

# Resonance-Stabilized Anion Exchange Polymer Electrolytes

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**Los Alamos National Laboratory**

**Project ID: FC112**

# Overview

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Our previous alkaline membrane fuel cell project was completed on September 30, 2010. This is one year project after two years of break. In this project, LANL focused on the development of anion exchange membrane and ionomer dispersion without subcontractors.

## Time line

- **Project Start:** October 2012
  - **Project End:** September 2013
  - **Percent Complete:** 100
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## Budget

- **FY13 DOE Funding (K)** 150
- **Planned FY 14 DOE Funding (K)** 0
- **Total Project Value (K)** 150

*No cost share*

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## Barriers

- B. Cost
- C. Electrode performance
- A. Durability

## Collaborators/Interactions

- **Sandia Nat. Lab.** Cy Fujimoto
- **DuPont** Shoibal Banerjee
- **Proton OnSite** Kathy Ayers
- **AIST (Japan)<sup>a</sup>** Yoong-Kee Choe
- **KIER (South Korea)<sup>b</sup>** Sung-Dae Yim

<sup>a</sup> National Institute of Advanced Industrial Science and Technology

<sup>b</sup> Korea Institute of Energy Research

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## Project lead

- **Los Alamos National Laboratory**  
Yu Seung Kim (PI)  
Kwan-Soo Lee  
Hoon Chung

# Relevance

## Objective

Develop stable perfluorinated hydroxide-conducting polymers that can be used in AEMFCs

## Technical Barriers

- ❑ Low hydroxide conductivity over the temperature range 40 to 80°C.
- ❑ Formation of mechanically-stable thin membranes.
- ❑ Poor cation & polymer backbone stability under AMFC operating conditions.

## Key Targets

Characteristics	Units	2012 Status <sup>a</sup>	2020 Target <sup>b</sup>
Hydroxide conductivity ( $\sigma$ ) at 80°C	mS/cm	80	125
Membrane formation ability	$\mu\text{m}$ (dry thickness)	60	< 25
Chemical stability after immersion in 0.5M, NaOH at 80°C for 100h	% $\sigma$ decrease	75	0

<sup>a</sup> From our previous project: polyphenylene membrane (ATM-PP): Fujimoto et al. *J. Memb. Sci.* 438-449 (2012)

<sup>b</sup> Based on PEMFC transportation application target; Corresponding areal resistance: < 0.02 Ohm cm<sup>2</sup>

## Milestone

Stable perfluorinated AEM: < 10%  $\sigma$  loss after 100 h in 0.5 M NaOH at 80°C. (Sep. 2013)

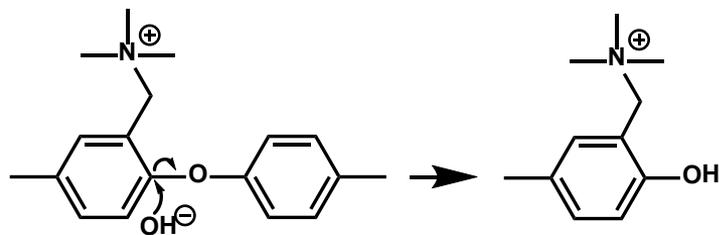
# Approach: Background

## Molecular design aspects for improved stability of alkaline polymers

### ■ Polymer backbone degradation

- ✓ not to use arylene ether polymer

#### Aryl-ether cleavage reaction<sup>a</sup>



Fujimoto et al. *J. Memb. Sci.* 438 (2012)

*In collaboration with Sandia National Laboratory*

### ■ Possible approach

- ✓ Wholly aromatic polyphenylene<sup>a</sup>
- ✓ Polyolefin<sup>b</sup>
- ✓ Perfluorinated polymer

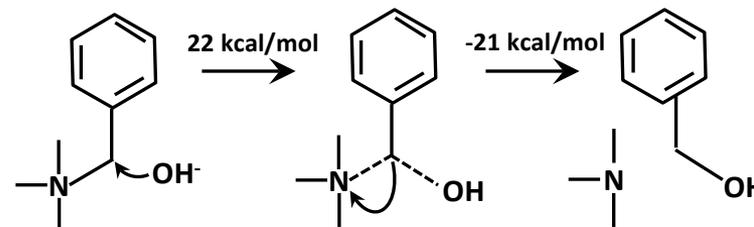
<sup>a</sup> Hibbs et al. *Macromolecules* 8316 (2009)

<sup>b</sup> Kostalik et al. *Macromolecules* 7147 (2010)

### ■ Cation degradation

- ✓ not to use benzyl trimethyl ammonium

#### S<sub>N</sub>2 degradation of hydroxide ion<sup>b</sup>



Choe et al. DFT calculation (2013)

*In collaboration with AIST (Japan)*

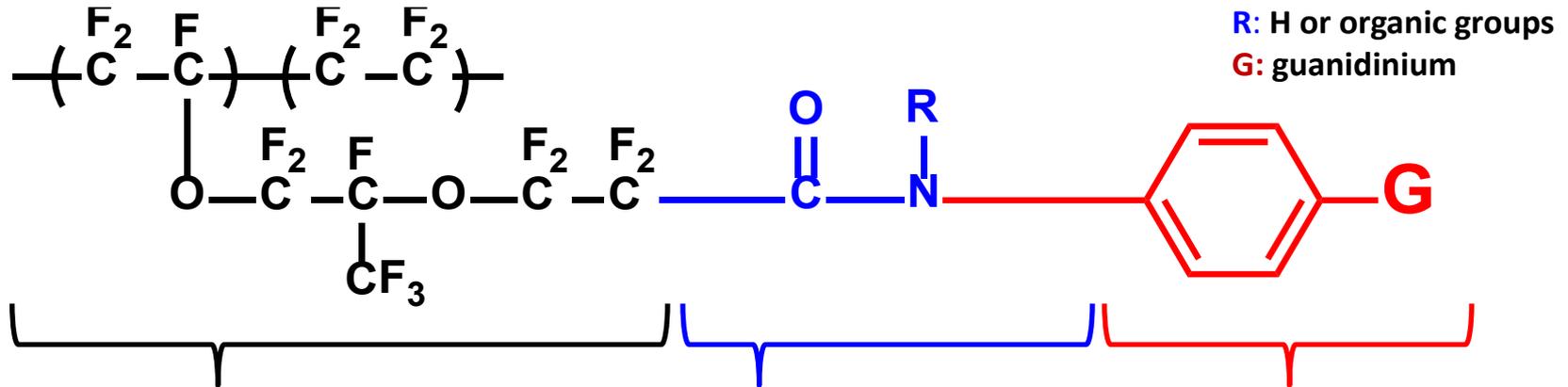
### ■ Possible approach

- ✓ Methyl imidazolium<sup>c</sup>
- ✓ Alkyl ammonium<sup>d</sup>
- ✓ Resonance stabilized guanidinium

