Resonance-Stabilized Anion Exchange Polymer Electrolytes

Yu Seung Kim
(yskim@lanl.gov)

Los Alamos National Laboratory
Los Alamos, NM, 87545

Project ID: FC043

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

Overview

Timeline

Project start	**September**	**2009**
Project end	**March**	**2012**
Percent complete	**100%**	

a. Polymer & ionomer synthesis (100%)
b. Catalyst preparation (100%)
c. MEA processing & testing (100%)
d. Degradation study (100%)

Budget

Total funding	**$ 1,320 K**
Funding for FY10	**$ 528 K**
Funding for FY11	**$ 330 K**

No cost shared

Barriers

B. Cost

C. Electrode performance

A. Durability

Partners

Project lead

Los Alamos National Laboratory

Yu Seung Kim (PI)
Dae Sik Kim
Andrea labouriau
Hoon Jung

Subcontractor

Sandia National Laboratory

Cy Fujiomoto (Ext. PI)
Michael Hibbs

Jet Propulsion Laboratory

Charles Hays (Ext. PI)
Daniel Konopka
Michael Johnson
Michael Errico
Poyan Bahrami

Interactions

Cellera Technologies (Shimpshon Gottesfeld)

Advanced Industrial Science and Technology (Yoong-Kee Choe)

Ovonic Fuel Cells (Rob Privette)

Relevance – Objectives, Technical Barriers, Technical Targets and Results

Objectives

Demonstrate an improved alkaline membrane fuel cell (AMFC) performance and durability using advanced polymer electrolyte membranes, ionomers and non-precious catalysts

Major tasks

- ❑ FY 09 & 10: Synthesis of anion exchange membranes and ionomers
- ❑ FY 10 & 11: Characterization of catalyst and AMFC performance
- ❑ FY 11 & 12: AMFC durability test and durability mechanism

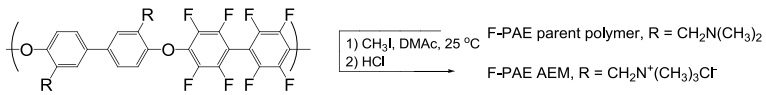
Technical Barriers, Targets and Results

ISSUES	Technical Barriers	Technical Target [a]	FY 09-10	FY 10-11	FY 11-12	Result
Membrane	Conductivity	σ: > 50 mS/cm	√	√	√	120 mS/cm
	Stability	> 500 h in NaOH soln. 60°C	×	√	√	672 h
	Tensile properties	Stress: > 10 MPa, Strain : > 10%	×	×	√	25 MPa, 30%
Ionomer	Backbone structure	Perfluorinated	√	√	√	M-Nafion®-FA-TMG
	Conductivity	> 50 mS/cm → 20 mS/cm[b]	×	√	√	20 mS/cm
	Stability	> 500 h in NaOH soln.	–	–	×	7% after 72 h
Catalyst	Element	*Non-precious metal or carbon*	–	√	√	CNT/CNP cat.
	ORR activity	> 0.9 V ($E_{1/2}$)	–	√	√	0.95 V ($E_{1/2}$)
AMFC performance	Maximum power	> 200 mW/cm^2 in H_2/Air	–	√	√	466 mW/cm^2
	Durability	< 10% for 800 h	–	–	×	~50% for 300 h[c]

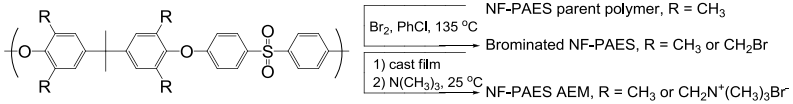
[a] Values in the original proposal
[b] Conductivity target for ionomer was lowered as we achieved MEA performance target with low conductive ionomers
[c] Mostly due to the cation stability and water management issue; ionomer and polymer backbone degradation is negligible

Synthesis of Polyaromatic Anion Exchange Membranes for Durability Study

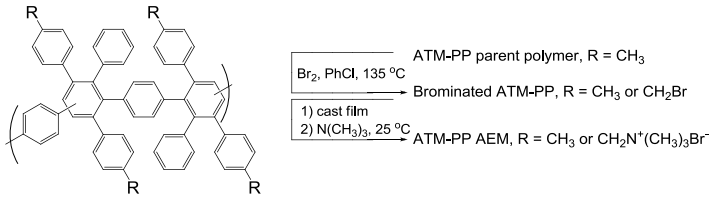
Synthesis and properties of polyaromatic AEMs



BTMA Functionalized Partially **F**luorinated **P**oly(**A**rylene **E**ther) (F-PAE)



BTMA Functionalized **N**on-**F**luorinated **P**oly(**A**rylene **E**ther **S**ulfone) (NF-PAES)



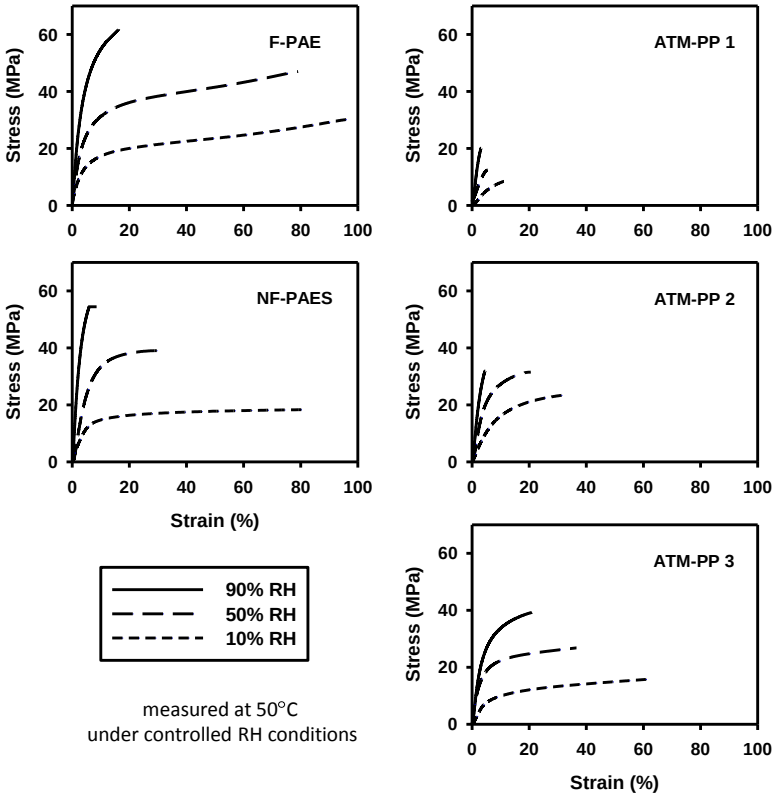
BTMA Functionalized Wholly Aromatic Poly(Phenylene) (**A**minated **T**etra**M**ethyl **P**oly**P**henylene (ATM-PP))

BTMA : Benzyl TetraMethyl Ammonium

Sample	Coun-ter ion	$M_w \times 10^3$ [a] (g/mol)	IEC (meq./g)	WU (wt.%)	σ [b] (mS/cm)
F-PAE	Cl^-	150	2.5	99	46
NF-PAES	Br^-	87	2.2	43	15
ATM-PP1	Br^-	61	1.7	72	30
ATM-PP 2	Br^-	77	1.6	64	35
ATM-PP 3	Br^-	196	1.7	70	37

[a] measured by GPC using the parent polymers
[b] measured at 80°C using salt form membranes

