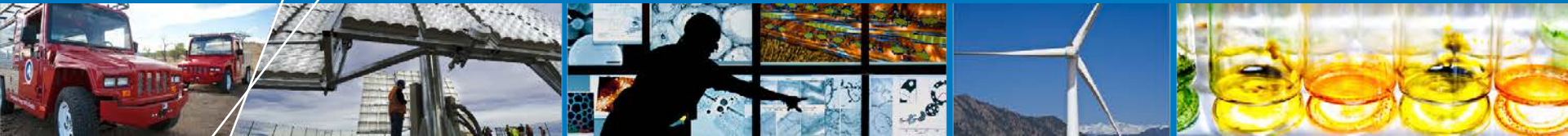


Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells



2014 DOE Hydrogen and Fuel Cells Program Review

Bryan Pivovar (PI)

June 18, 2014

FC108

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- **Start: April 2013**
- **End: April 2015**
- **% complete: 30%**

Barriers

- A. Durability**
- B. Cost**
- C. Performance**

Budget (\$K)

DOE Cost Share	Team Cost Share	TOTAL
2000	500	2500

- **FY13 DOE Funding: \$600K**
- **Planned FY14 DOE Funding: \$1M**
- **Total Project Value: \$2.5M**
- **Cost Share Percentage: 20%**

Partners – Principal Investigators

CellEra – Shimshon Gottesfeld

3M – Krzysztof Lewinski

Colorado School of Mines – Andy Herring

First year reviewed no response to previous year's reviewer comments.

Relevance

DOE Milestones for Alkaline Membrane Fuel Cells (AMFCs)/ Goals

http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf pages 3.4-42 and 3.4-44

Task 1: Electrolytes

1.4

Demonstrate an anion-exchange membrane that retains 99% of original ion exchange capacity for 1000 hours in hydroxide form at $T > 80^{\circ}\text{C}$. (2Q 2013)

Task 3: Membrane Electrode Assemblies, Gas Diffusion Media, and Fuel Cells

3.8

Demonstrate anion-exchange membrane technologies in MEA/single cells with non-PGM catalysts that maintain performance higher than 350 mW/cm^2 for 2000 hours at $T > 80^{\circ}\text{C}$. (4Q, 2016)

Relevance: Alkaline membrane development as an enabling aspect of non-precious catalysis in fuel cells without the concerns of liquid alkaline electrolytes.

Team Project Goals

Synthesize novel perfluoro (PF) anion exchange membranes (AEMs) with high temperature stability and high water permeability. (past year's focus)

Employ novel PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells. (current/future focus)

Demonstrate high performance, durability, and tolerance to ambient carbon dioxide. (future focus)

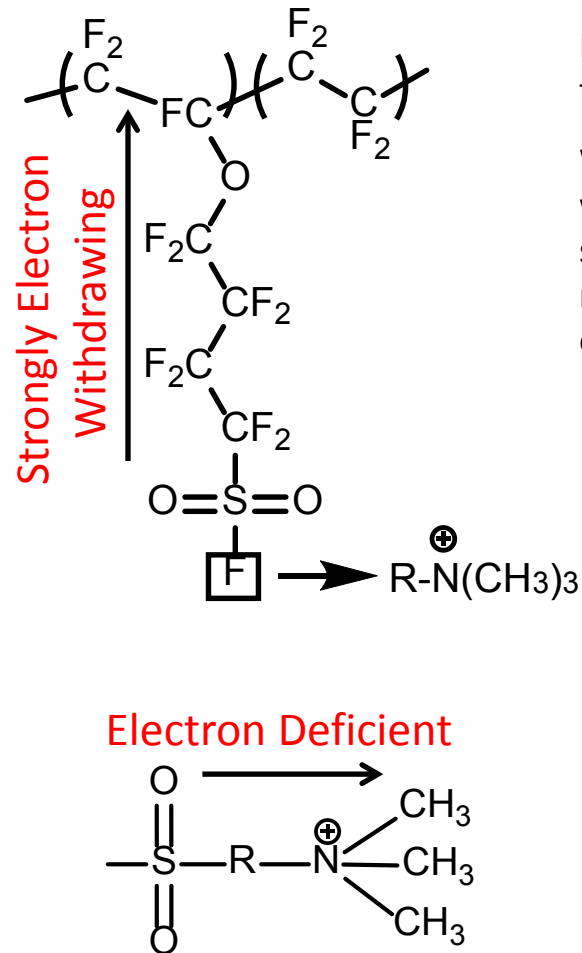
Approach

FY 14 Milestones

Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
Q1	12/31/2013	Go/No-Go	Evaluate Grignard reagent chemistry for its applicability to produce target chemical modifications to sulfonyl fluoride precursor form ionomer Decision Criteria: If Grignard chemistry has produced AEMs with >90% conversion of anion exchange groups and/or hydroxide ion conductivities >20mS/cm ² at room T, continue Grignard chemistry otherwise cease.	Go Decision (Estimated >94% of the SF bonds were converted from IR)
Q2	3/31/2014	Regular	Supply at least 3 novel PF AEM membranes (greater than 3" by 3") to CellEra for fuel cell testing and characterization	Completed on time
Q3	6/30/2014	Regular	Report (and compare to CellEra baseline) AMFC performance of 3 novel MEAs using PF AEM materials.	
Q4	9/30/2014	Stretch	Demonstrate PF AEMs with 5×10^{-10} m ² /s water self-diffusion coefficient (a 150% increase in water transport self-diffusion coefficient versus traditional hydrocarbon AEMs, critical in enabling higher fuel cell performance due to the increased water transport dependence of AMFCs vs PEMFCs)	

Approach

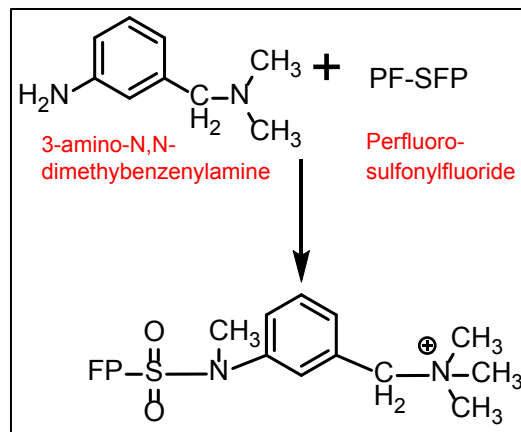
PF AEM Materials – Targeted Sulfonyl Linkages and Specific Chemistries



Perfluoro (PF) polymer electrolytes exhibit chemical robustness, enhanced water transport and conductivity properties.

