2010 DOE Hydrogen Program and Vehicle Technologies Program
Annual Merit Review and Peer Evaluation Meeting
June 7-11, 2010, Washington, D.C.

Resonance-Stabilized Anion Exchange Polymer Electrolytes

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Project ID: fc043

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Overview

Timeline

- Project start – September 2009
- Project end – September 2011
- Percent complete – 35%
  - Polymer synthesis (50%)
  - Catalyst synthesis (20%)
  - MEA processing (10%)

Budget

- Total Project Funding: $ 1,320k
- Funding Received in FY 09: $ 462k
- Funding for FY 10: $ 528k

  No cost shared

Barriers

B. Cost
C. Electrode Performance
A. Durability

Partners

Project Lead:

Los Alamos National Laboratory

- **Yu Seung Kim**
- Dae Sik Kim
- Andrea Labouriau

Collaborators:

Sandia National Laboratories

- **Cy Fujimoto**
- Michael Hipps

JPL

- **Sri Narayan**
- Chuck Hays

Interactions:

- Cellera Technologies (**S. Gottesfeld**)
- Ovonic Fuel Cell Company (**R. Privette**)
- Virginia Tech. (**J. McGrath**)
- Univ. New Mexico (**P. Atanassov**)
- NREL (**B. Pivovar**)
- Canada NRC (**M. Guiver**)

Relevance

Objectives

- **Develop anion exchange polymer electrolytes that have <u>high hydroxyl conductivity</u> and <u>stability</u> in high pH conditions.**
- **Demonstrate an improved single cell performance of solid-state alkaline fuel cells using the polymer electrolytes and non-precious metal catalyst.**

Impact on Technical Barriers

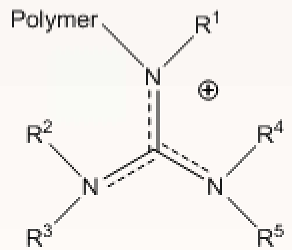
ISSUES	Technical Barriers	Recent Reported Value	Technical Target
Conductivity	Significantly low due to low mobility of OH^-, carbonate formation etc.	27 mS/cm (20°C) [1] 34 mS/cm (50°C) [2]	> 50 mS/cm at 80°C
Stability	Fast degradation of AEM at high PH conditions	> 48 h 1M KOH at 60°C [1]	> 500 h at 80°C in 1 M NaOH solution
Electrode Processing	Poor solubility of AEM and lack of understand electrode structure	196 mW/cm^2 H_2/O_2, 80°C [1] 130 mW/cm^2 H_2/O_2, 50°C [3] 94 mW/cm^2, H_2/O_2, 50°C [2]	> 200 mW/cm^2 H_2/air at 80°C.

1. Y. Yan et al., *Angewandte Chem*. **121**, 6621-6624, (2009)
2. Varcoe et al., *Chem. Mater*. **19**, 2686-2693, (2007)
3. Varcoe et al., *Electrochem. Comm*. **8**, 839-843, (2006)

Approach - Stability

- **Major degradation route of anion exchange polymer electrolytes is nucleophilic substitution (S_N2). The reaction rate usually inverse to the basicity of the tertiary amine.**

Guanidine base AEM

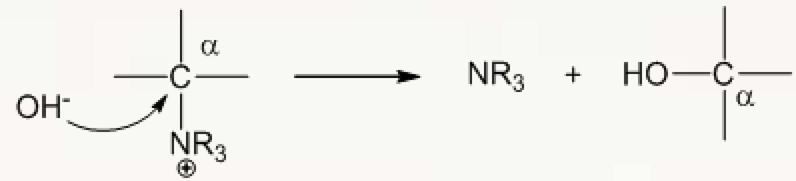


- **Guanidine base is 10,000 times more basic* than tri-alkyl amine (TAA) base.**

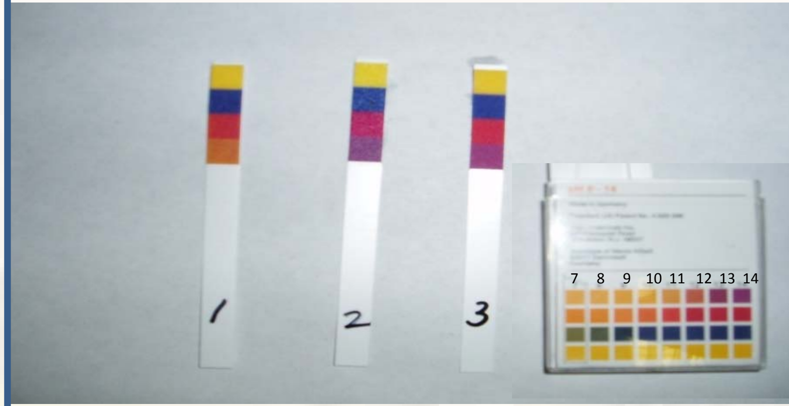
- **Resonance structure of guanidine base possibly further enhances the cation stability and hydroxyl conductivity.**

- **Guanidine bases are commercially available and cheap. ($300/kg, Aldrich)**

Nucleophilic Substitution (S_N2)



Basicity



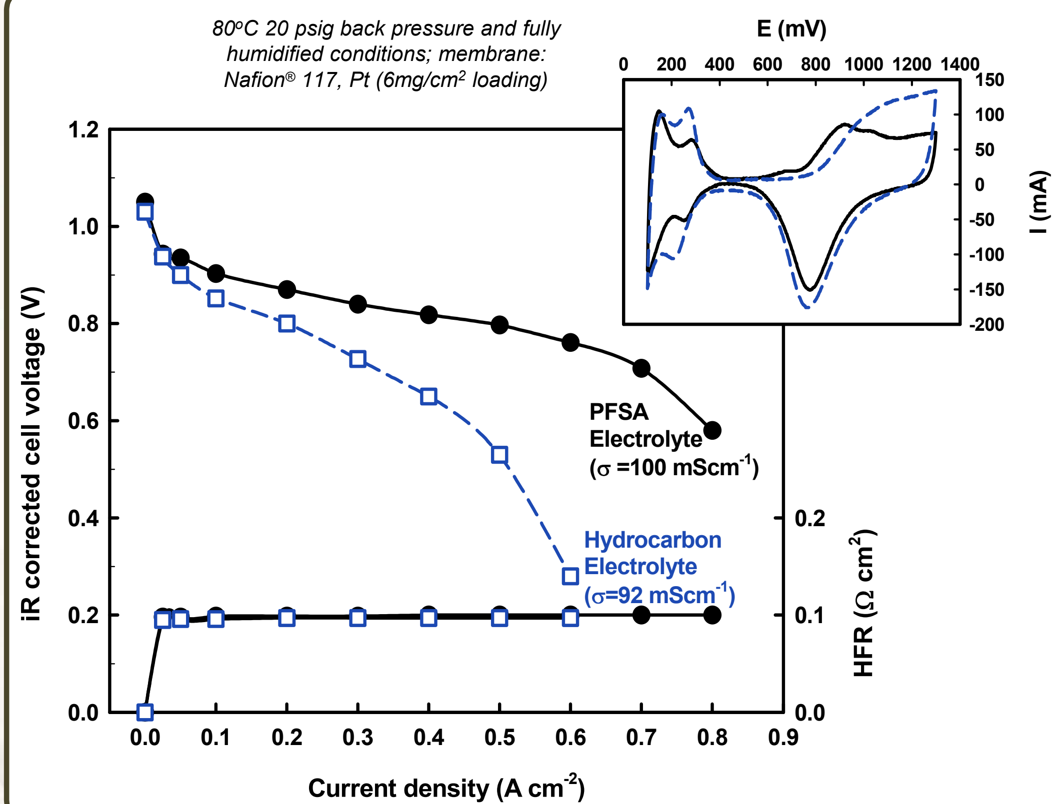
1: Triethylamine: H_2O (1:1 v/v)
2: Tetramethylguanidine: H_2O (1:1 v/v)
3: 1 M NaOH

* http://www.cem.msu.edu/~reusch/VirtualText/amine1.htm

Approach – Electrode Performance

- Hydrocarbon (HC) based polymer electrolytes have <u>lower gas permeability</u> (and chain mobility) than perfluorinated (PF) based polymer electrolytes.
- **Low gas permeability** is desirable to membrane but undesirable to electrode binder since it gives a detrimental effect on electrode performance.