<sup>c</sup> Lin et al. *Chem. Mater.* 1858 (2013)

<sup>d</sup> Hibbs, *J. Polym. Sci. Part B* 1736 (2013)

# Approach: Resonance Stabilized Perfluorinated Polymers



## Perfluorinated backbone

- Chemically stable
- Hydrophobic
- Good chain mobility
- Inert to catalytic reaction<sup>1</sup>
- Optimized for MEA
- Commercially available

<sup>1</sup> Reviewers' only (Slide 26)

## Amide linkage

- Chemically stable
- Neutral - not dissociate hydrogen<sup>2</sup>
- High reaction yield
- Hydrogen bonding
- Minimal hydrolysis under high pH conditions<sup>3</sup>

<sup>2</sup> Technical backup (Slide 27)

<sup>3</sup> Slide 12

## Phenyl Guanidinium

- Chemically stable
- High basicity, pKa = 13.6<sup>4</sup>
- Resonance structure<sup>5</sup>
- Low HOR inhibition<sup>6</sup>
- High reaction yield<sup>7</sup>
- Minimal steric hindrance
- Inexpensive

<sup>4</sup> Perrin, Dissociation Constant of Organic Bases, 1972

<sup>5</sup> Technical backup (Slide 22)

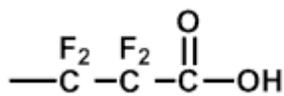
<sup>6</sup> Slide 14

<sup>7</sup> Kim et al. *Chem. Mater.* 3795 (2011)

# Preparation of Membrane & Ionomer Dispersion

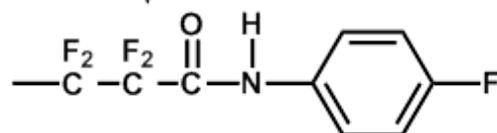
## Synthetic procedure, e.g., PF-Amide-G2

Nafion®  
Precursor\*



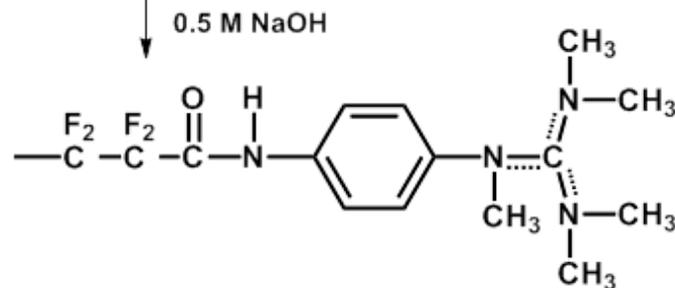
TBAOH  
4-Fluoroaniline at 150°C

Amide  
formation



TMG 150°C, 12 h  
DMS, room temp.

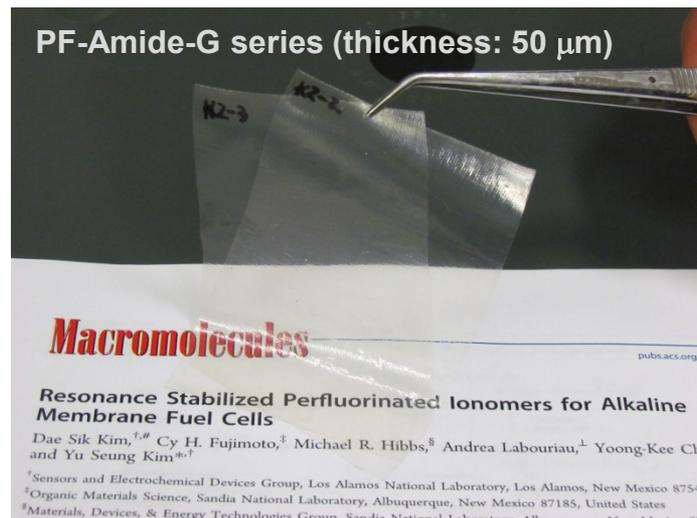
F-amine  
reaction/  
methylation



Spectroscopic data provided in Technical Back-up (Slide 21)

\* *In-kind material support from DuPont*

For general synthetic method, see  
Kim et al. *Macromolecules*, 7826 (2013)



Membrane thickness range: 20 - 50 μm

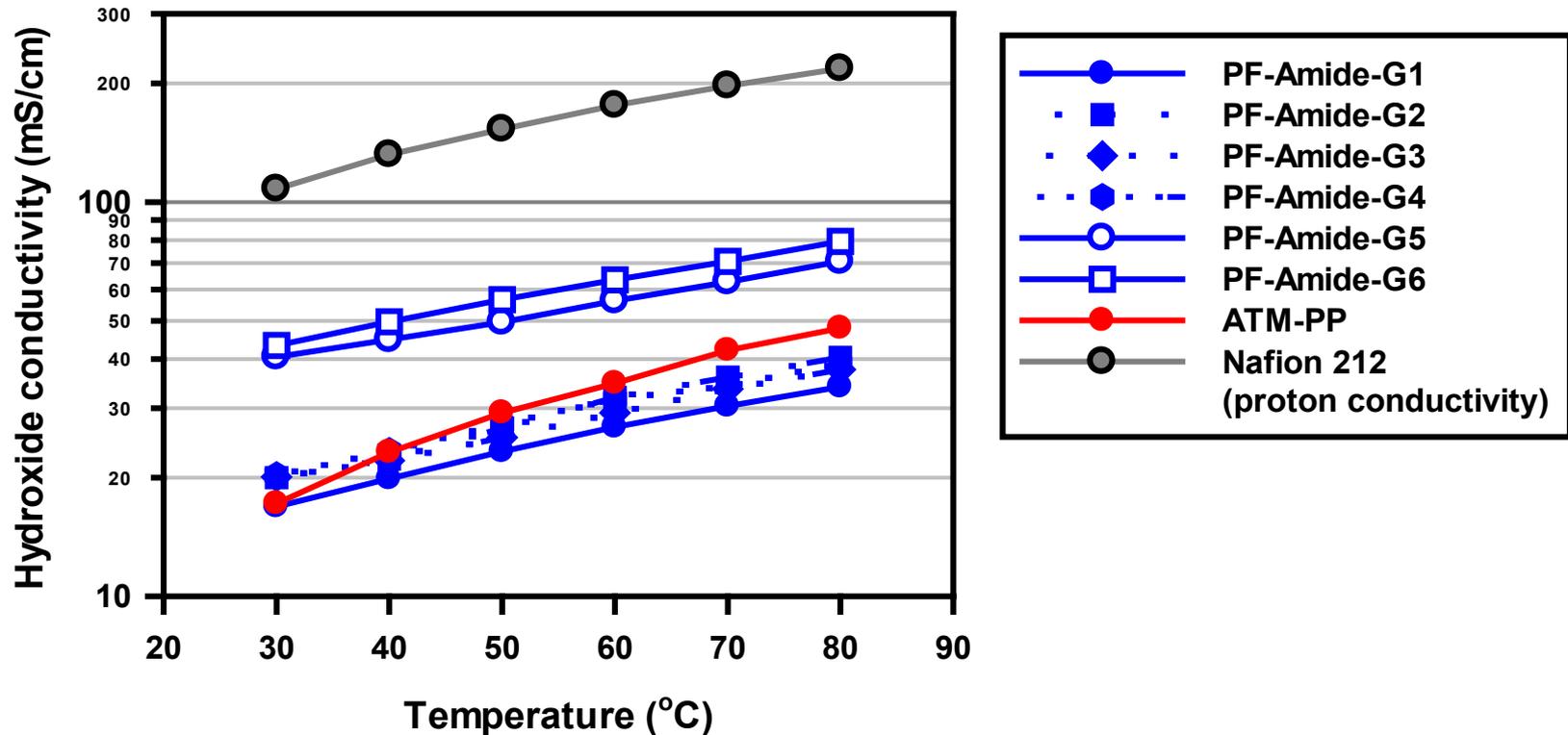
Polymer	IEC <sup>a</sup> (meq/g)	Application
PF-Amide-G1	0.8	Ionomer dispersion
PF-Amide-G2		
PF-Amide-G3		
PF-Amide-G4		
PF-Amide-G5	1.5	Membrane
PF-Amide-G6		