Stress-strain behavior of AEM parent polymers



measured at 50°C
under controlled RH conditions

- **High molecular weight polyaromatic AEMs were prepared**
- **Mechanical properties of the AEMs are strongly influenced by chemical structure and molecular weight**
- **Highlight: Stress: > 25 MPa & Elongation: > 30% at 50% RH**

Membrane mechanical milestone (> 10 MPa stress & 10% strain) achieved with F-PAE, NF-PAE and ATM-PP 3

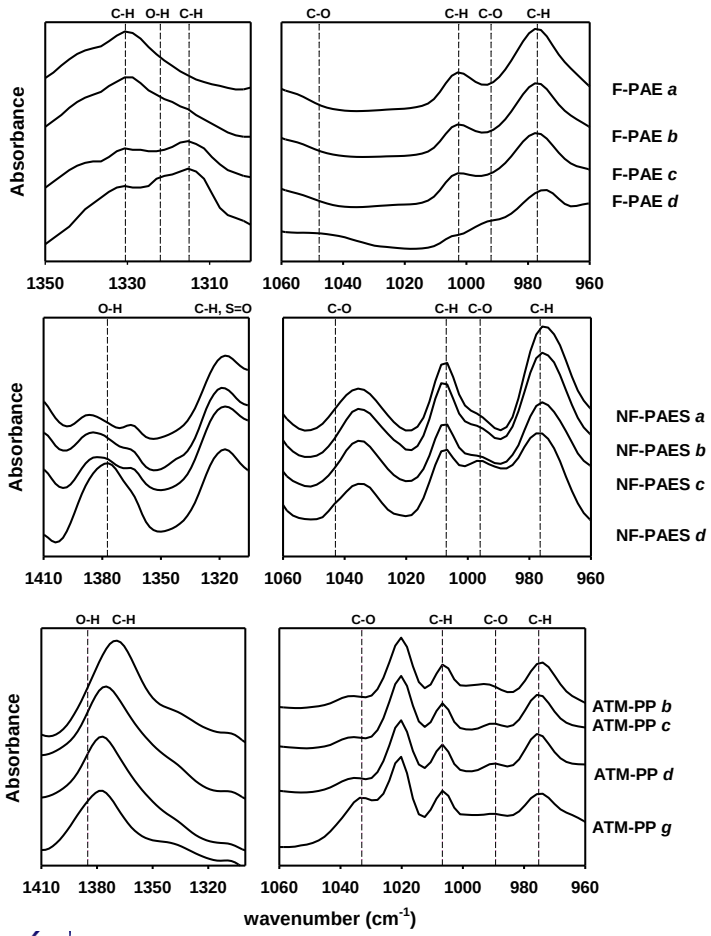
Aryl-Ether Cleavage of Poly(arylene ether) AEMs*

Membrane treatment

a: 0.5 M HCl (or HBr) for 30 min (or 2 h);
c: 0.5 M NaOH for 30 min, room temp. after ***a***
e: 0.5 M HCl (or HBr) for 30 min (or 2 h) after ***d***
g: 0.1 M NaOH for 2 h & 0.5 M NaOH for 100 h at 80° C

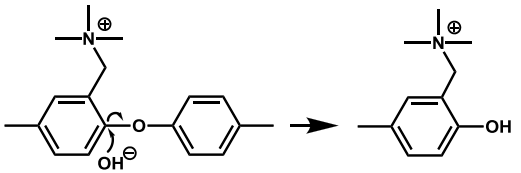
b: 0.1 M NaOH for 1 h, room temp. after ***a;***
d: 0.5 M NaOH for 1 h, 80°C after ***a***
f: 0.5 M NaOH for 1 h 80°C after ***e***

Phenol formation (FTIR) after treatment

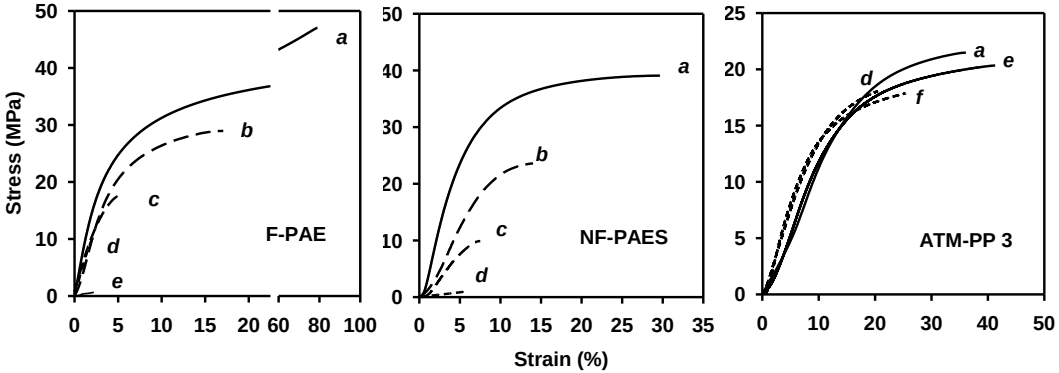


Proposed backbone degradation mechanism

Nucleophilic displacement of aryl-ether linkage



Mechanical property change after membrane treatment



- **FTIR results indicated phenol formation of poly(arylene ether) (PAE) based AEMs after membrane treatment → Nucleophilic displacement takes place in the aryl-ether linkage of the PAE backbones**
- **Mechanical properties of the AEMs are greatly influenced by the AEM backbone degradation**

Highlight: No backbone degradation observed in poly(phenylene) AEMs

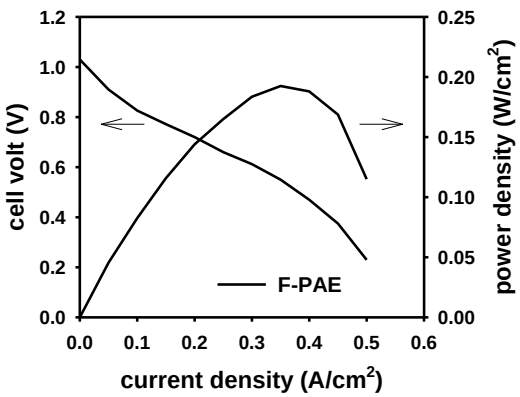
*C. Fujimoto et al. manuscript was submitted 2012

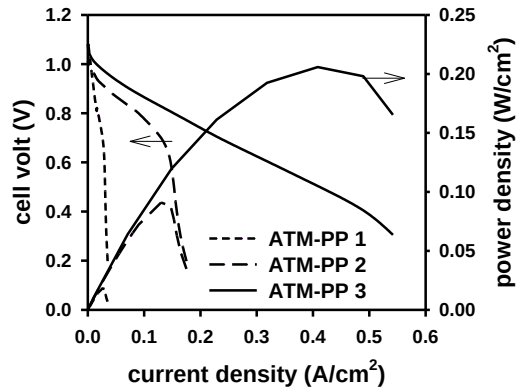
Impact of Polymer Structure on AMFC Performance*

Membrane: *fluorinated poly(arylene ether) AEM (F-PAE, LANL) and poly(phenylene)-based AEMs with three different molecular weight (ATM-PP, SNL);* ***Test conditions****: H_2/O_2 at 80 ℃*

Membrane: *F-PAE and ATM-PP 3;* ***Test conditions****: H_2/O_2 at constant voltage of 0.3 V, at 80 ℃*

Effect of molecular weight on AMFC performance





Sample	F-PAE	ATM-PP1	ATM-PP 2	ATM-PP 3
$M_w \times 10^3$ [a] (g/mol)	150	61	77	196
HFR (Ω cm^2)	0.23	1.67	1.23	0.21