H_2/air PEMFC performance*



Ideal combination

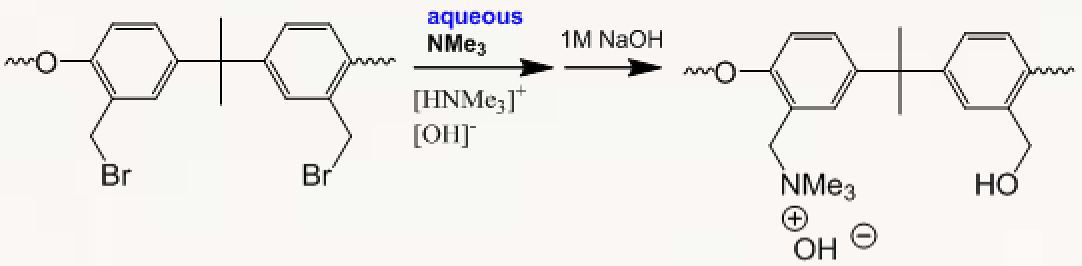
HC membrane (SNL, LANL) + Perfluorinated ionomer (LANL)

+ Non-precious metal catalyst (JPL)

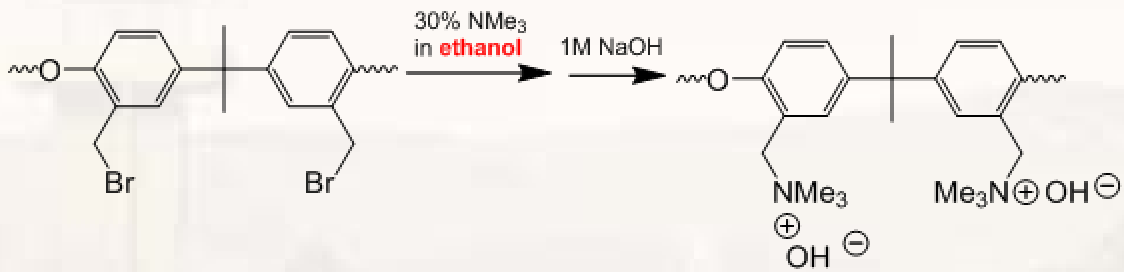
* High temperature membrane working group meeting, US DOE AMR Meeting, Arlington, Virginia, May 18-22, 2009.

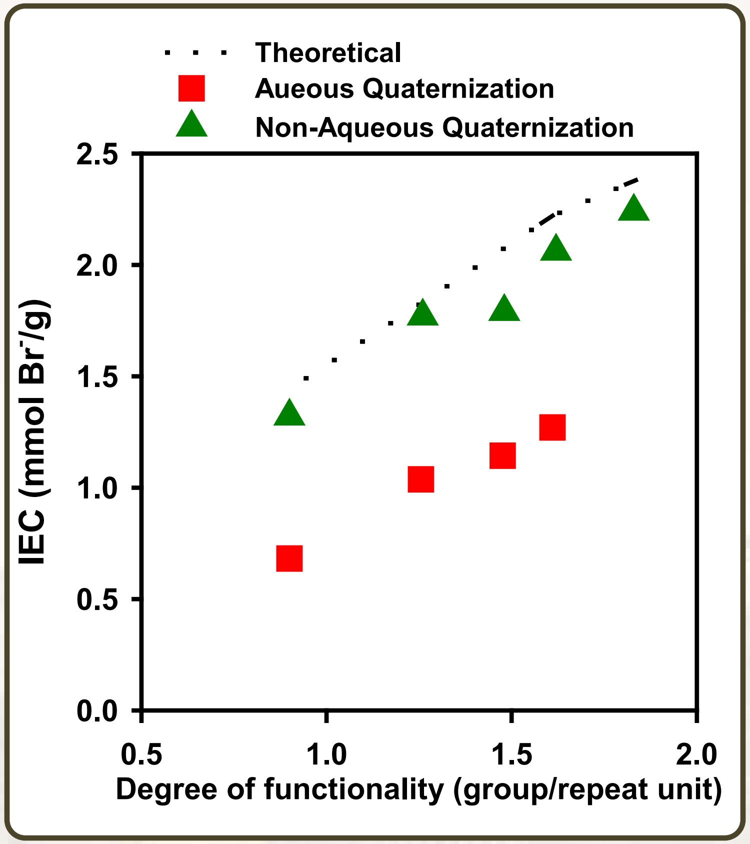
Non-aqueous Quaternization

Traditional aqueous quaternization*



Non-aqueous quaternization

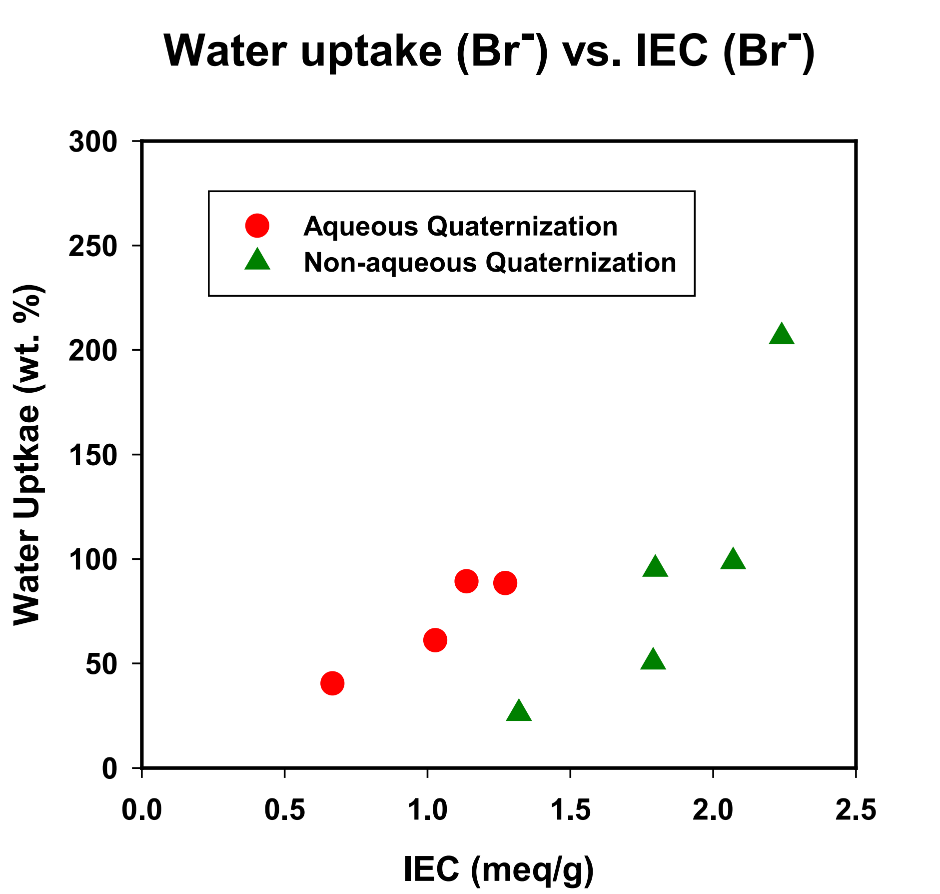




Traditional aqueous quaternization produces large discrepancy between theoretical IEC and actual IEC while non-aqueous quaternization provides precise control of amination.

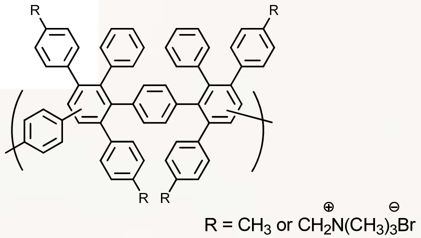
* Zarcoe et al. *Chem. Mater*. 19, 2686 (2007).
Wu et al. *J. Memb. Sci*. 310, 577, (2008).
Hickner et al. *Macromolecules*, 43, 2349 (2010).