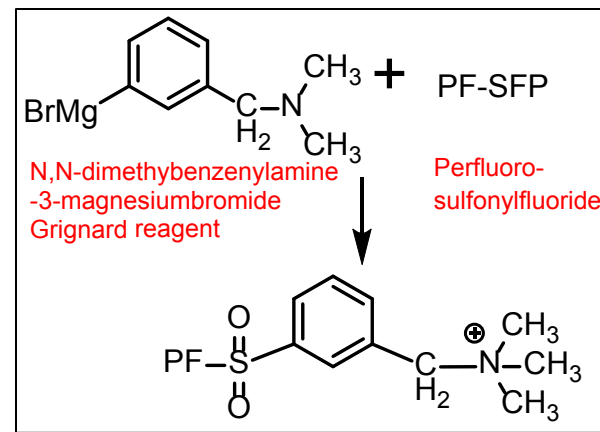
While PF chemistry improves PF sulfonic acid (PFSA) acidity, the strongly electron withdrawing PF backbone creates challenges for anion exchange membrane stability. We have focused on spacer groups (R) to increase stability. From the readily available perfluoro sulfonyl fluoride precursor (PF-SFP), different strategies can be employed to tether cations to the PF-SFP.

Amide Linkage



The sulfonamide linkage is demonstrated chemistry¹ and has been employed industrially to synthesize PF AEMs such as Tosflex®.

Aryl Linkage



Strategies for amide-free linkages are less developed. We have targeted Grignard reagents as a type of “clip on” chemistry amenable to several different well defined end groups onto PF-SFP sidechains.

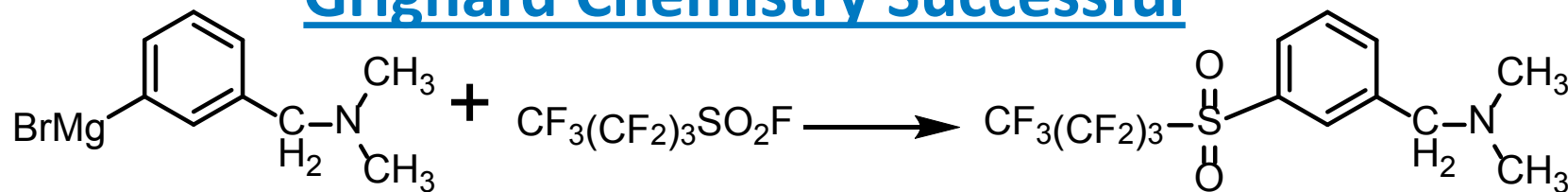
¹Matsui, K. (1987). U.S. Patent No. 4659744.

Accomplishments and Progress

Verifying Grignard Chemistry – Small Molecule Analog

Perfluorobutanesulfonylfluoride ($\text{CF}_3(\text{CF}_2)_3\text{SO}_2\text{F}$) was utilized as a small molecule analog to PF-SFP. NMR/FTIR analysis confirmed desired reaction product.

Grignard Chemistry Successful



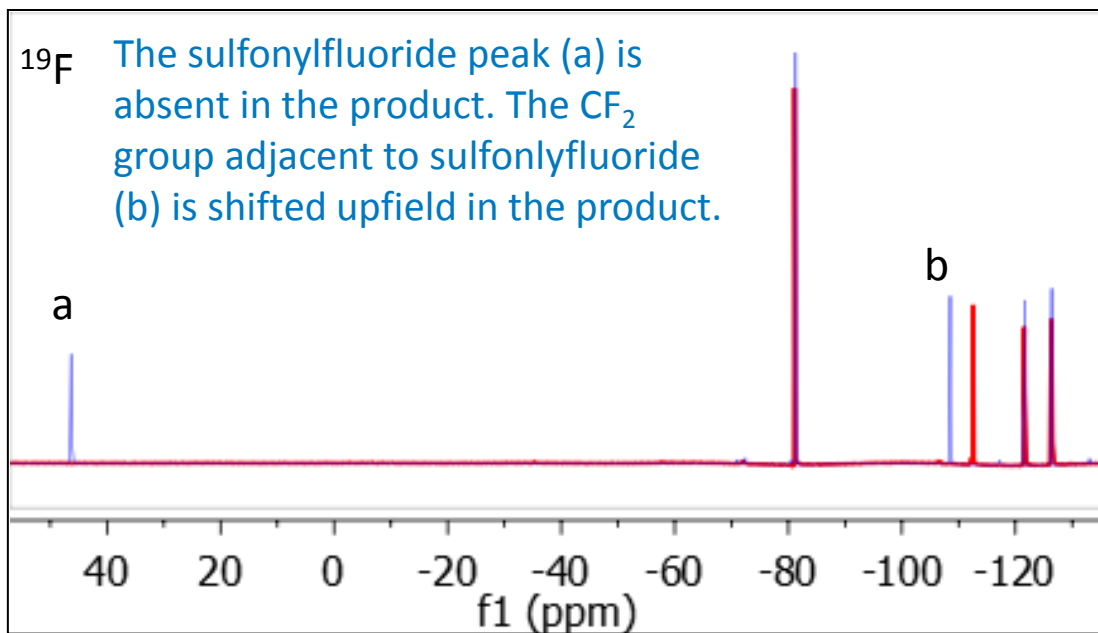
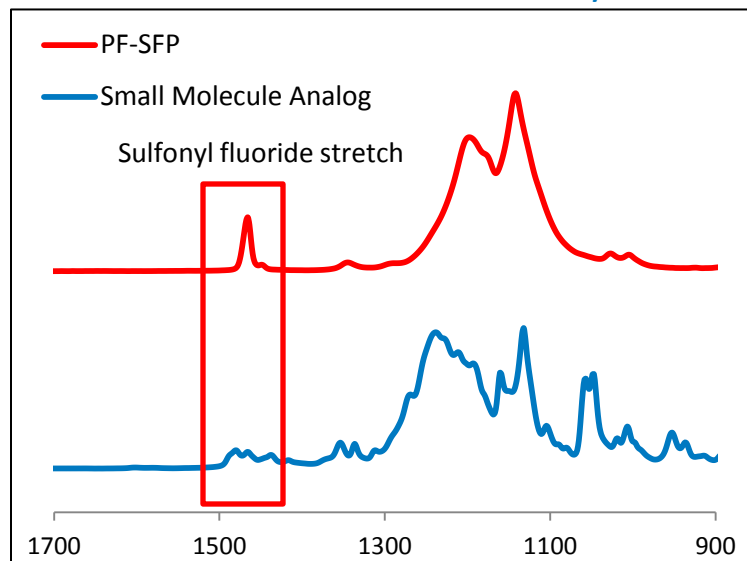
N,N-dimethylbenzenylamine
-3-magnesiumbromide
Grignard reagent

