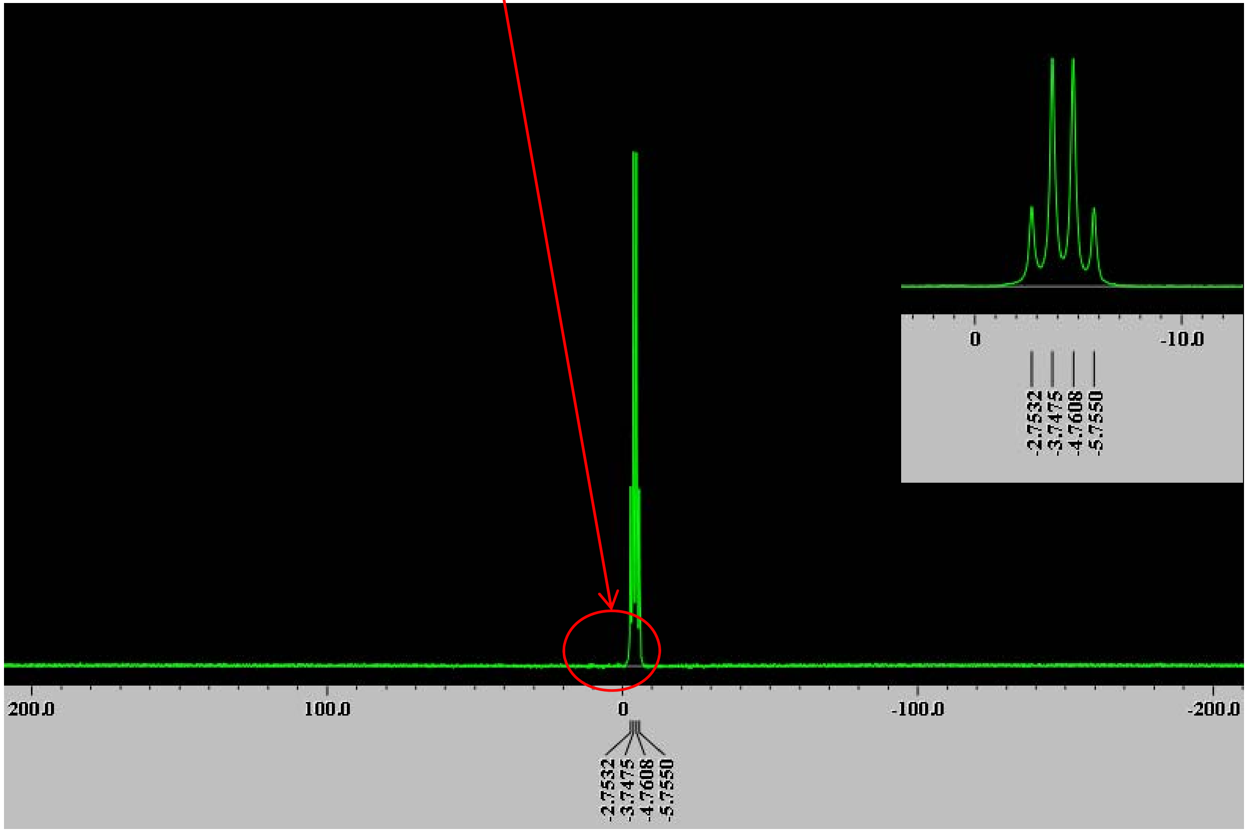
Possible presence of pyrophosphates

- ***Pyrophosphates of H_3PO_4 and R-PO_3H_2 are expected to show resonances shifted upfield by approx. 9 ppm relative to the acids (see ref. below).***
- ***The absence of such resonances in our fluoroalkyphosphonic acid sample in CD_3CN solvent suggests that pyrophosphates do not form.***

Reference : Ohms, G.; Grossmann, G.; Schwab, B.; Schiefer, H. Phosphorus, Sulfur and Silicon and the Related Elements 1992, 68(1-4), 77-89.



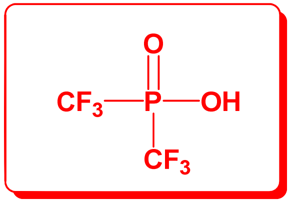
$CF_3-P(=O)(OH)-OH$



^{31}P-NMR of compound as solution in CD_3CN

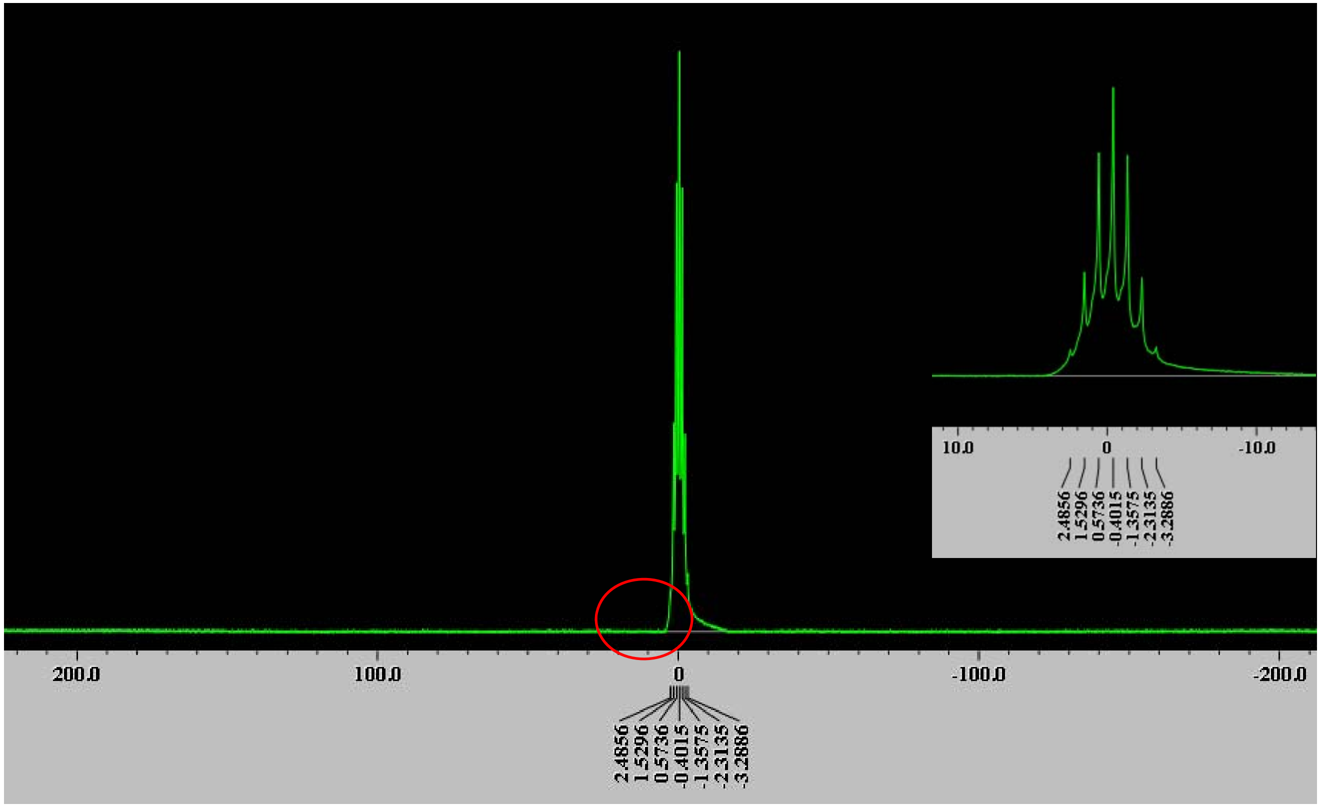
Possible presence of pyrophosphates

- ***Similar results were obtained for our fluoroalkyl phosphinic acids from NMR spectra obtained both in CD_3CN solution and on neat samples, as in the NMR spectrum below.***



$(CF_3)_2P(O)OH$

^{31}P-NMR of neat compound using CD_3CN as external lock solvent

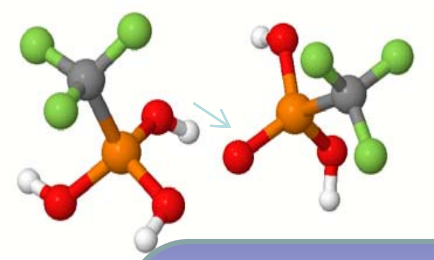


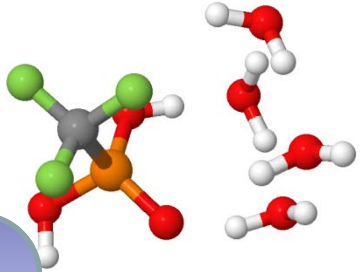
Technical Accomplishments

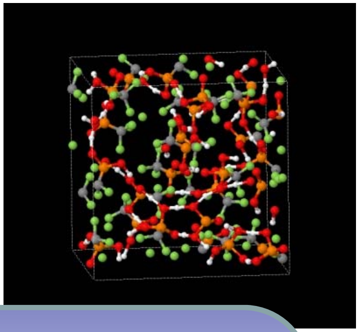
1B. Small molecule studies; modeling

- ***(New) Q-HOP, simulations of proton hopping***
- ***(New) FPA aggregation / phase separation, analysis of acid-group aggregate network size***
- ***How many waters to dissociate acid?***
- ***Water-mediated internal proton transfer***
- ***BO-MD, local structure and proton hopping***

Simulations Approach



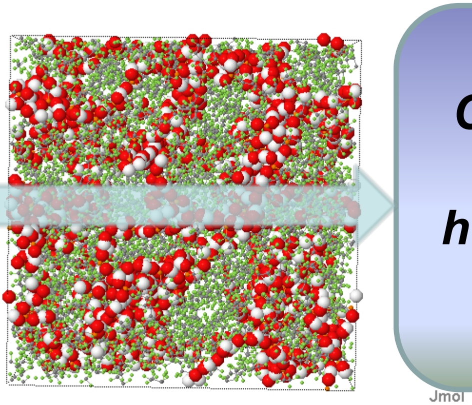




Quantum Chemistry Calculations on Representative Gas-Phase Clusters (1-10 molecules)

DFT-based Born Oppenheimer Molecular Dynamics (BOMD) simulations using BLYP. 27molecules - $CF_3PO_3H_2$ 24 molecules -$(CF_3)_2POOH$

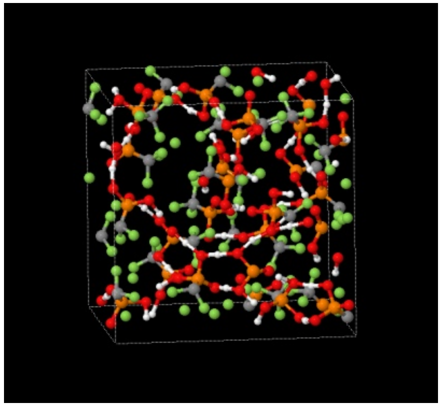
Classical MD simulations (no explicit proton hopping) (100s of molecules)

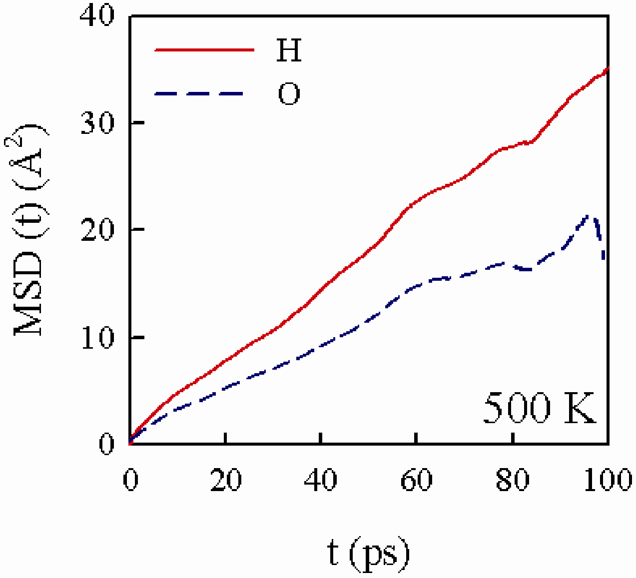


Classical MD simulations with explicit proton hopping (Q-HOP, MS-EVB) (100s of molecules)

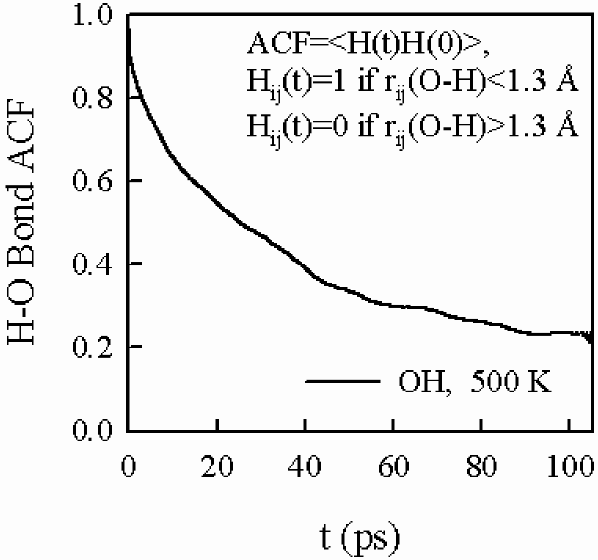
Born-Oppenheimer Molecular Dynamics (BOMD): Proton Transport in $CF_3PO_3H_2$

Simulation box





O-H bond lifetime=75 ps

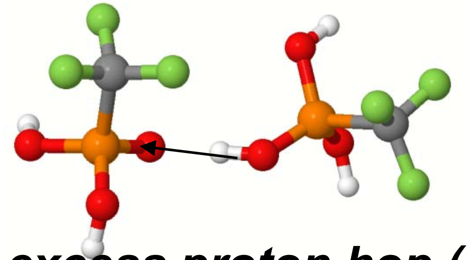


- BOMD performed using BLYP DFT on a cell containing 27 molecules at average temperature 393 K and 500 K
- Proton diffusion is significantly faster than diffusion of oxygen atoms to which the protons are bonded. Diffusion coefficients at 500 K are $D(H)=5.9 \times 10^{-10}$ m^2/s, $D(P)=3.0 \times 10^{-10}$ m^2/s consistent with the extrapolated experimental values
- The average O-H bond lifetime is 75 ps indicative of the proton hopping rate of 0.013 ps^{-1}.
- On average, autoionization ~20% at 393K and 500 K.
- Charged species (anions and cations) were found to have a short life time.

