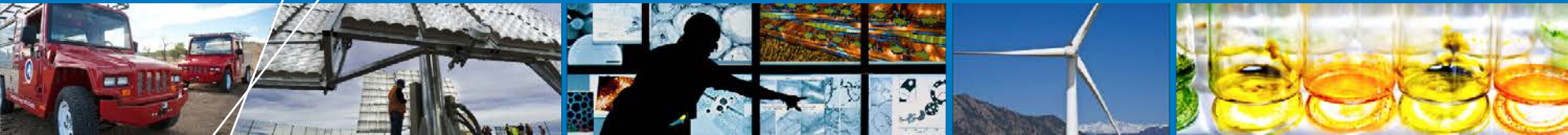# Advanced Ionomers & MEAs for Alkaline Membrane Fuel Cells

2015 DOE Hydrogen and Fuel Cells Program Review

Bryan Pivovar (PI)

June 11, 2015

FC108

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

Overview

Timeline

- **Start: April 2013**
- **End: Oct 2015**
- **% complete: 60%**

Barriers

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

Budget ($K)

DOE Cost Share	Team Cost Share	TOTAL
2000	500	2500

- FY14 DOE Funding: $1000K
- Planned FY15 DOE Funding: $400K
- Total Project Value: $2.5M
- Cost Share Percentage: 20%

Partners – Principal Investigators

CellEra – Shimshon Gottesfeld
3M – Krzysztof Lewinski
Colorado School of Mines – Andy Herring

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°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°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.
- Employ high performance PF AEM materials in electrodes and as membranes in alkaline membrane fuel cells.

Approach
FY 14/15 Milestones

Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
Q3	6/30/2014	Regular	Report (and compare to CellEra baseline) AMFC performance of 3 novel MEAs using PF AEM materials.	**Completed on time (See technical Back up Slide # 28)**
Q4	9/30/2014	Stretch	Demonstrate PF AEMs with 5 x 10-10 m2/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)	**Completed on time**

| Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
Q1	12/31/2014	Quarterly progress measure	Produce at least 2 m2 of novel PF AEM membranes for systematic studies of properties including mechanical and chemical stability.	**Completed on time**
Q4	9/30/2015	Milestone	Demonstrate MEA performance >350 mW/cm2 employing novel PF AEMs in CO2 free environments.	**TBD**

Approach
PF AEM Materials – Targeted Sulfonyl Linkages and Specific Chemistries
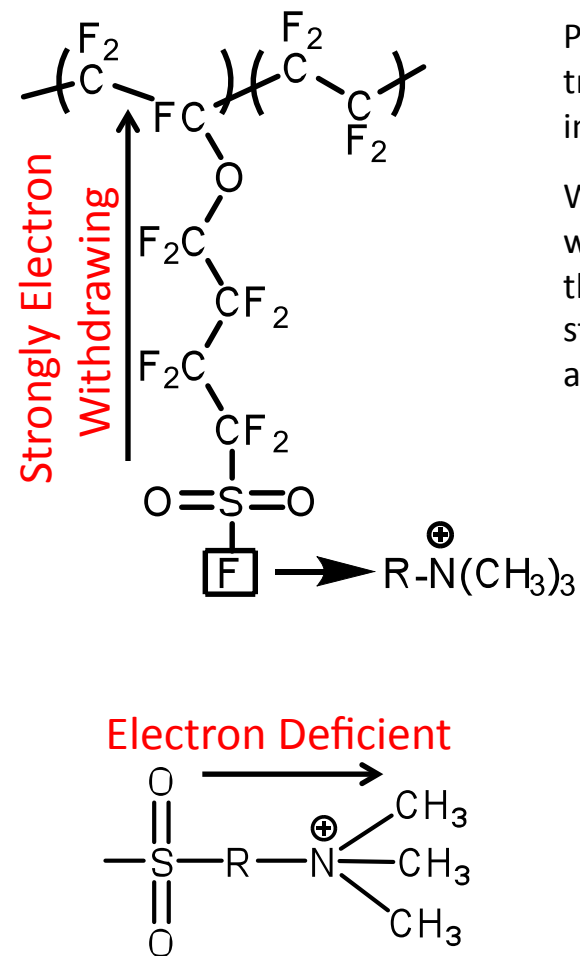
Perfluoro (PF) polymer electrolytes exhibit chemical robustness, enhanced water transport and conductivity properties (see slides 18 and 24 for further supporting information).

While PF chemistry improves PF sulfonic acid (PFSA) acidity, the strongly electron withdrawing PF backbone creates challenges for anion exchange membranes. From the readily available perfluoro sulfonyl fluoride precursor (PF-SFP), different strategies can be employed to tether cations to the PF-SFP. We have focused on 2 an amide linkage and an aryl/alkyl linkage employing Grignard reagents.

Strongly Electron Withdrawing

Electron Deficient

Amide Linkage

3-amino-N,N-dimethybenzenylamine + PF-SFP Perfluoro-sulfonylfluoride
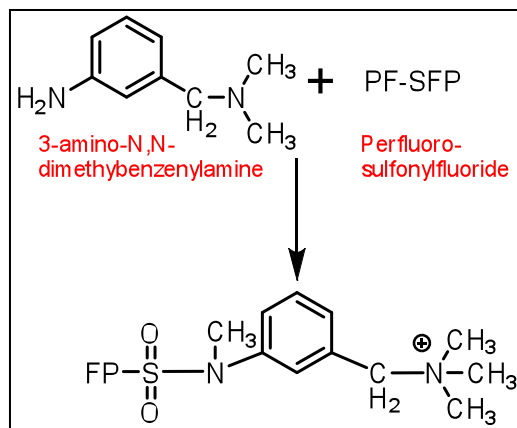
The sulfonamide linkage is demonstrated chemistry[1] and has been employed industrially to synthesize PF AEMs such as Tosflex®.

Aryl/Alkyl Linkage

N,N-dimethybenzenylamine-3-magnesiumbromide Grignard reagent + PF-SFP Perfluoro-sulfonylfluoride
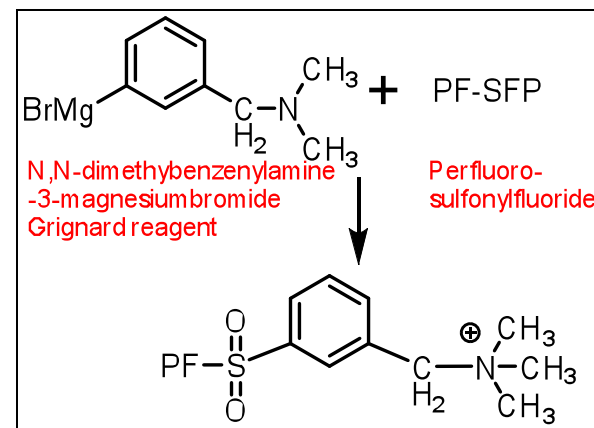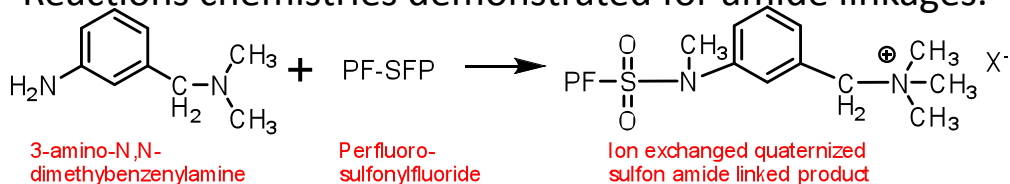
Strategies for amide-free linkages are less developed. We have targeted Grignard reagents as a type of "clip on" chemistry amenable to several different well defined end groups onto PF-SFP sidechains.
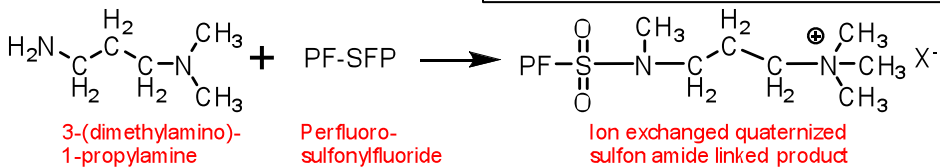
[1]Matsui, K. (1987). *U.S. Patent No.* 4659744.

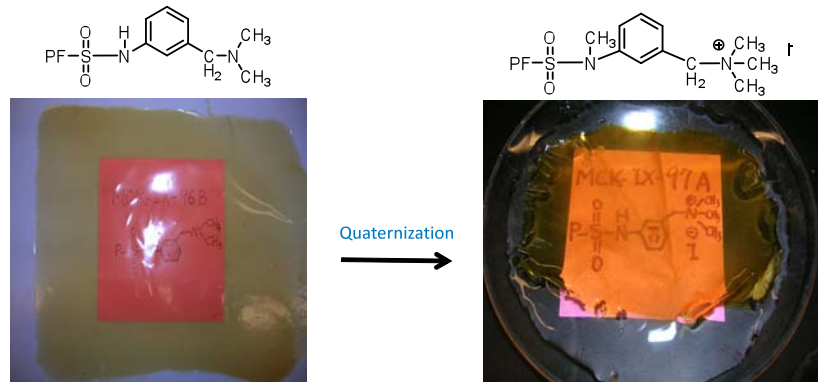# Accomplishments and Progress
Amide linkages (2014 AMR)

Reactions chemistries demonstrated for amide linkages.