<sup>a</sup> estimated from precursor and <sup>1</sup>H NMR



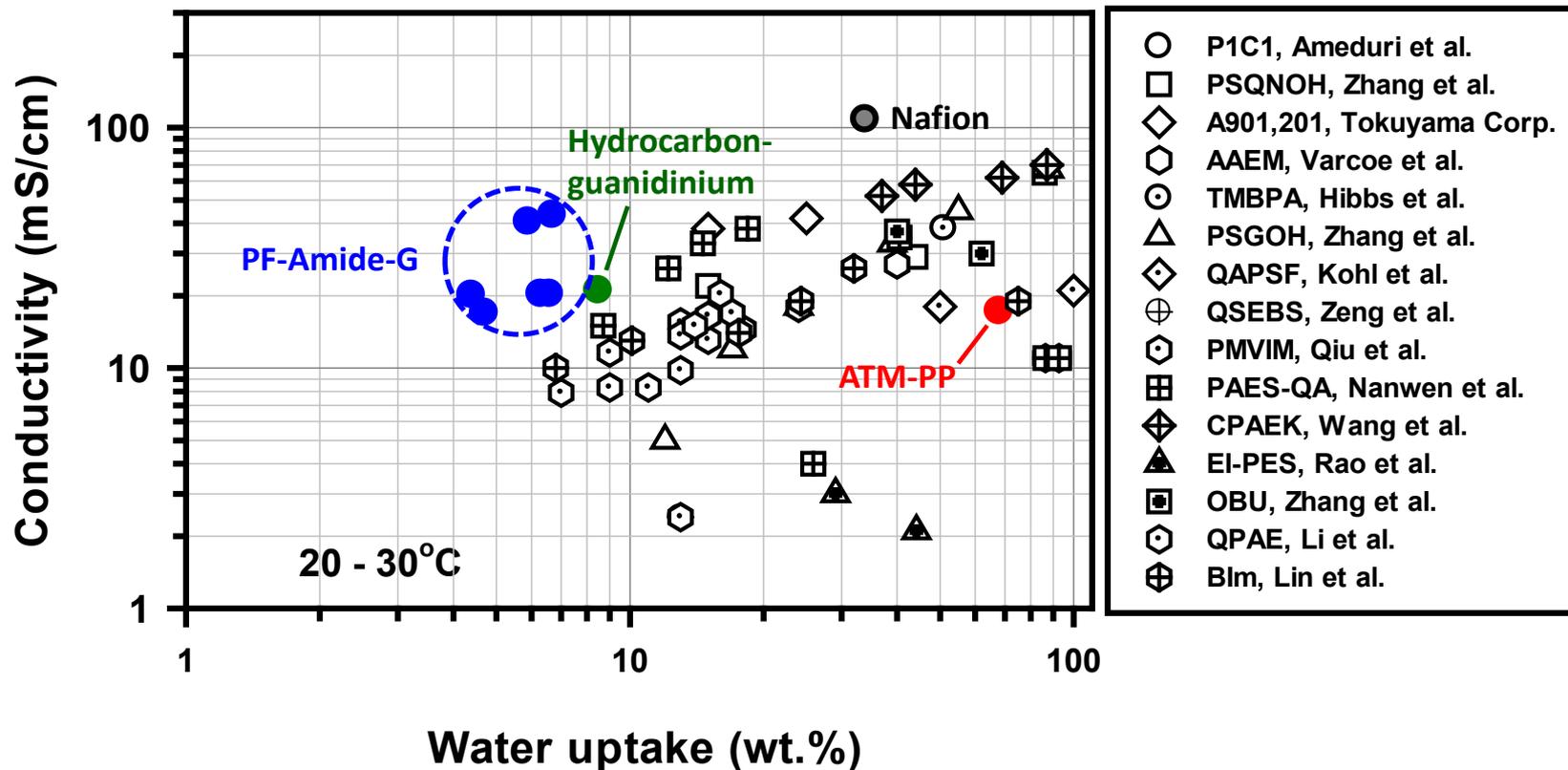
# Hydroxide Conductivity

Membrane: hydroxide form (AEM thickness: 50  $\mu\text{m}$ ); Pre-treatment: boiling water for 3 h; measured in deionized water



- Good hydroxide conductivity of *PF-Amide-G* series is 20–40 mS/cm (IEC = 0.8 meq/g) and 40–80 mS/cm (IEC = 1.5 meq/g) with temperature range of 30–80°C