Blue spectrum

Small Molecule Analog

Red spectrum

FT-IR confirms conversion of sulfonyl fluoride



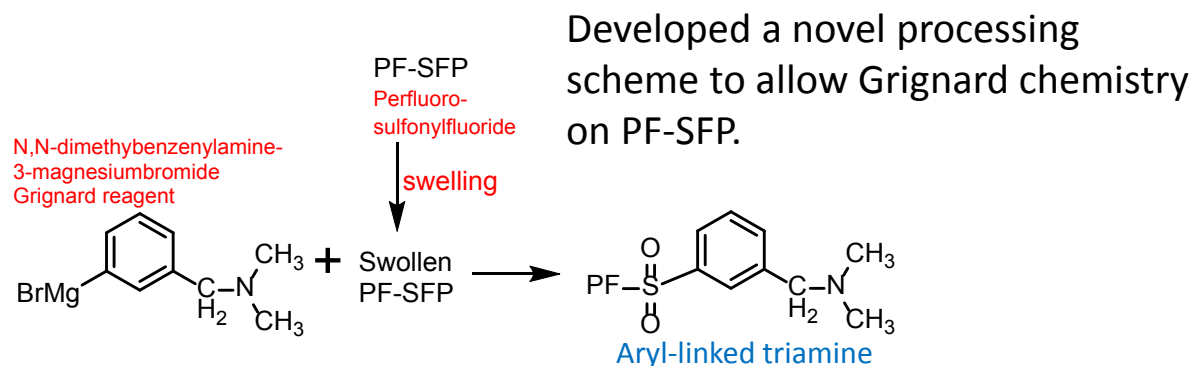
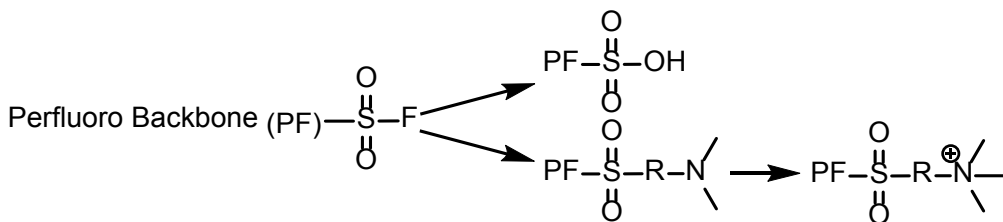
Accomplishments and Progress

Overcoming Reactant Accessibility in Grignard Chemistry

Challenge: Reactant Accessibility

For PFSA's, the conversion of $-\text{SO}_2\text{F}$ to $-\text{SO}_3\text{H}$ sites results in a highly swellable polymer.

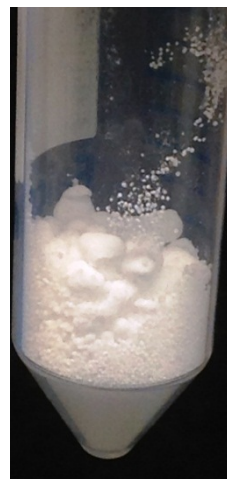
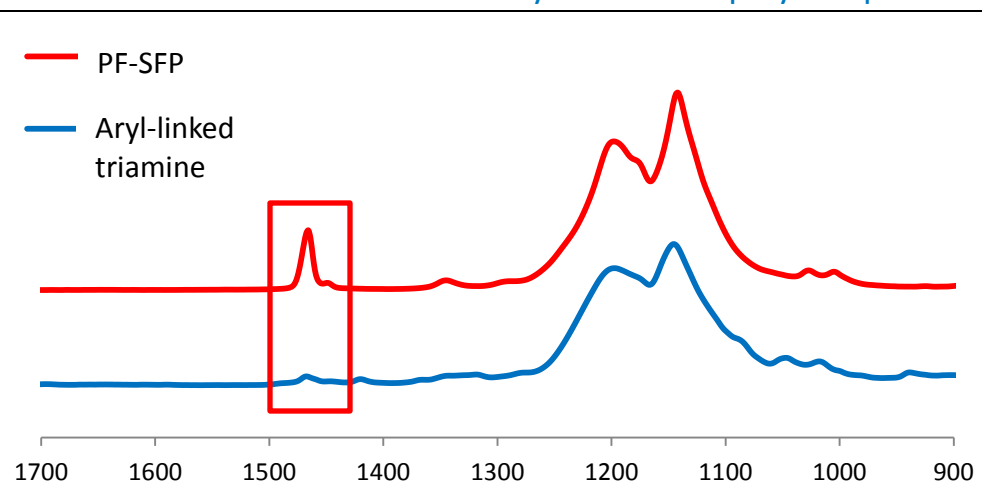
PF AEM chemistries rely on a neutral intermediate that does not easily swell, creating reactant accessibility challenges.



Swollen PF-SFP



FT-IR confirms conversion of sulfonyl fluoride in polymer product.



PF-SFP



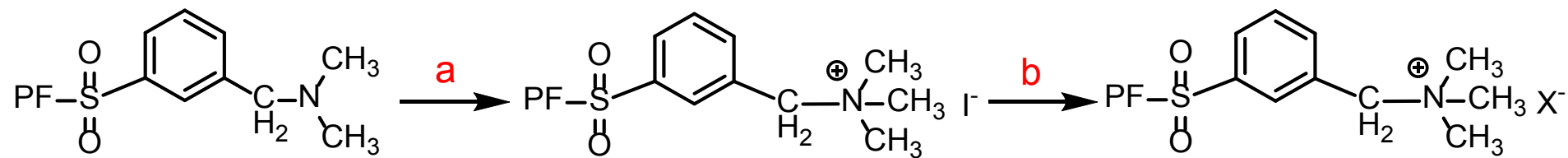
Crude Product



Dried product

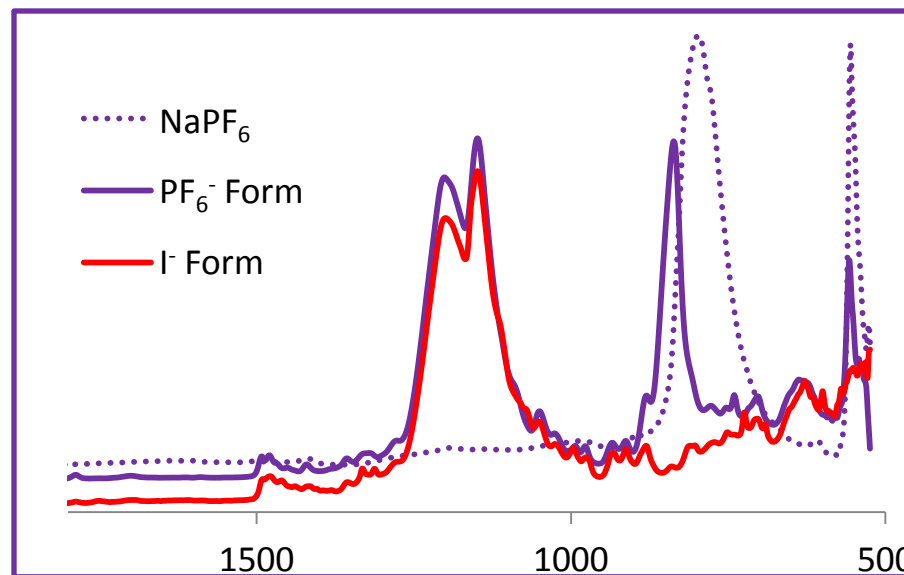
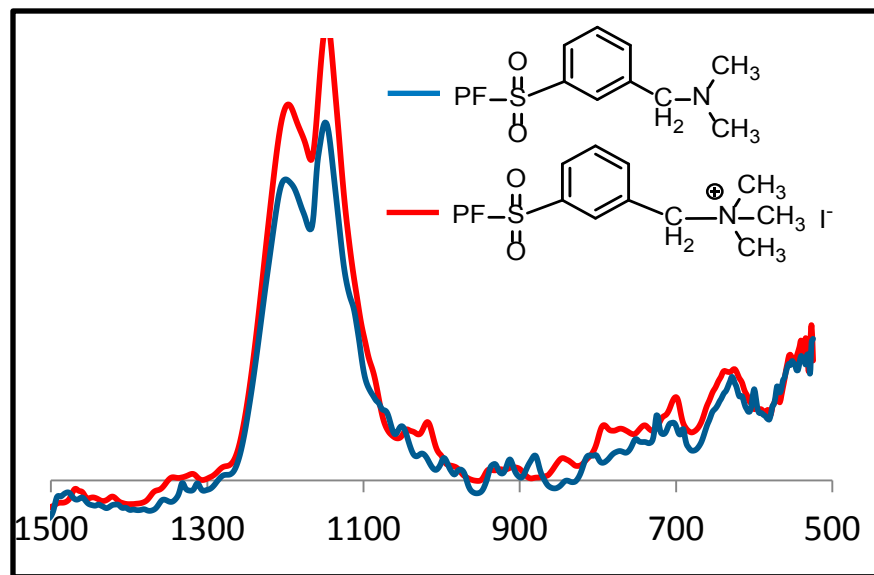
Accomplishments and Progress