3-amino-N,N-dimethybenzenylamine + PF-SFP → Ion exchanged quaternized sulfon amide linked product

3-amino-N,N-dimethybenzenylamine

Perfluoro-sulfonylfluoride

Ion exchanged quaternized sulfon amide linked product

X = I, Br, Cl
Total of 50 g synthesized (April 2014).

3-(dimethylamino)-1-propylamine + PF-SFP → Ion exchanged quaternized sulfon amide linked product

3-(dimethylamino)-1-propylamine

Perfluoro-sulfonylfluoride

Ion exchanged quaternized sulfon amide linked product

X = I, Br, Cl, PF6
Total of 30 g synthesized (April 2014).
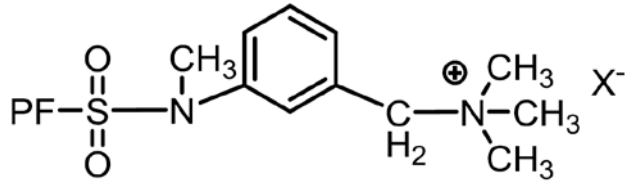

Pink paper is 3" x 3"

Quaternization

Membranes supplied to CellEra

As of 2014 AMR, we had synthesized many grams of amide linked polymer, cast films and shown good water uptake and conductivity in halide salt form membranes.
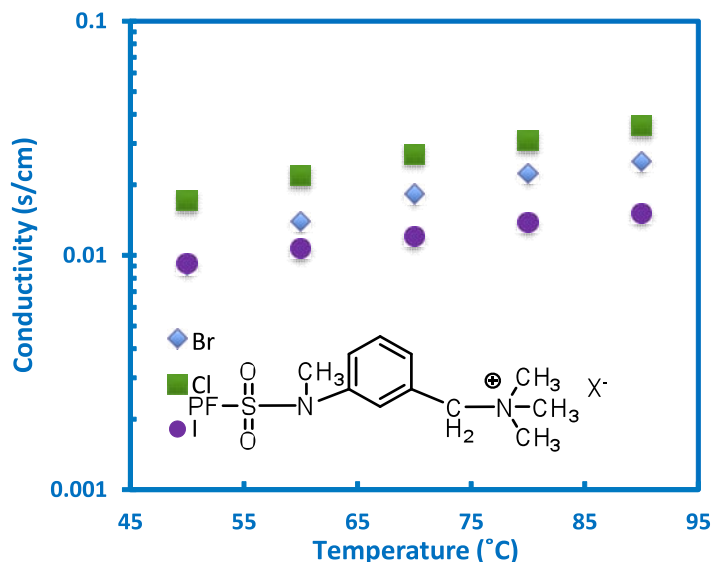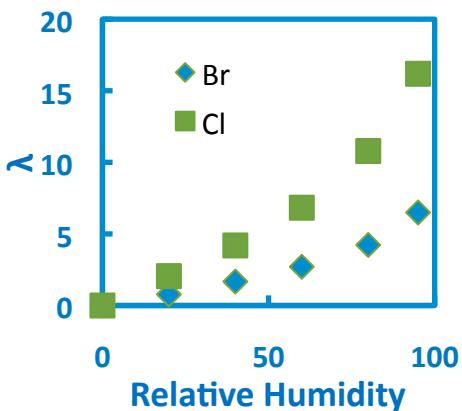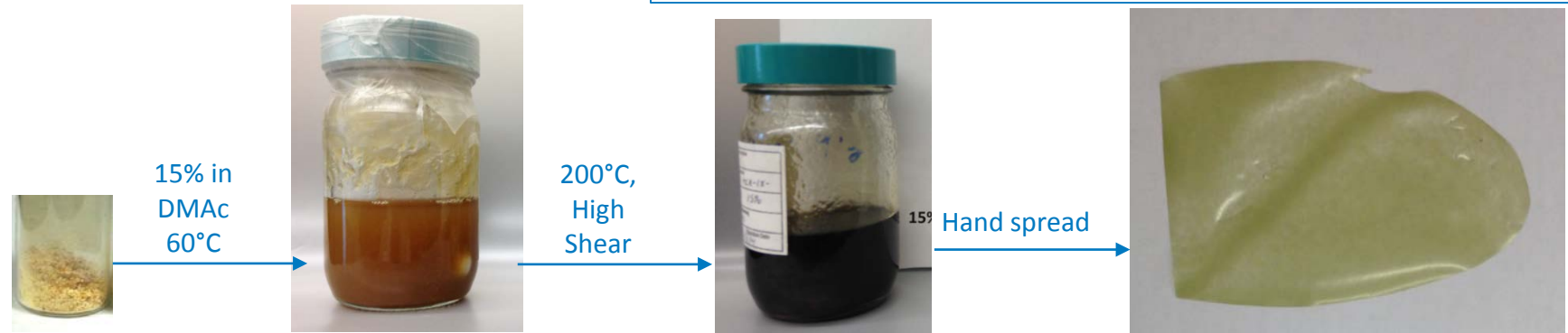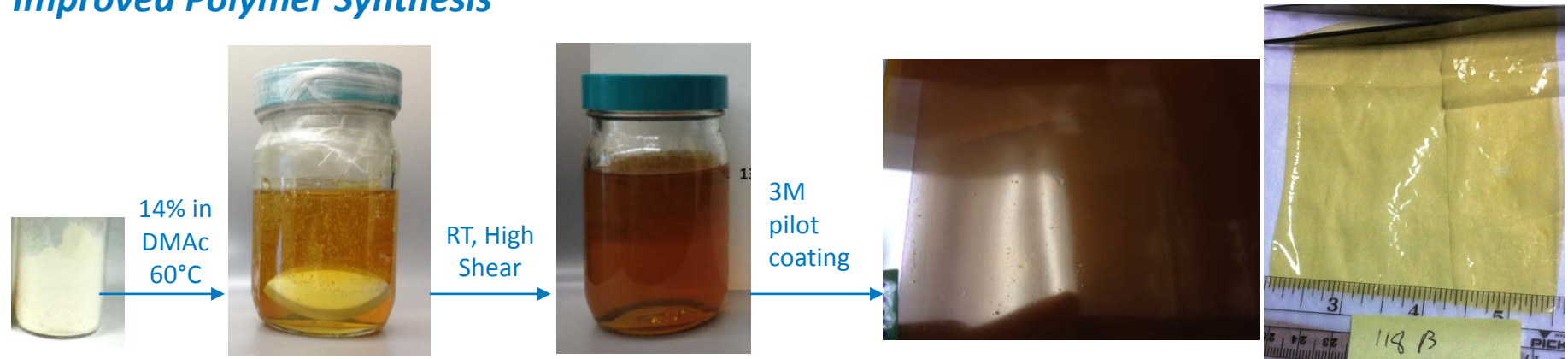
Accomplishments and Progress
Improved polymers, polymer solutions, and membranes

- Early polymers were difficult to dissolve and cast into high quality films
- Improved synthesis resulted in better solutions and pilot scale casting
- Increased quantities (100's grams polymers and sq. meters membrane) obtained

First Polymer Synthesis

15% in DMAc 60°C → 200°C, High Shear → 15% → Hand spread

Improved Polymer Synthesis

14% in DMAc 60°C → RT, High Shear → 3M pilot coating

118 β

Accomplishments and Progress
Polymer chemical structure identified including zwitterionic polymer

**'Target' methylated sulfonamide**

10%

+

Protonated sulfonamide

90%
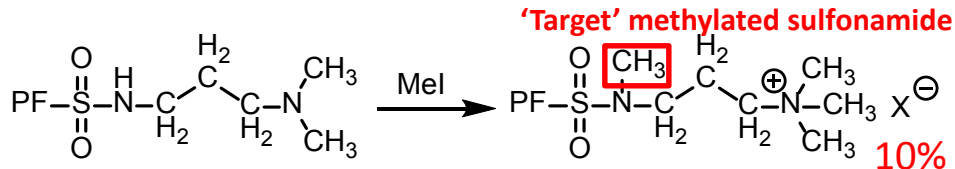
The highest sulfonamide methylation quantified in early materials was only 10% (shown in ^{1}H NMR). Many samples showed no signs of methylation.
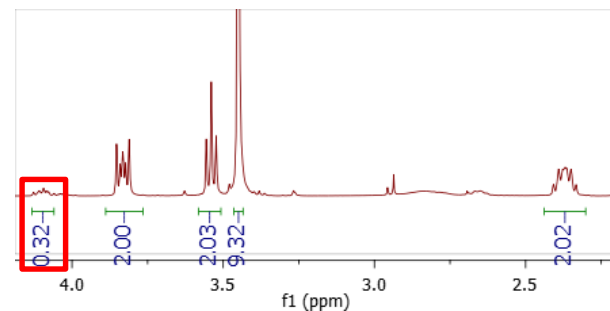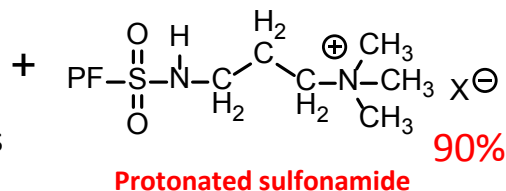
Identification of zwitterionic polymer: The protonated sulfonamide has high, recoverable conductivity in the halide salt form (Cl form shown). But on exposure to base (OH⁻), forms a zwitterion due to acidity of sulfonamide proton (with significantly decreased conductivity).