# Hydroxide Conductivity vs. Water Uptake



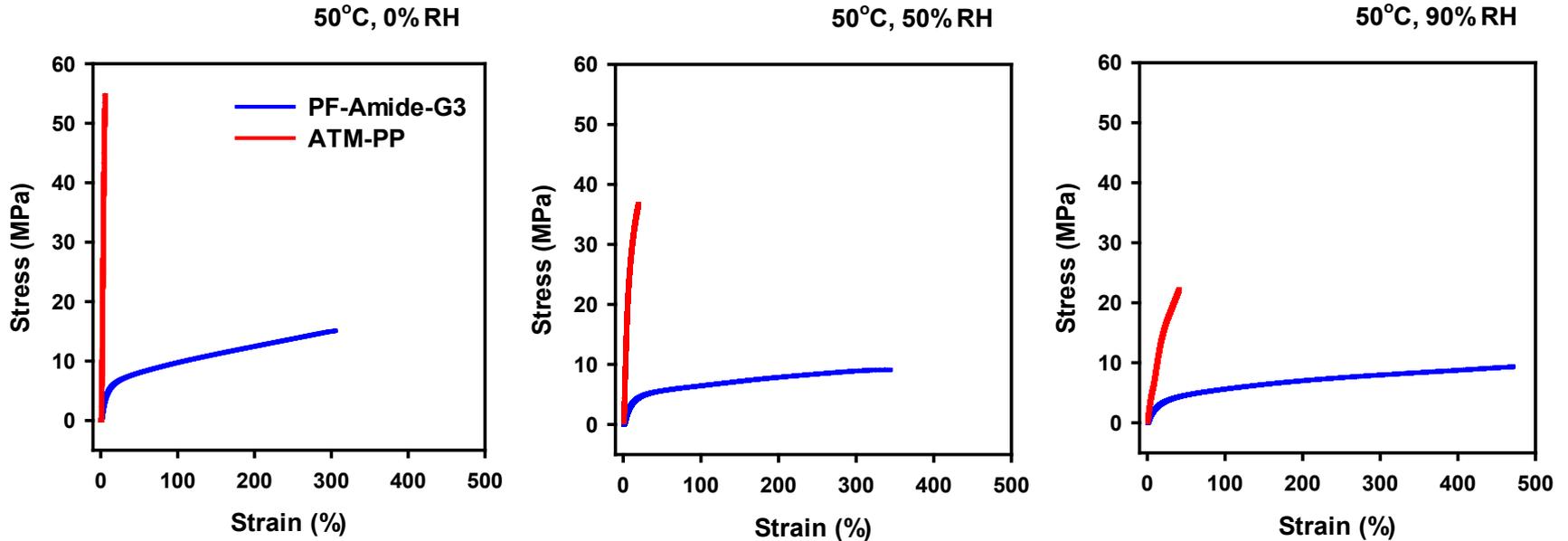
- Extremely low water uptake of *PF-Amide G* series due to 1) hydrophobicity of perfluorinated polymer backbone and ii) low hydration energy of guanidinium\*

**Highlight:** Best efficiency on hydroxide conductivity of *PF-Amide-G*

\* Mason et al. *P. Natl. Acad. Sci.* 4557 (2003)

# Stress-Strain Behaviors

Membrane dimension: 0.5 cm × 3 cm × 50 μm; ramp rate 0.5 MPa/min; RH equilibrium time: 30 min; Hydroxide form AEM



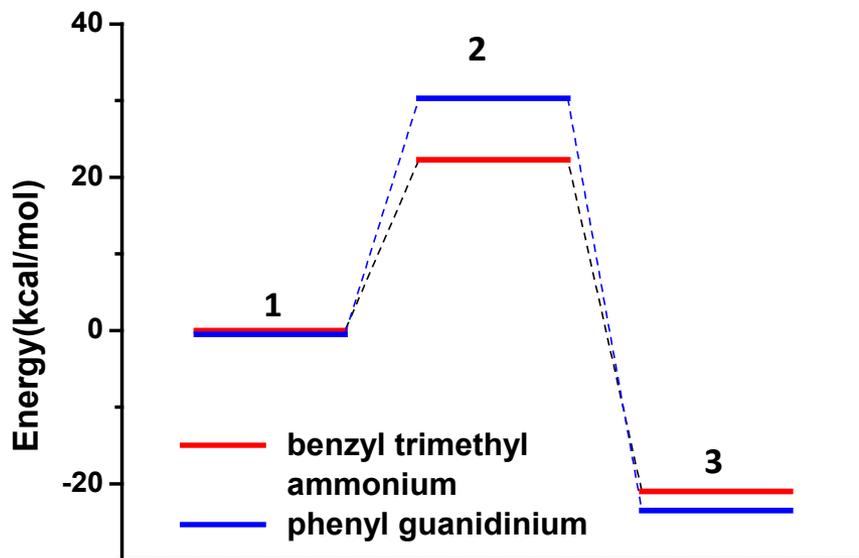
## Tensile Toughness (MPa)

Polymer	RH (%)		
	0	50	90
PF-Amide-G3	2.3	2.5	3.2
ATM-PP	0.1	0.5	0.5

- Elastic behavior with *PF-Amide-G* series (no brittleness under dry conditions)
- Highlight:** The best mechanical toughness with *PF-Amide-G* series among those reported.

# Chemical Stability: DFT Modeling

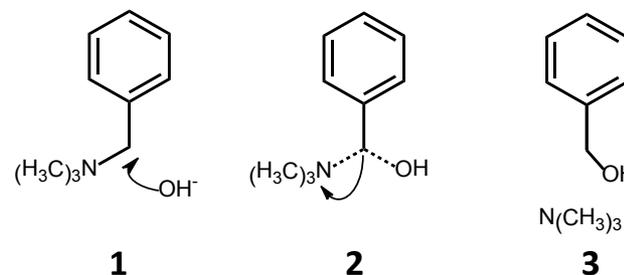
## Energy profiles of cation degradation



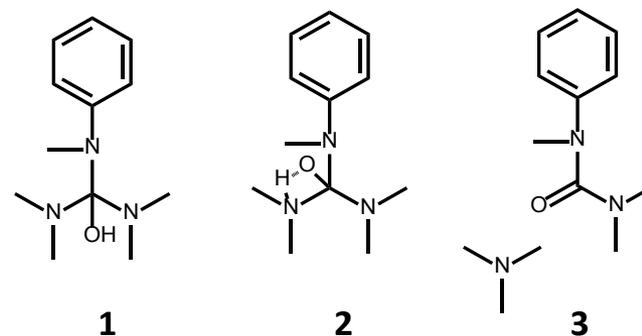
- Resonance stabilized phenyl guanidinium has 8 kcal/mol greater barrier energy than conventional benzyl trimethyl ammonium.
- The difference in barrier energy makes the guanidinium cation half-life approximately 6000 times longer at 200°C (See Reviewers' only Slide 24).