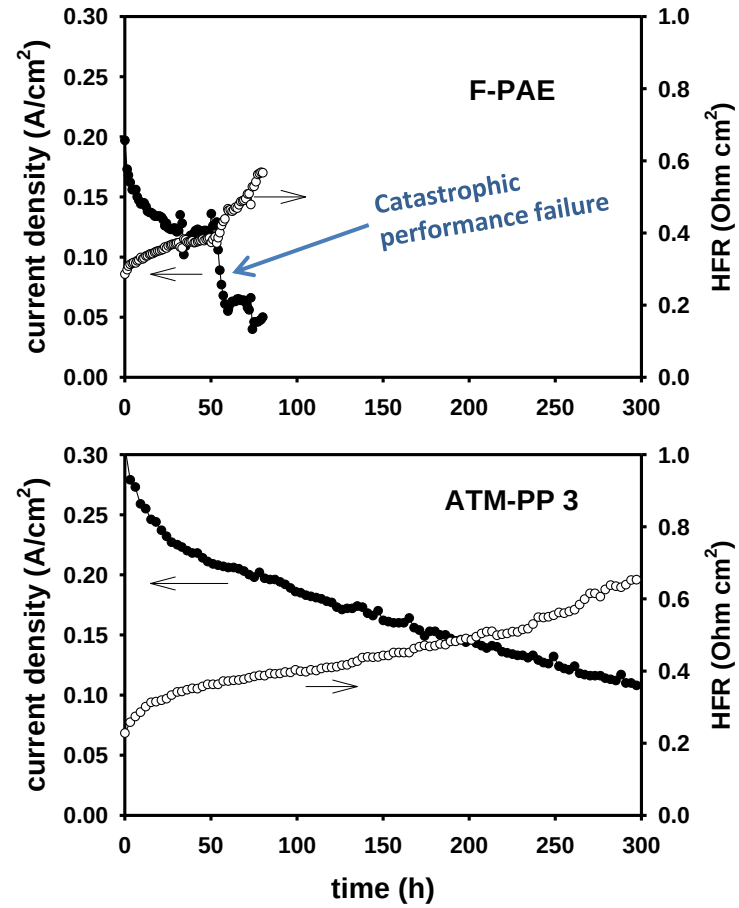
[a] measured by GPC using the parent polymers

- **The AEMs having low Mw (*ca.* < 100 K) showed poor AMFC performance due to the possible interfacial failure during MEA processing**
- **Negligible interfacial issue for high Mw F-PAE and ATM-PP**
- **F-PAE MEA showed catastrophic failure at 55h probably due to the AEM degradation**

Highlight: No catastrophic failure for ATM-PP 3 MEA during 300 h life test

*C. Fujimoto et al. manuscript was submitted 2012

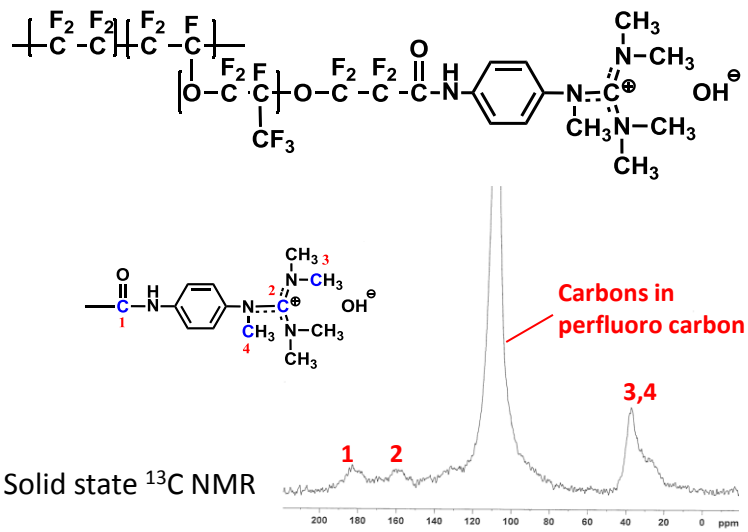
Effect of backbone degradation#



supporting information for analysis methodology

Stability of Perfluorinated Anion Exchange Ionomers

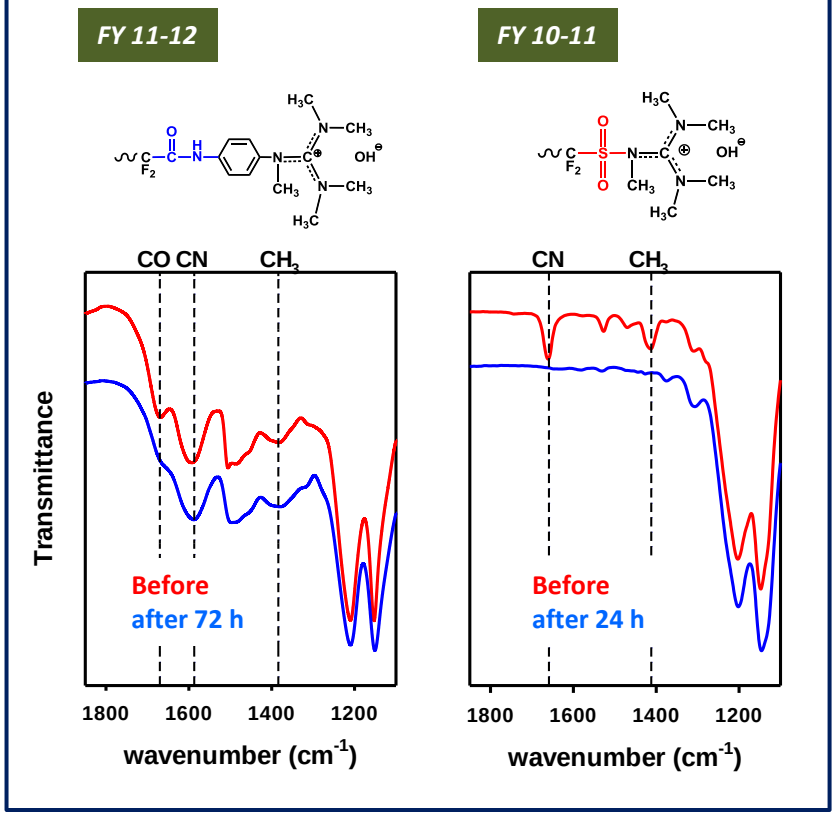
Synthesis and properties of perfluorinated AEMs



Sample		IEC (meq./g)	WU (wt.%)	σ [a] (mS/cm)
FY 11-12	M-Nafion®-FA-TMG	0.70	10	20
FY 10-11	M-Nafion®-TMG	0.90	18	45

[a] measured with hydroxide form at 80°C

Stability after soaking in 0.5 M NaOH at 80°C



- **Phenyl guanidinium has much better stability than sulfone guanidinium under high pH conditions**
- **Trace of degradation after the treatment for phenyl guanidinium functionalized perfluorinated ionomers is due to the hydrolysis of amide group rather than polymer backbone or cation degradation**

Highlight: **Stable perfluorinated ionomers were prepared by introducing electron donating spacer**