Q-HOP Methodology

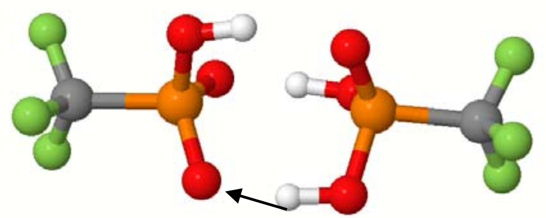
- ***Q-HOP method allows explicit consideration of proton hopping within a classical MD framework.***
- ***Hopping rate estimates come from barriers for proton transfer for different geometries with different approach distances.***
- ***Mechanisms 1 – 3 below are implemented in the code.***
- ***Details are in a supplementary slide.***

1)



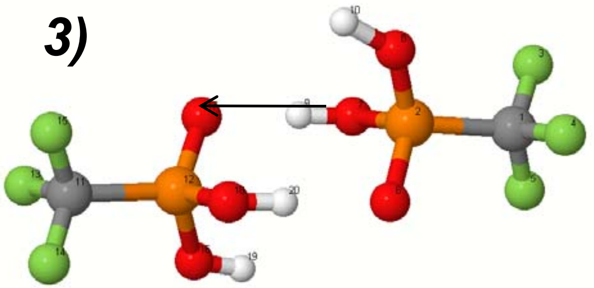
excess proton hop (+)

2)



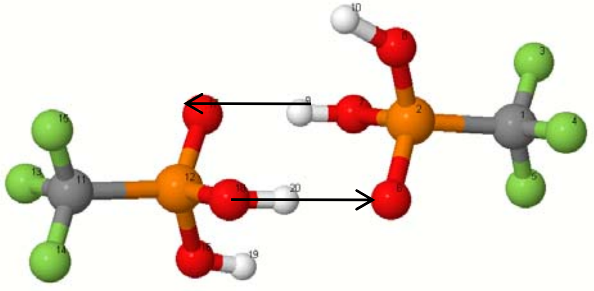
proton (hole) hop (-)

3)



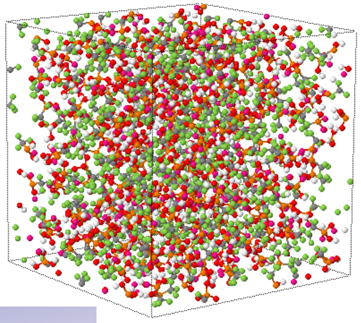
self-dissociation/recombination

4)



local proton re-arrangement

Q-HOP Simulations of Liquid $CF_3PO(OH)_2$

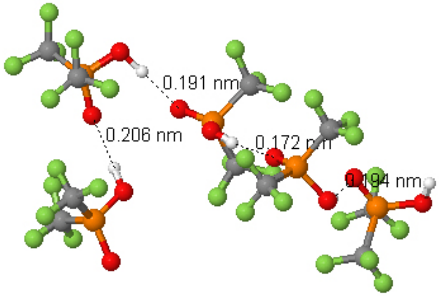


- Simulation box consisted of 360 molecules.
- Many-body polarizable force field was used with self-dissociation (recombination), excess proton and hole hopping included in the model.

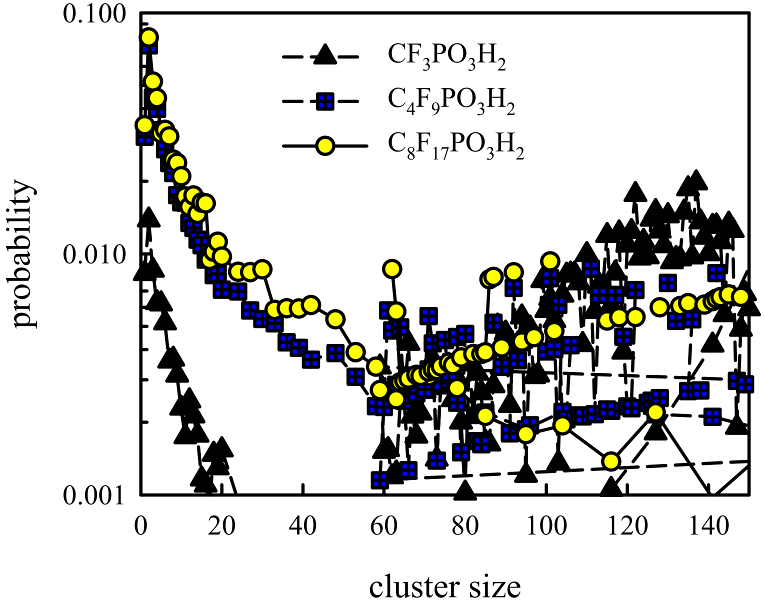
Method	**D (CF_3) 10^{-10} m^2/s**	**$D(H_O)/D(CF_3)$**
NMR, 358 K	**0.5**	**2.25**
MD (Q-HOP), 358 K	**0.98**	**2.1**

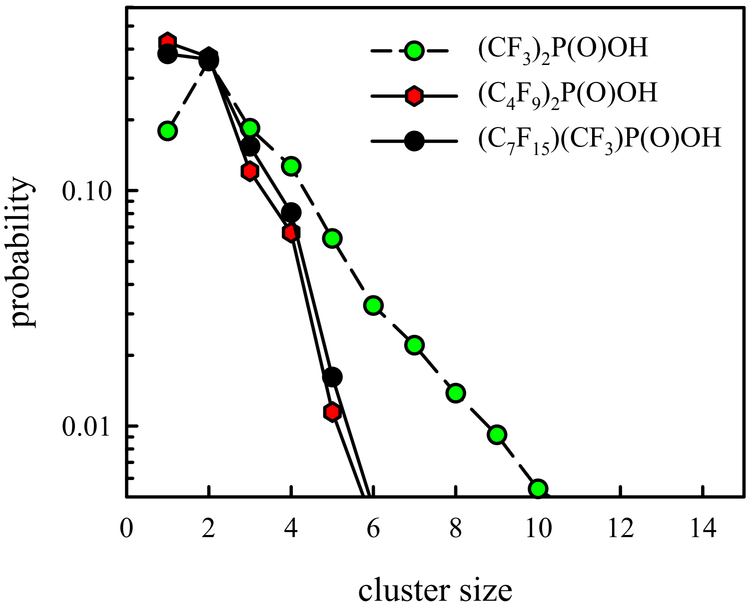
- MD (QHOP) simulations yielded molecular diffusion coefficients and the ratio $D(H_O)/D(CF_3)$ is in excellent agreement with experiments.
- The rate of excess proton hops was found ~ 0.05 hops/(ps molecule) not including immediate (<1 ps) back transfers. This rate is comparable to the rates of the excess proton transfers found in water at 298 K.
- The highest rate was found for the excess proton transfer followed by hole transfer.
- Environment (changes of the solvation shell hydrogen bonding structure) is strongly correlated with the probability of hopping events.

Analysis of acid-group aggregate network sizes



- ***For mono-fluoroalkyl phosphonic acids (from $CF_3PO_3H_2$ to $C_8F_{17}PO_3H_2$) the hydrogen bonding network is large and percolates over the whole simulation box***
- ***For bis-fluoroalkyl phosphinic acids.... $(CF_3)_2POOH$ has a significant fraction of large acid group aggregates (3<n<9), while $(C_4F_9)_2POOH$ acid has only very small acid aggregates (n<5) suggesting that no extended pathways exist for Grotthuss proton transport in $(C_4F_9)_2POOH$.***
- ***All these results are consistent with recent PFG-NMR experiments.***





Summary of FPA model compound studies

- FPA model compounds have higher anhydrous conductivity than triflic acid even though they are weaker acids and have higher viscosity.
- Proton hopping (structure diffusion) is shown by PFG-NMR to occur in all anhydrous FPA model compounds tested, but not in fluoroalkyl sulfonic or carboxylic acids.
  - *BO-MD and QHOP-MD modeling confirm this result for CF_3-$PO(OH)_2$*
- Pyrophosphates do not form to any great extent in FPA model compounds under normal handling conditions.
- Adding fluorocarbon character usually decreases anhydrous conductivity and extent of proton hopping.
  - *Classical MD modeling indicates that proton-transport networks are smaller and shorter for FPA model compounds having two R_f groups on P, especially for long R_f chains.*
- Adding water (up to 20 waters / acid) increases conductivity for all acid model compounds studied.

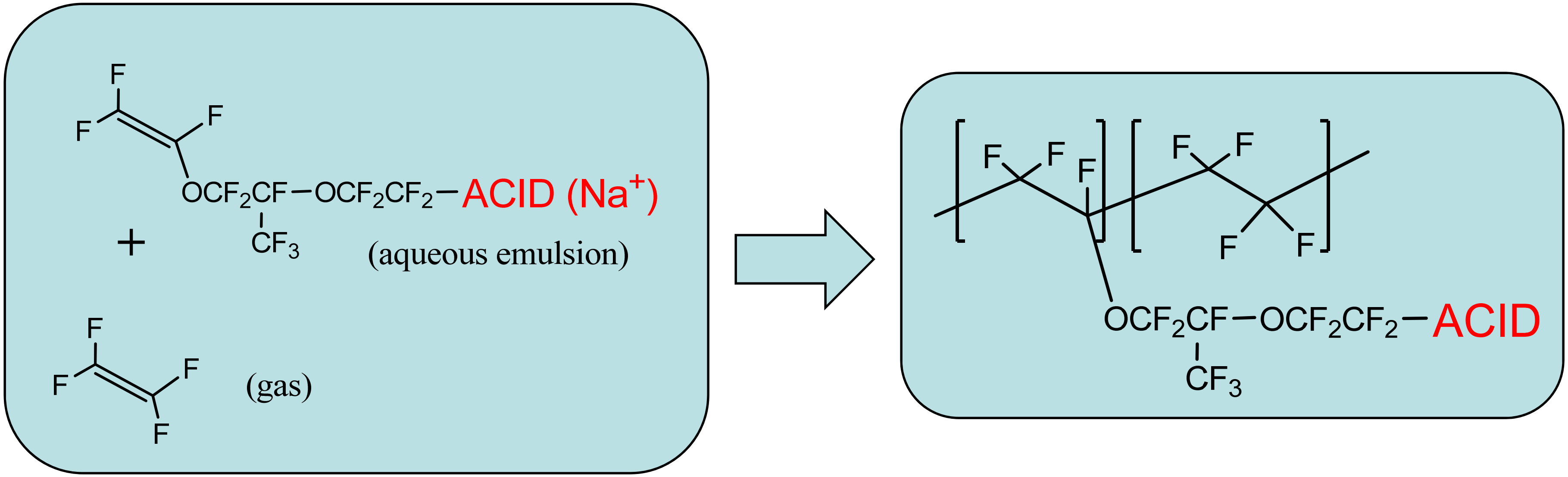
Technical Accomplishments

THE CHALLENGE: Prepare FPA Fluoropolymer Ionomers That incorporate the Favorable Properties of Molecular FPAs