## Molecular structure of stationary points

### Benzyl trimethyl ammonium



### Phenyl pentamethyl guanidinium



Cf. Degradation of non-conjugated guanidinium occurs very fast (see Technical Back-up Slide 21)

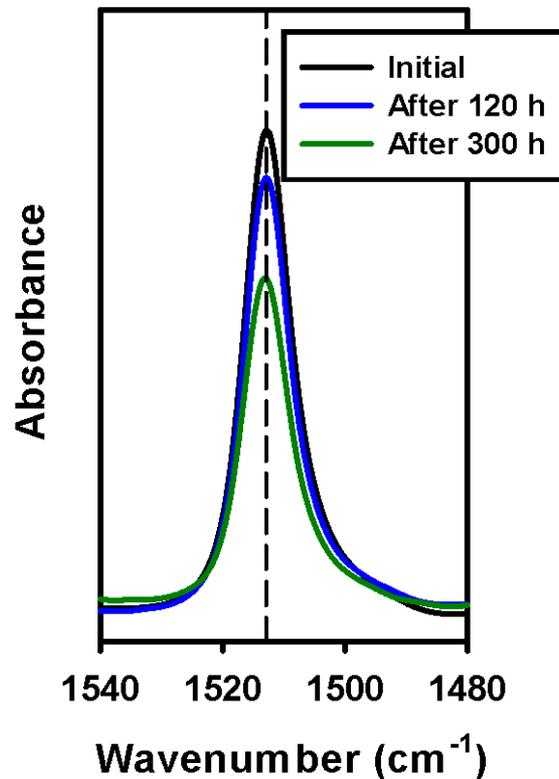
*In collaboration with AIST (Japan)*

# Chemical Stability: Ex-situ Testing

Stability Test: Immersed hydroxide form AEMs in 0.5 M NaOH at 80°C; Observed the chemical structural change by FTIR

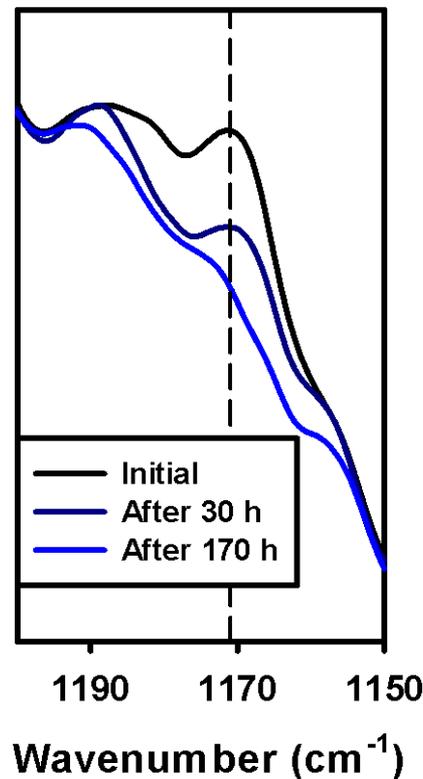
## PF-Amide-G4

C-C stretches  
in the aromatic ring



## ATM-PP

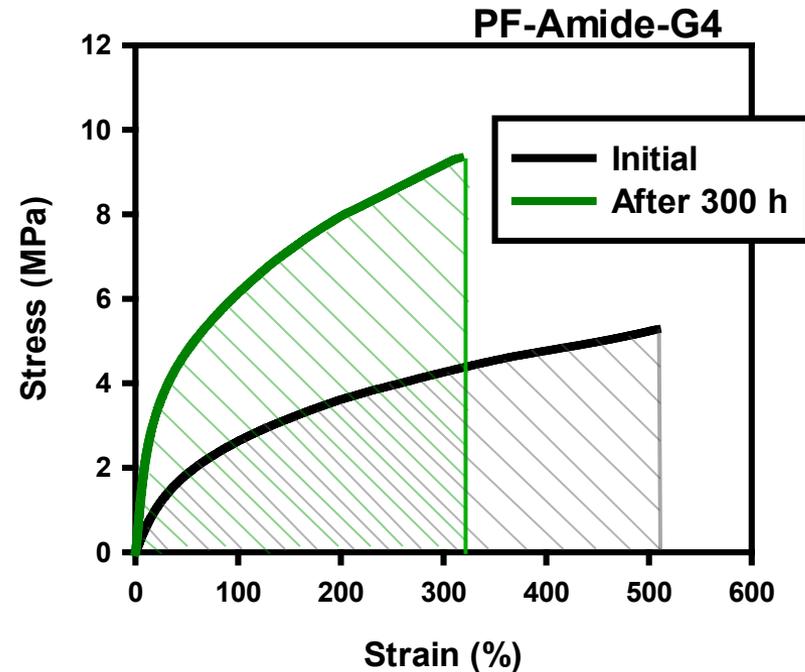
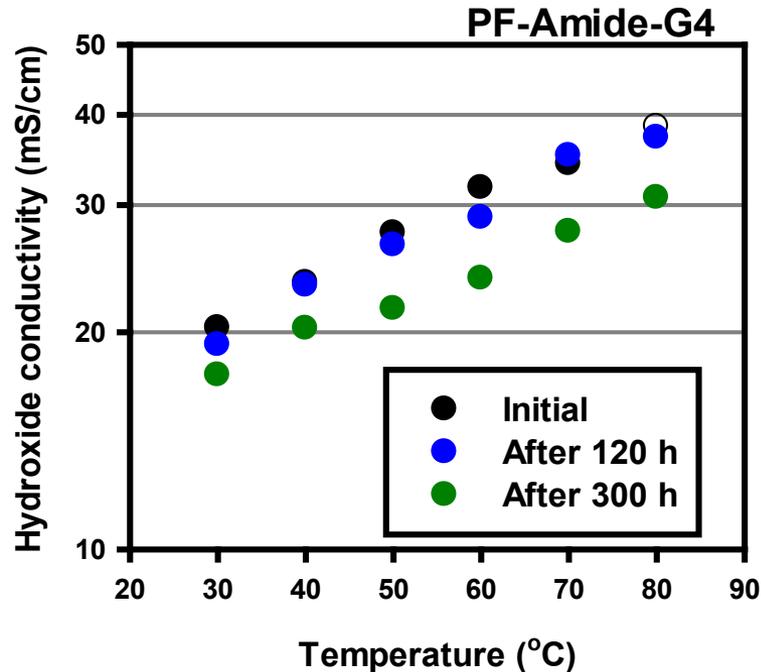
C-N stretches  
in the aromatic ring



- **PF-Amide-G4:** Amide hydrolysis occurs before guanidinium cation degradation (no guanidinium degradation observed).
  - **ATM-PP:** Degradation of benzyl ammonium occurs first.
  - PF-Amide-G4 shows better stability than ATM-PP.
  - With demonstration of > 2100 h life for ATM-PP in alkaline electrolysis, prolonged life for PF-Amide-G4 is expected (see Reviewers Only Slide 25).
- Next:** Confirmation of stability of PF-Amide-G4 in AMFC.