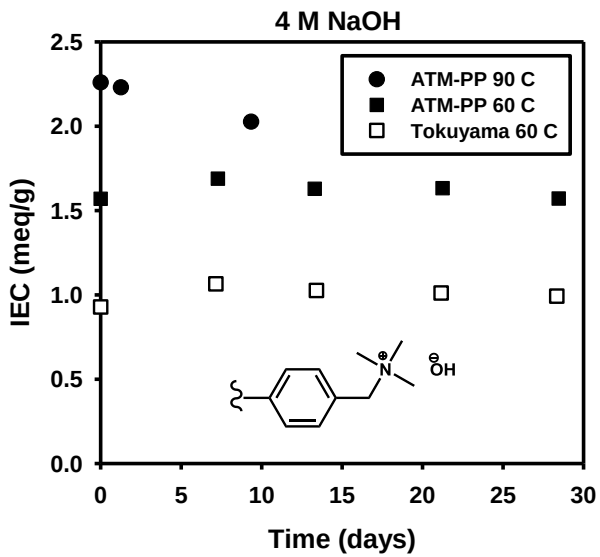
Ionomer milestone (perfluorinated ionomer with conductivity > 20 mS/cm and stability) achieved

Stability of Benzyl Tetramethyl Ammonium Cations (*ex-situ*)

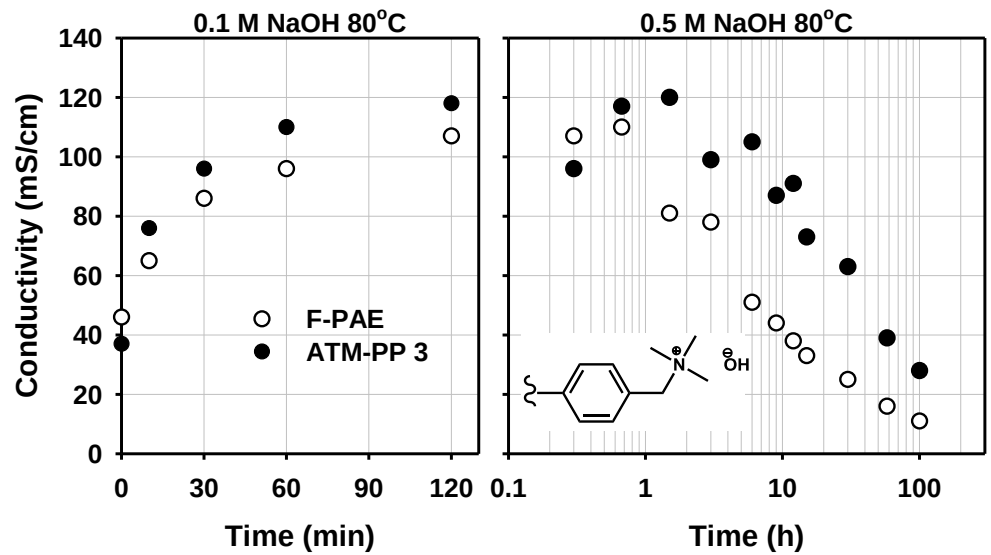
Membrane: *poly(phenylene) based AEM (ATM-PP, SNL) and crosslinked polystyrene based AEM (AHA, Tokuyama) (cf. PAE based AEMs became too brittle to handle after 1-2 days);* ***Test conditions****: 4 M NaOH (aqueous), no stirring; IEC measured with back titration*

Membrane: *Poly(phenylene) based AEM (ATM-PP, SNL) and poly(arylene ether) based AEM (F-PAE, LANL);* ***Test procedures****: 1st step: AEMs* were prepared in their salt forms and were immersed in 0.1 M NaOH at 80°C for 10, 30, 60 and 120 min and followed by rinsing those in boiling water for 1 h to remove any residual NaOH; 2nd step: AEMs were immersed in 0.5 M NaOH solution at 80°C for various time intervals

IEC change as a function of time



Anion conductivity change as a function of time*



- **Benzyl tetramethyl ammonium (BTMA) is stable at 60°C; However, ~ 10 % IEC loss after 9 days at 90°C was observed under high pH conditions**
- **Anion conductivity loss of BTMA functionalized F-PAE and ATM-PP 3 was observed at 0.5 M NaOH at 80°C over 100 h**
- **Polymer backbone degradation has a little impact on conductivity**
- **Comparing the ether cleavage degradation of PAEs, the BTMA cation degradation was much slower**

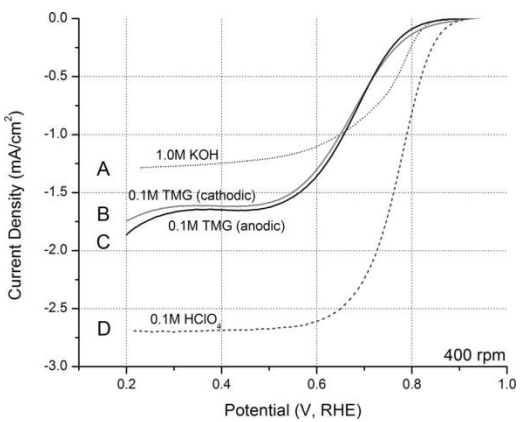
*C. Fujimoto et al. manuscript was submitted 2012

Stability Tetramethyl Guanidine Aqueous Solution (*ex-situ*)

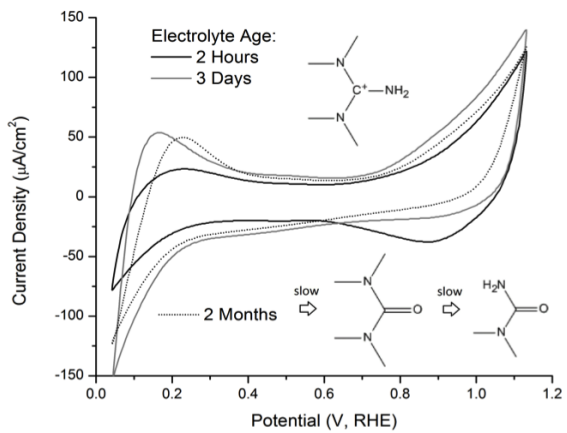
***ORR study**: under O_2 sparging with anodic and cathodic scans at a rate of 1 mV/s, between a potential range of 1.0 V to ~ 0.2 V; A separate set of scans between 1.0 and 0.8 V for the kinetically limited region*

***CV Cycling**: 0.0 to 1.1 V RHE (clockwise cycles) in 0.1 M TMG purged with sparging and blanketing Ar gas; Durability test 2 L of 0.1 M TMG was mixed and allowed to sit in open air for 2 months*