2. Ionomer studies

- *(New) FPA ionomers with new acid protecting groups*
- *(New) SEM / TEM imaging*
  - *Micron-scale membrane structure*
  - *Nano-scale domain structure*
- *Phosphonic / phosphinic acid ionomer; synthesis, characterization, conductivity*

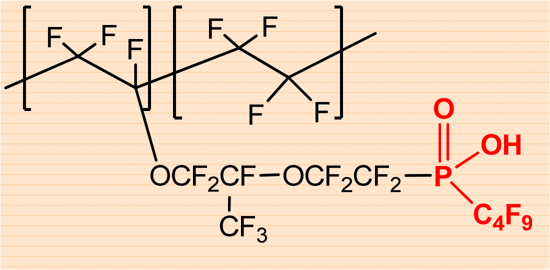
Co-polymerization of TFVE monomer with TFE



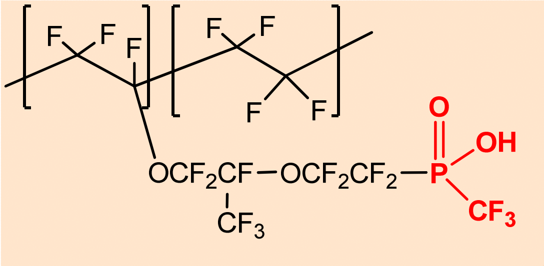
Reactions are typically run in a 450 mL autoclave;

- ***Approx 2 g monomer in 260 mL water; TFE gas at 75 – 180 psi;***
- ***Aqueous emulsion co-polymerization: persulfate initiator, ammonium PFO surfactant, phosphate buffer, temp = 65 °C.***
- ***Requires acid monomer (as Na$^+$ salt) to have good surfactant character for co-polymerization reactions to run well.***

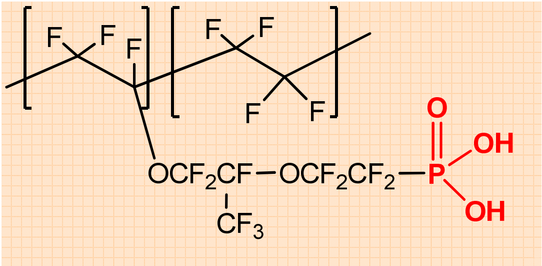
Ionomer Structures



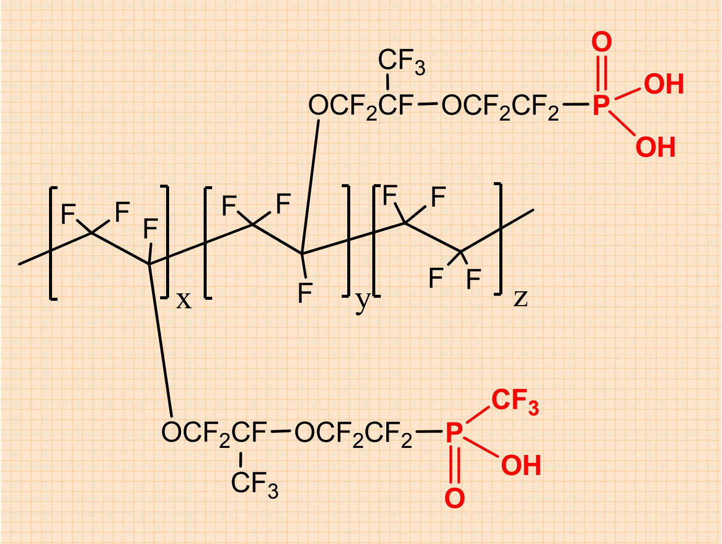
P-10, P-12, P-14, P-15



P-18

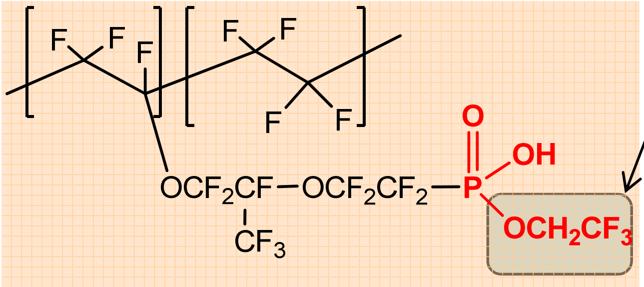


P-23, P-24



P-20, P-21, P-22

A hydrolyzable protecting group!



P-26, P-27, P-29

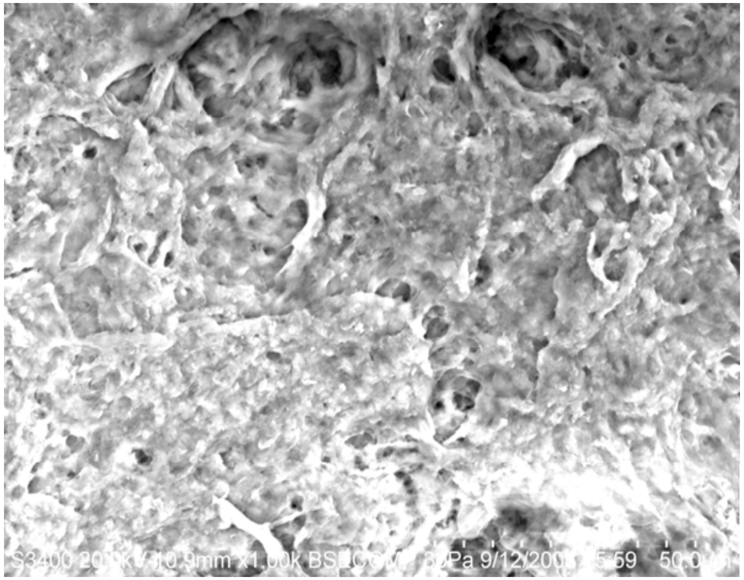
Ionomer properties; conductivity at 100% RH

membrane	P10	P12	P18	P21	P23	P24	P26	P27	P29	Nafion® 112
EW; g / equiv	750	1300	1000	1400	1450	740	580[a]	1000[a]	490[a]	1100
H_2O uptake; 100 C	123%	13%	30%	-	-	-	-	-	-	-
Conductivity; 25 C, 100% RH	0.025	0.006	0.045	0.044	0.0005	0.006	0.028	0.012		0.060
Conductivity; 80 C, 100% RH	0.025	0.018	0.12	0.10	0.00023	0.017	0.034	0.010	0.12	0.12

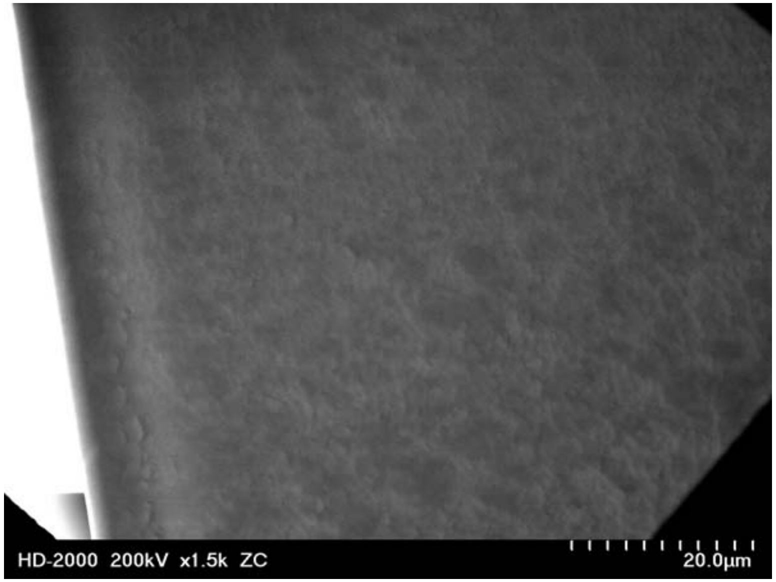
a. Membranes after hydrolysis

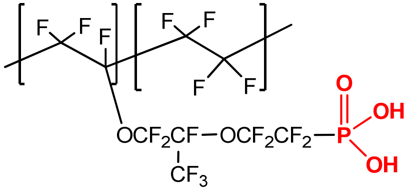
SEM images of membranes P23 and P18

- *Sample P-23 exhibits a complex morphology on a large length scale. P-24 behaves similarly. We believe this fact reflects the relatively poor solubility of P-23 / P-24, and is partially responsible for the poor conductivity of membranes of these polymers.*
- *Sample P-18 is smoother on a similar length scale both visually and by SEM. We believe this fact reflects the better solubility of P-18 in the casting solvent and contributes to the improved conductivity of P-18 over P-23 / P-24.*