NaOH

HCl

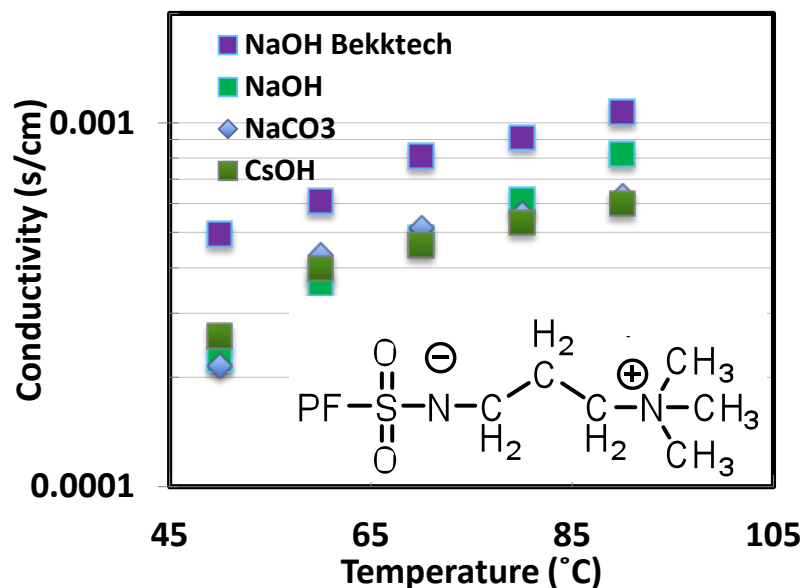**zwitterionic polymer**

Recoverable Conductivity

HCl

NaOH

HCl_1
NaOH
HCl_2

Conductivity (s/cm)

Temperature (°C)
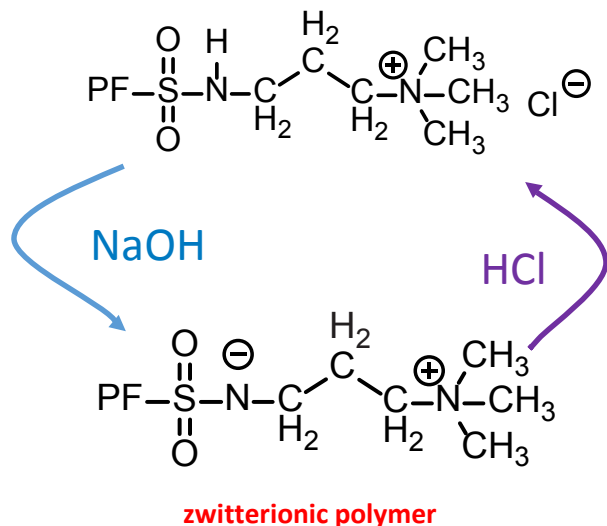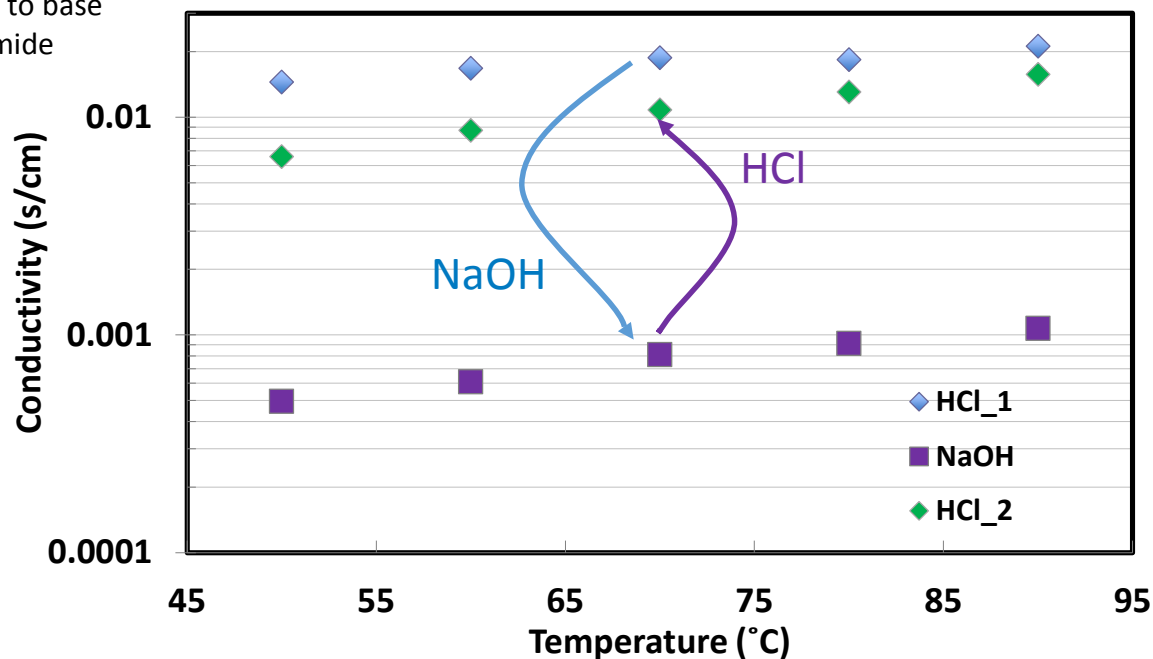
Accomplishments and Progress
Probing zwitterionic conductivity to understand process and limits

Zwitterionic membrane still showed measurable conductivity. Anion and cation exchange was used to probe the state of the polymer. Only when CO_2 was excluded did the conductivity of the membrane change (Bekktech). Suggesting anion conduction through the membrane (with hydroxide converting to carbonate form upon exposure to air).
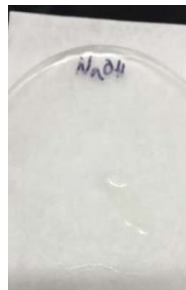

Titration with HCl

Thymophthalein treatment (pH 9.4-10.6)
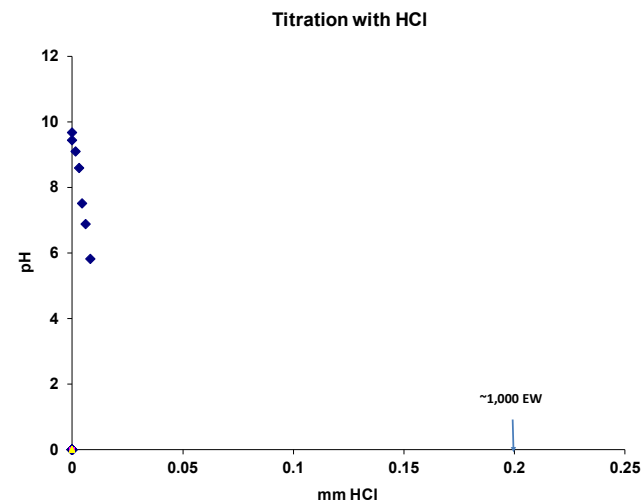

In N_2 glove box (visible blue color)

Outside glove box for 15 min (slight blue color)

Outside glove box for 1 hour (no blue color)

pH sensitive dye, showed a basic membrane that converted to a less basic form upon exposure to CO_2.
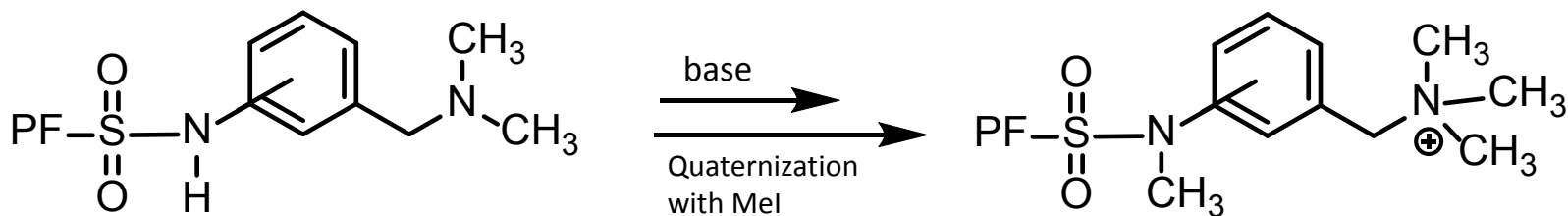
Ion exchange with NaCl followed by titration with acid showed an ion exchange capacity ~20x less than side chain density. Demonstrating that only a small fraction of side chains remained in a hydroxide/carbonate associated state.
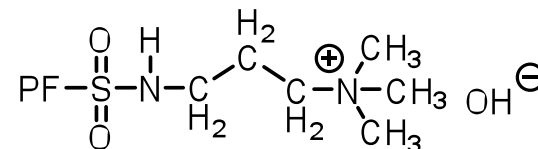
Accomplishments and Progress
## Methylation of sulfonamide linkage

Improved methylation of sulfonamide linkage has been pursued by modified methylation strategy. An added step to activate the N-H bond with a base has resulted in improved reaction efficiency.