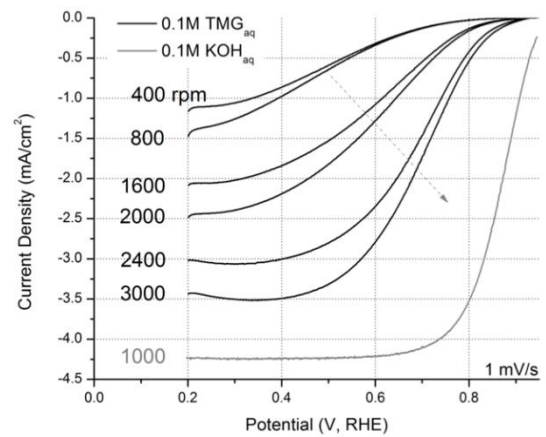
Oxygen reduction reaction on Pt



H_2O redox features of TMG



Effect of rpm on oxygen reduction



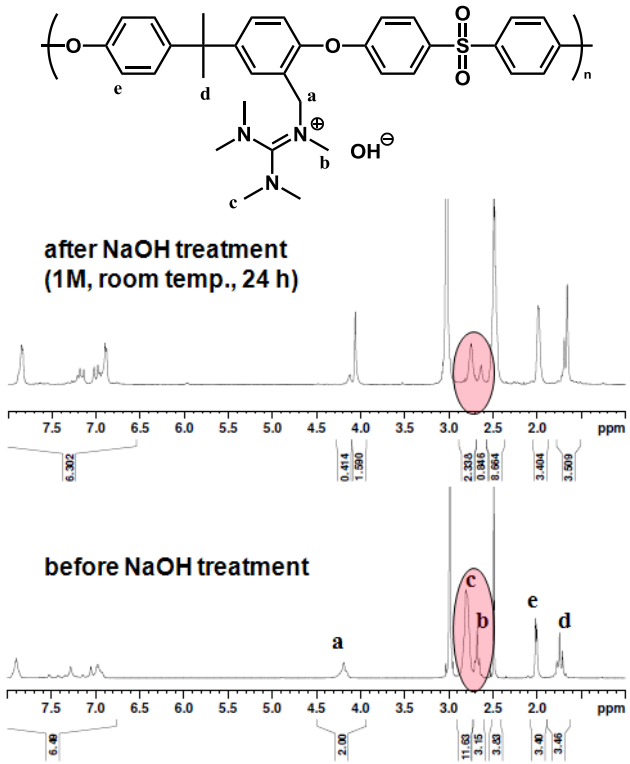
- **Tetramethylguanidine (TMG) showed electro-catalytic activity; The current at 0.9 V is similar to conventional KOH electrolytes but is less favorable at lower potential due to the probable adsorption to the Pt surface**
- **TMG and its byproducts can adsorb onto the Pt surface below ~0.8 V, obscuring the transition between typical kinetic and mass-limiting regions during oxygen reduction; This effect is especially pronounced at low rpm (low oxygen concentrations)**

Highlight: The TMG electrolyte showed remarkable stability after two months, with some signs of increasing resistivity such as the positive potential shift of the H-desorption peak

*D. Konopka et al. *Electrochem. Solid-State Lett,* **15**, B17 (2012)

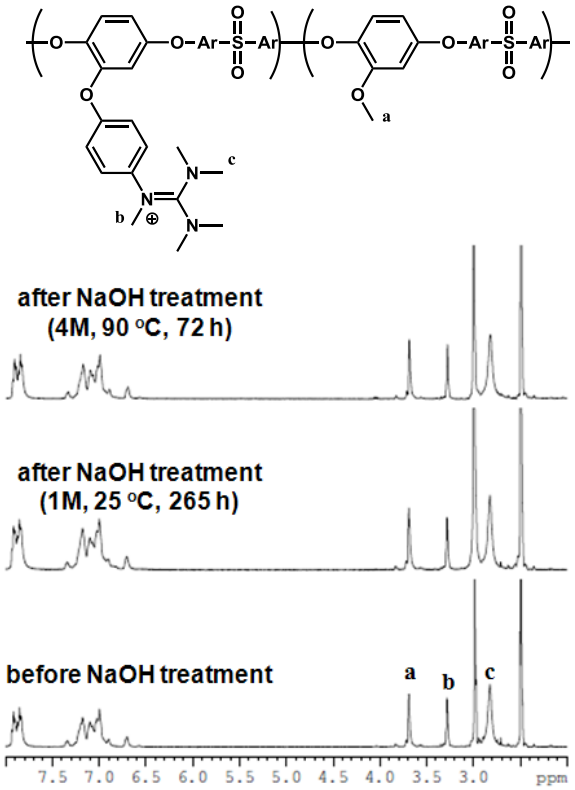
Stability of Benzyl and Phenyl Guanidinium (*ex-situ*)

Stability of benzylpentamethyl guanidinium*



The relative areas of **b** and **c** peaks decrease drastically after NaOH. But **b** to **c** area ratio does not change

Stability of phenylpentamethyl guanidinium*



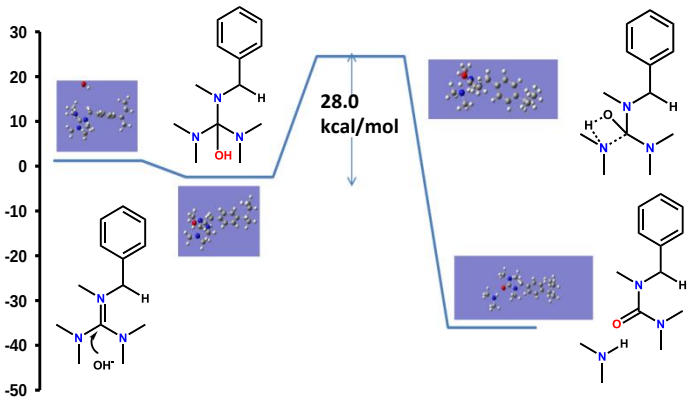
- **Benzylpentamethyl guanidinium was slowly decomposed while phenylpentamethyl guanidinium was stable under high pH conditions and elevated temperatures**

Highlight: Phenylpentamethyl guanidinium was stable at 4 M NaOH, 90°C for 72 h

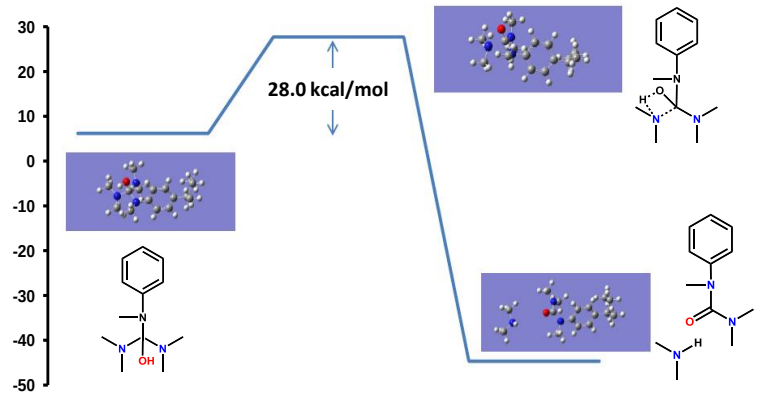
*M. Hibbs, C. Fujimoto, T. Lambert, D.S. Kim, Y.S. Kim, NAMS 2011, June 6, 2011

Quantum Chemical Modeling for Guanidinium Degradation*

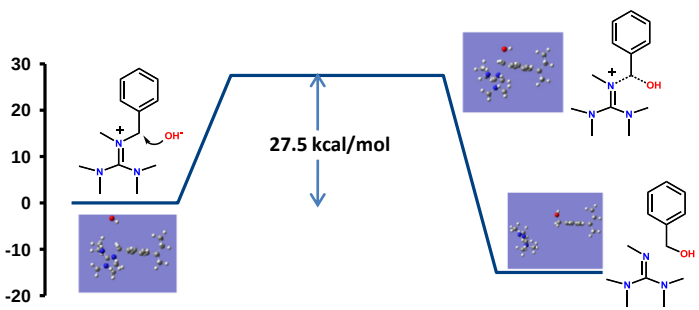
Benzyl-guanidinium (Addition + Carbonyl formation)



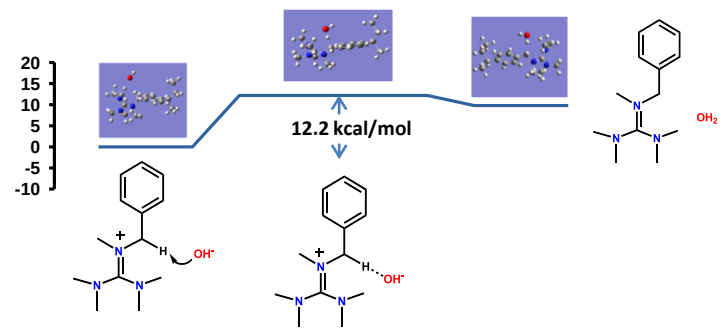
Phenyl-guanidinium (Addition + Carbonyl formation)