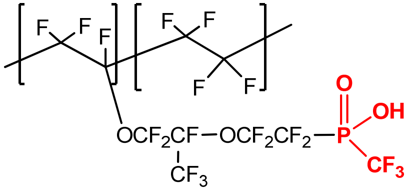


50 micrometers



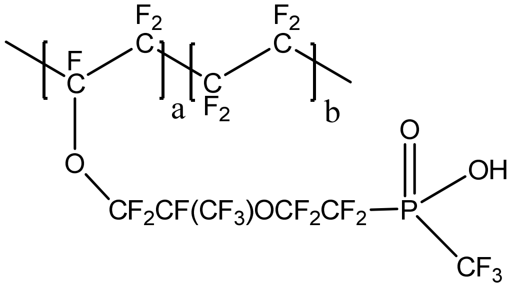


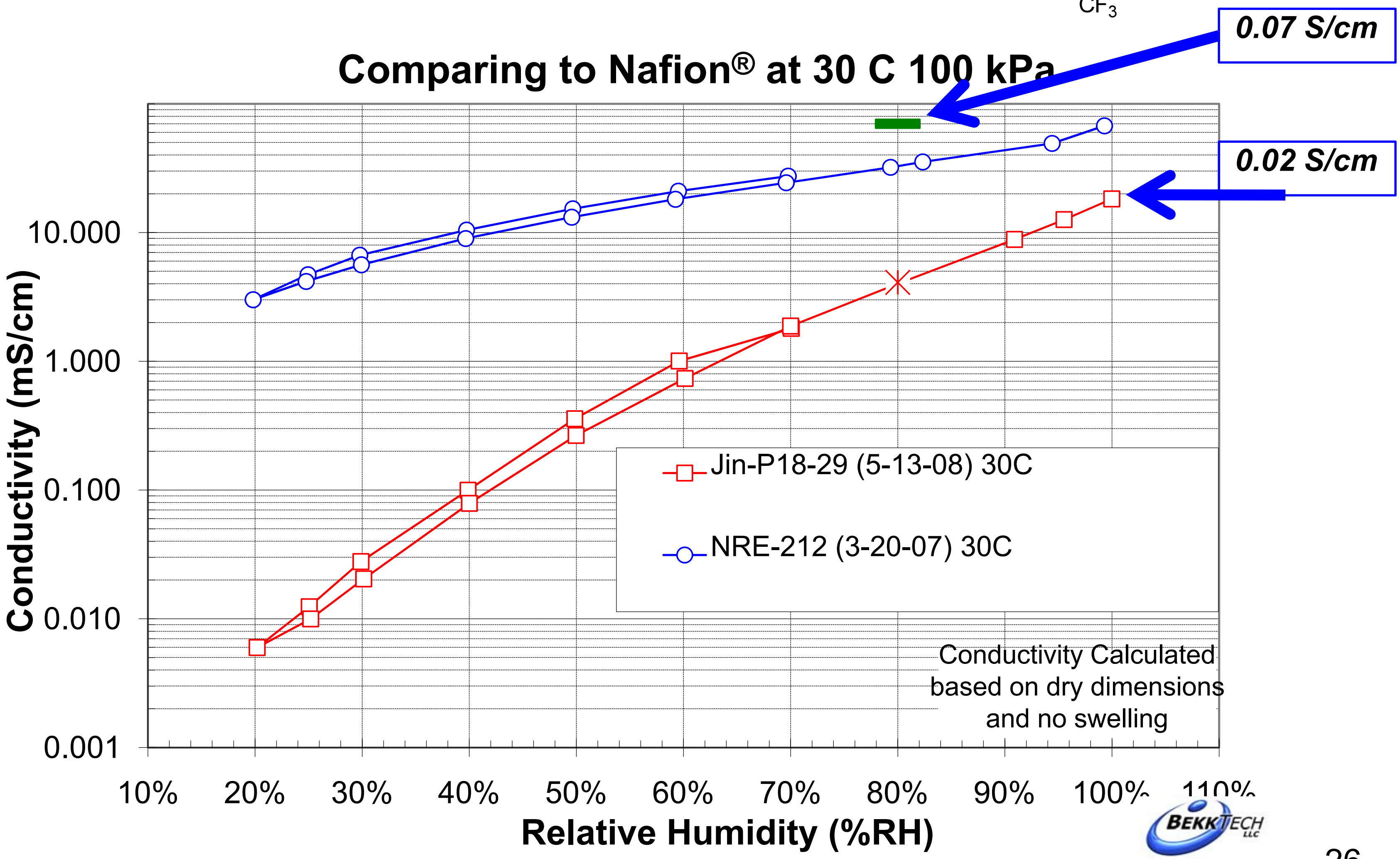
P23



P18

Membrane Sample P-18, testing by Bekktech LLC




Comparing to Nafion® at 30 C 100 kPa

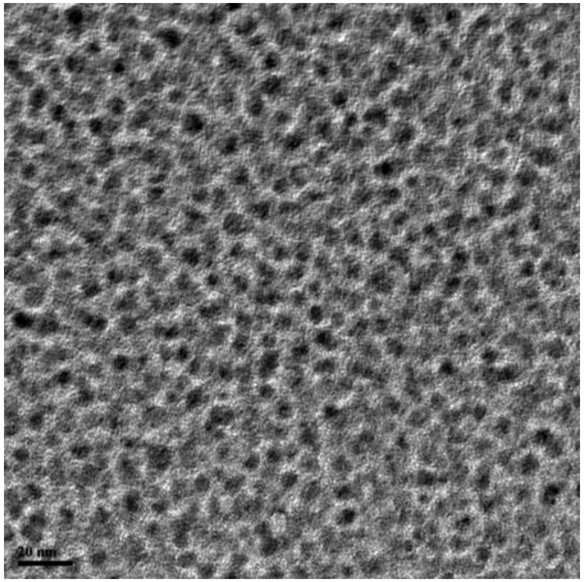
0.07 S/cm

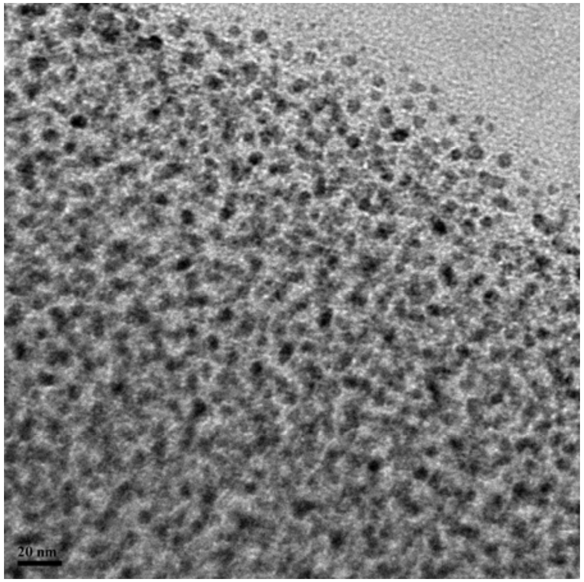
0.02 S/cm

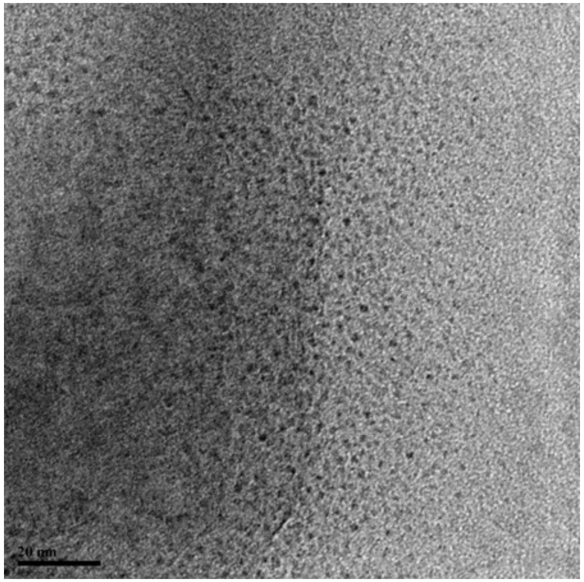
Conductivity Calculated based on dry dimensions and no swelling

TEM images of ionomer domain structure

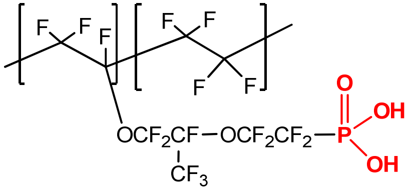
- ***FPA sample P-18 after Pb^{2+} staining appears to have a weaker domain structure (weaker contrast) with smaller ionic domains than Pb^{2+}-stained Nafion® and related FPA ionomers.***



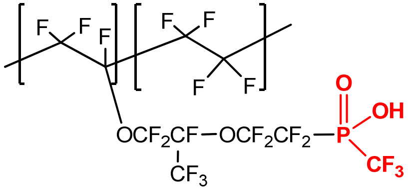




Nafion® 1000 EW

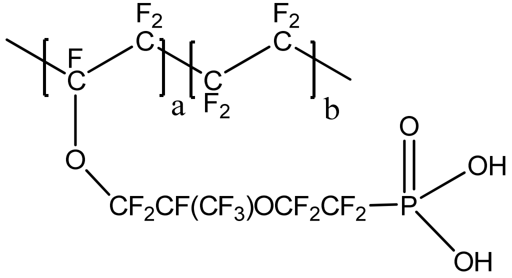


P-27, 1000 EW



P-18, 1000 EW

Membrane Sample P-29, testing by Bekktech LLC



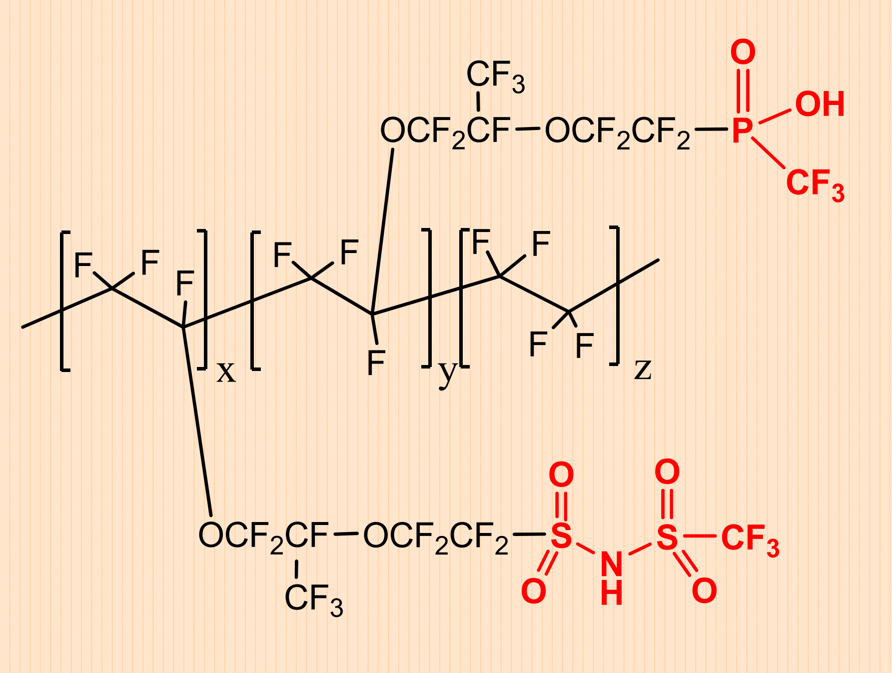
EW = 490, 2 acidic protons per acid group.
Conductivity in our hands was 0.12 S/cm at 100% RH, 80 C.

- ***Conductivity test at Bekktech on this membrane failed. The sample became brittle while being dried when mounted in the conductivity cell and cracked, causing test to abort.***

- ***We are currently exploring ways to stabilize this material and/or to prepare tougher and more pliable membranes to obtain reliable conductivity data at different RH values.***

- ***Strategies being explored include <u>crosslinking</u> (both chemical and via nano-particles); and <u>blending</u> with higher EW ionomers.***

A fluorosulfonimide / fluoroalkyl-phosphonic acid terpolymer ionomer



- Could offer a particularly favorable combination of properties;
  - ✓ *Fluoro-sulfonimide superacid provides protonation capability even at low water content*
  - ✓ *Fluoro-phosphonic acid could provide capability for proton hopping at low water content*
  - ✓ *Fluoro-phosphonic acids could provide internal crosslinking to stabilize especially low EW ionomers against swelling / dissolution*
- Initial synthesis was completed in March 2009

Summary of ionomer studies

- Co- and ter-polymerization of a variety of FPA TFVE monomers with TFE was accomplished and shown to give processible and ionically conductive polymer membranes.
- Monomers with hydrolyzible protecting groups provide a new route to ionomer membranes with R_f-PO_3H_2 acid groups.
- Conductivity values for FPA membranes are below milestones but are steadily improving.
- TEM characterization is revealing important things about the relationship between ionomer primary structure and ionic domain structure
- First-generation FPA ionomers are promising and with further optimization could be very promising.
- Ter-polymers of FPA monomers with TFE and other acidic monomers, e.g. sulfonimide superacids, are possible and could be promising for stabilizing very low EW ionomer membranes.

Overall Summary

- Small-molecule studies (experiments and computer modeling) indicate that FPA acids groups should be effective in promoting rapid proton transport under low-humidity conditions
- Ionomers with FPA acid groups have been synthesized but superior conductivities have so far not been realized.
- Optimization with respect to acid composition, ionomer molecular weight, ionomer equivalent weight, and crosslinking are being pursued to provide materials that can meet DOE targets for conductivity and water swelling.

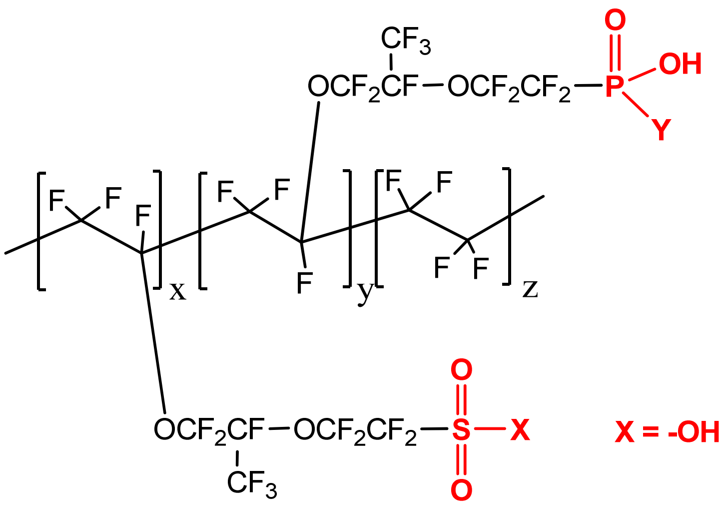
Interactions / Collaborations

- **PFG NMR measurements;**
  - Dr. Alex Kitaygorodskiy, Clemson
  - Dr. Ashok Krishnaswami, JEOL
  - Professor Klaus D. Kreuer, Max Planck Institute, Stuttgart, GE
- **Water uptake;**
  - Dr. Cortney Mittelsteadt, Giner Inc.
- **Electron Microscopy;**
  - Dr. JoAn Hudson, Clemson
- **Alternate protogenic groups**
  - Dr. John Kerr, LBNL. Collaboration is with the computation group at Utah to understand anhydrous proton conduction in related ionomers having other protogenic groups.

- A major PFSA producer is in talks with us, aimed at moving this and related fluoro-ionomer membrane work forward.