Ion Exchange Solution:	Ionic Conductivity (mS/cm)
I⁻ form	3
1 M NaOH	10
1 M NaCl (after 1 M NaOH)	17
1 M HCl	19
1 M NaOH (after 1 M HCl)	8

When tested under DI water equilibrated conditions at room temperature, hydroxide conductivities greatly increased compared to zwitterionic form. Higher conductivity of Cl⁻ form suggest incomplete reaction or stability concerns.

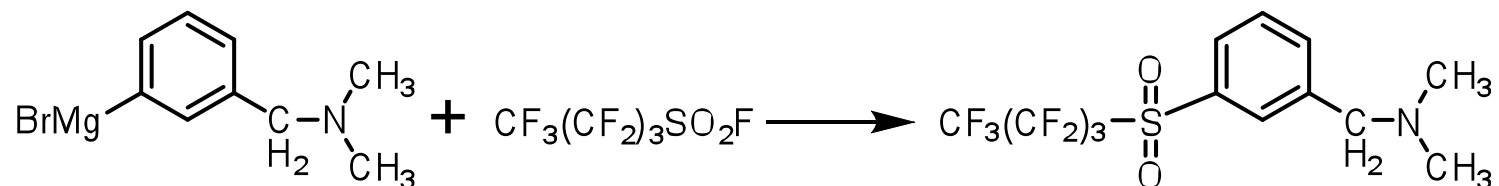Films exhibited good mechanical properties.
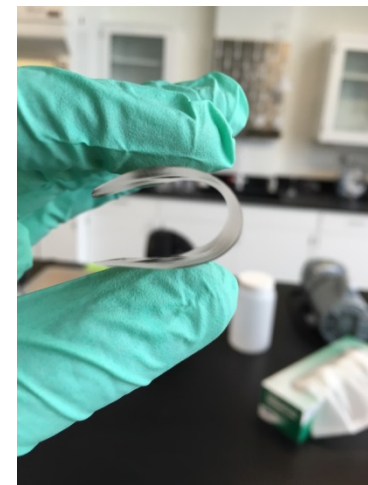
Secondary amine route presented in supplemental slide #27.

Accomplishments and Progress
Grignard Chemistry

Grignard chemistry successful in small molecules

Grignard chemistry avoids the formation of acidic sulfonamide proton, but has significant challenges in applying to polymeric systems in large part due to solubility issues at different stages of reaction. Typical PF ionomers synthesis benefits from swelling of reacted phases.

Products verified via NMR and IR (2014 AMR)

hydrolysis

amide

Grignard
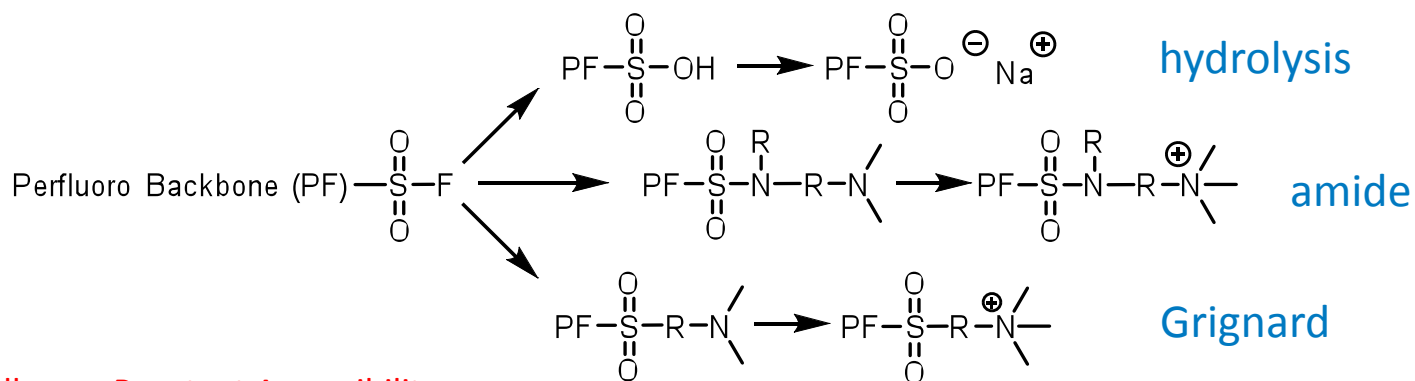
Challenge: Reactant Accessibility

For PFSAs, the hydrolysis conversion of $-SO_2F$ to $-SO_3H$ sites results in a soluble polymer.

The amide linkage creates a swellable intermediate that is processable in carbonyl amide solvents (DMF, NMP, DMAc).

Grignard chemistries are not compatible with carbonyl amide solvents and therefore have to proceed through an intermediate that does not easily swell, creating reactant accessibility challenges.

Accomplishments and Progress
Varying Grignard Chemistry Approaches

Explored known Grignard solvents (2014)

THF was used in the production of the Grignard reagent but would not swell PF-SFP polymer.
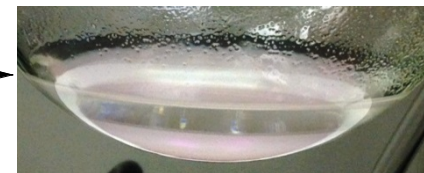
Preswelling PF-SFP in dimethoxy ether (DME) resulted in increased swelling/reaction compared to THF, but still incomplete sulfonyl fluoride conversion.

Product polymer could not be processed into ionomer solution.

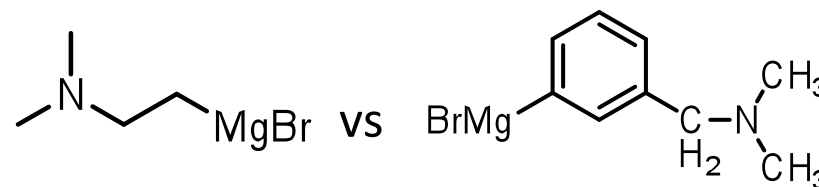Swollen PF-SFP

PF-SFP

Crude Product

Dried product

Heterogeneous pressed film

Modifying Grignard reagents

Explore reagents with less steric hindrance.

VS

Exploring alternative solvents

Few solvents are known to dissolve PF-SFP form polymer. Solvents also need to be suitable for Grignard chemistry.

Modified Grignard Reagents

Short, straight chain dimethylamino – alkyl Grignard reagents were explored to potentially alleviate solubility/steric concerns.

Targeted ethyl and butyl chain lengths were found to be unstable.
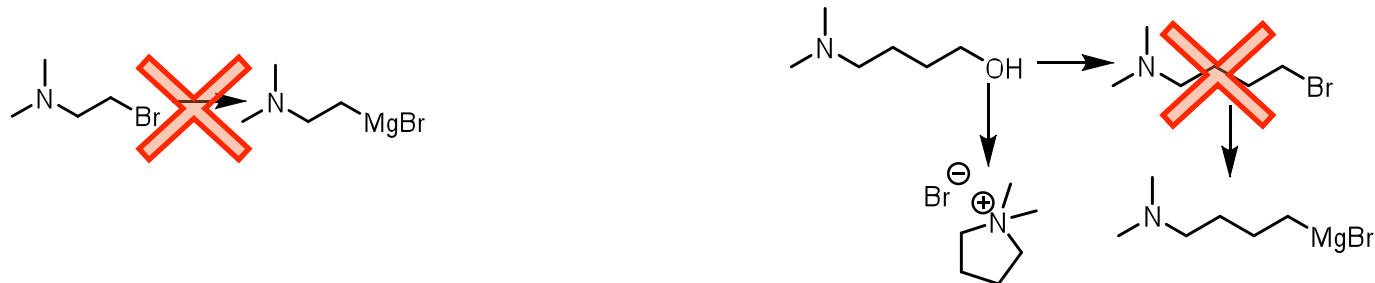
Longer alkyl chains may be stable, but have increased solubility/steric concerns for polymer incorporation, as well as increased hydrophobicity.