# Property Changes after Ex-situ Stability Test

Stability Test: Immersed hydroxide form AEM in 0.5 M NaOH at 80°C; Observed the chemical structural change by FTIR

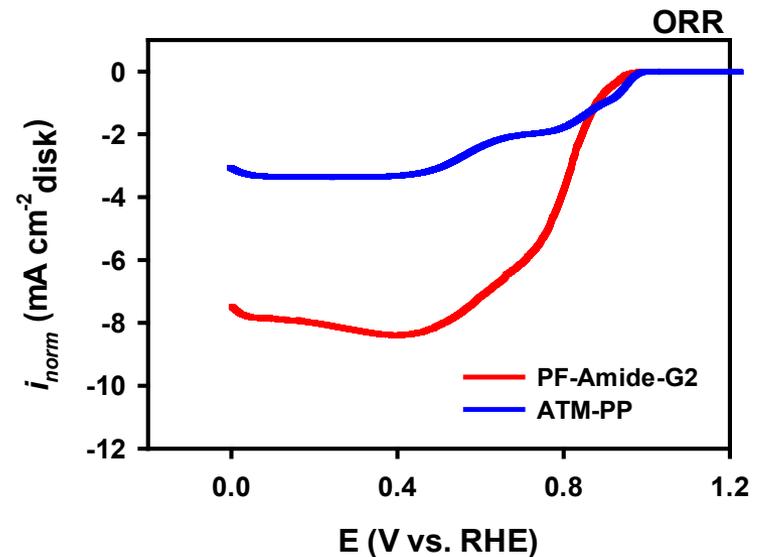
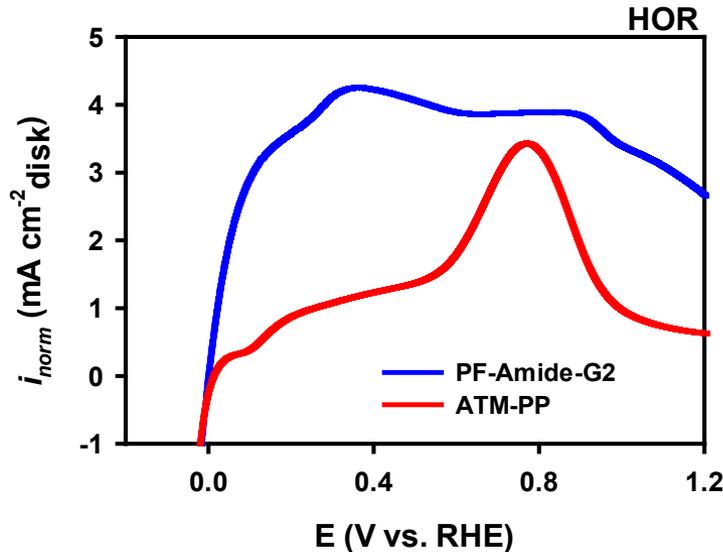


- Conductivity loss after stability test; 120 h:  $3.3 \pm 4$  %, 300 h:  $19.0 \pm 4$  %
- Maintained the mechanical toughness of membrane (shaded area) after 300 h stability test: 0 h: 19 MPa, 300 h: 22 MPa

**Highlight:** Meet FY14 milestone:  $< 10\%$  conductivity loss after 100 h in 0.5 M NaOH at 80°C (Sep. 30, 2013)

# Ionomer Performance: Micro-electrode experiments

**Pt microelectrode experiments (Reviewers Only Slide 26):** Pt micro-electrode (100  $\mu\text{m}$  diameter); scanning rate: 5 mV/s, gas: water saturated  $\text{H}_2$  and  $\text{O}_2$ , for HOR and ORR, respectively, temp.: 40°C; pre-conditioning: 1.4 V for 10s; current is normalized to film thickness



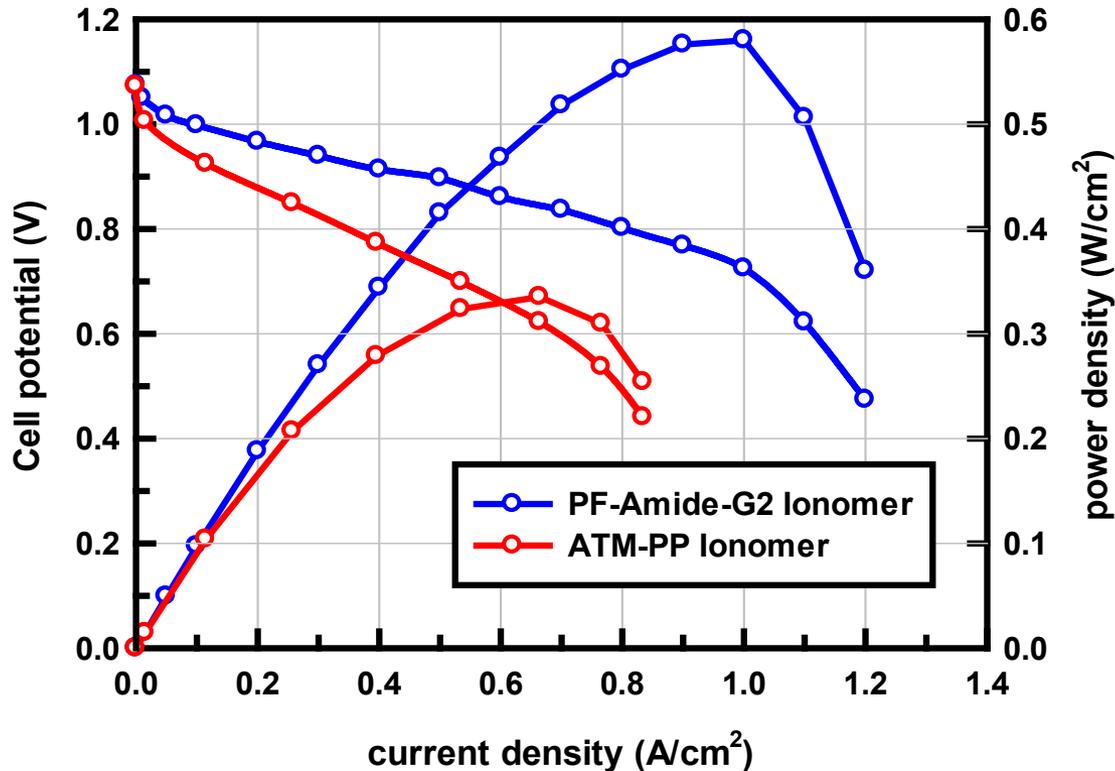
Polymer	HOR current at 0.01 V (mA cm <sup>-2</sup> )	ORR half-wave potential ( $E_{1/2}$ )	Oxygen permeability ( $\text{mol s}^{-1} \text{cm}^{-1}$ )
PF-Amide-G2	0.51	0.78	$2.25 \times 10^{-12}$
ATM-PP	0.23	0.79	$0.91 \times 10^{-12}$

- Better HOR behavior and oxygen permeability with *PF-Amide-G2*
- Highlight:** Better performance of *PF-Amide-G2* explains better AMFC performance (Slide 15)

*In collaboration with KIER (South Korea)*

# AEMFC Performance

Membrane: ATM-PP (50  $\mu\text{m}$  thick); Catalysts: Pt (3.4 and 6.5  $\text{mg}/\text{cm}^2$  for anode and cathode, respectively); Gas supply:  $\text{H}_2/\text{O}_2$ ; cell temperature: 80°C