Future work

We propose the following terpolymer ionomers:



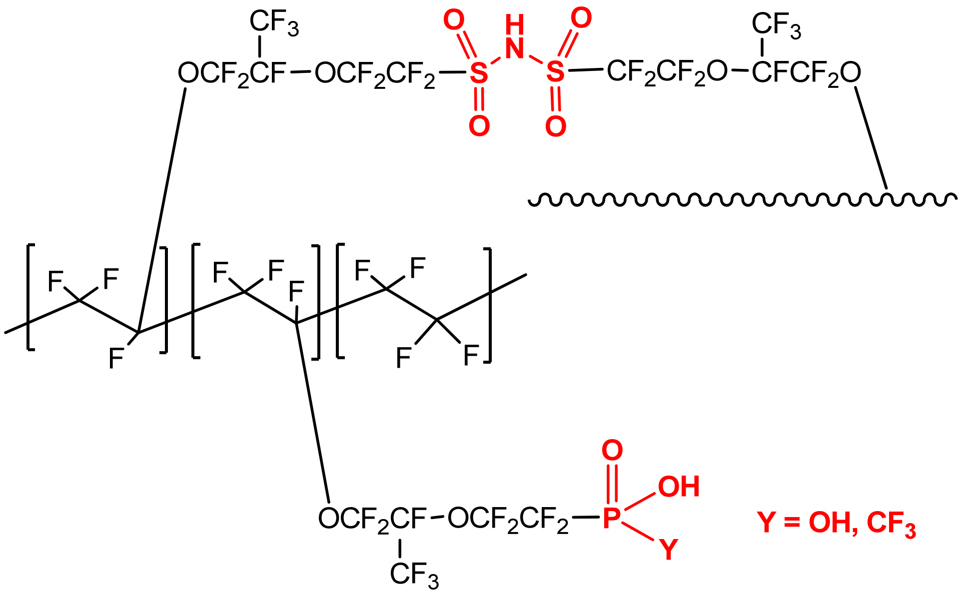
Y = -OH, CF_3

X = -OH, -N(H)SO_2-R_f

- *Sulfonic and/or sulfonimide acid groups will impart high acidity, high water uptake, good stability, and rapid proton transport.*
- *Phosphonic acids will impart sites for crosslinking via strong hydrogen bonding and/or selective metal ion chelation, e.g. Zr^{4+}.*
- *Controlled crosslinking will enable use of very low EW ionomers without problems from too much swelling / dissolution*
- *Combination of controllable crosslinking and very low EW will promote water retention and give high conductivity at high temp and low RH.*

Future work

We propose the following crosslinked ionomer:



- *This strategy has previously been used by us to prepare lightly crosslinked versions of fluorosulfonimide ionomers.*
- *Similar crosslinking strategies could prove useful for stabilizing low EW versions of fluoroalkylphosphonic acid ionomers which could have high conductivity and also low swelling and dissolution.*

The End

Selected supporting slides to follow.....

Key remaining barriers and approach(s) to solve them

Acid group aggregation / domains

- *Better casting solvents are needed to give dense membranes with intact continuous pathways for proton transport*
- *TEM studies (possibly without Pb^{2+} staining) are needed to better correlate domain structure with ionomer structure / membrane treatment*
- *Studies combining TEM imaging with directed strategies to create / stabilize domain structure are needed*

Water uptake / retention

- *Water uptake studies for model compounds and ionomers are underway with Giner Inc. (Thanks to Cortney Mittelsteadt!).*
- *Strategies are needed for improving water retention without promoting ionomer swelling / dissolution.*

Key remaining barriers and approach(s) to solve them

Low equivalent weight ionomers with controllable crosslinking

- *Very low EW ionomers are needed to meet DOE conductivity targets*
- *Even very light crosslinking can stabilize very low EW ionomers against excess swelling / dissolution.*
- *Crosslinking will be accomplished using difunctional TFVE monomers during polymerization, and possibly FPA monomers coupled with Zr^{4+}-based crosslinking following polymerization.*
- *See next slides for some proposed examples.....*

Ionomer conductivity

- *Improved conductivity under all conditions will follow from improved understanding of the relationship between ionomer structure and proton transport properties*

PFG NMR Measurments Experimental Details:

Pulsed field gradient nuclear magnetic resonance (PFG NMR) experiments were performed on a Bruker avance 300 spectrometer with 5 mm 13C/19F/31P-1H QNP z-gradient liquid probes at 300.13 MHz for ^{1}H, 282.7 MHz for ^{19}F at 25 and 85 ^{o}C. The measurements were done using closed Wilmad-Labglass cylindrical bulb micro Cell (110 microliters vol., bulb length 12 mm) with sample lengths of less than 1cm to ensure high rf homegeneity. Temperatures were regulated by a BVT3000 temperature controller and calibrated against ethylene glycol. Samples were neat acids and the experiments were performed without deuterium lock and without sample rotation. The stimulated echo sequence using one spoil gradient (stegp1s from the Bruker library) was used in pseudo-two dimensional mode with constant diffusion time and a linearly ramped gradient from 5 to 95% of maximum power in 16 increments. Diffusion parameters, diffusion time, Δ was kept constant at 100 ms, gradient pulse length, δ was optimized for each sample, nucleus, and temperature using the one-dimensional variant of the pulse sequence stegp1s1d. The data were processed in pseudo-two-dimensional mode, then analyzed using SimFit included with Bruker (v 3.5), fitting the signal integration (area) to gradient strength.

Proton hopping; PFG-NMR 25 C

- ***PFG-NMR spectroscopy was used to estimate self-diffusion coefficients for ^1H and ^{19}F in model acids***
- ***A higher diffusion coefficient for ^1H provides clear evidence for proton hopping in FPA acids at ambient temperature!!***

Table 1. Diffusion Coefficients for select nuclei in the model compounds (m^2/s) at 25 °C.

	At 25 °C		
Compound	$10^{10}D(H_{OH})$	$10^{10}D(F_{CF3})$	$D(H_{OH})/D(F_{CF3})$
$CF_3PO(OH)_2$	-----	-----	------
$(CF_3)_2POOH$	0.47	0.21	2.27
CF_3SO_3H	1.00	0.84	1.19
CF_3COOH	12.17	12.17	1.00

Acid Strength Effects

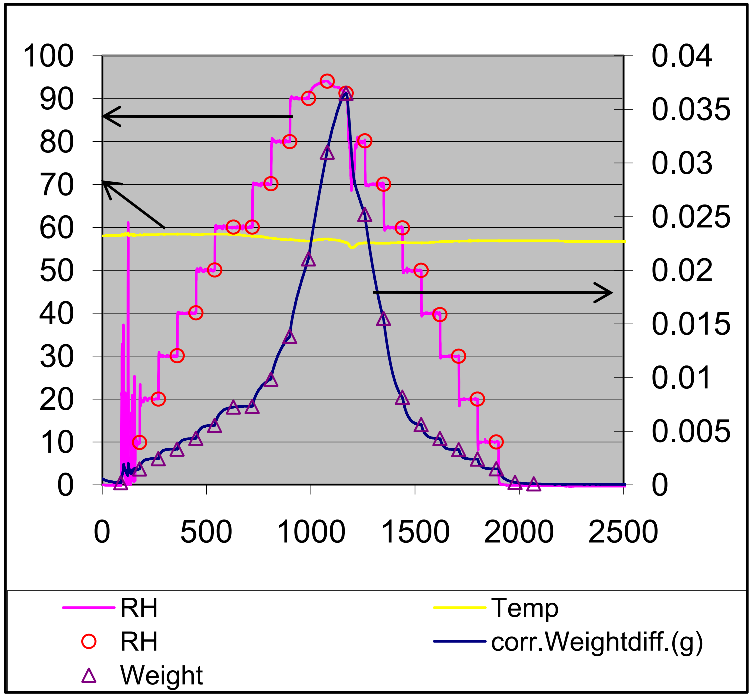
- ***Fluoroalkylphosphonic and phosphinic acids are intermediate in strength between fluoroalkyl carboxylic and sulfonic acids.***
- ***YET they show the highest ionic conductivity.***
- ***Conductivity does not directly correlate with acid strength, as long as the acid is strong.***

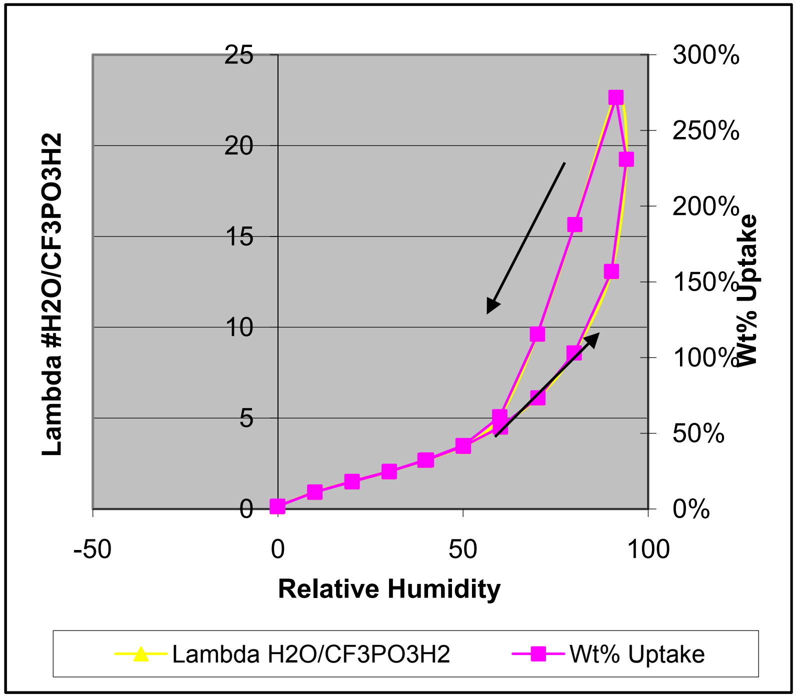
Compound	**Hammett Acidity (This study)**	**Hammett Acidity (Lit.)**
CF_3COOH	-3.03	-3.03[a,b]
$CF_3PO(OH)_2$	-7.10	
$(CF_3)_2POOH$	-7.95	
$C_4F_9PO(OH)_2$	-4.36	
$(C_4F_9)_2PO(OH)$	-5.34	
$C_4F_9SO_3H$	-11.20	-12.7[c]
CF_3SO_3H	-13.70	-14.6[b,c]

(a) Farcasiu, D.; Ghenciu, A.; J. Am. Chem. Soc. 1993, 115, 10901
(b) Farcasiu, D.; Ghenciu, A.; Prog. Nucl. Magn. Reson. Spectrosc. 1996, 29, 129-168
(c) Olah, G. A.; Prakash, G. K. S,; Sommer, J. Science 1979, 206 , 13-20.

Water uptake by CF_3-PO_3H_2

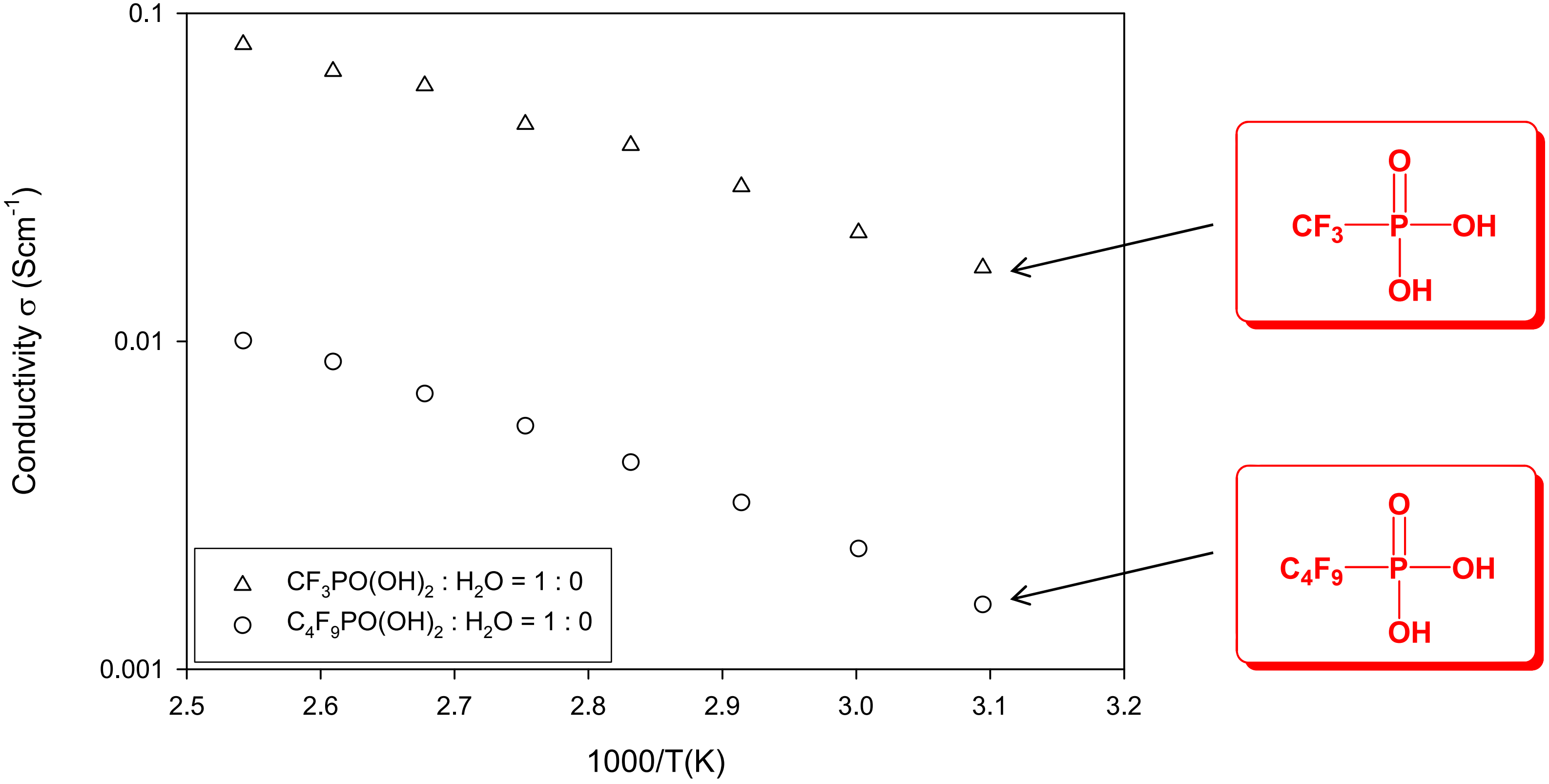
- *Performed by variable-RH thermogravimetry at 60 C at Giner Inc.; Many thanks to Corky Mittelsteadt!*
- *Water uptake at 50% RH is approx. 3.5 waters per acid, which is similar to that seen for many sulfonic acids.*
- *Measurements on ionomers are in progress.*