Accomplishments and Progress
Hydro Fluoro Ethers (HFEs) as alternate solvent systems

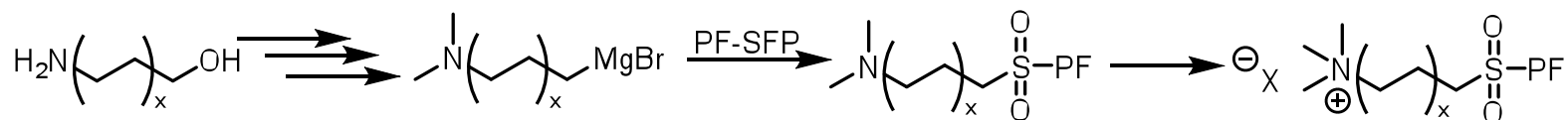Increasing EW →

Increasing hydrocarbon character of solvent ↓

620 EW (8%)
3M Novec™ 7100
C_4F_9-O-CH_3

702 EW (5%)
3M Novec™ 7100
C_4F_9-O-CH_3

798 EW (5%)
3M Novec™ 7100
C_4F_9-O-CH_3

702 EW (5%)
3M Novec™ 7200
C_4F_9-O-C_2H_5

798 EW (5%)
3M Novec™ 7200
C_4F_9-O-C_2H_5

HFE General Structure:
C_nF_{2n+1}-O-C_mH_{2m+1}
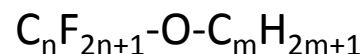
Dissolving PFSA sulfonyl fluoride starting polymer

- Polymer is soluble in a limited number of highly fluorinated fluids.
- Both polymer and reactants need to be soluble.
- 3M Novec™ Engineered HFE fluids are good candidates for reaction solvents due to semi-fluorinated character.
- <725 EW ionomer forms true solution in Novec™ 7100 & 7200 fluids

Accomplishments and Progress
Screening Grignard chemistry in HFEs

¹H and ¹⁹F NMR used to evaluate Grignard chemistry in HFEs.

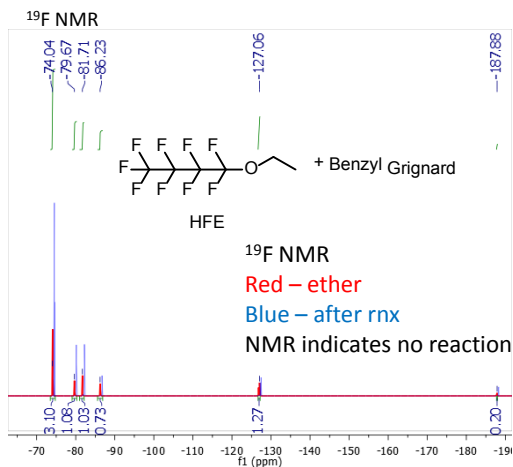Grignard reactants found to be stable/non-reacting with HFEs.

Solubility of Grignard reagent/HFE combinations tested to date, have displayed some solubility limitation that improved with temperature.
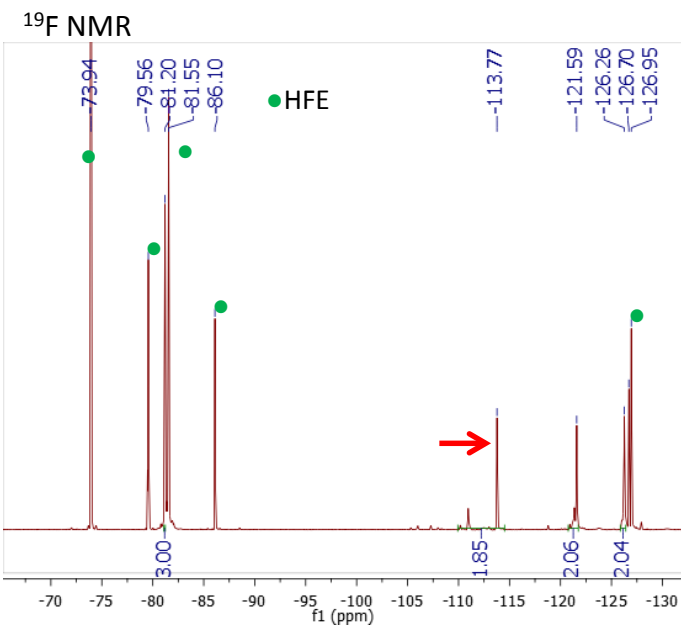
Initial small molecule screening studies have shown Grignard chemistry in HFE to be successful.
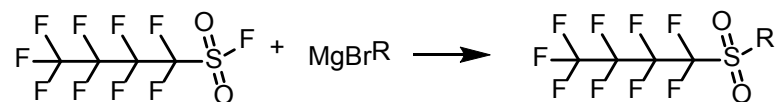
Perfluoro sulfonyl fluoride model compound (C4F9SO2F) was reacted with a Grignard reagent in HFE. Shift of 108 ppm peak to 113.77 ppm (red arrow) interpreted as conversion of sulfonyl fluoride to alkyl group.

Accomplishments and Progress
Modeling of carbonate formation and equilibrium in AEMs

Carbonate formation is a known source of performance loss for hydroxide conducting fuel cells.

Scrubbing CO_2 from air has been employed as a mitigation technique, but self-purge has also been promoted as a viable approach to prevent carbonate related losses. Fundamentally, the carbonate/bicarbonate/hydroxide equilibrium is poorly understood.
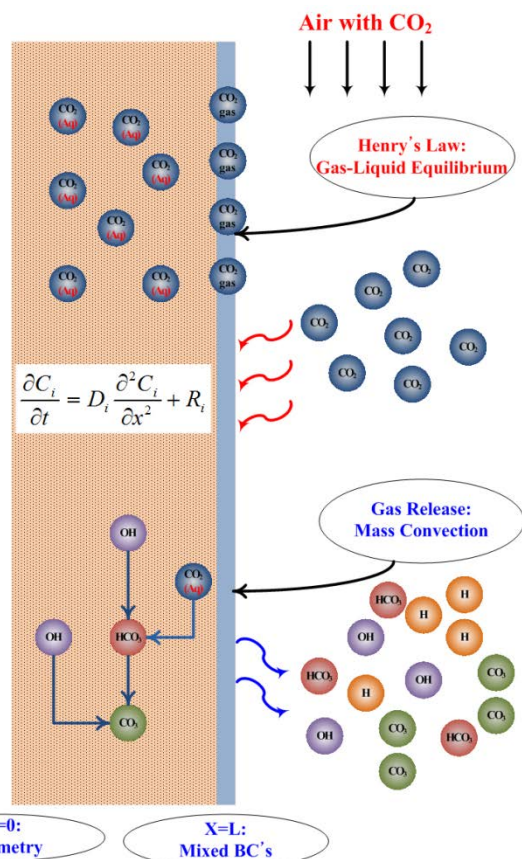

Gas-Liquid Equilibrium: Henry's Law
→ Explains CO_2 dissociation into water (membrane)

R0: $$CO_{2(g)} \xleftrightarrow{K_0} CO_{2(AQ)}$$
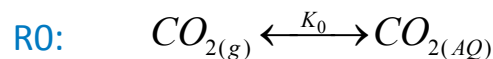
Reaction Equation of Membrane Neutralization
→ Kinetics of CO_2 dissociation

R1: $$CO_2 + OH^- \xrightarrow{k_{OH}} HCO_3^-$$

R2: $$HCO_3^- + OH^- \xleftrightarrow{k_{2f}, k_{2b}} CO_3^{2-} + H_2O$$

R3: $$H^+ + OH^- \xleftrightarrow{k_{3f}, k_{3b}} H_2O$$

R4: $$CO_2 + H_2O \xleftrightarrow{k_{4f}, k_{4b}} HCO_3^- + H^+$$
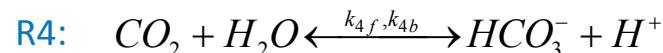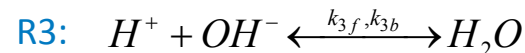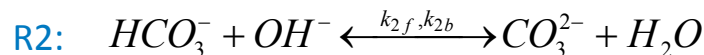
In collaboration with Prof. Sangseok Yu (Chungnam National University)

Accomplishments and Progress
Modeling of carbonate formation and equilibrium in AEMs
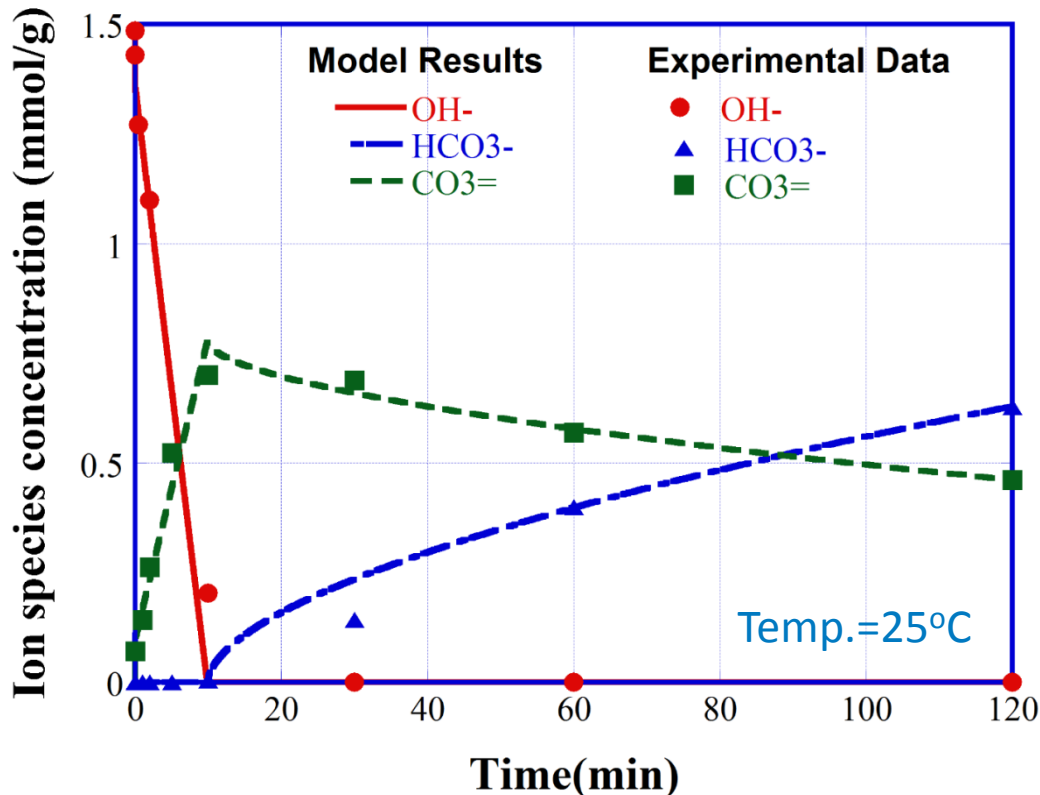
Experimental data from Yanagi, H. and K. Fukuta, ECS Transactions, 2008. **16**(2): p. 257-262.