Impact of Quaternization on Polymer Properties

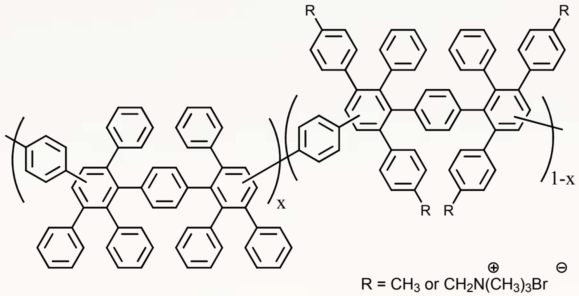


Impact of Quaternization on Polymer Properties

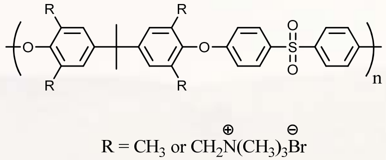
ATMPP



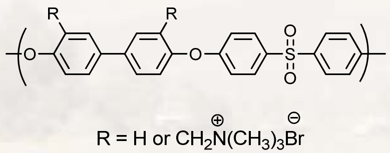
DAPP:ATMPP 1:1

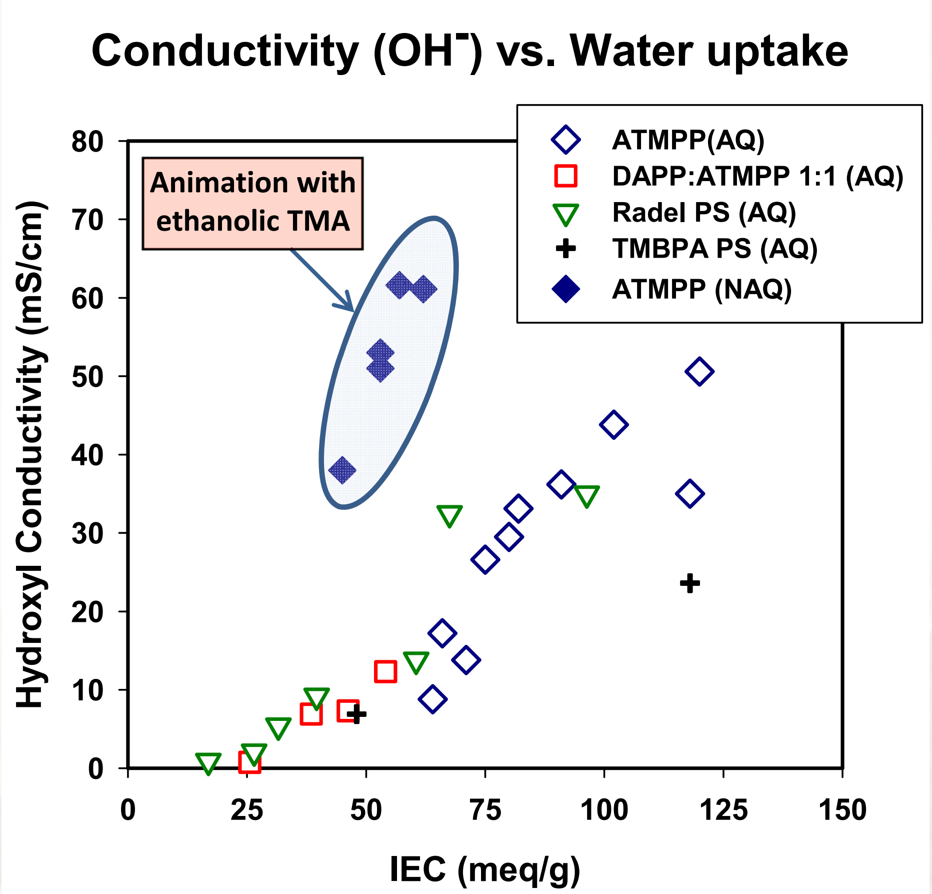


TMBPA PS



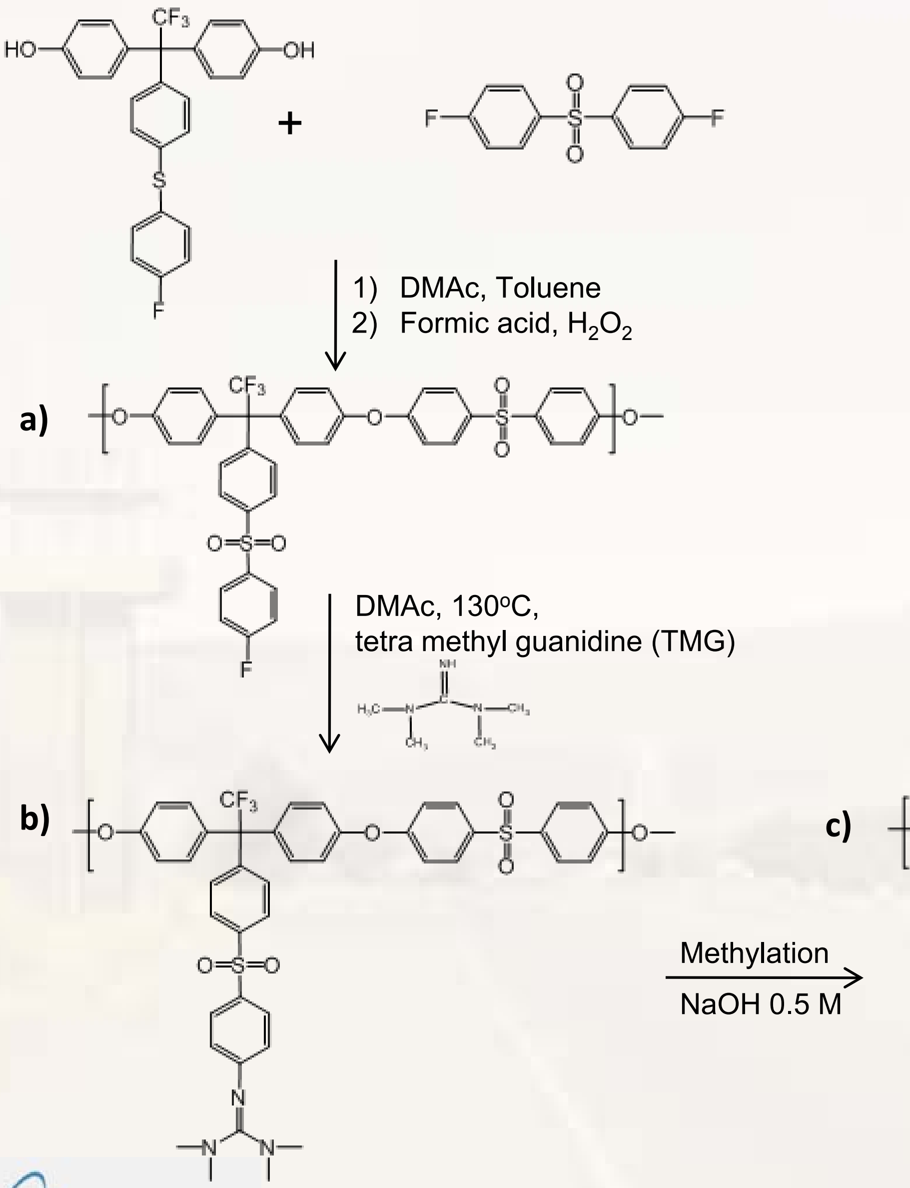
Radel PS

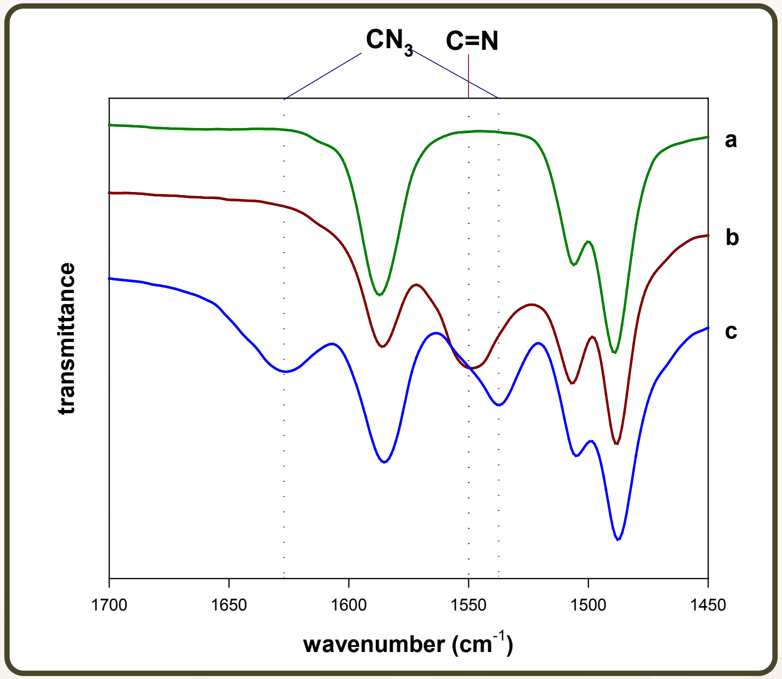


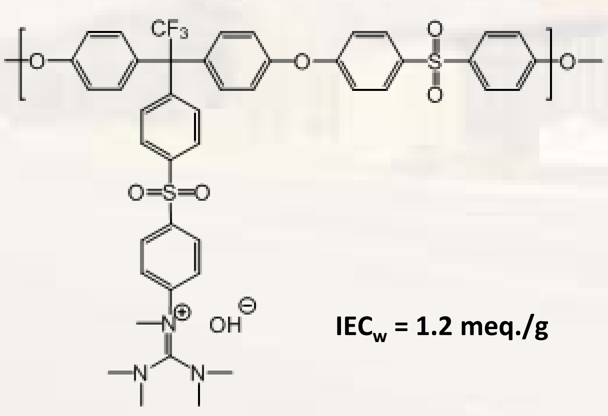


Uniformity of cation distribution can reduce water uptake and enhance the anionic conductivity under fully hydrated conditions!!!