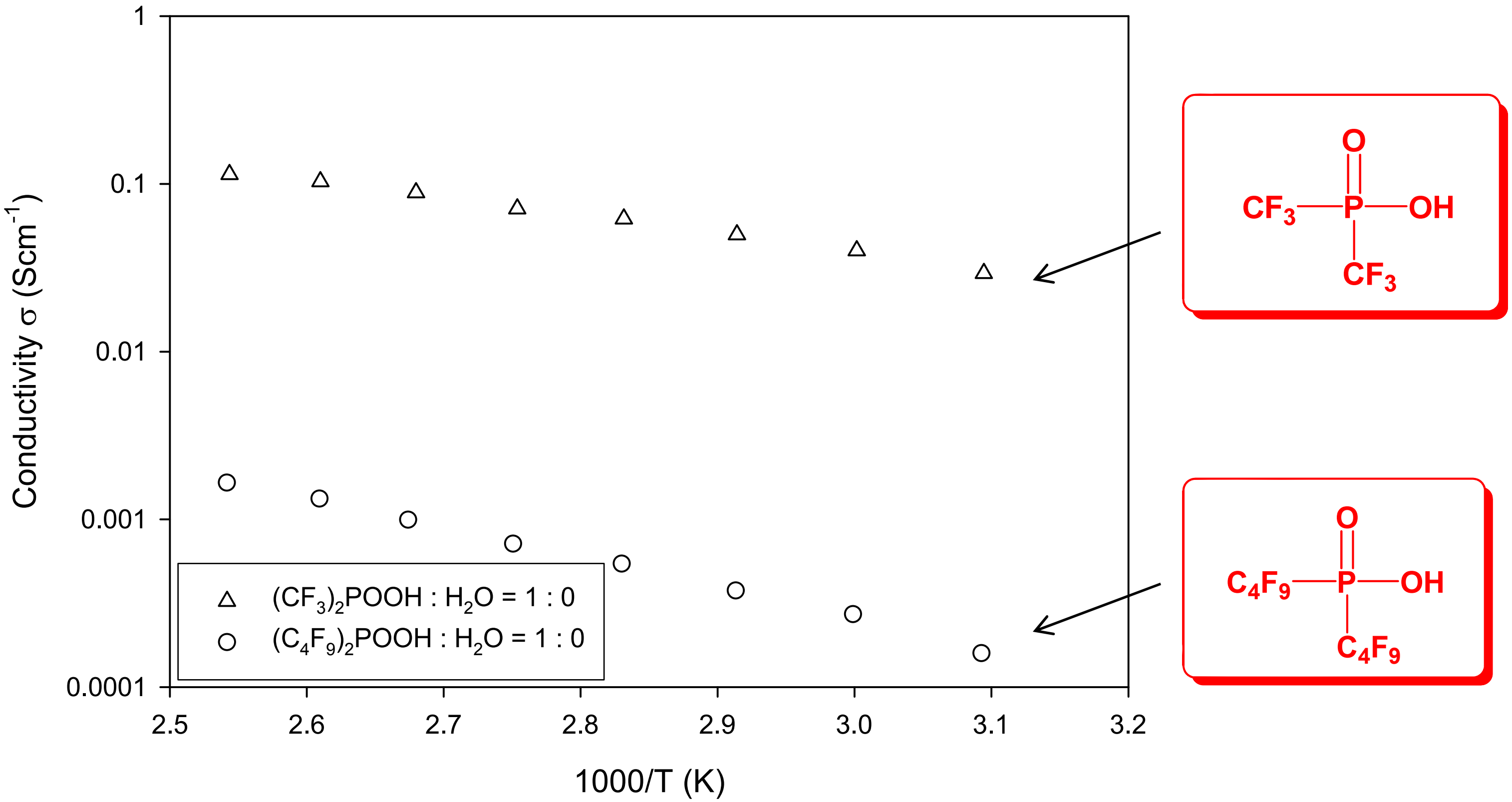
Fluoroalkyl group chain length effect

- ***Lengthening the fluoroalkyl chain in fluoroalkyl phosphonic acid model compounds diminishes anhydrous ionic conductivity***



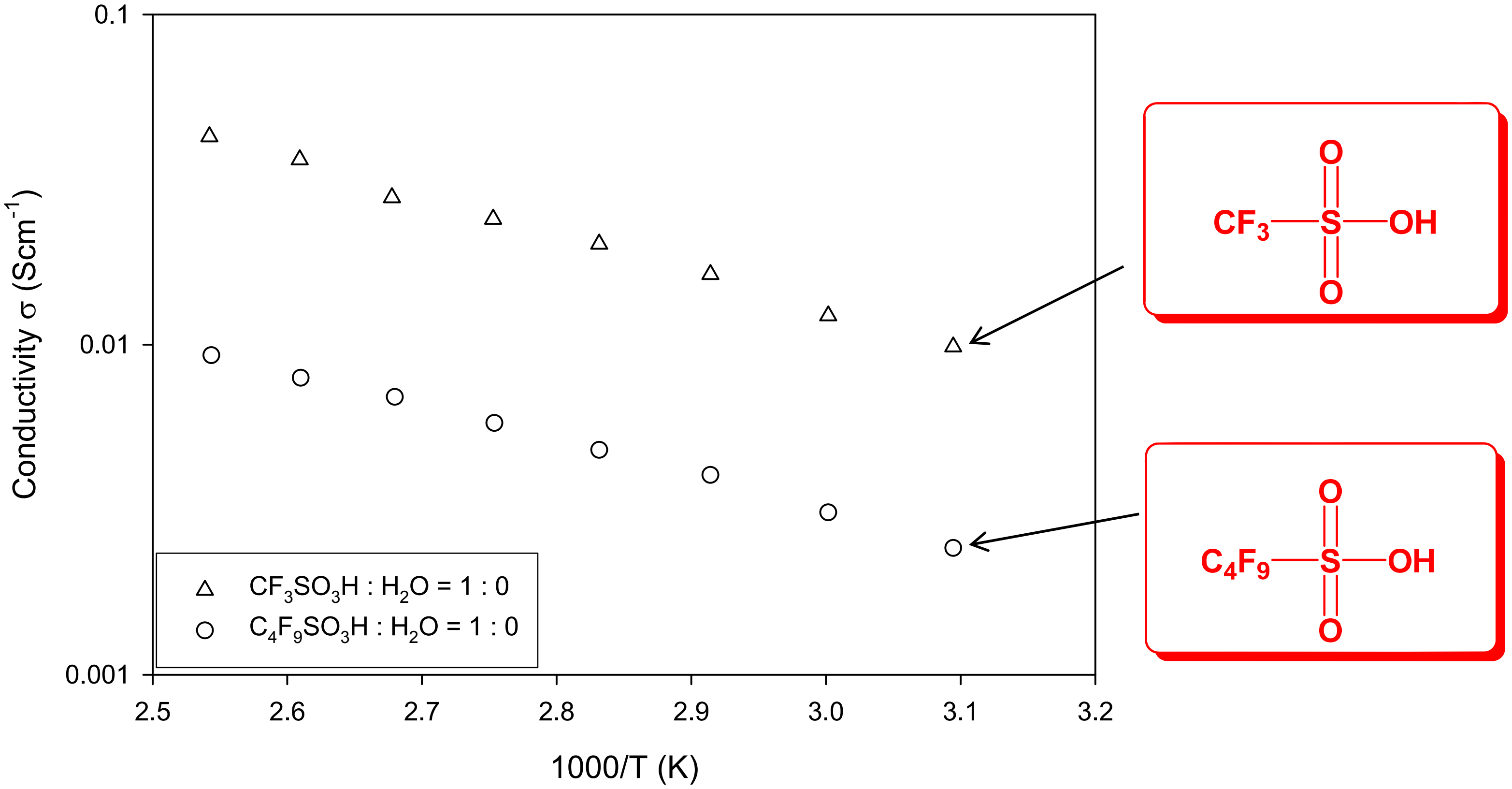
Fluoroalkyl group chain length effects

- ***Same is true for fluoroalkyl phosphinic acids…***



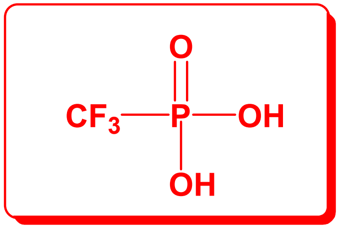
Fluoroalkyl group chain length effects

- ***... And, for fluoroalkyl sulfonic acids.***
- ***And yet, Nafion® and other fluoroionomers with relatively high fluoro-carbon content have relatively high conductivity. Why is this so?***
- ***Because they absorb water, and they adopt domain structures wherein acid groups aggregate to form continuous ion-conducting channels.***

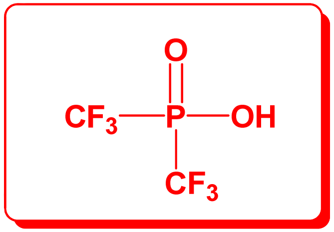


Conductivity with water present

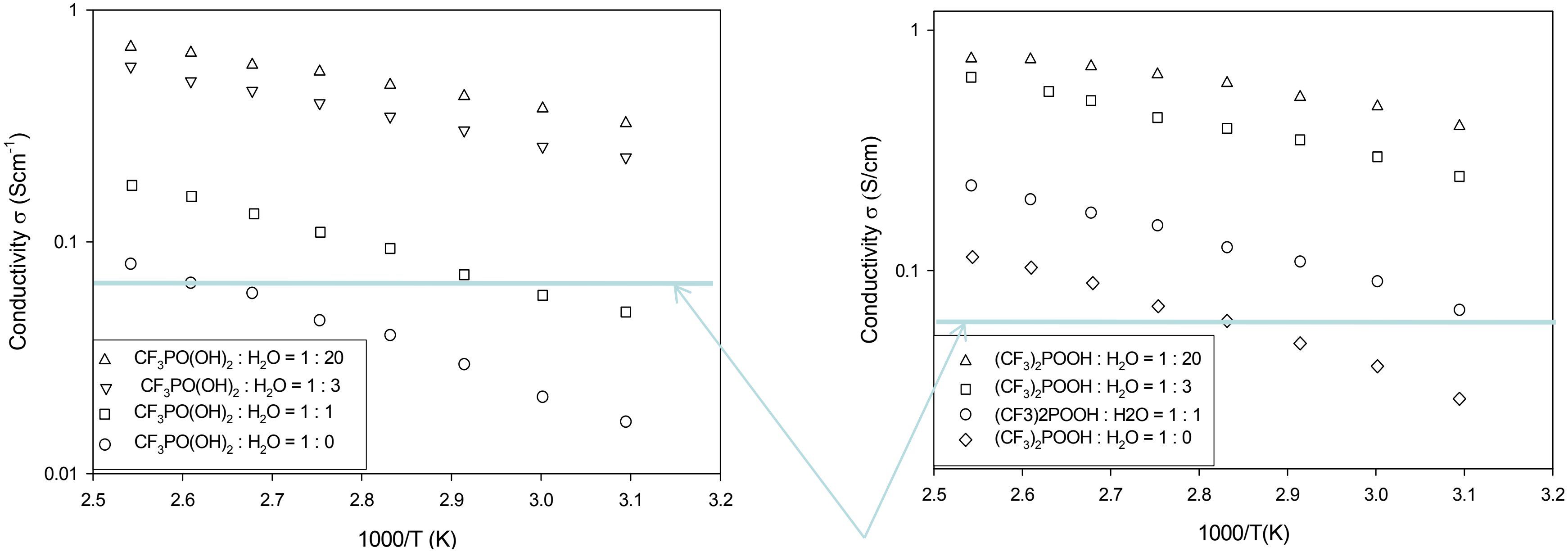
- ***Adding water always increases ionic conductivity.***