Quaternization and Ion Exchange



50g have been synthesized to date.

Once synthesis of triamine was complete and verified via FT-IR, the product was then quaternized (a). The counter anion is then exchanged (b) to verify ion exchange capability, PF_6^- counterion clearly ion exchanged.



Accomplishments and Progress

Membrane Formation (Grignard Approach)

Appropriate processing conditions to form membranes using PF AEMs with Grignard chemistry have not succeeded. Material has been supplied to 3M to further investigate polymer dispersion and membrane casting.

Three approaches have been attempted so far: solution based, chemical modification of preformed films, and melt (thermal) processing.

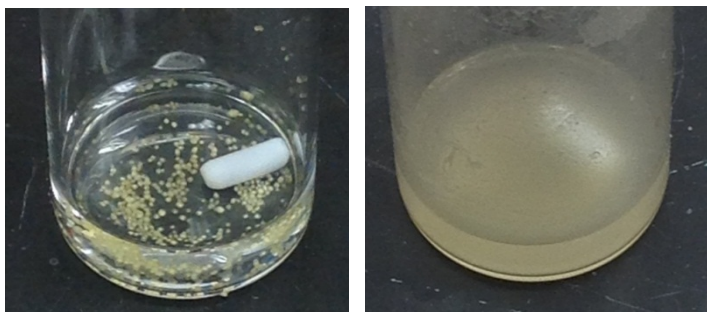
Solution

An appropriate solvent has not been found for preparation of dispersion or solvent casting. Batch to batch variability (including PF-SFP) and concerns over extent of reaction are issues remaining to be resolved.

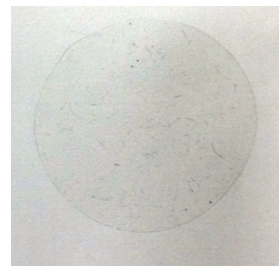
SFP membrane processing

The SFP form membrane can be placed into membrane form through thermal (melt) processing. Attempts to perform chemistry on pre-made films have been unsuccessful due to reactant access throughout the polymer film.

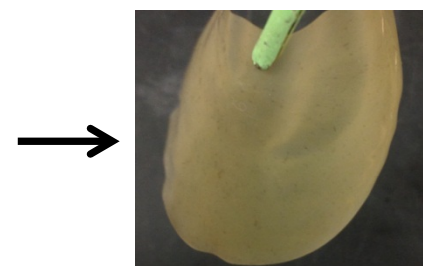
Triamine product in $(CF_3)_2CHOH$



SFP membrane



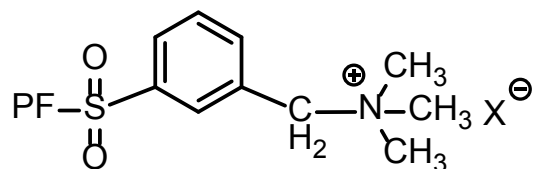
Post-Grignard Chemistry



Accomplishments and Progress

Salt form exchange to investigate thermal processing of PF AEMs

Limitations encountered in the solvent processing of polymers synthesized through Grignard chemistry led to the investigation of thermal routes to investigate thermal properties of films (the tetrabutylammonium form of Nafion® is known to be melt processable, so large organic counterions were the primary focus using TGA and DSC).

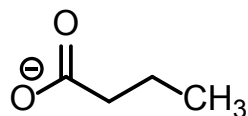


X = I[⊖]

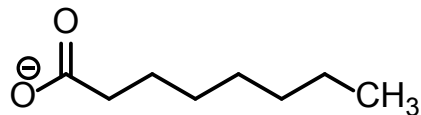
Iodic



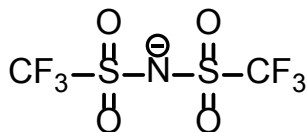
Hexafluorophosphoric



Butyric



Octanoic

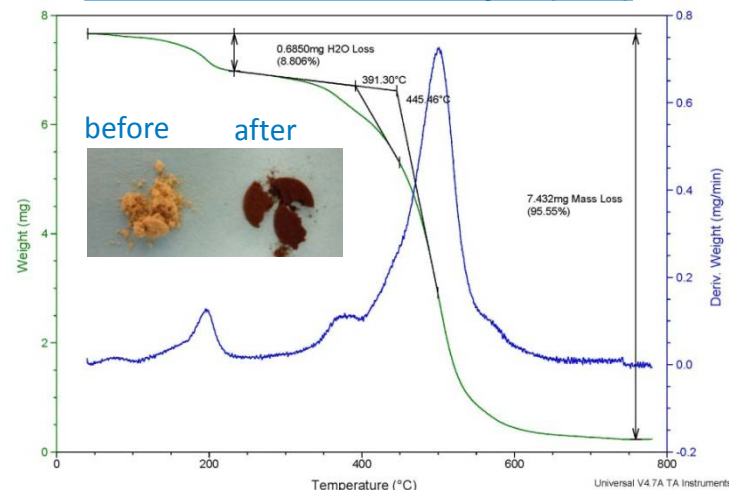


Bis-trifluoromethyl
Sulfonamide

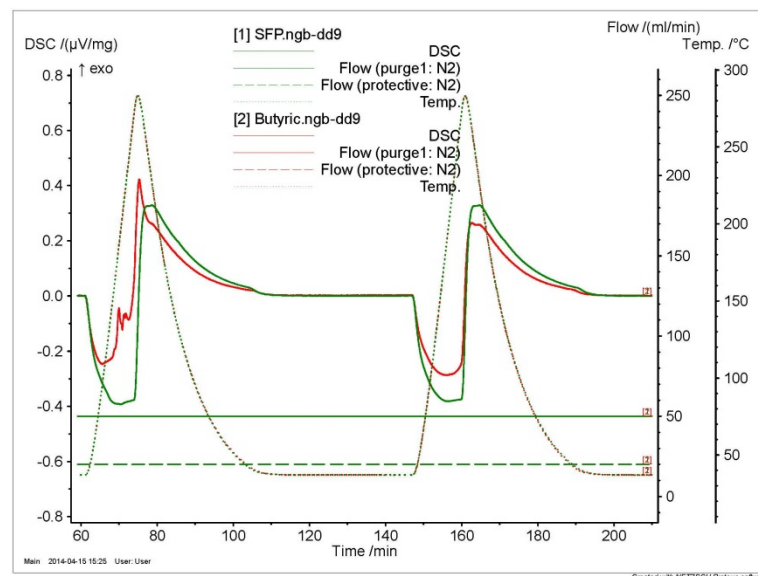
Melt processing not achieved

See Technical Backup slide #23 for summary of results

Thermal Gravimetric Analysis (TGA)