Synthesis of Hydrocarbon Guanidine Base (HCGB) Homopolymer

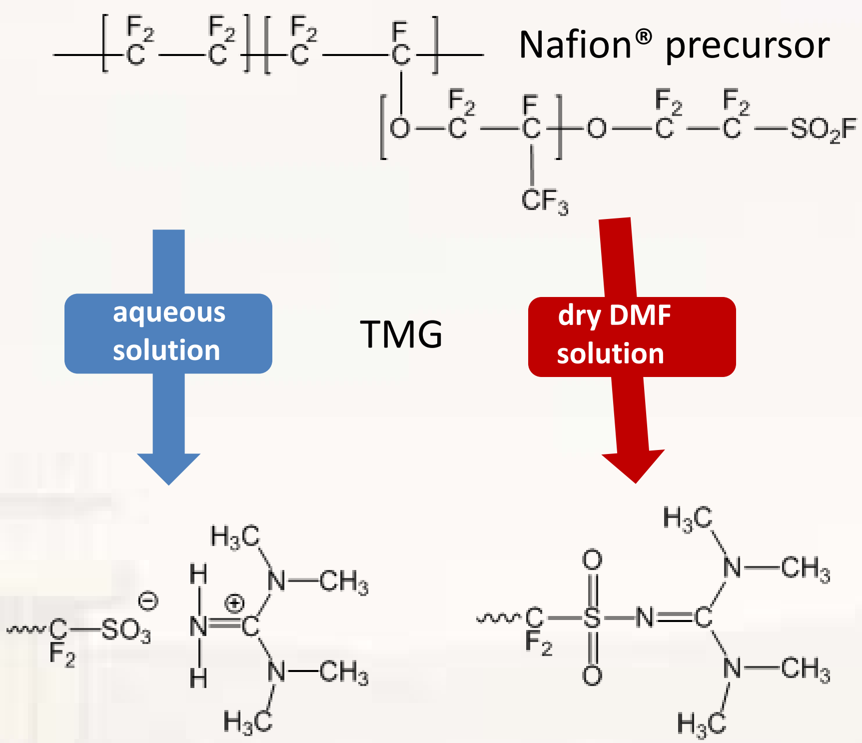






IEC_w = 1.2 meq./g

Incorporation of Guanidine Base into Nafion® Precursor



Nafion®-TMG salt form

Converted to proton form after acidification

⇩

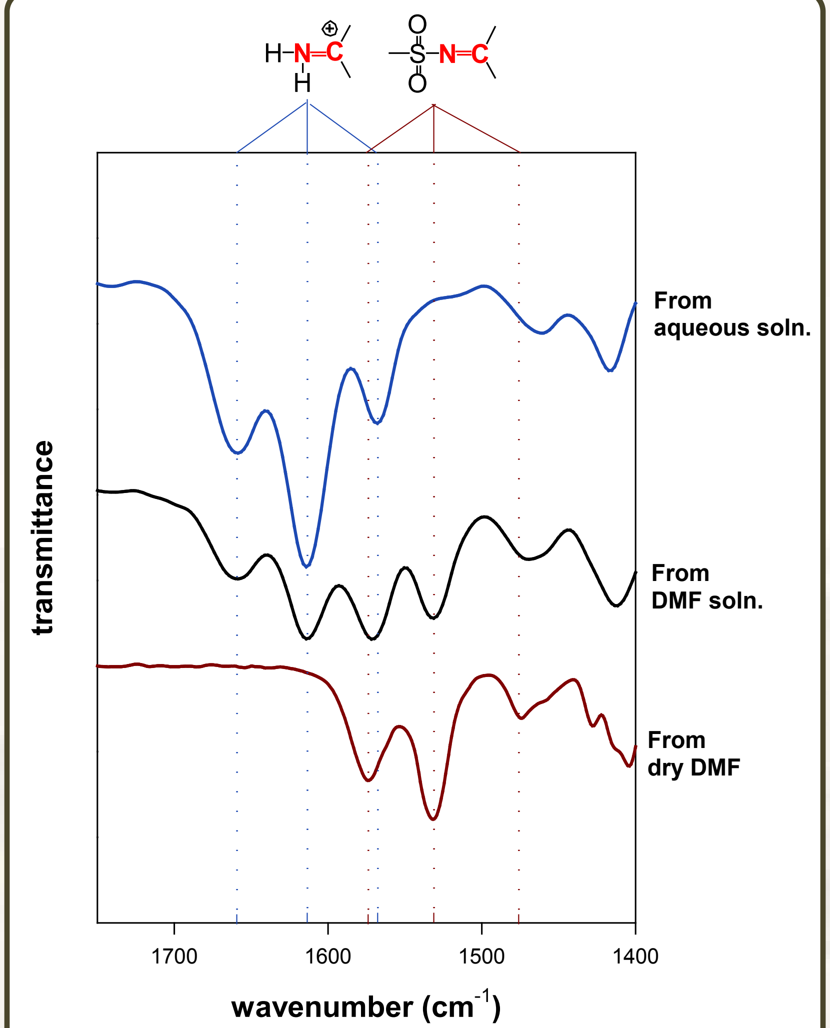
Cation exchange polymer electrolyte

PFGB precursor

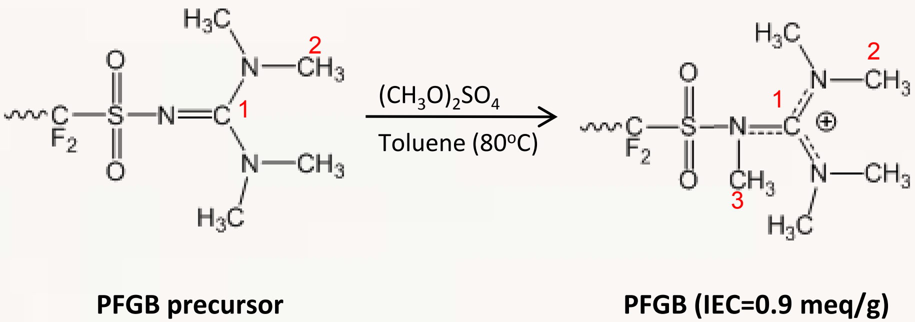
Converted to hydroxyl form after methylation