$CF_3P(O)(OH)_2$

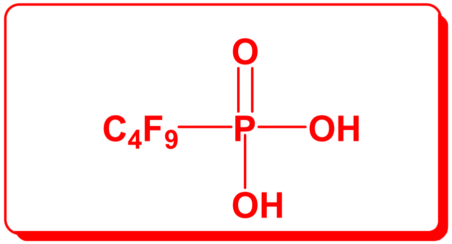


$(CF_3)_2P(O)OH$

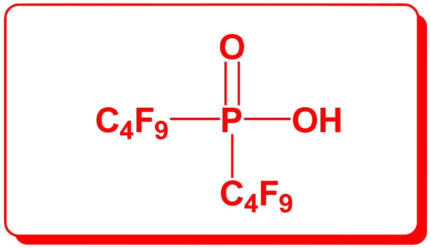


0.07 S / cm

Conductivity with water present

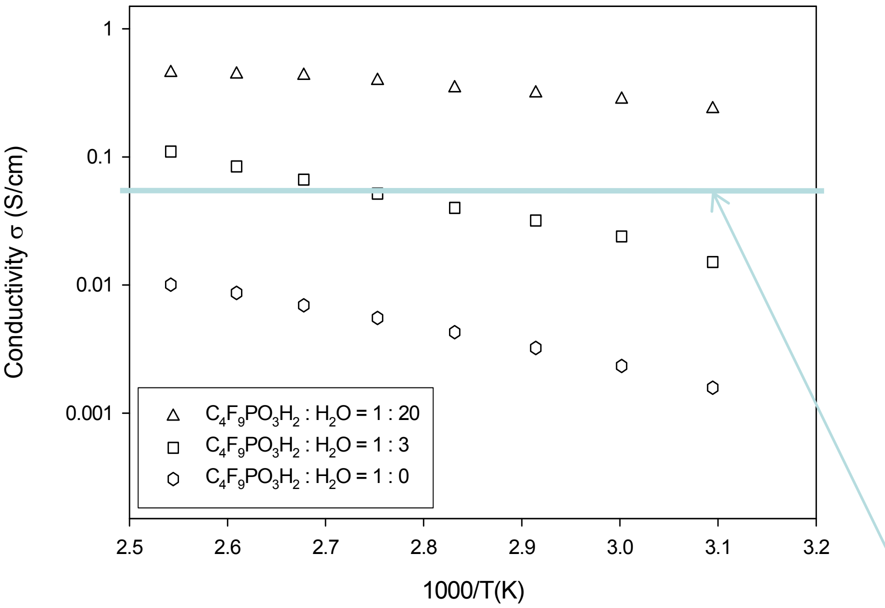


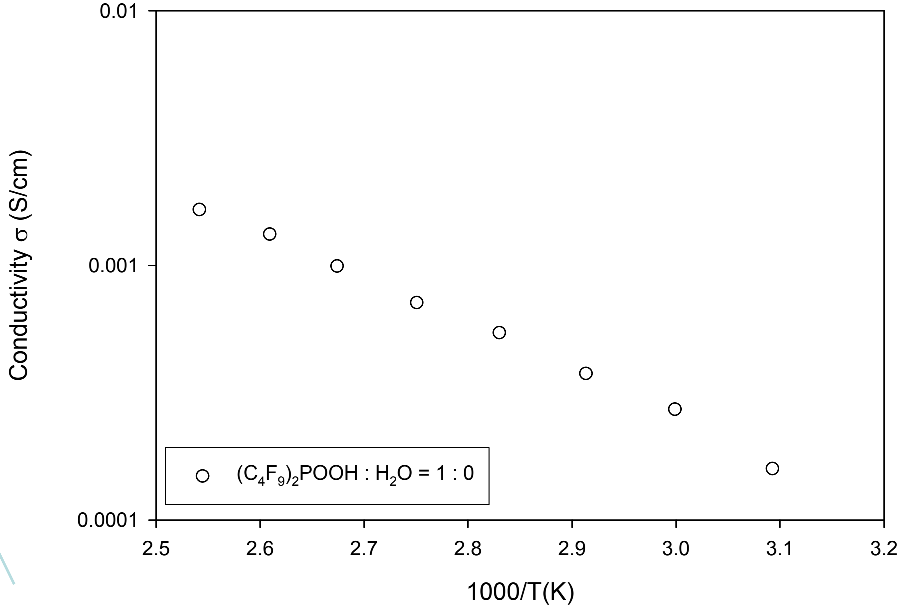
$\mathrm{C_4F_9{-}P(=O)(OH){-}OH}$



$\mathrm{C_4F_9{-}P(=O)(C_4F_9){-}OH}$

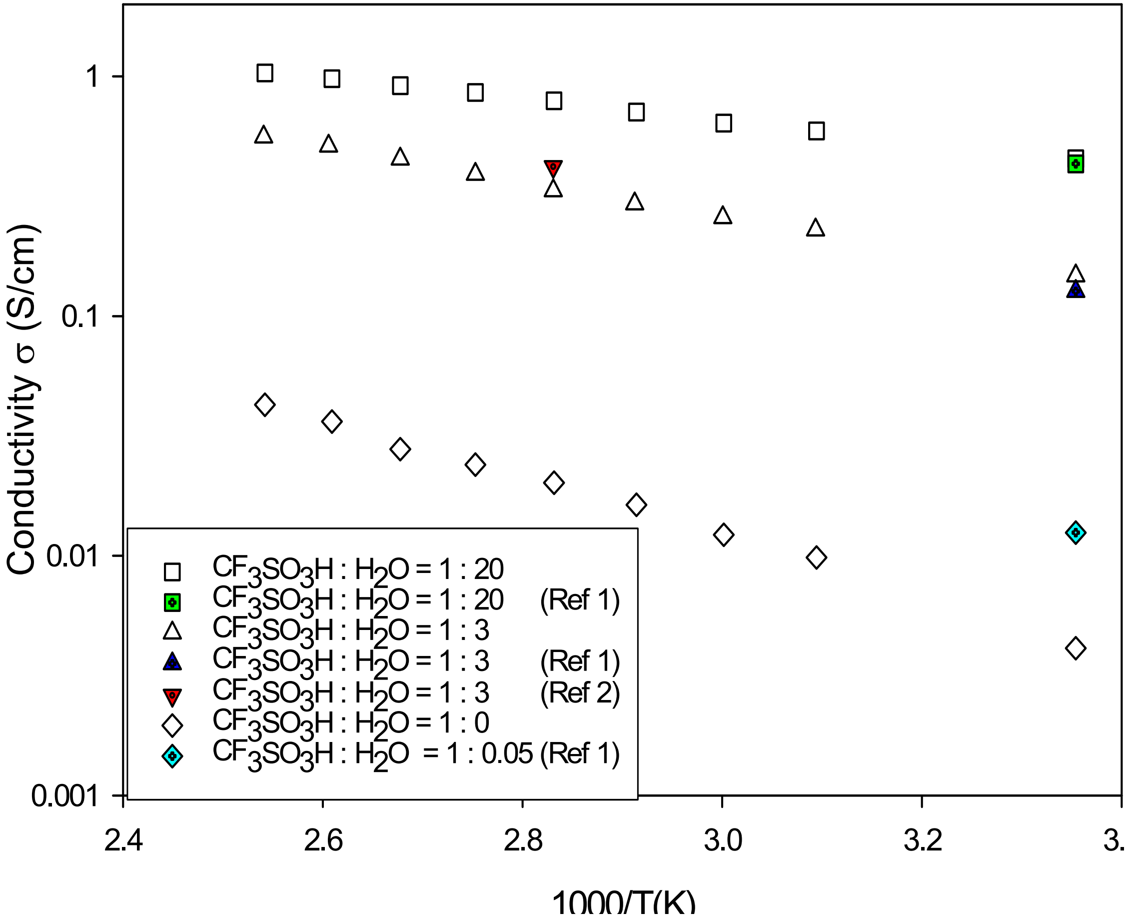
Water would not dissolve in this material…

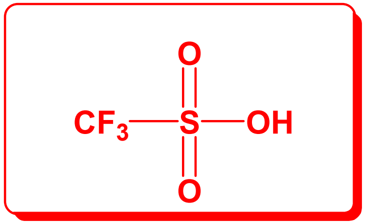




0.07 S / cm

Conductivity with water present

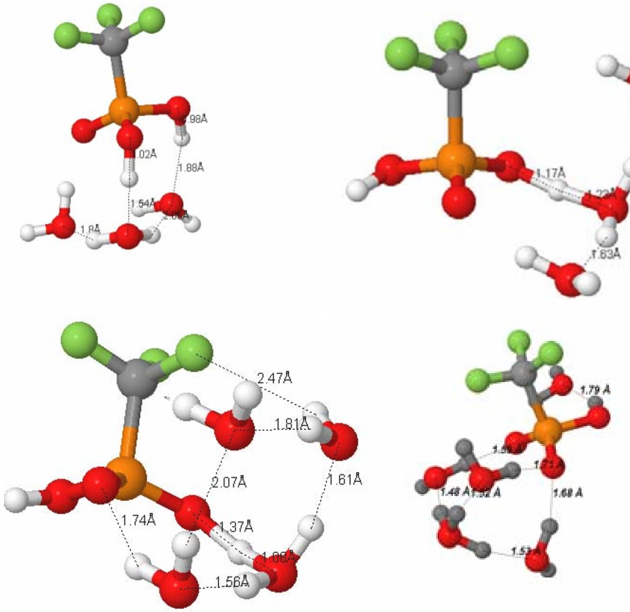




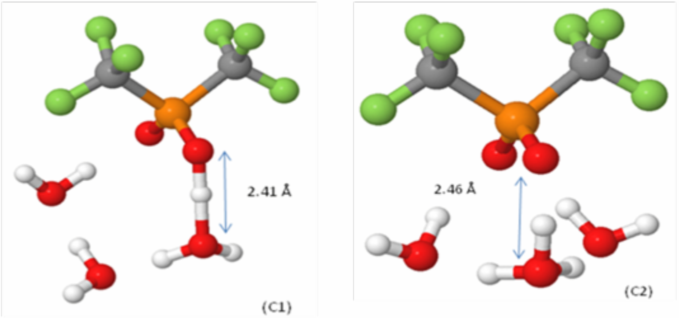
Ref 1: Canadian Journal of Chemistry (1978), 56(13), 1832-5.

Ref 2 : Giner Electrochemical systems LLC. DOE Hydrogen review 2007 pg 8

Quantum Chemistry Studies FPA/water Clusters



$CF_3PO(OH)_2$



$(CF_3)_2POOH$

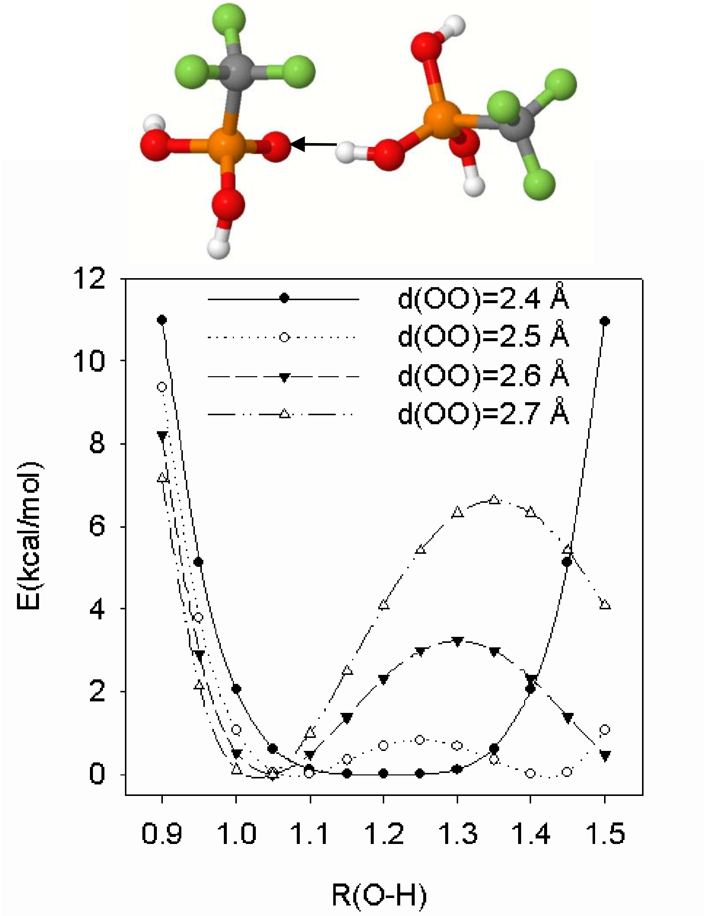
complex	Binding energy* (kcal/mol)	r(P**O-H**...Ow-Hw)^a (Å)	r(PO-**H…O**$_w$-H$_w$)^a (Å)
$CF_3PO(OH)_2$		0.96	
$CF_3PO(OH)_2 + H_2O$	-11.0	1.0	1.67
$CF_3PO(OH)_2 + 2\ H_2O$	-20.8	1.04	1.5
$CF_3PO(OH)_2 + 3\ H_2O$	-31.8	***1.17***	***1.23***
$CF_3PO(OH)_2 + 4\ H_2O$	-41.4	1.01	1.62
$CF_3PO(OH)_2 + 4\ H_2O$	-43.2	***1.37***	***1.08***
$CF_3PO(OH)_2 + 5\ H_2O$	-52.6	2nd solv. shell	
$CF_3PO(OH)_2 + 6\ H_2O$	-64.7	2nd solv. shell	