Data from Tokuyama has shown that hydroxide form membranes is quickly converted to carbonate/bicarbonate when exposed to ambient air (400 ppm CO_2).

The thermodynamics and kinetics of this uptake had not yet been explained computationally. Our modeling results show good agreement with experimental measurements, and can be extended to longer times (equilibrium conditions) and be used to perform parametric studies investigating membrane thickness, CO_2 concentration and temperature.

The model developed can be combined with a fuel cell performance model to probe the needs for CO_2 scrubbing, the losses associated with carbonate formation, and the limits of self-purge under ambient conditions to remove CO_2 from the system.

Accomplishments and Progress
Responses to Previous Year (2014 AMR) Reviewer's Comments

- **Reviewer Comment:** While the PIs are correct that the PF-based electrolyte was proved superior in cation exchange membranes, this does not directly translate into AEMs. In fact, as the PIs pointed out, PF can cause chemical stability issues in AEM due to strong electron-withdrawing PF backbones. It is also debatable whether to expect higher OH- conductivity by using PF backbone in AEMs. Again, the strong electron-withdrawing backbone helps to form stronger acid in proton exchange membranes, but in AEMs, the same PF backbone may cause a weaker base.

- **Reviewer Comment:** The base for the project is questionable. It is unclear why fluorinated polymer is needed with the hydrocarbon polymer. Amide alkyl has C-H bonds. The whole idea does not make sense.

- **Response:** While, in general, the approach to the project was seen very favorably by reviewers in the 2014 AMR (2 review bullets out of 11 had strong criticism for the approach). Perhaps, in part, because the rationale for the approach was presented less in the 2014 AMR compared to the 2013 AMR. A specific slide has been added to the Technical Backup Slide Section (#24) to address this, but the 2013 AMR presentation also goes into deeper detail. Regarding the first reviewers comments above. PF electrolytes impart higher water transport and conductivity due to improved phase separation not acid or base strength (unless very weak acids or bases are used). Base strength in these systems is related to the stability of the cations used, as hydroxide, unlike protons, cannot form a covalent bond with the ionic group without degrading the ionic group (nuetral acid forms exist that can later deprotonate, but hydroxide attacks and degrades cations typically forming alcohols). Therefore, if the cation is stable the hydroxide is available for conduction. For the second reviewers comment, in acidic systems it is important to remove C-H bonds from the system due to stability concerns with peroxide that aren't the same in basic conditions (C-H bonded systems can be stable). The use of PF polymers is to take advantage of PF transport properties and is presented in more detail on slide #24.

- **Reviewer Comment:** Particularly disappointing is the lack of characterization capabilities at this point in the project. Using other anions as a proxy is OK; however, eventually these characterizations have to be done in the -OH form.

- **Response:** This has been addressed throughout this year's presentation. The recognition of zwitterions was critical to our understanding of performance and our earlier concerns with hydroxide stability.

- **Reviewer Comment:** The only clear contribution of NREL is the DFT modeling. The PI should indicate on each slide, where appropriate, the material and information coming from each organization. The roles of the participants in the project are unclear.

- **Response:** The team has regular (biweekly) web based meetings where NREL and CSM are in the same room and 3M joins virtually and there is significant overlap in the contributions of NREL, CSM and 3M. The specific roles have been called out more specifically on the collaboration slide (#19).

Collaborations

Institutions	Role
National Renewable Energy Laboratory (NREL): Bryan Pivovar (PI), Matt Sturgeon, Dan Ruddy, Andrew Park, Zbyslaw Owczarczyk, Hai Long	**Prime, Oversees the project, lead novel PF AEM synthesis (all Grignard, majority of small molecule, and some amide work), PF AEM characterization, modeling**
Colorado School of Mines (CSM): Mei-Chen Kuo, Zach Page-Belknap, Andy Herring	**Sub; synthesis of PF AEM polymers (amide linkage), membranes characterization (water uptake and conductivity).**
3M (3M): Krzysztof Lewinski, Mike Yandrasits, Steve Hamrock	**Sub; Consulting on novel chemistries; preparation of solutions and dispersions; membrane fabrication.**
CellEra (CellEra): Shimshon Gottesfeld, Dario Dekel	**Sub; MEA fabrication; fuel cell testing and characterization (reduced role past year)**
Chungnam University Sangseok Yu	**In kind; modeling of carbonate poisoning.**

Remaining Challenges and Barriers

- ## Polymer Synthesis:
  - Solubility/chemistry concerns for PF AEM synthesis
    - Amide linkages
    - Aryl/Alkyl linkages (Grignard)

- ## Dispersion/Solution Preparation:
  - Optimize solution/dispersions for electrodes and membrane fabrication.
  - Durability testing of membranes
  - Mechanical properties of membranes

- ## Fuel Cell Testing:
  - Application of membranes and dispersions as fuel cells and fuel cell membranes including performance and durability testing.

Future Work

- ## Membrane Synthesis:
  - Improved methylation/Secondary amine tethering for non-protic sulfonamide linkage.
  - Grignard (or related) chemistry in HFEs

- ## Characterization:
  - Continued characterization along the lines of that currently on-going

- ## Modeling
  - Parametric studies looking at temperature, membrane thickness, and CO_2 concentration

- ## Dispersion Preparation, Membrane Casting, MEA fabrication/Fuel Cell Testing:
  - To be performed after target polymers are achieved

Summary

- **Relevance:** Developing advanced PF AEMs for improved performance AMFCs.

- **Approach:** Developing novel PF AEM chemistry based on readily available sulfonyl fluoride precursor.

- **Accomplishments and Progress:** The project has explored multiple PF AEM chemistries for amide and aryl/alkyl linkages (Grignard). We have improved our polymer synthesis and membrane casting, but have obtained only zwitterionic polymers from amide linkages. We have further investigated novel Grignard chemistry, and have shown PF-SFP solubility and Grignard viability in HFEs. We have developed and applied models to evaluate carbonate uptake/poisoning in AMFCs.

- **Collaborations:** We have a diverse team of researchers including 1 national labs, 2 universities, 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 polymer synthesis as the critical enabling element toward AEMs in energy applications.

Technical Backup Slides

Our approach focuses on achieving **higher-temperature, higher-power-density AMFC operation** through implementation of **novel alkaline perfluoro (PF) membranes and ionomeric dispersions**. The PF materials proposed are expected to enhance water transport capabilities and electrode performance/durability significantly, thereby enabling higher temperature and power density operation. The combination of high current density and operating temperature will improve the ability of these devices to tolerate ambient CO_2, potentially enabling complete tolerance to ambient CO_2.
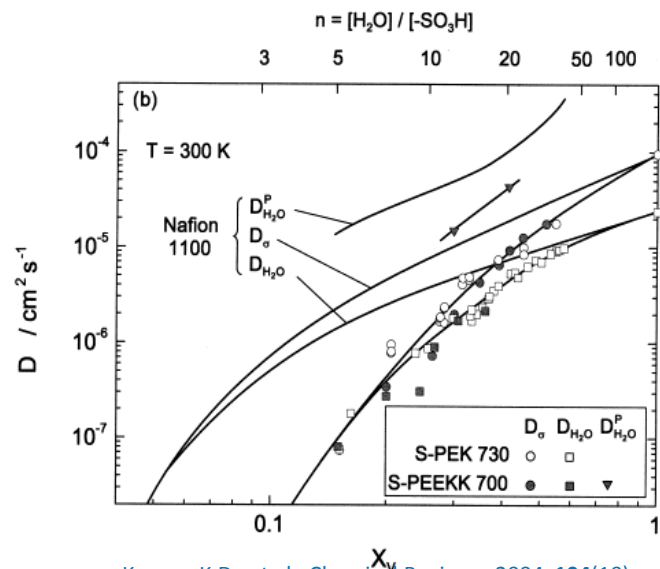
Kreuer, K.D., et al., Chemical Reviews, 2004. **104**(10): p. 4637-4678

Most AEMs are based on hydrocarbon polymer chemistry. From significant work in the area of PEMs, water transport and conductivity has been shown to be **significantly higher in PF polymers**, particularly at lower hydration levels.