Benzyl-guanidinium (Nucleophilic substitution)



Benzyl-guanidinium (Elimination reaction)



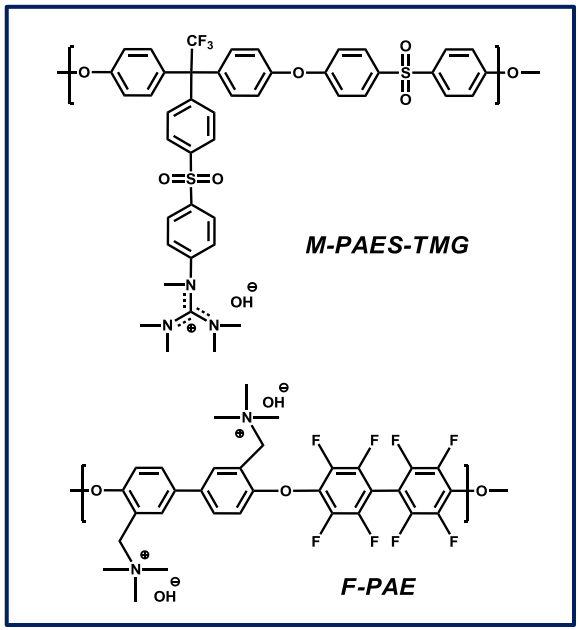
- **Alpha carbon in benzyl-guanidinium is weak site due to the nucelophilic substitution. Also hydrogen on the alpha carbon is very acidic**
- **Activation energies of center carbon of benzyl and phenyl guanidinium for addition and carbonyl formation are similar**

Next: The stability comparison with benzyl tetraalkyl ammonium is under investigation at AIST

*Yoong-Kee Choe, unpublished results, AIST

Stability Comparison BTMA vs. Phenyl Guanidinium (*in-situ*)

Cation functionalized ionomers

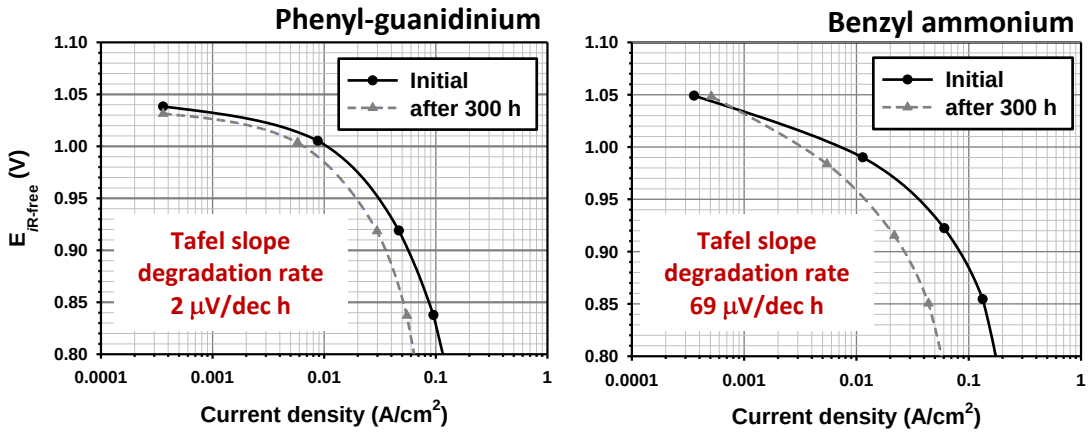


* Polymers were synthesized from FY 11 tasks

Sample	IEC (meq./g)	WU (wt.%)	σ (mS/cm)
M-PAES-TMG	1.0	10	35
F-PAE	2.4	85	100

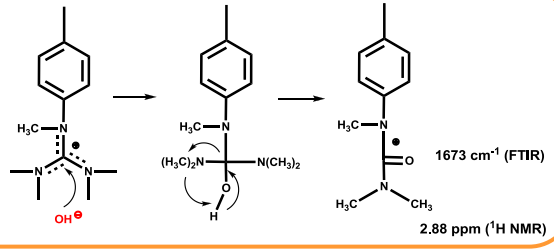
Membrane: *Benzyl tetramethyl ammonium functionalized poly(phenylene) (ATM-PP 3, 50 μm thick); Catalyst: Pt black (3 mg/cm²) for anode and cathode; Ionomer for catalyst layer: M-PAES-TMG and F-PAE; testing conditions: H_2/O_2 at 60 ℃; Durability test: Constant voltage of 0.3 V for 300 h*

Durability of ionomer (phenyl guanidinium vs. benzyl ammonium)



Proposed phenyl pentamethyl guanidinium degradation mechanism

Addition and carbonyl formation
Nucelophilic attack to the central carbon



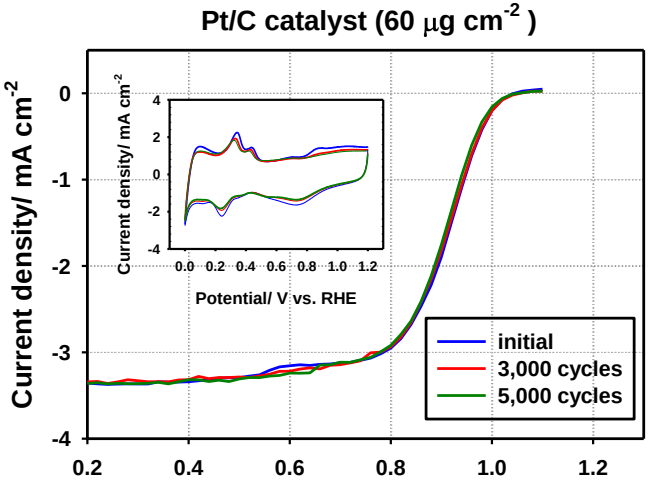
- **The stability of phenylpentamethyl guanidinium and benzyltetramethyl ammonium functionalized PAEs were compared when used as ionomer in the catalyst layer**
- **Spectroscopic results indicated that central carbon of pentamethyl guanidinium is the weakest site which is consistent with quantum chemical modeling**

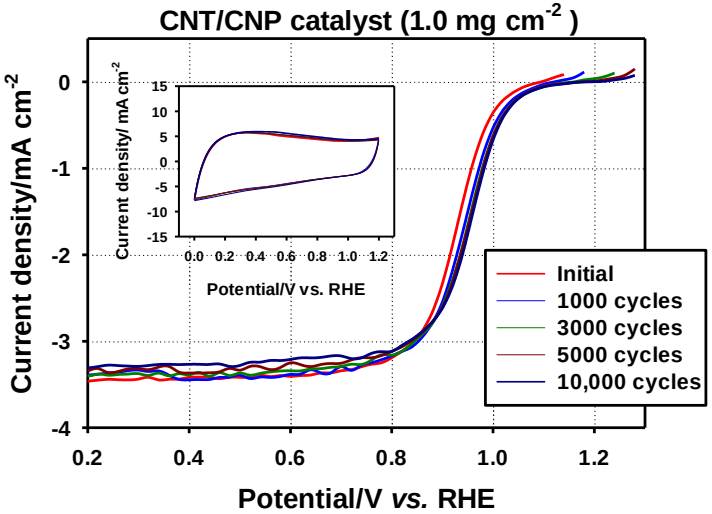
Highlight: Phenyl guanidinium cation was substantially more stable than BTMA after 300 h durability test (2 vs. 69 μV/dec h)

Stability of Pt and CNT/CNP Composite Catalyst (*ex-situ*)