Differential Scanning Calorimetry (DSC)

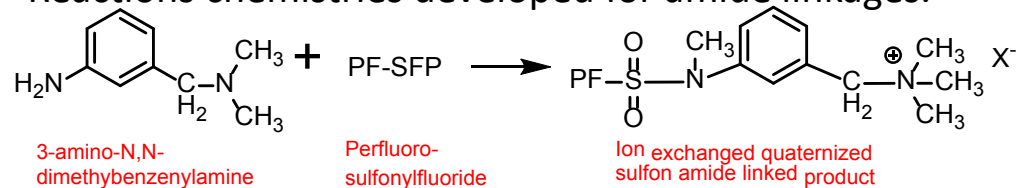


Accomplishments and Progress

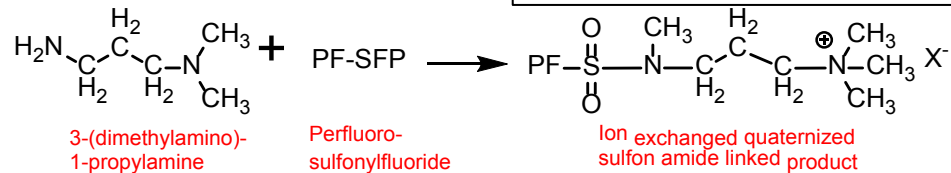
Amide linkages/ DFT results

Grignard chemistry was investigated due to its high degree of control and the ability to avoid sulfonamide linkages. Amide linkages were developed in parallel and initial DFT calculations suggest slightly enhanced stability of sulfonamide linkage.

Reactions chemistries developed for amide linkages.



X = I, Br, Cl
Total of 50 g synthesized to date.



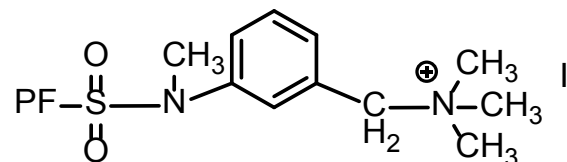
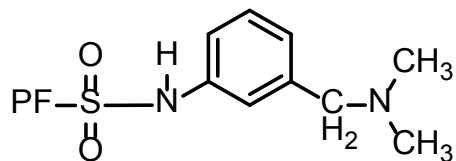
X = I, Br, Cl, PF6
Total of 30 g synthesized to date.

Three AEM chemistries primarily investigated to date

R	Linkage	DFT Hydroxide Stability (kcal/mol)		
		Benzyl CH ₂	Ammonium CH ₃	β elimination
	Amide	NA	24.7	19.7
	Amide	23.4	24.5	NA
	Aryl	22.1	24.1	NA

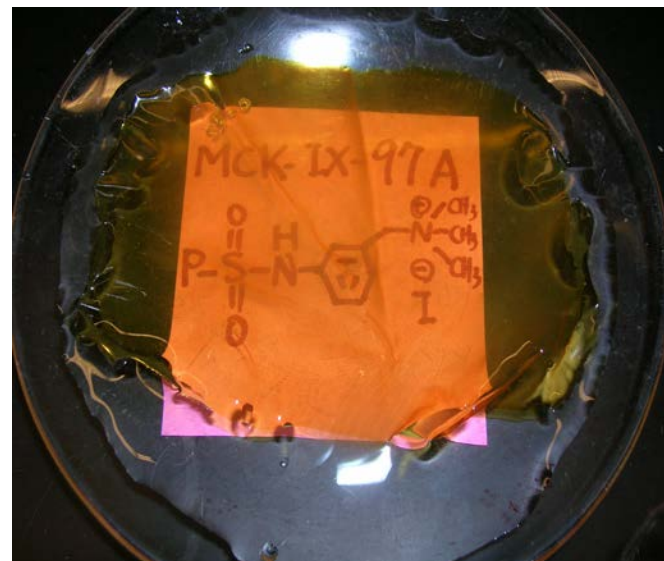
Accomplishments and Progress

Casting and Quaternizing Amide Films/Membranes



Pink paper is 3" x 3"

Quaternization



Membranes supplied to CellEra

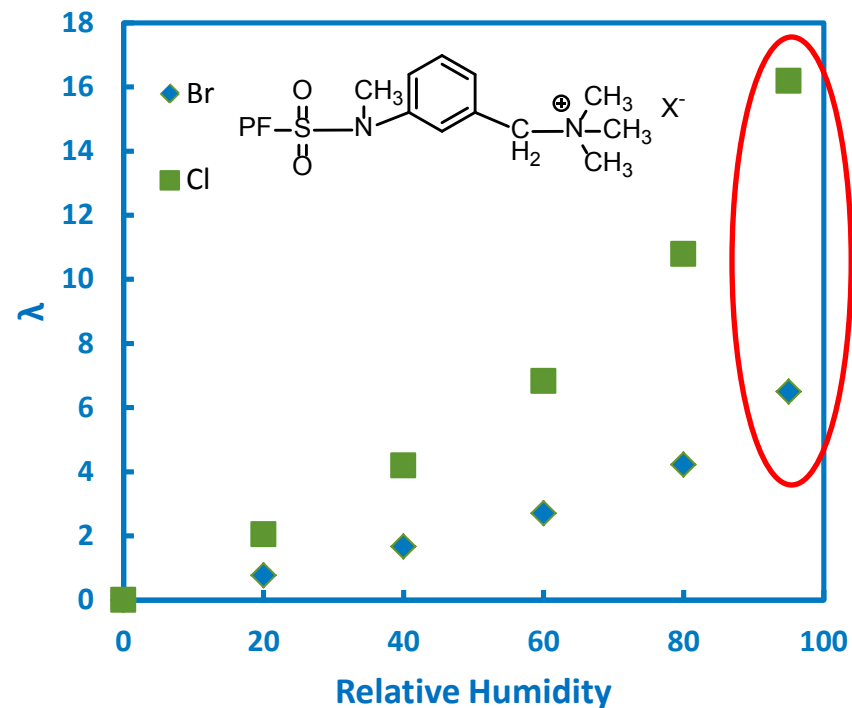
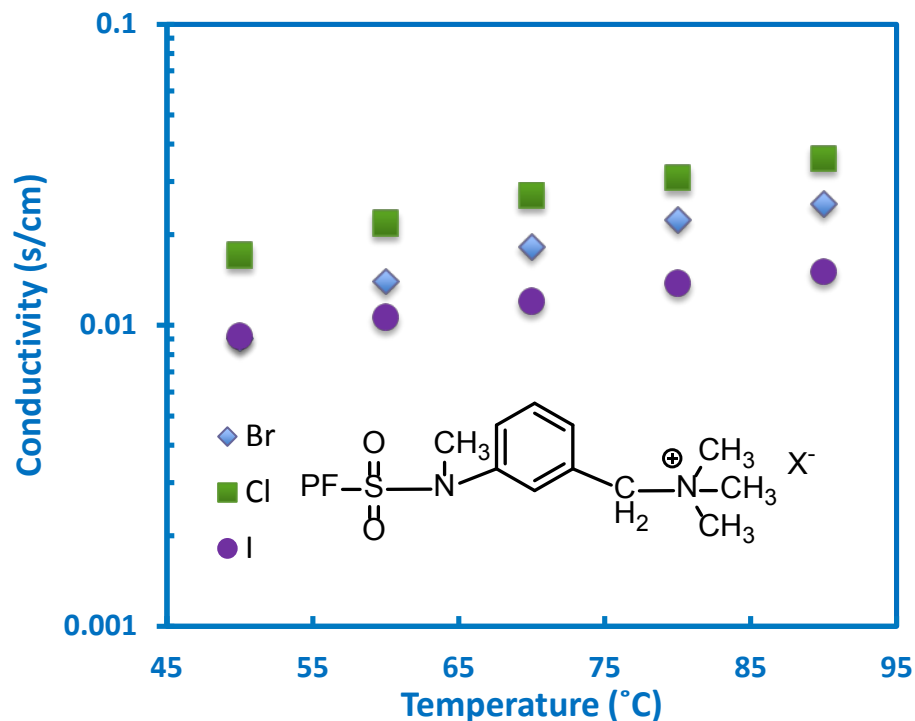
Polymer membranes were cast on the Teflon® plate from DMAc solutions.