While perfluoro membranes are electron withdrawing, as long as cations remain chemically stable, hydroxide is a free cation and should not have losses associated with decreased basicity compared to hydrocarbon membranes.

Perhaps the most exciting advance in the AEM area in the past decade has come from the high hydroxide stabilities of covalently tetherable cations recently reported. At this point in time, we feel clear that cations with high hydroxide stability have been demonstrated. Demonstrating these cations in high performance polymers is the remaining challenge

Our team through BES funded efforts in cation stability have quantified benzyltrimethyl ammonium (BTMA$^+$) stability at 80°C of less than 10% degradation after 5,000 hours, and a half-life of over 4 years. Stability capable of enabling several applications.
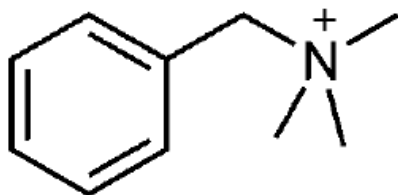
Kreuer and Marino have shown multiple cations with increased stability relative to BTMA$^+$, with 6-azonia-spiro[5.5]undecane showing a 20x improvement in base stability.
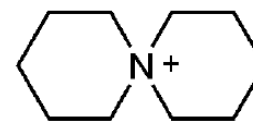
6-azonia-spiro[5.5]undecane

Marino, M.G. and K.D. Kreuer, Chemsuschem, 2015. **8**(3): p. 513-523

BTMA$^+$

M Sturgeon, C Macomber, C Engtrakul, H Long, and B Pivovar, J. Electrochem. Soc., 162 (4) F366-F372 (2015).

# Accomplishments and Progress
Mechanical Property Investigation

Sample	Tensile Strength (Mpa)	Young's Modulus (Mpa)	Elongation (%)	Thickness (μm)
Non-Annealed	6.2 ± 0.9	289 ± 73	3.6% ± 1.4%	34 ± 2.1
Annealed	49 ± 3.2	389 ± 63	13% ± 2.4%	26 ± 1.1

- Drop cast membranes, once removed from the Teflon® substrate, were observed to be highly brittle (iodide form)
- Membranes were annealed at 160 °C and 400 psi for 10 minutes
- Tensile tests were performed at 60 °C and <0% relative humidity
- Non-annealed samples disintegrated before measurement could be conducted at >90% relative humidity
- Annealed samples possessed 8x the tensile strength, 1.3x the Young's modulus and nearly 4x times the degree of elongation
- Cl^- and OH^- ($CO3^{2-}$/$HC03^-$) ion forms were also tested
- Slight decreases in the tensile strength at dry conditions were observed following ion exchange

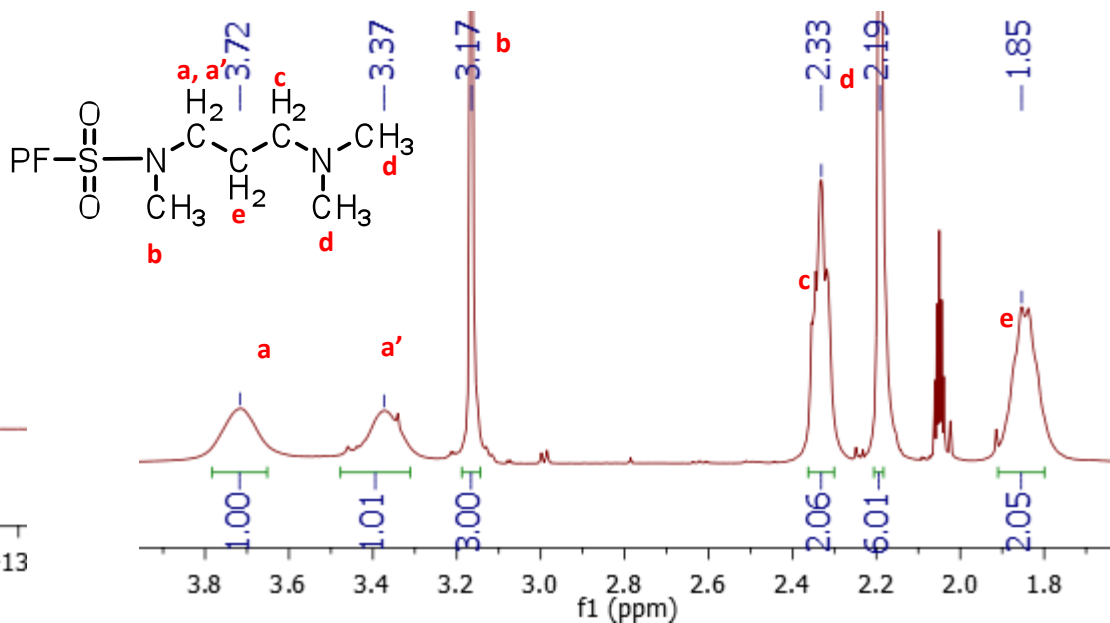| Sample	Tensile Strength (Mpa)	Young's Modulus (Mpa)	Elongation (%)	Thickness (μm)
< 0% Relative Humidity				
HCl	26 ± 2.6	417 ± 44	10% ± 1.9%	57 ± 10
KOH	45 ± 7.2	583 ± 83	15% ± 1.0%	34 ± 2.8
> 90% Relative Humidity				
HCl	5.8 ± 0.8	60 ± 5.8	28% ± 8.2%	41 ± 6.8
KOH	13 ± 2.0	87 ± 16	75% ± 9.1%	29 ± 3.4

Secondary amine as amide reactant
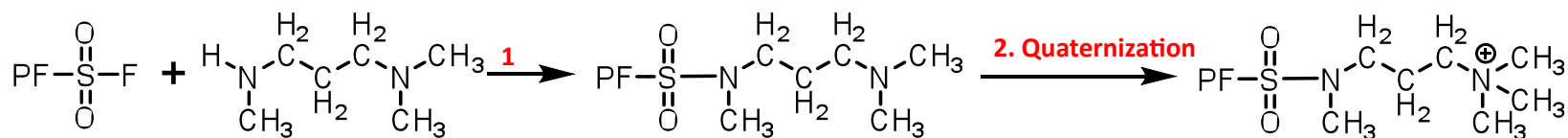
Employing a secondary reactant amine ensures that product obtained is methylated at the sulfonamide position.
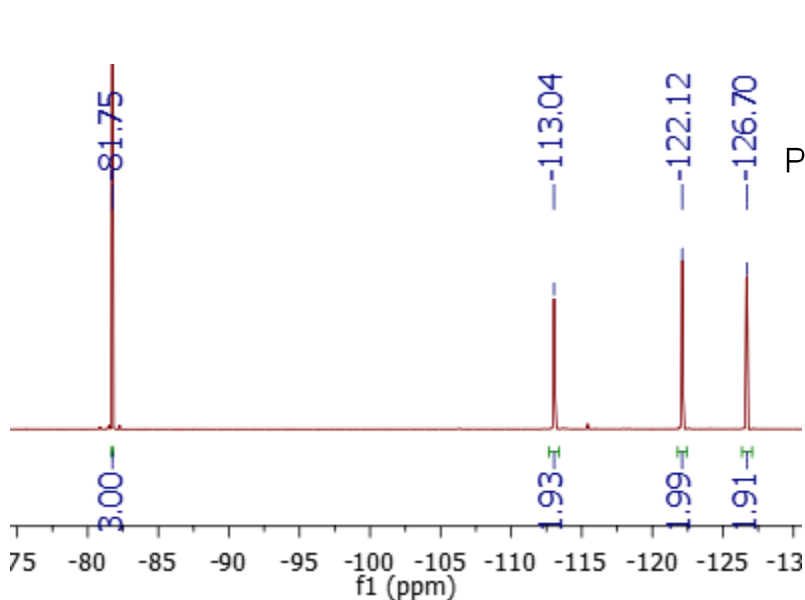
^{19}F NMR of dimethylamino product (after step 1). S-F at 46.12ppm is gone and -108ppm shifted to -113.04ppm.
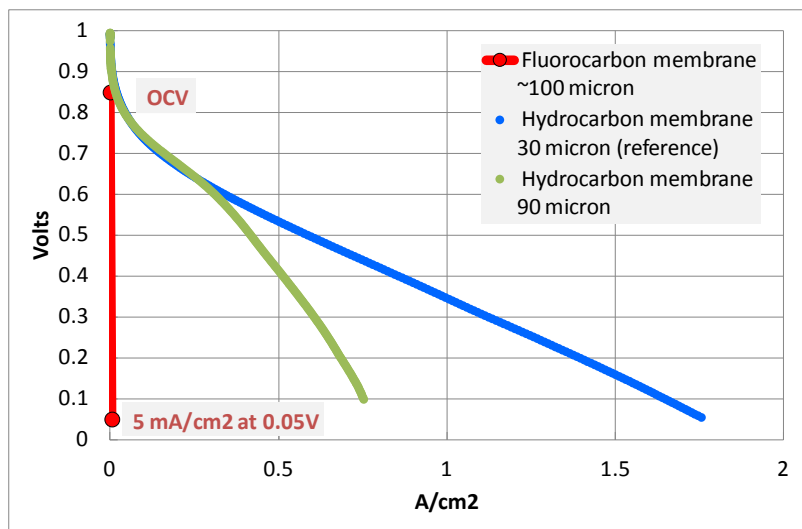
^{1}H NMR dimethylamino product (after step 1). Diastereotopic protons due to limited rotation around sulfonyl linked amine.