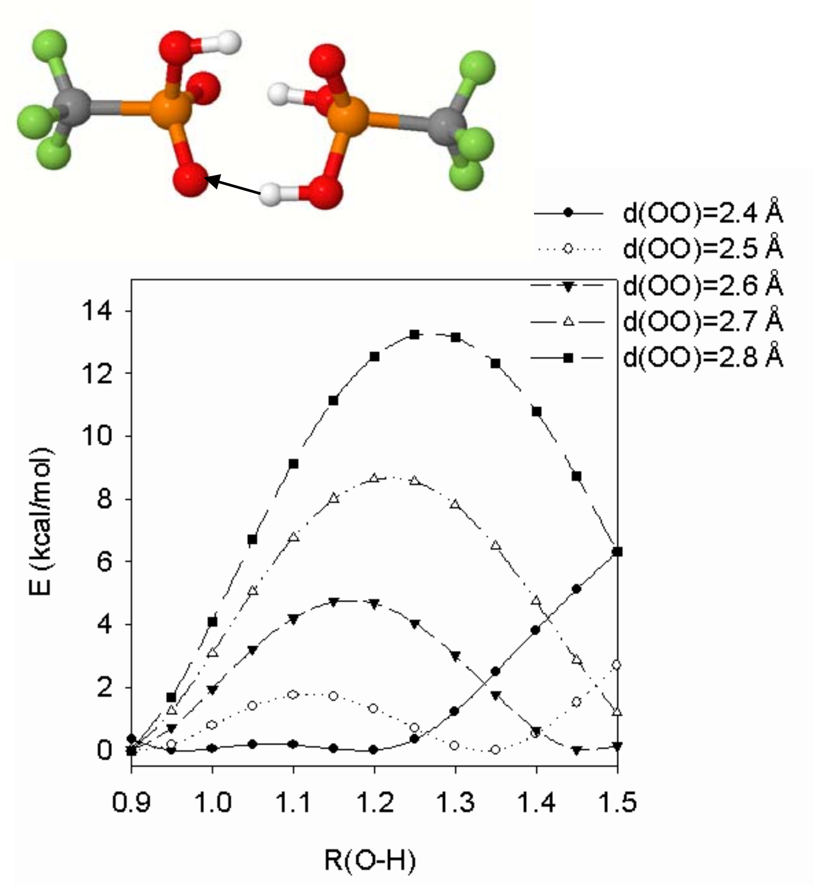
***Binding energy is calculated at the mPW1PW91/aug-cc-pvDz level*

- ***$CF_3PO(OH)_2 + 3\ H_2O$: proton is shared between $CF_3PO(OH)_2$ and water;***
- ***$CF_3PO(OH)_2 + 4\ H_2O$: $CF_3PO(OH)_2$ becomes deprotonated***
- ***$(CF_3)_2POOH + 3\ H_2O$: the complex with a shared proton between acid and water is ~ 1kcal/mol more stable than a complex with a deprotonated acid***
- ***Previous studies have shown that for $CF_3SO_3H + 3H_2O$ the acid group is sponteneously deprotonated***

These results are consistent with the experimentally measured acid strength

Example of Q-HOP Parameterization: Barriers for Proton Hopping

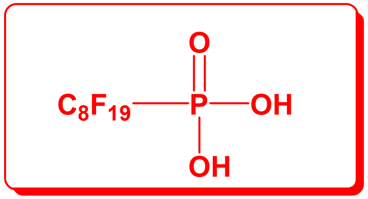




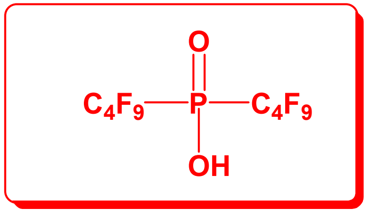
- The gas-phase barrier was fit to $\mathbf{E^0_{12}(DA)= a+b*d(DA)+c*d(DA)^2}$, where d(DA) is the distance between the donor (D) and acceptor oxygen (A).
- QC calculations were performed at mPW1PW91/6-31+G(d,p) level

Classical MD; acid group aggregation

- ***$C_8F_{17}PO_3H_2$ exhibits good acid group aggregation giving rise to possible proton conducting pathways.***
- ***$(C_4F_9)_2POOH$ does <u>not</u> exhibit good acid group aggregation indicating that Grotthuss-type proton hopping is improbable in the later.***

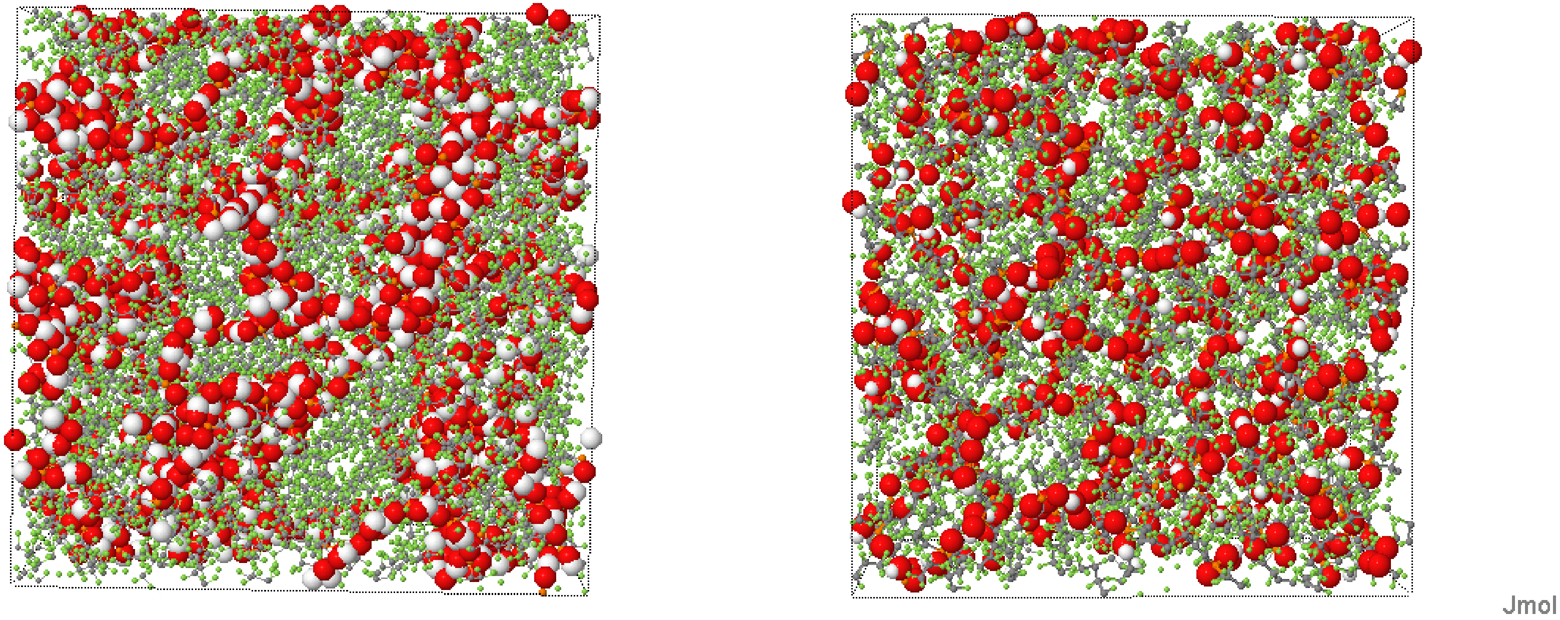


$$\mathrm{C_8F_{19}{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}OH} \quad \text{with } \mathrm{OH} \text{ below P}$$

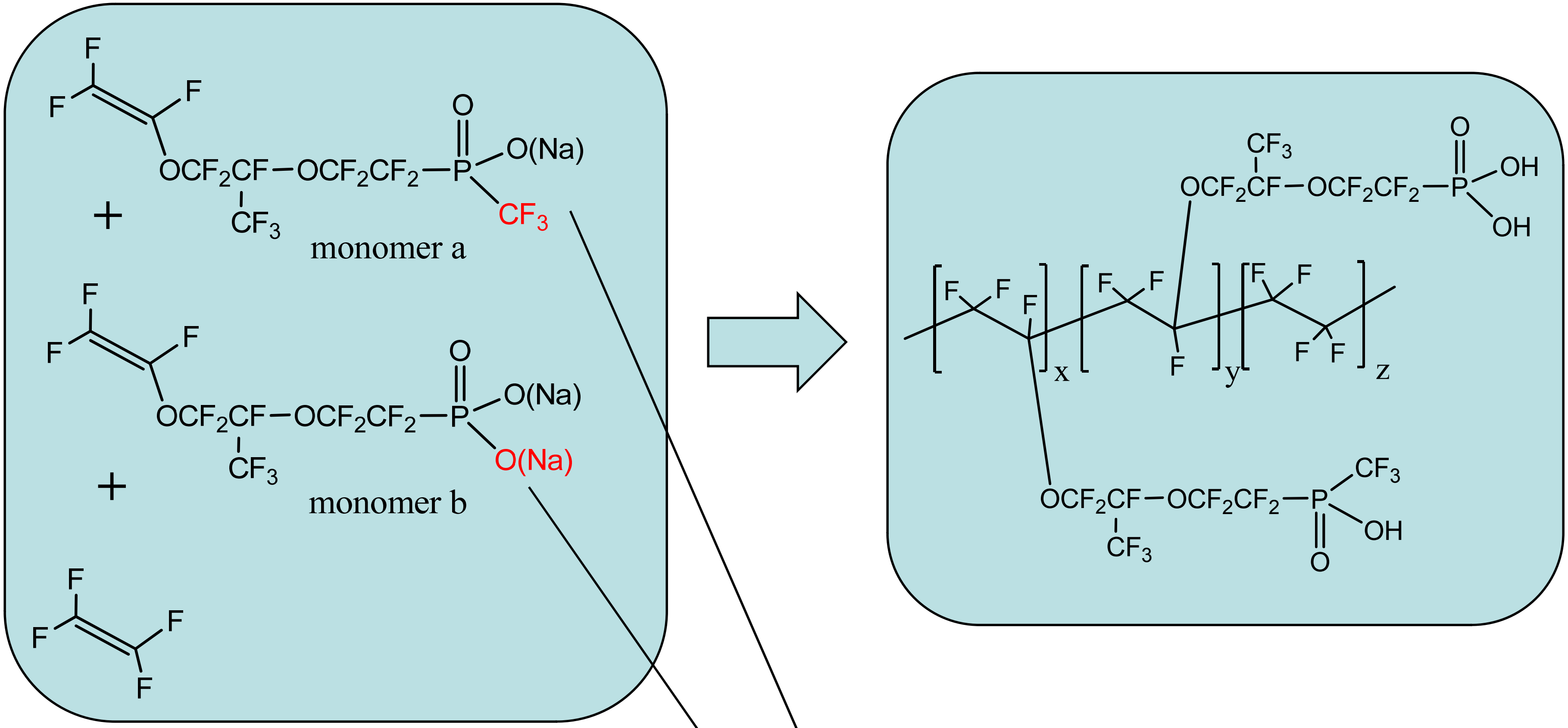


$$\mathrm{C_4F_9{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}C_4F_9}$$

Hydrogen and oxygen have been increased in size to highlight acid group aggregation



Co- and Terpolymerization



	P18	**P20**	**P21**	**P22**	**P23**
Monomer **a** (wt%, g)	100, 4	97, 2	83, 2	17, 0.4	0, 0
Monomer **b**(wt%, g)	0, 0	3, 0.06	17, 0.4	83, 2	100, 2