Quaternized product could be recast from DMAc (a solvent unsuitable for Grignard Chemistry).

Membrane robustness post-quaternization is a concern, but initial membranes have been characterized for conductivity and water uptake.

Accomplishments and Progress

Amide (aryl) linkage – most stable from DFT calculations

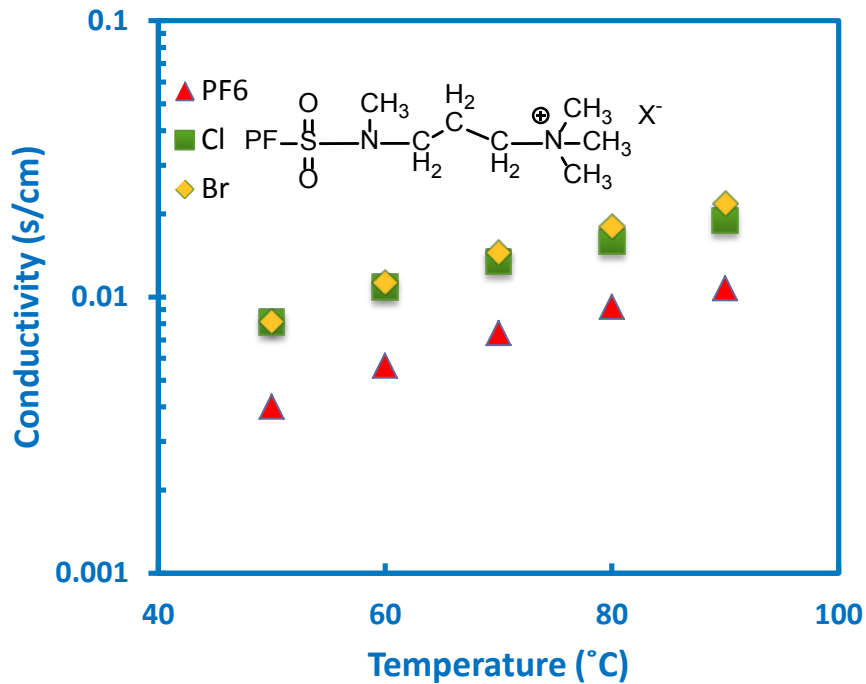


Reasonable conductivities (95% RH) measured. Different salt forms investigated to validate anion exchange, hydroxide avoided to date to minimize complications of carbonate formation and remove degradation concerns. Expect conductivity increase when in OH⁻ form.

Water uptake values show strong dependence on salt form. Reasonable trends when compared to PFSA, conductivity differences qualitatively consistent with differences in water uptake and counterion mobility.

Accomplishments and Progress

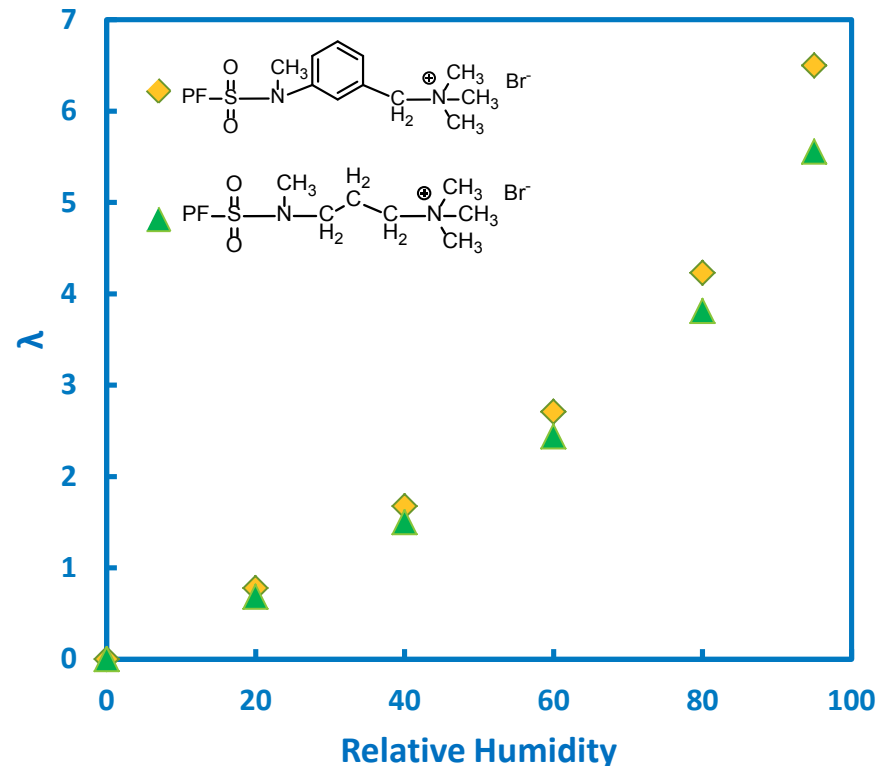
Amide alkyl linkage



Alkyl linked system also investigated, but of lower interest due to potential of Hoffman attack (β hydrogen elimination). Br-form conductivities (alkyl linked system) somewhat lower than those of aryl linked systems, in spite of nearly identical water uptake values.