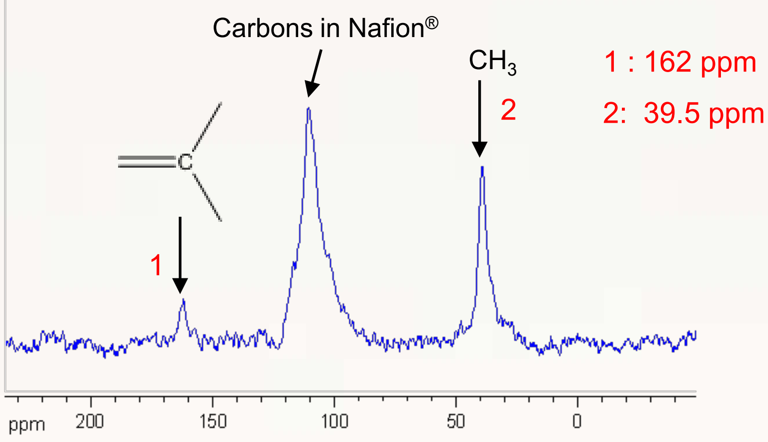
⇩

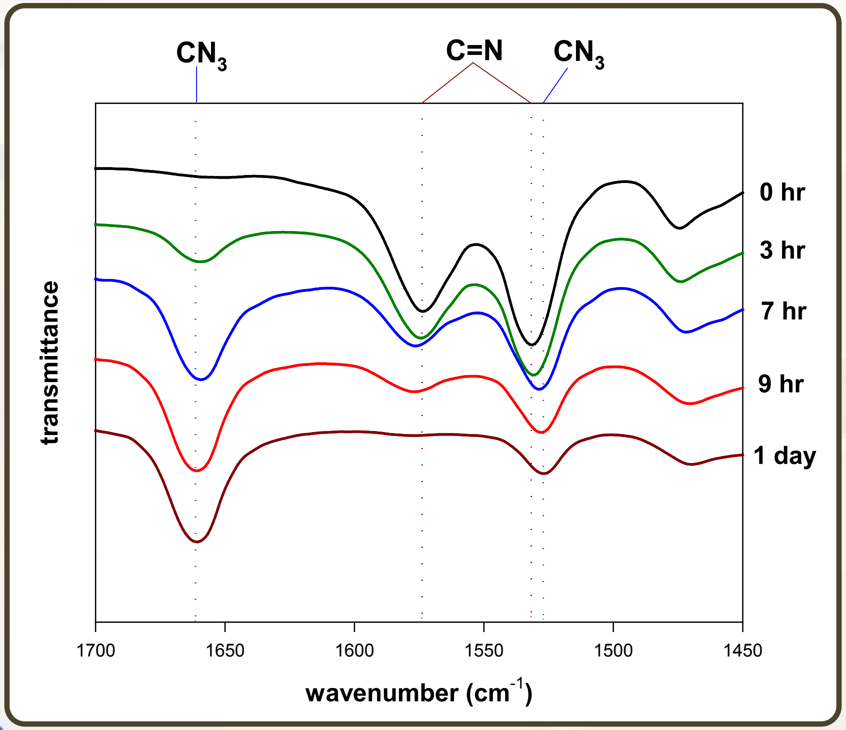
Anion exchange polymer electrolyte

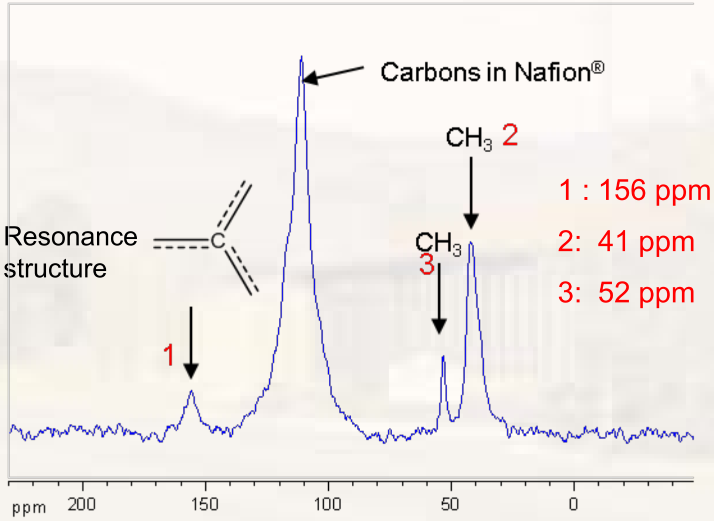


Methylation of PFGB Precursor



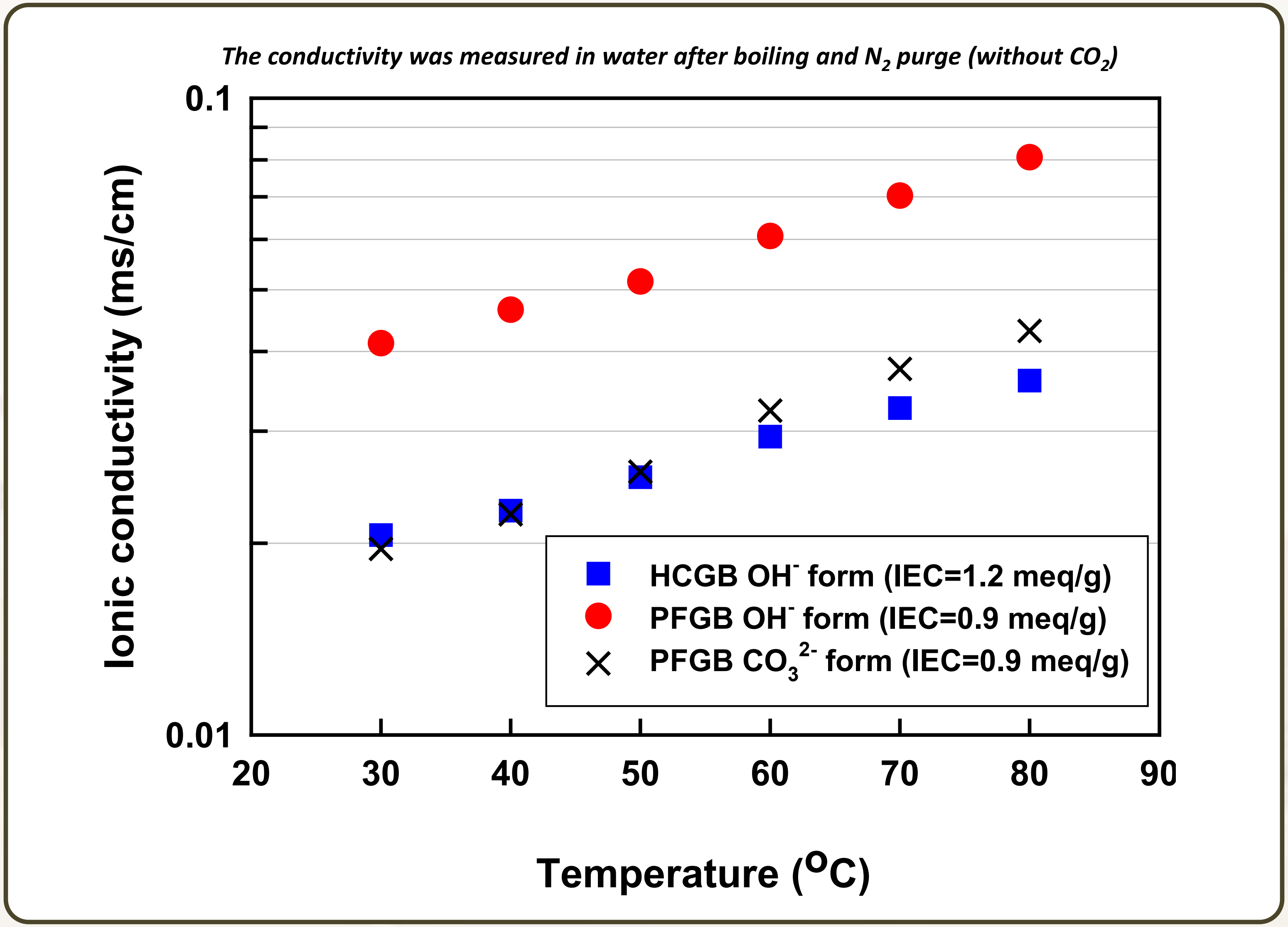




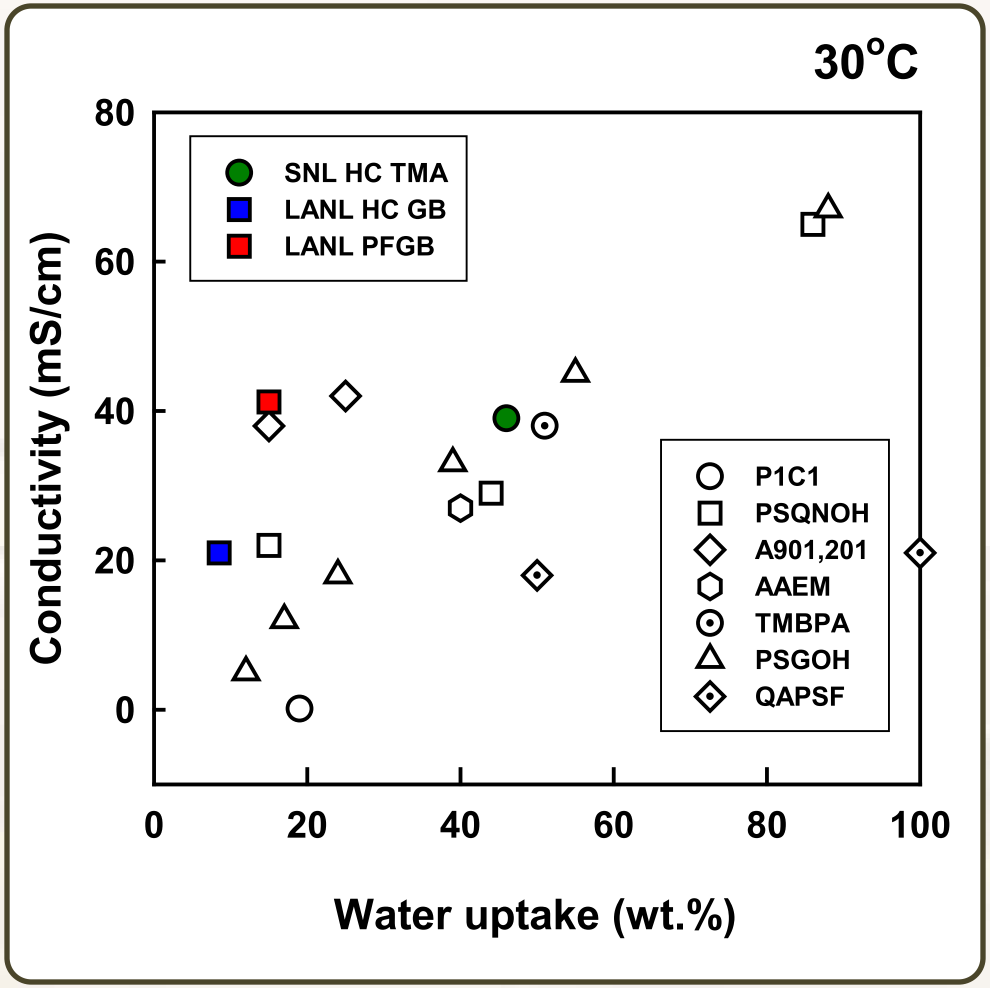


^{13}C solid state NMR

Ionic Conductivity of HCGB and PFGB as a Function of Temperature



Hydroxyl Conductivity Comparison at RT



Sample	Water uptake (wt.%)	IEC (meq./g)	σ (mS/cm)
P1C1[a]	19	0.5	0.13
PSQNOH50 [b]	15	1.9	22
PSQNOH80 [b]	86	2.8	65
A901 [c]	15	2.6	38
A201 [c]	25	1.7	42
AAEM [d]	40	-	27
TMBPA [e]	51	0.7	38
PSGOH [f]	17	1.2	12
PSGOH [f]	55	1.9	45
QAPSF1 [g]	50	-	18
QAPSF2 [g]	100	-	21
SNL HC TMA	**46**	**1.32**	**39**
LANL HC GB	**8.5**	**1.2**	**21**
LANL PFGB	**15**	**0.9**	**41**