- Much better electrode performance for perfluorinated ionomer compares with wholly aromatic ionomer.
- These data consistent with the superior HOR and gas permeability of perfluorinated ionomer are superior (Slide 14)

- **Highlight:** Demonstrated excellent AMFC performance using PF-Amide-G2 ionomer at 80°C

# Collaborations/Interactions

Institutions	Type	Extent	Role and Importance
Los Alamos National Laboratory	Federal Laboratory	Prime	<ul style="list-style-type: none"> <li>DOE Hydrogen and Fuel Cell Program, Project lead</li> <li>Synthesis and preparation of polymers and ionomer dispersion</li> <li>Membrane, electrode and fuel cell performance test</li> </ul>
Sandia National Laboratories	Federal Laboratory	Major	<ul style="list-style-type: none"> <li>DOE Hydrogen and Fuel Cell Program</li> <li>Supply hydrocarbon AEMs <b>(Slide 7)</b></li> <li>Access to the state-of-the-art polyphenylene AEMs <b>(Slide 9-11)</b></li> </ul>
Proton OnSite	Industry	Medium	<ul style="list-style-type: none"> <li>DOE ARPA-E Program</li> <li>Membrane evaluation for alkaline water electrolysis <b>(Slide 25)</b></li> <li>Expand AEM technology to water electrolysis application</li> </ul>
DuPont	Industry	In-Kind	<ul style="list-style-type: none"> <li>DOE Hydrogen and Fuel Cell Program</li> <li>Supply Nafion precursors <b>(Slide 6)</b></li> </ul>
Korea Institute of Energy Research	Foreign National Laboratory	Medium	<ul style="list-style-type: none"> <li>KIER Visiting Scholar Fellowship</li> <li>Micro-electrode studies <b>(Slide 14 and 26)</b></li> <li>Experimental validation for alkaline electrode performance</li> </ul>
National Institute of Advanced Industrial Sci. and Technol.	Foreign National Laboratory	Medium	<ul style="list-style-type: none"> <li>LANL Cooperative Research and Development Agreements</li> <li>DFT modeling <b>(Slide 11 and 24)</b></li> <li>Design perspective for stable alkaline membrane structure</li> </ul>
<p><b>Rutgers University, University of New Mexico, Celler, Giner and Ion Power</b>            Minor interactions through NDA &amp; Material Transfer Agreement</p>			

# Summary: Property Comparison with Nafion

*We prepared advanced hydroxide conducting membranes and ionomer dispersions;  
Property compares with industrial standard acid-based Nafion membrane*

Property	Nafion		PF-Amide G series		Target
Thickness ( $\mu\text{m}$ )	25 - 250	✓	25 - 50	✓	$\leq 25$
Ion Conductivity at 80°C (S/cm)	0.22	✓	0.05 – 0.09		$> 0.15$
IEC (meq./g)	0.9	✓	0.8 - 1.5	✓	2.5
WU (wt.%)	33		4 -10	✓	$< 30\%$
Mech. Toughness (MPa)	1.7		2.3	✓	Reached
Chemical Stability Cont. fuel cell run (h)	Up to 5,000 h (80°C)	✓	$> 2500 \text{ h}^{\text{a}}$ (25-60°C)		5,000 h (80°C)
Ion Contamination	Moderate	✓	$\text{HCO}_3^-$ and $\text{CO}_3^{2-}$		
Ionomer Dispersion	Up to 20 %	✓	Up to 5 %	✓	Reached

<sup>a</sup> Projected value: See Reviewer's Only Slide 25

# Remaining Challenges and Barriers

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## ▪ Membrane

- **Stability:** Polymer backbone and cation stability of *PF-Amide-G series* is excellent. Remaining technical challenge is further enhancement of amide polymer-cation linkage.
- **Conductivity:** Current conductivity of *PF-Amide-G series* is 25-40% of Nafion. Further increase of hydroxide conductivity is desirable.

## ▪ Ionomer

- **Solubility:** *PF-Amide-G series* membranes have poor solubility (excellent solvent resistance). More advanced dispersion techniques are required for more uniform dispersion and mechanical properties of solid-state electrode.
- **Ionomer-catalyst interface:** We demonstrated good interaction of *PF-Amide-G series* of Pt electrode. However, more systematic studies to improve HOR and ORR behaviors are needed.

## ▪ AMFC performance

- **In-situ long term test:** Long term stability of Nafion® and ionomer-bonded electrode is needed to confirm the *ex-situ* data.
- **(Bi) carbonate contamination:** Performance loss due to (bi) carbonate contamination may be problematic for end-use applications. Mitigation strategy needs to develop.
- **Non-precious metal catalysts:** Performance demonstration using non-precious metal catalysts is remaining challenges. Extensive works with MEA fabrication and fuel cell testing are required.
- **Water management:** *PF-Amide-G series* are expected to have moderate water diffusion coefficients unlike acid-based Nafion. However, flooding and water management in AEMFCs is more challenging than PEMFCs. Further study is needed.

# Proposed Future Work

*In order to obtain the equivalent performance to the state-of-the-art acid systems, below are the proposed work.*

## Reducing Resistance

*Level of difficulty*

- Increasing membrane conductivity up to 0.15 S/cm at 80°C (Near term) High
- Reducing membrane thickness down to 10 μm (Near term) High
- Increasing cell operation temperature to 90°C (Longer term) High

## Increasing Durability

- Designing more stable cation-polymer linkage (Near term) High
- Introducing more stable cations (Longer term) Medium

## Better Cell Performance

- Increasing low RH stability and conductivity (Near term) High
- Improving HOR and ORR kinetics with NPGM catalysts (Longer term) Medium
- Increasing (bi)carbonate tolerance (Longer term) Medium