Infinite Dilution Diffusion Coefficient D_{∞} (cm²/s)

Cl ⁻	Br ⁻	I ⁻	PF ₆ ⁻
2.032	2.080	2.045	1.515



Collaborations

Institutions	Role
<u>National Renewable Energy Laboratory (NREL):</u> Bryan Pivovar (PI), Matt Sturgeon, Clay Macomber, Dan Ruddy, Hai Long	Prime, Oversees the project, lead novel PF AEM synthesis (Grignard); thermal characterization of polymers, DFT calculations
<u>Colorado School of Mines (CSM):</u> Mei-Chen Kuo, Zach Page-Belknap, Andy Herring	Sub; synthesis of PF AEM polymers/ membranes; water uptake and conductivity.
<u>3M (3M):</u> Krzysztof Lewinski, Mike Yandrasits, Steve Hamrock	Sub; Consulting on novel chemistries; preparation of solutions and dispersions; membrane fabrication.
<u>CellEra (CellEra):</u> Shimshon Gottesfeld, Dario Dekel	Sub; MEA fabrication; fuel cell testing and characterization

Remaining Challenges and Barriers

Polymer Synthesis/Membrane Fabrication:

- Reproducibility/Better quantifications of properties
- Investigation including OH⁻ form
- Titration to evaluate IEC
- Durability testing of membranes
- Higher quality membranes

Dispersion/Solution Preparation:

- Ability to form or optimize solution/dispersions for electrodes and membrane fabrication.

Fuel Cell Testing:

- Application of membranes and dispersions as fuel cells and fuel cell membranes including performance and durability testing.

Future Work

Membrane Synthesis:

Scaling up of established chemistry, focus on aryl amide linkage

Characterization:

Expand membrane characterization to include OH⁻ form and more complete data set including (titration to evaluate IEC). Durability testing of membranes

Dispersion/Solution Preparation:

Ability to form or optimize solution/dispersions for electrodes and membrane fabrication. Higher temperature processing. Increase solvents

Membrane Fabrication:

Higher quality membranes

Fuel Cell Testing:

Application of membranes and dispersions as fuel cells and fuel cell membranes including performance and durability testing.

Summary

- **Relevance:** Developing advanced PF AEMs for improved performance AMFCs.
- **Approach:** Developing novel PF AEM chemistry, transitioning to membrane fabrication, and fuel cell performance.
- **Accomplishments and Progress:** The project has demonstrated multiple PF AEM chemistries that have spacer groups separating cation from PF backbone. We have synthesized significant quantities of polymers (>150g). We have developed and demonstrated novel Grignard chemistry to allow more facile functionalization of the PF-SFP. Polymers/membranes have been characterized using a variety of techniques including IR, NMR, TGA, DSC, conductivity, and water uptake.
- **Collaborations:** We have a diverse team of researchers including 1 national labs, 1 university, and 2 industry participants that are leaders in the relevant fields of PF polymer electrolytes/dispersions(3M) and AMFC stack and system development (CellEra).
- **Proposed Future Research:** Focused on improved membrane fabrication and increased fuel cell testing with novel PF AEMs as membranes and ionomers in electrodes.

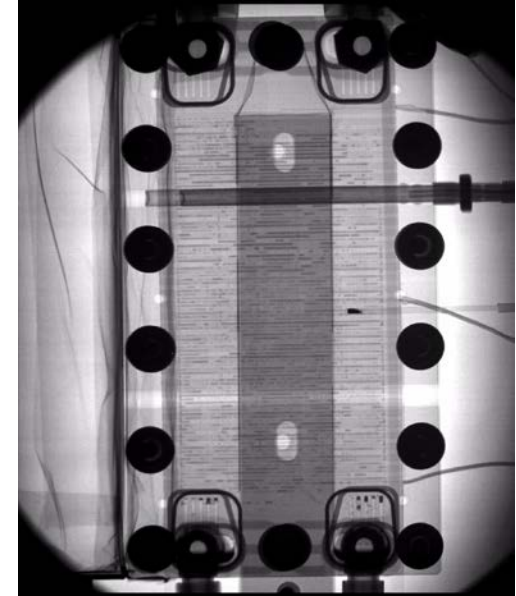
Technical Backup Slides

Relevance/Approach

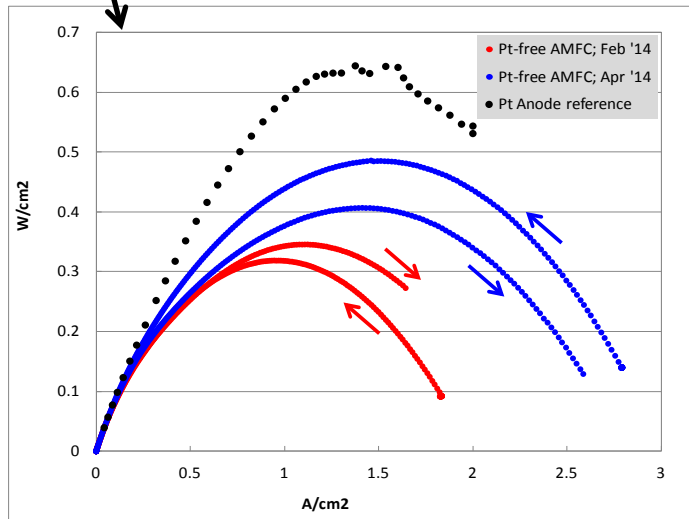
CellEra advances made outside of this DOE funded project

- Significant advances made at Cellera in 2014, working for the moment with state-of-the-art hydrocarbon AEMs*.
- They include:
 - Reaching high fuel utilization by dead-ended anode operation, assisted by neutron imaging
 - Substantial improvement in longevity
 - Further closing of the performance gap vs. PEMFCs (next slide)
 - Operation w/o any Pt catalyst in the cell

* This 2014 work (supported from non-DOE sources) keeps pointing to the great value of higher water transport rates in the ionomer and membrane of the AMFC and, hence, the expected important role of a PF AEM as an enabling element.

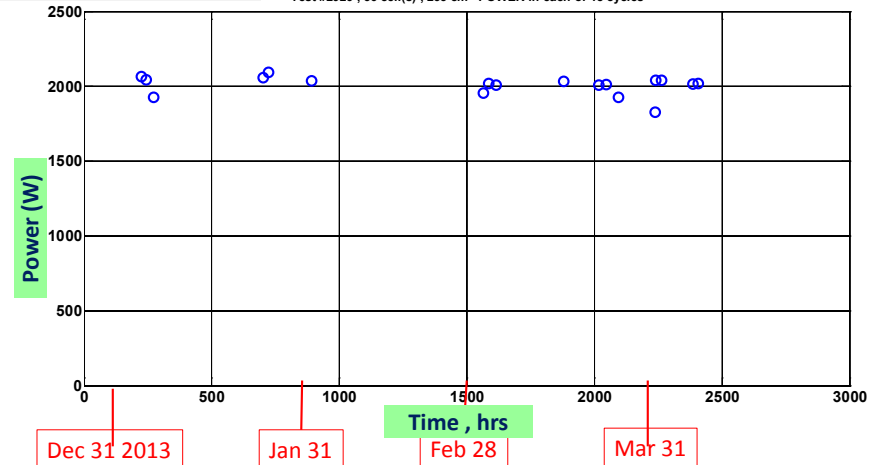


2kW AMFC H₂/Air Back-up Power Stack



• Voltage: 0.55V/cell;