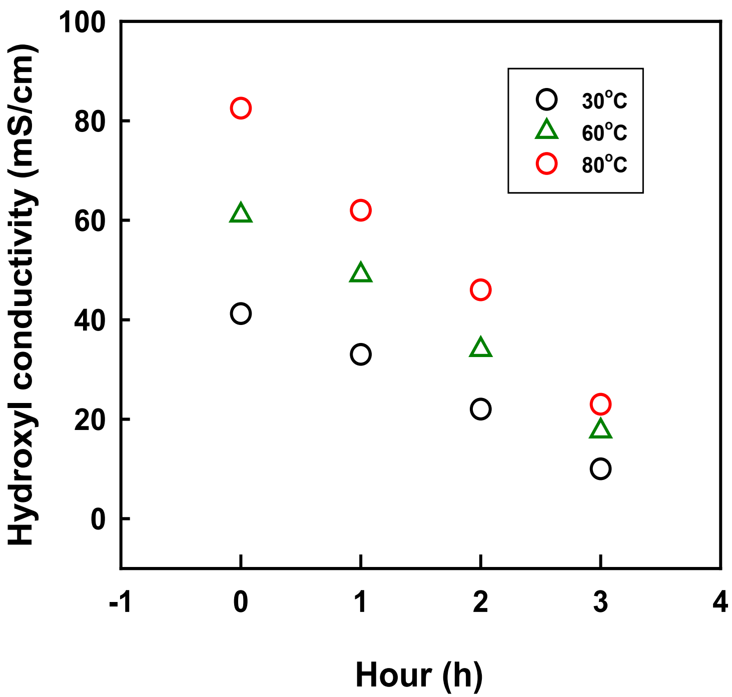
a. Poly(CTFE-alt-VE) - Bruno Ameduri
b. Poly(arylene ether sulfone) - Suobo Zhang group
c. Hydrocarbon polymer – Tokuyama Corporation
d. Poly(ethylene-co-tetrafluoroethylene) – John R. Varcoe
e. Poly(arylene ether sulfone) – Michael Hipps
f. Poly(arylene ether sulfone) – Suobo Zhang group
g. poly(arylene ether sulfone) - Paul A.Kohl group