NMR of small molecule analogue shows that sulfonyl group has been converted and that the sulfonamide position contains a methyl group.

90 μ PF membrane (red) , 30 μ HC membrane (blue) and 90 μ HC membrane (green) – all with standard cellera GDEs

CellEra tested early amide linked polymers in fuel cells (before we had clear understanding of zwitterionic nature of amide linked materials). Exceptionally low performance now attributed to exceptionally low conductance.

When applied to electrodes, the performance of even the zwitterionic polymers showed surprisingly good performance for low conducting material, even outperforming standard materials at high potential/low current density.
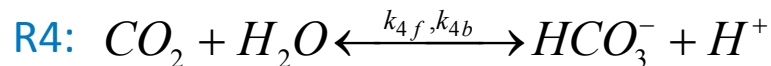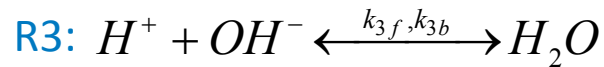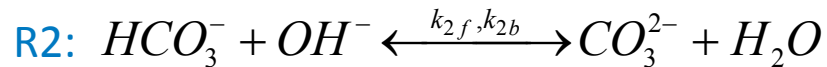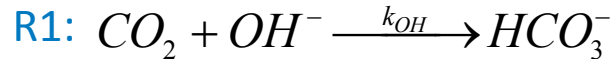
GDE w. recast PF ionomer (red) &GDE with recast HC material (blue); Same HC membrane in both cases
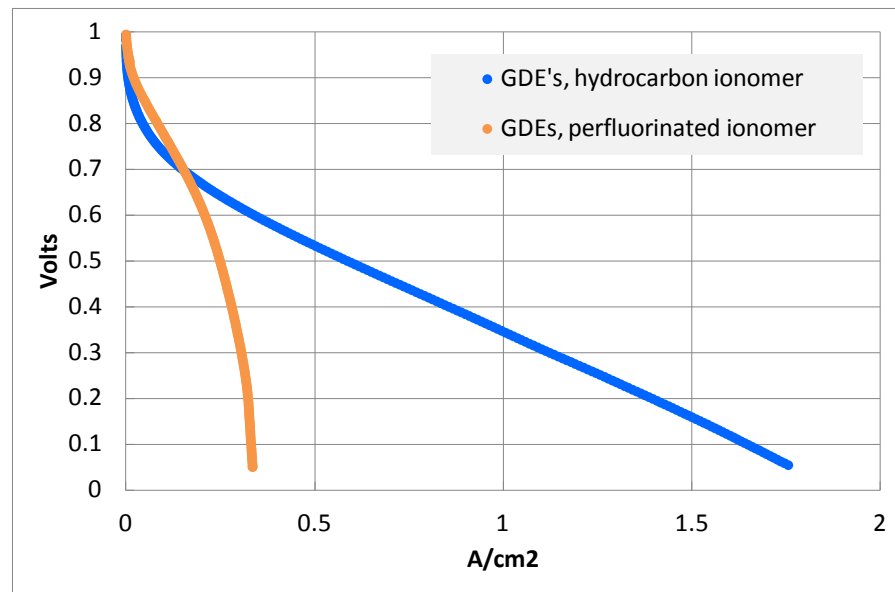
Modeling of carbonate formation and equilibrium in AEMs - Reactions

Species: A: CO_2 B: OH   C: HCO3   D: OH   E: H   F:H_2O

R1: $CO_2 + OH^- \xrightarrow{k_{OH}} HCO_3^-$

R2: $HCO_3^- + OH^- \xleftrightarrow{k_{2f},k_{2b}} CO_3^{2-} + H_2O$

R3: $H^+ + OH^- \xleftrightarrow{k_{3f},k_{3b}} H_2O$

R4: $CO_2 + H_2O \xleftrightarrow{k_{4f},k_{4b}} HCO_3^- + H^+$

$-r_{1A} = +k_{OH}C_A C_B$

$-r_{2C} = +k_{2f}C_B C_C - k_{2b}C_D C_F$

$-r_{3E} = +k_{3f}C_B C_E - k_{3b}C_F$

$-r_{4A} = +k_{4f}C_A C_F - k_{4b}C_C C_E$

Stoichiometric Relation

$$r_A = r_{1A} + r_{4A} = k_{OH}C_A C_B - k_{4f}C_A C_F + k_{4b}C_C C_E$$

$$r_B = r_{1B} + r_{2B} + r_{3B} = k_{OH}C_A C_B - k_{2f}C_B C_C + k_{2b}C_D C_F - k_{3f}C_B C_E + k_{3b}C_F$$
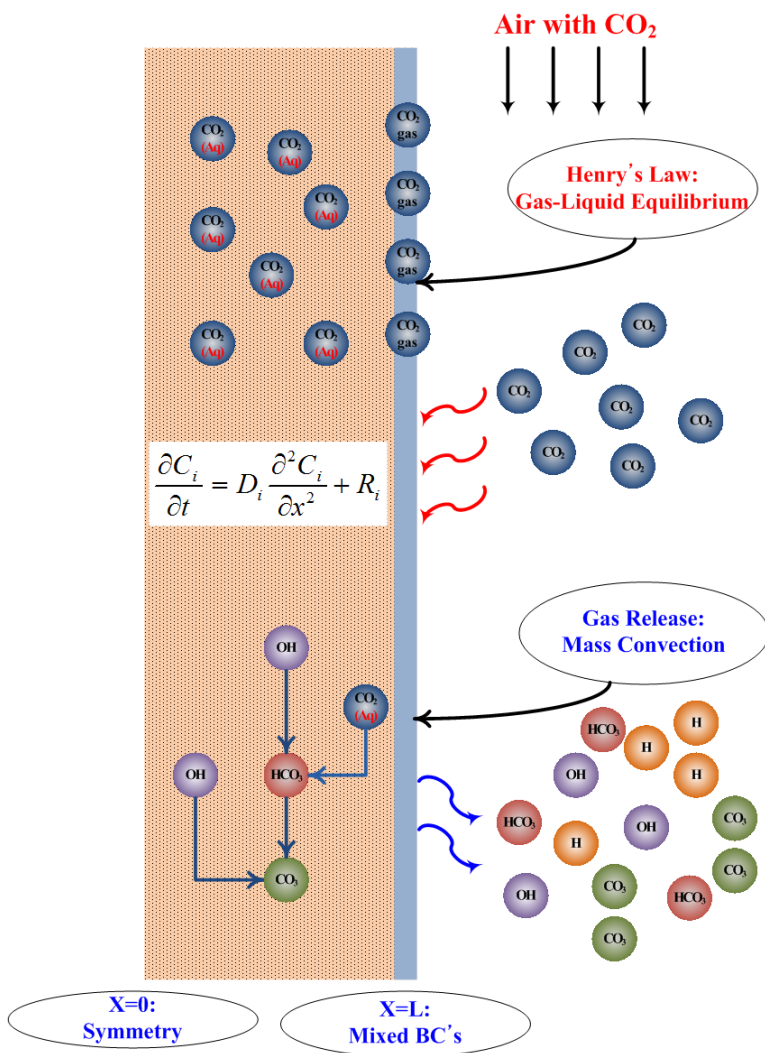
$$r_C = r_{1C} + r_{2C} + r_{4C} = k_{OH}C_A C_B - k_{2f}C_B C_C + k_{2b}C_D C_F + k_{4f}C_A C_F - k_{4b}C_C C_E$$

$$r_D = r_{2D} = k_{2f}C_B C_C - k_{2b}C_D C_F$$

$$r_E = r_{3E} + r_{4E} = -k_{3f}C_B C_E + k_{3b}C_F + k_{4f}C_A C_F - k_{4b}C_C C_E$$

Air with CO_2

Henry's Law:
Gas-Liquid Equilibrium

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + R_i$$

Gas Release:
Mass Convection

X=0:
Symmetry

X=L:
Mixed BC's

$$x = 0 : i = CO_2, OH, HCO_3^-, CO_3^{2-}, H$$

$$\frac{\partial C_i}{\partial x} = 0$$

$$x = L : i = CO_2$$

$$N_{flux,in} = N_{flux,out}$$

$$-D_i \frac{\partial C_i}{\partial x} = h_{d,i} \left(\frac{C_i(L,t)}{Henry} - C_{i,\infty} \right)$$

$$x = L : i = OH, HCO_3^-, CO_3^{2-}, H$$

$$N_{flux,in} = N_{flux,out}$$

$$-D_i \frac{\partial C_i}{\partial x} = h_{d,i} \left(C_i(L,t) - C_{i,\infty} \right)$$