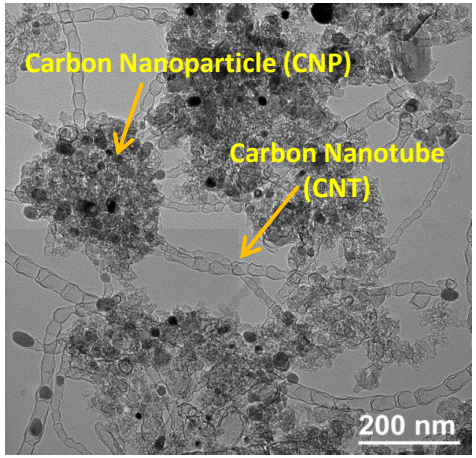
RDE: *E-TEK Pt/C, Pt loading: 60 µg cm^{-2}; N-M-C, 1.0 mg cm^{-2}; 0.1 M NaOH; 900 rpm; room temperature; Ag/AgCl (3 M NaCl) reference electrode; steady-state potential program (OCP for 120 s first, then 20 mV steps, 25 s/step); Cycling: 0.6 -1.0 V, 50 mV s^{-1}, O_2-saturated solution*

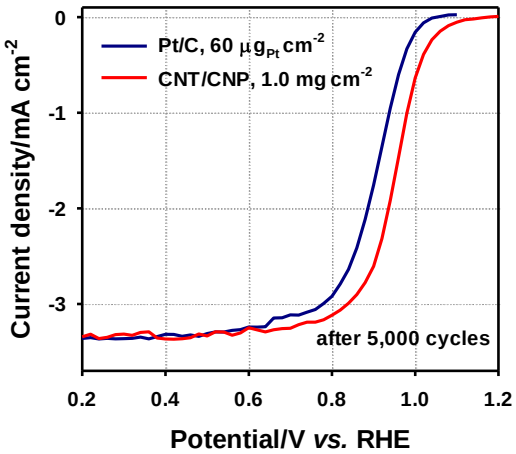
Cycling stability in 0.1 M NaOH





Morphology and ORR activity of CNT/CNP catalyst





- **Novel CNT/CNP composite catalyst was prepared from nitrogen containing compound and carbon black**
- **Both Pt and CNT/CNP catalyst showed excellent stability under high pH conditions up to after 10,000 potential cycles**
- **The CNT/CNP showed high activity after 5,000 potential cycles (*ca.* $E_{1/2}$ = 0.95 V)**

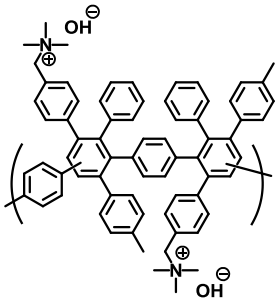
Highlight: Durability of electro-catalyst is no issue and the electrochemical activity of CNT/CNP catalyst is excellent

Catalyst ORR activity milestone ($E_{1/2}$ > 0.9 V) achieved

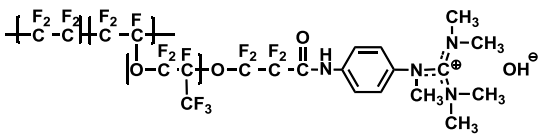
H_2/O_2 AMFC Performance

Materials for MEA fabrication

AEM & hydrocarbon ionomer: ATM-PP 3

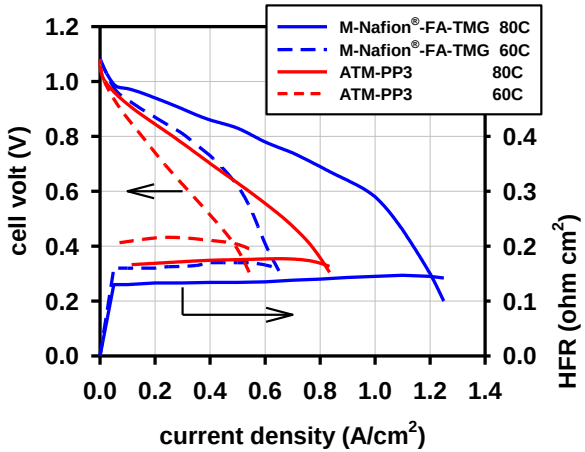


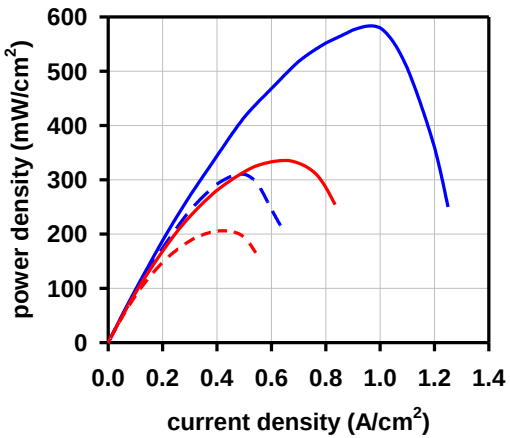
PF ionomer: M-Nafion®-FA-TMG



Membrane: *BTMA functionalized poly(phenylene) (ATM-PP 3, 50 μm thick);* ***Catalyst****: Pt black (3 mg/cm²) for anode and cathode;* ***Ionomer*** *for catalyst layer: M-Nafion-FA-TMG and ATM-PP 3*

H_2/O_2 initial performance comparison between HC and PF ionomer





Ionomer	IEC (meq./g)	WU (wt.%)	σ [a] (mS/cm)	HFR (ohm cm²)		Maximum Power density (mW/cm²)	
				60°C	80°C	60°C	80°C
ATM-PP 3	1.7	100	120	0.215	0.174	206	335
M-Nafion®-FA- TMG	0.7	10	20	0.165	0.134	306	577

[a] measured with hydroxide form at 80°C

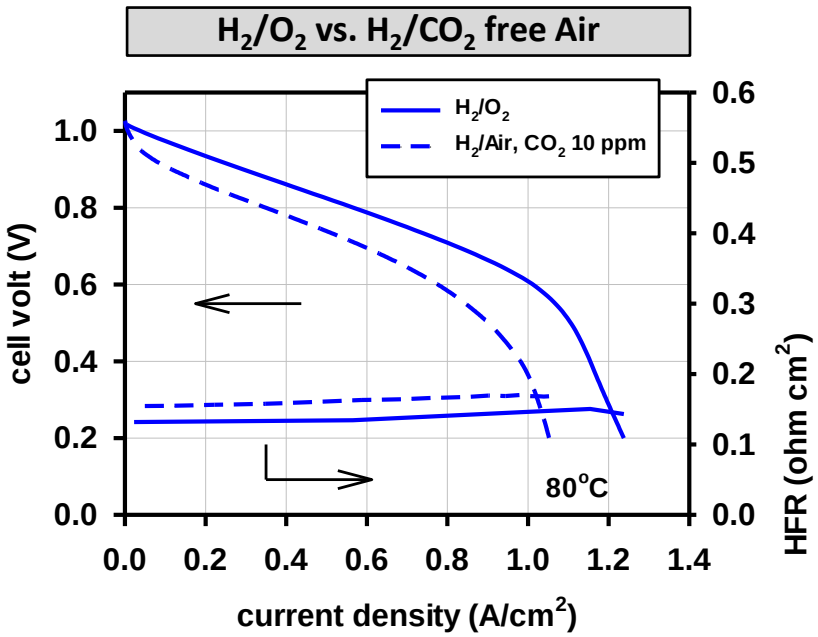
- **Membrane electrode assemblies for AMFC were prepared from LANL decal process using the AMFC materials**
- **The MEA using M-Nafion®-FA-TMG showed superior performance to the MEA using ATM-PP 3**