## Commercialization

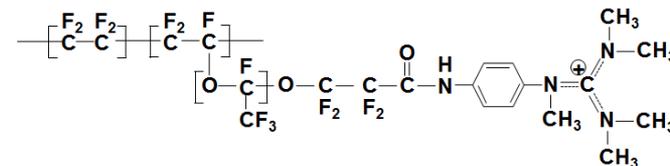
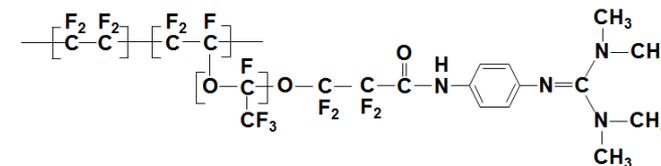
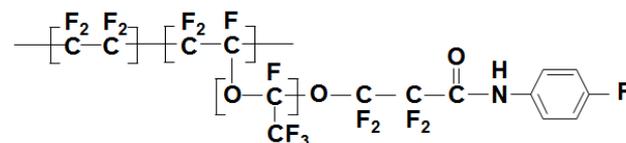
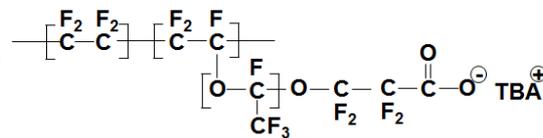
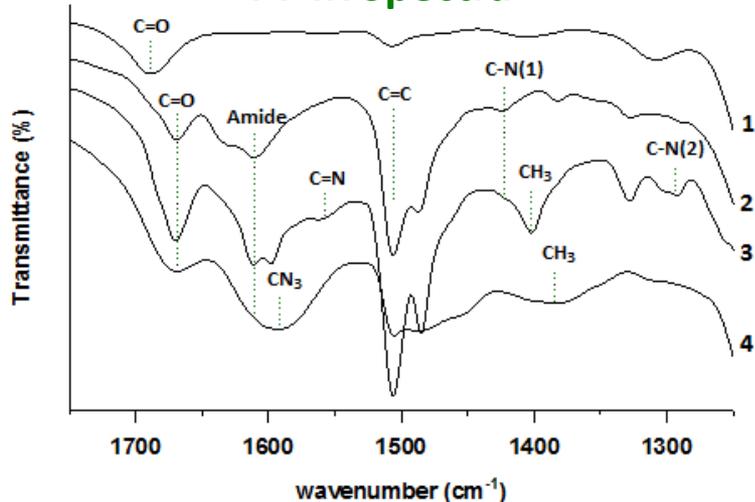
- Strengthening collaborations and licensing (Near term)
- Reducing cost by increasing volume and using less expensive perfluorinated polymer precursor (Longer term)

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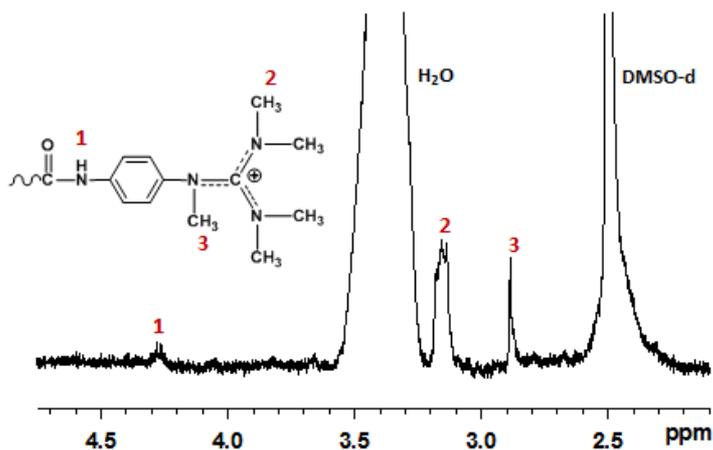
# Technical Back-Up Slides

# Spectroscopic Data

## FT-IR Spectra



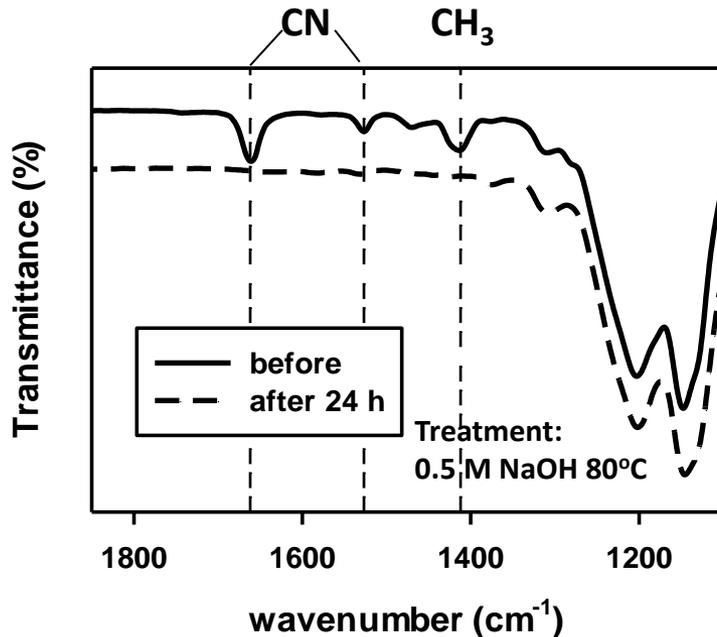
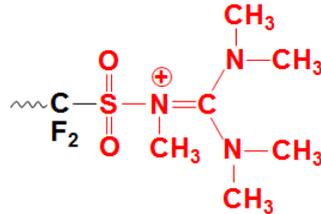
## Solid-state <sup>1</sup>H NMR



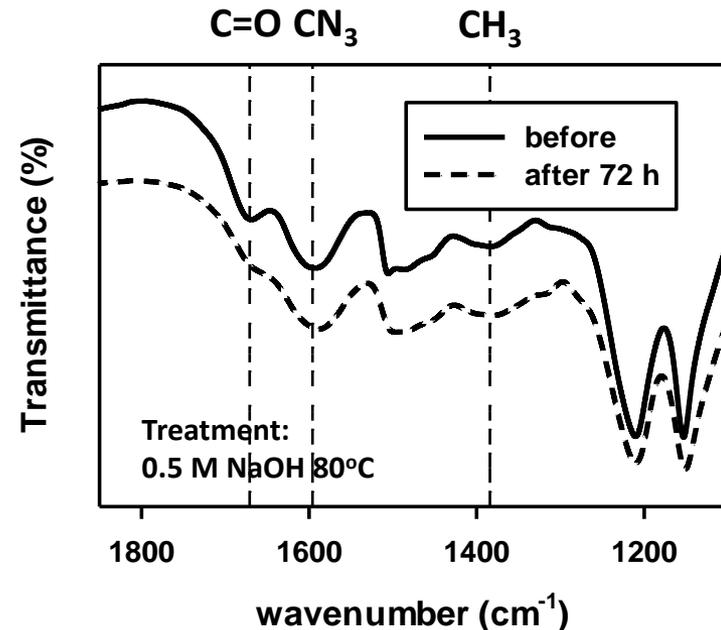
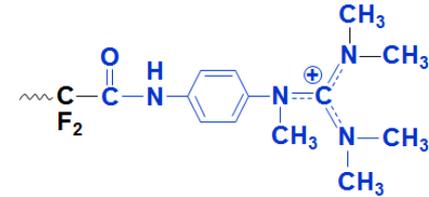
- Confirmed the chemical structure of each step of the reaction by FT-IR or <sup>1</sup>H NMR.
- Reaction yield is 100%** → no mixed ion form membrane is generated.

# Resonance Stabilization

Sulfone  
guanidinium  
(non-conjugated)



Phenyl  
guanidinium  
(conjugated)



- Non-conjugated sulfone guanidinium due to the electron withdrawing sulfone group
- Improved cation stability by the resonance structure of guanidinium