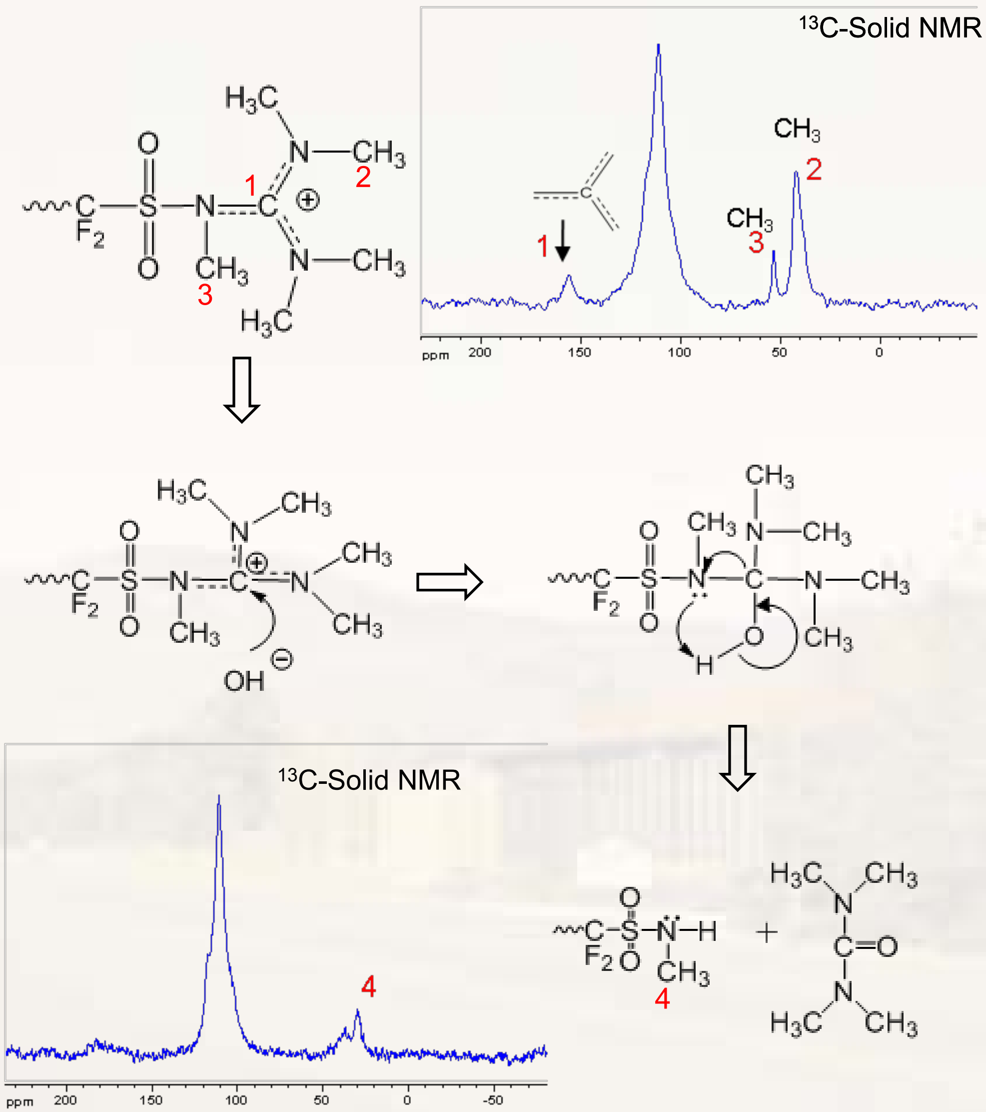
Stability of PFGB

Proposed Degradation Mechanism

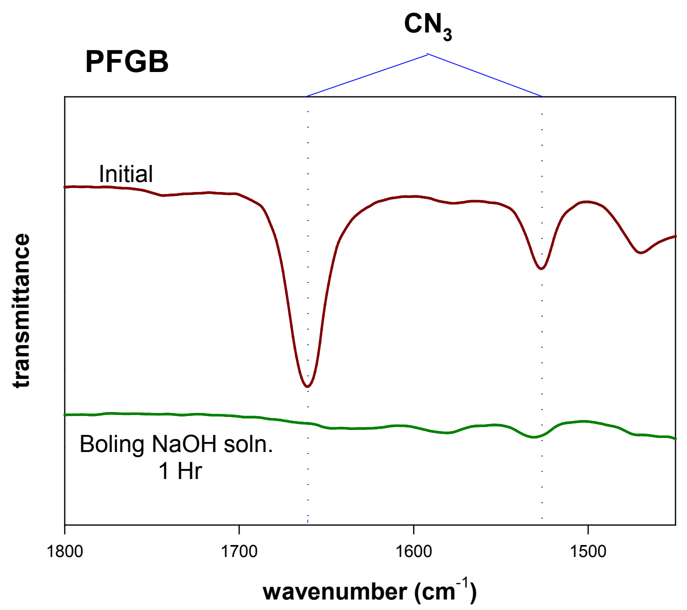
- Nucleophilic *Suicidal* attack

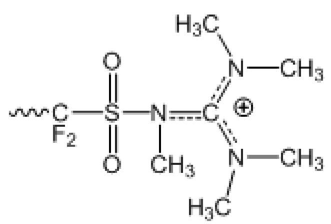
Conductivity of PFGB in boiling water



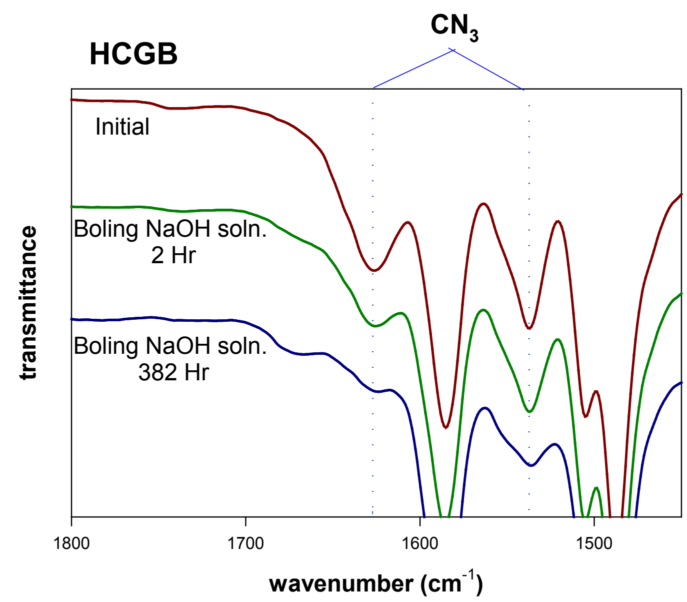


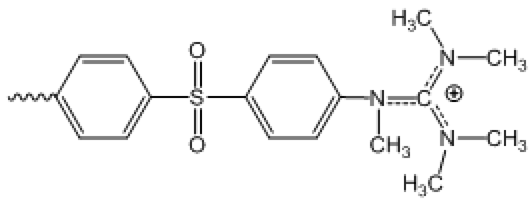
Effect of Electron Density on Stability





Electron withdrawing





Electron withdrawing

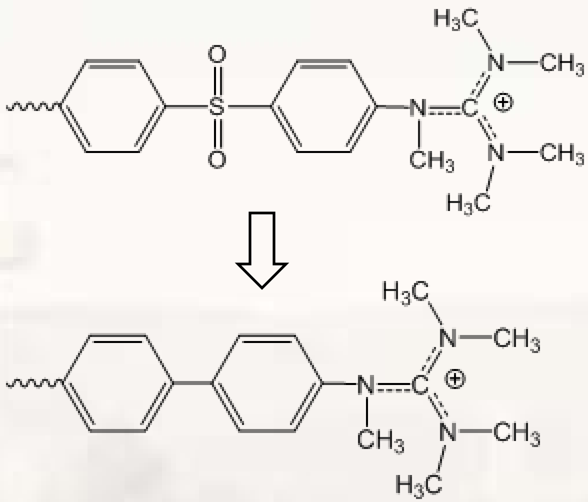
Stability increased by higher electron density!!

Future Works – Polymer Chemistry

Major focus

- **Cation Stability (LANL, SNL)**

  Electron donating spacer



Other issue

- **Proton conductivity (LANL, SNL)**

  Increasing ion exchange capacity

  Partial fluorination

  Copolymer architecture

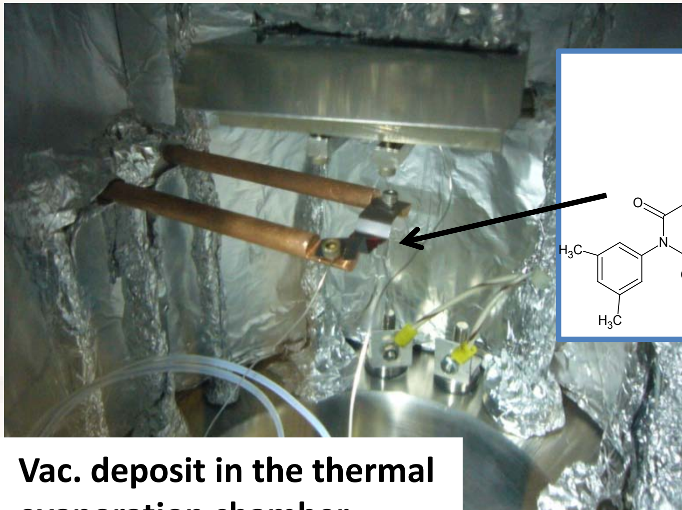
- **Polymer stability (LANL, SNL)**

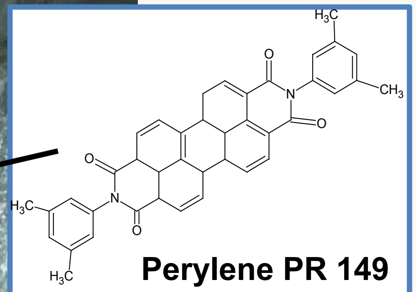
  Removing sulfone group

- **Continuing investigation of TMA based system (SNL)**

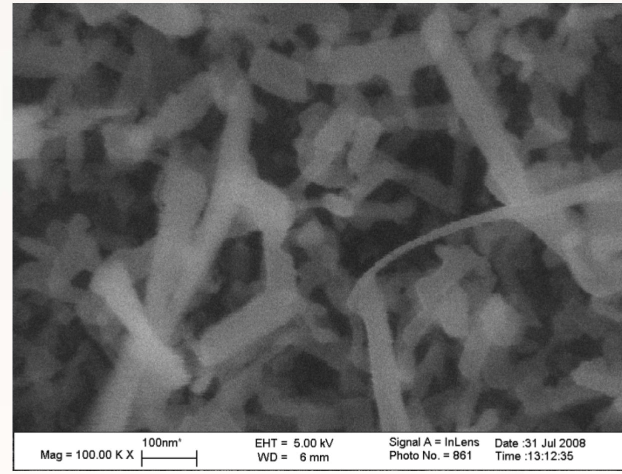
Future Works – Electrode and MEA

- **Synthesis of Nano-structured thin films (JPL)**





Vac. deposit in the thermal evaporation chamber



Converted Nano-structured Whiskers

Prepare sputter-deposited coating on multi-electrode array

Electrochemical screening tests and down select catalyst

Sputterdeposite catalysts on to NSTF materials

- **Electrode optimization and MEA fabrication (JPL, LANL)**

- **Fuel cell test (JPL, LANL)**

Collaborations

Sub Contractors

- Sandia National Laboratory: Polymer Synthesis, extensive collaboration.
- Jet Propulsion Laboratory: Electrode Preparation, extensive collaboration.

Industry

- Cellera Technologies (S. Gottesfeld): Material characterization and licensing issue, moderate interaction.
- Ovonic Fuel Cell Company (R. Privette): Material characterization, occasional.

University

- Virginia Tech. (J. McGrath) and Penn State (M. Hickner): Polymer synthesis, occasional.
- Univ. New Mexico (P. Atanassov): Catalyst synthesis, occasional.

Federal Laboratory

- National Renewable Energy Laboratory (B. Pivovar) through DOE BES Program: cation stability, occasional.
- Los Alamos Neutron Science Center (R. Hjelm) through DOE Applied Science Program: SANS experiments and modeling, moderate interaction.
- Los Alamos National Laboratory (P. Zelenay) through DOE Advanced Catalyst Program: Catalyst issue in alkaline fuel cells, moderate interaction.
- Canada NRC (M. Guiver) through DOE Technical Assistant Program): Polymer synthesis, occasional.

Summary

Project start
Sep. 1, 2009

Synthesis of high MW guanidine base membrane
Milestone 1
March 1, 2010

Go →

Highly conductive/stable anion exchange membrane
Milestone 2
September 1, 2010

→

Optimized electrode formulation and MEA processing Procedure
Milestone 3
June 1, 2011

Current Status (as of April 8, 2010)

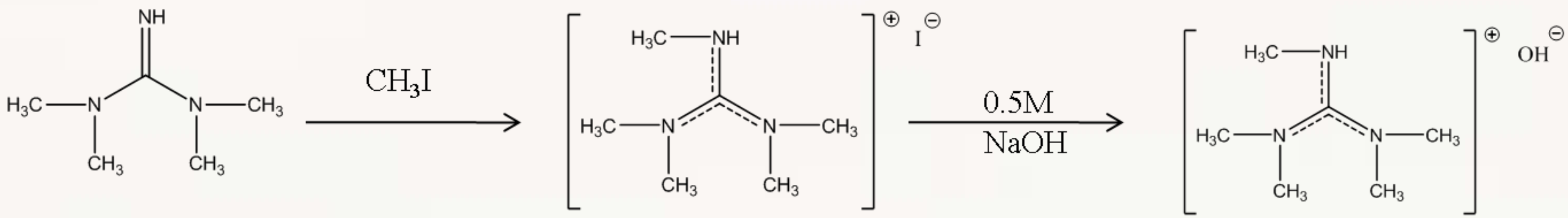
	M2 Criteria	HCGB	PFGB
σ (S/cm)	0.05	0.04	0.08
WU (wt.%)	60	9	15
σ reduction (80°C, 1M NaOH)	10% (500 h)	42 % (380 h)	Not stable