Test #2926 ; 56 cell(s) ; 235 cm² POWER in each of 18 cycles

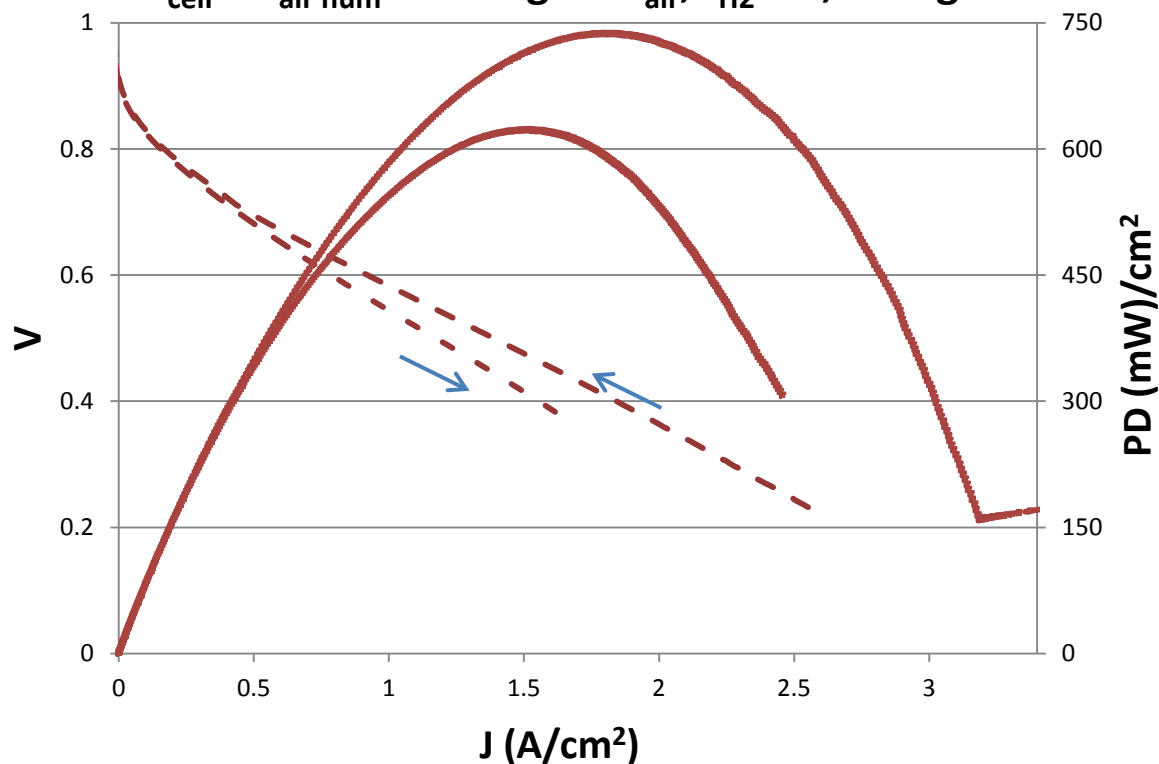


Relevance/Approach

Need for PF AEMs with higher water transport rates

Polarization curve for 5 cm² Cellera AMFC (polyhydrocarbon membrane)

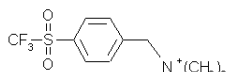
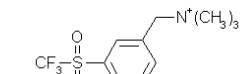

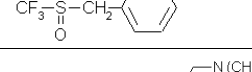
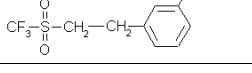
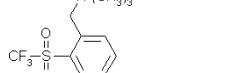
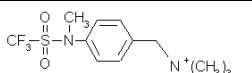
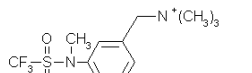
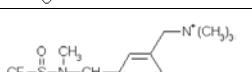

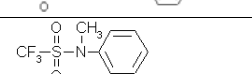
$T_{\text{cell}} = T_{\text{air hum}} = 60 \text{ degC.}$ $P_{\text{air}}; P_{\text{H}_2} = 0; 3 \text{ barg.}$



In a small cell, Cellera's AMFC performance approaches that of a PEMFC. Water management conditions including a fully humidified air stream and excessive flow of hydrogen to offset the decreased water transport properties of hydrocarbon polymer electrolytes compared to PF electrolytes. This means that given the potential water management advantages of PF AEMs, performances approaching those of PEM systems should be achievable.

Accomplishments and Progress

Summary of DFT studies

	Attack on benzyl	Attack on methyl	Attack on SO ₂ N(CH ₃) methyl	Attack on S
	21.4	23.1	NA	13.5
	22.1	24.1	NA	13.8
	24.6	26.1	NA	19.7
	23.6	25.2	NA	16.9
	22.4	24.2	NA	15.5
	22.6	24.4	27.7	19.4
	23.4	24.5	29.5	22.0
	24.1	26.0	34.2	20.7
	24.1	25.2	32.7	27.4(?)
	27.1	24.1	25.5	18.9
	Not calculating	Not calculating	30.1	23.4

DFT calculations (showing hydroxide attack energy barriers) on 11 (out of more than 30) PF sulfonyl ammonium salts containing potential linkage chemistries are shown. These calculations are used as a guide to our synthetic approach. Two main linkages (direct aryl and amide) were pursued.

Methods:

- DFT calculation using Gaussian 09.
- Reactants and transition state structures were optimized at B3LYP/6-311++G(2d,p) level with PCM solvation and their free energies (G) were computed.
- The transition state free energy barrier was calculated by $\Delta G^\ddagger = G([A-B]^\ddagger) - G(A) - G(B)$

Reference:

- Pivovar *et al*, *J. Phys. Chem. C*, v116, 9419-9426.

Accomplishments and Progress

Salt form exchange to investigate thermal processing of PF AEMs

Material	Td in air [°C]	Decomp steps	Tg in Argon [°C]	Mp [°C]	%H2O Loss RT-200°C	% Loss Total	Comments
SFP	402	2	N/O	N/O	0	99.5	Pre/post melt, flow
Iodide	400	5	N/O	N/O	12	81.5/93.5	Pre/post powder darker
Octanoate	409	4 to 5	N/O	N/O	13	79/92	Pre/post powder darker
Hexafluoro	330	2	N/O	N/O	0	94	Pre/post chunks darker
Butyric	401	2 to 3	N/O	N/O	9	86.5/95.5	Pre/post chunks darker
Sulfonimide	349	3	N/O	N/O	2	95/97	Pre/post chunks darker
Triamine	402	2	N/O	N/O	0	98	Pre/post glob darker
3M PFSA Ionomer (H ⁺)	360/451	4	N/O	N/O	6.5	99	Pre/post odor flow, charring

Summary of TGA/DSC results investigating different salt forms has been unable to find a melting point for any of the ionomers investigated with all results relatively consistent except for the decomposition temperature (T_d) and water uptake (although initial hydration conditions were not closely controlled).