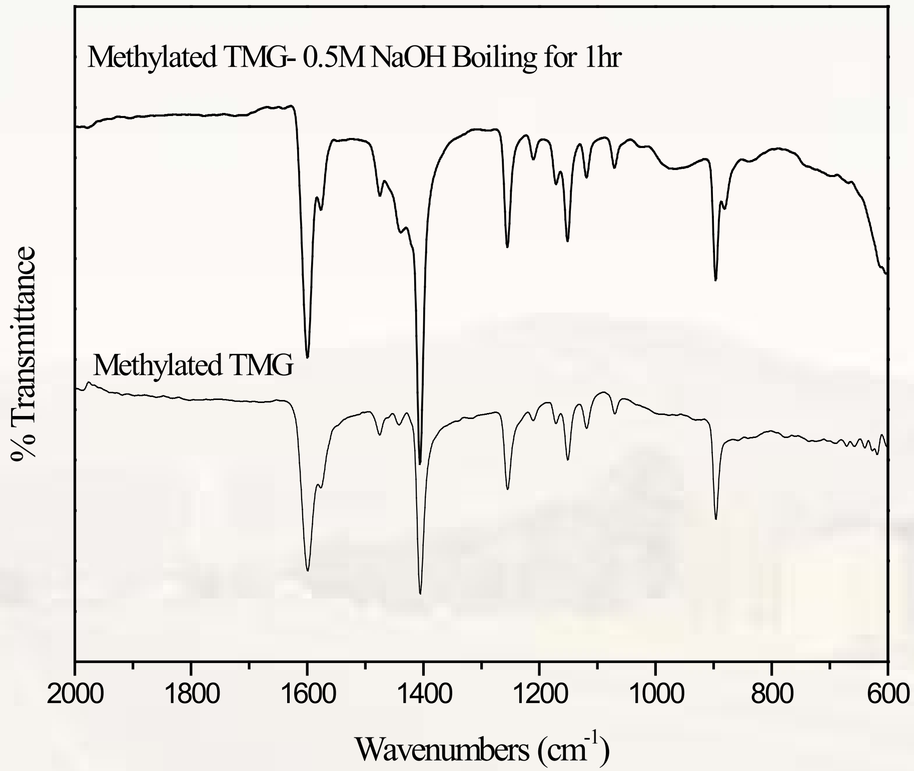
If stable PFGB ionomer is unavailable,

Development of NSTF Electrode
Opt. Milestone 2
September 1, 2010

Supplemental Slides

Stability of Methylated TMG in 0.5 M NaOH Solution

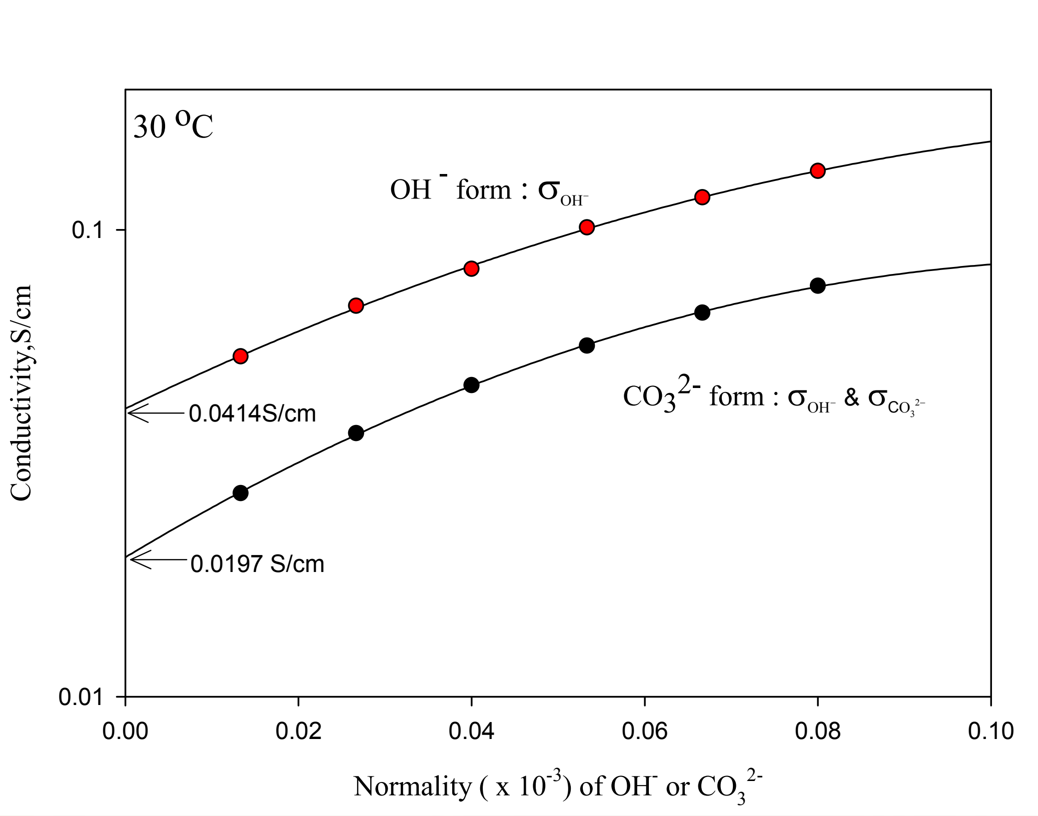




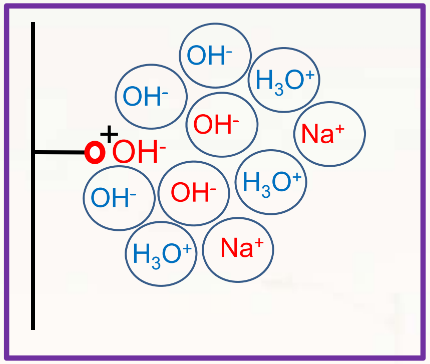
Methylated tetermethyl guanidine is stable in alkali conditions!!!

Conductivity of different Counter ion 1

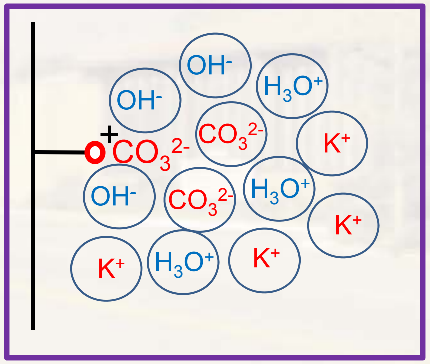
- *The conductivity was measured in water after boiling and N_2 purge(without CO_2)*



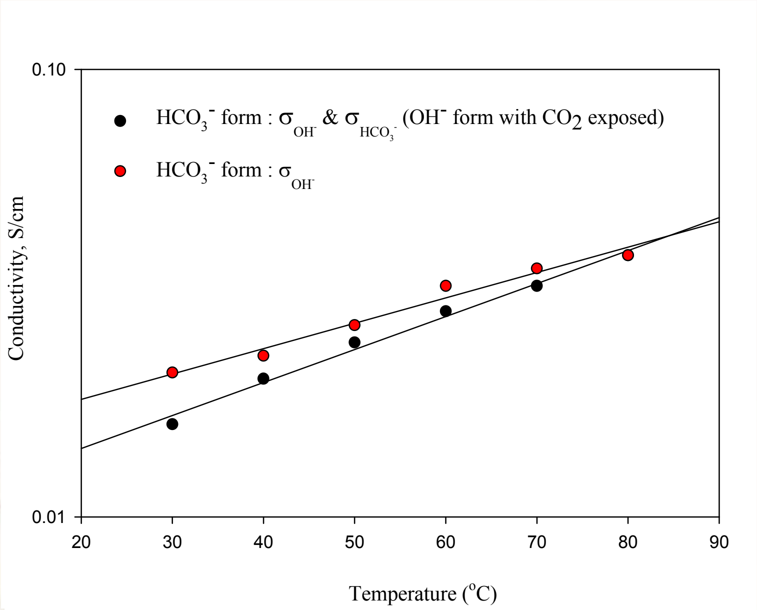
OH⁻ Form : σ_{OH^-}

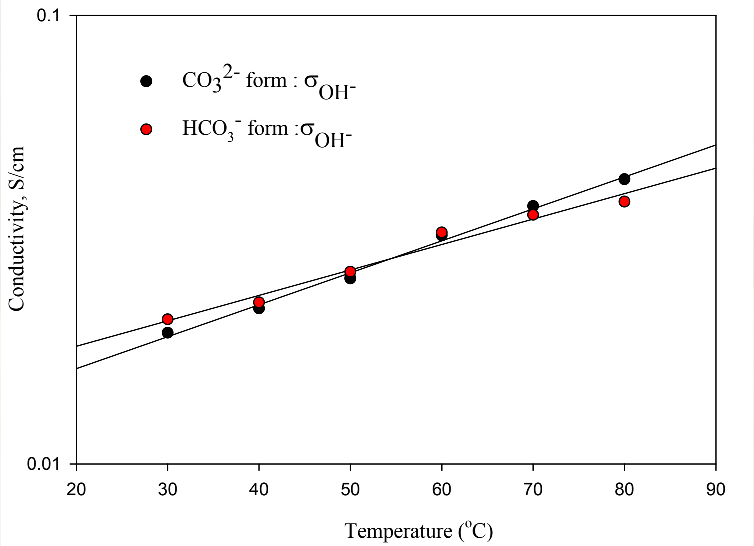


CO_3^{2-} Form : $\sigma_{OH^-} + \sigma_{CO_3^{2-}}$



Effect of CO_2 on Conductivity





pH			
> 6.5	$CO_2 + H_2O$	⟷	H_2CO_3
	H_2CO_3	⟷	$H^+ + HCO_3^-$
pH > 10.4	HCO_3^-	⟷	$H^+ + CO_3^{2-}$

- OH^- Form was replaced with HCO_3^- form by the absorption of CO_2 from air