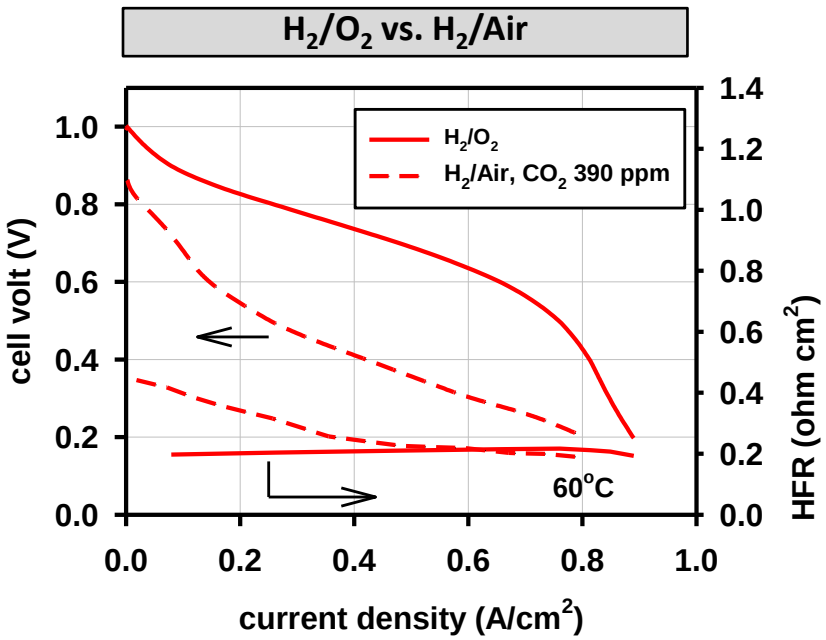
Highlight: Maximum power density reached to 577 mW/cm² at 80°C under H_2/O_2 conditions

High AMFC performance using hydrocarbon AEM and resonance stabilized perfluorinated ionomer was demonstrated

H_2/Air AMFC Performance

Membrane: *BTMA functionalized poly(phenylene) (ATM-PP 3, 50 μm thick);* ***Catalyst****: Pt black (3 mg/cm²) for anode and cathode;* ***Ionomer*** *for catalyst layer: M-Nafion®-FA-TMG*



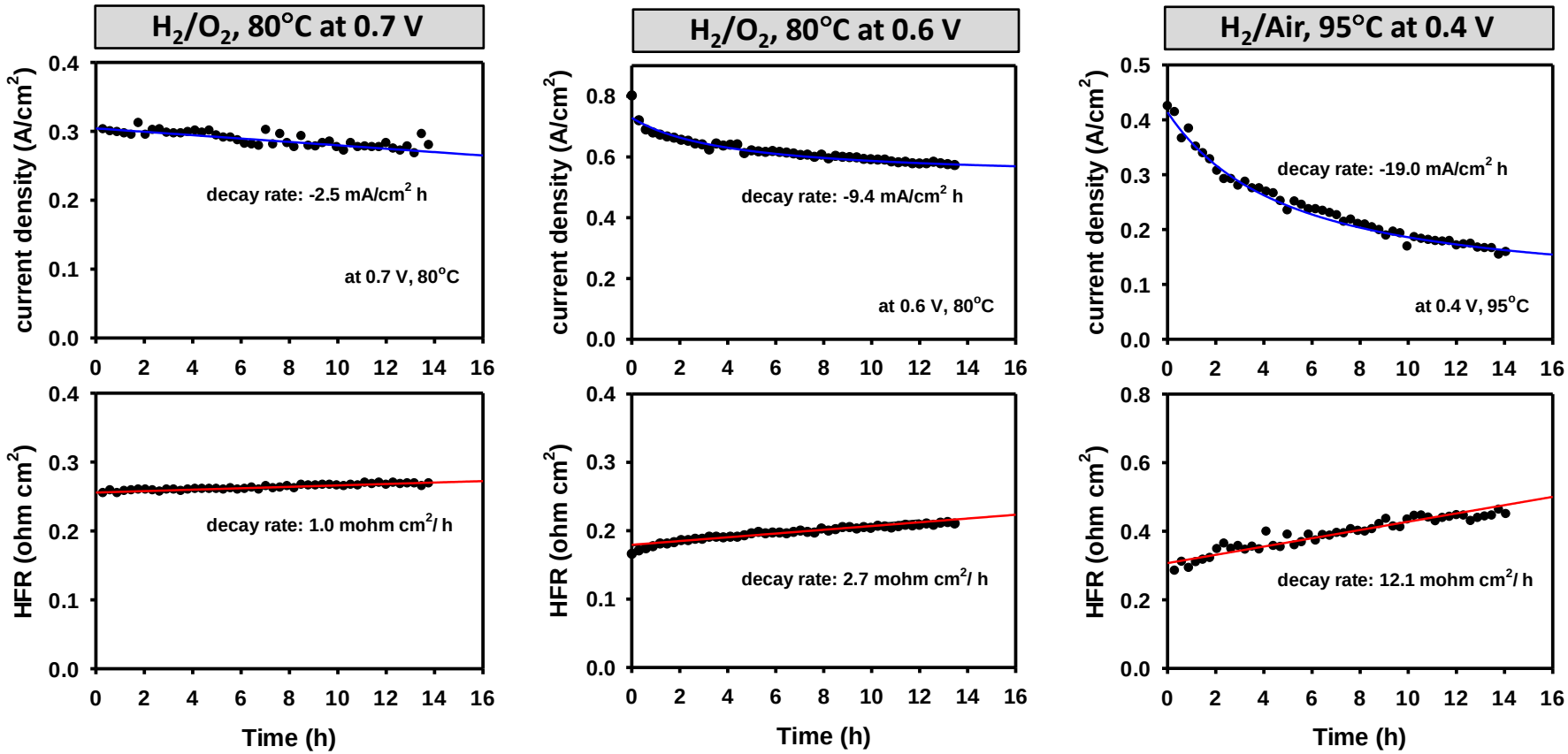


- **H_2/CO_2 free air AMFC performance showed excellent performance**
- **Additional loss for H_2/normal air (CO_2 = 390 ppm) conditions was observed; The performance loss was significant at low current region, indicating some water management problems possibly due to the bicarbonate/carbonate issue at lower current density. Further study for the performance loss is required**

Highlight: Maximum power density reached to 466 mW/cm² at 80°C under H_2/CO_2 free Air conditions

Durability of BTMA-functionalized Poly(phenylene)s (*in-situ*)

Membrane: *BTMA functionalized poly(phenylene) (ATM-PP 3, 50 μm thick);* ***Catalyst****: Pt black (3 mg/cm²) for anode and cathode;* ***Ionomer*** *for catalyst layer: M-Nafion®-FA-TMG; Life test conditions: constant voltage under full hydration*



- **The AMFC performance degradation depends on cell operating conditions; Large portion of current loss at low voltage conditions is due to water management issue which is recoverable loss.* However, HFR increase mostly reflects the AEM degradation**
- **AEM degradation rate increased with decreasing cell voltage and increasing operating temperature**

*see supporting information

AMFC Degradation Summary

Ex-situ testing in NaOH aqueous solution

Compo-nent	Type	Degradation* (time, NaOH, Temp.)	Slide page
Polymer	Poly(arylene ether) Aryl ether linkage	Fast (*g*) (< 1 h, 0.5M, 80°C)	5
	Poly(phenylene)	Stable	5
	Perfluorinated	Stable	7
	Amide linkage	Slow (*g*) (72h, 0.5M, 80°C)	7
Cation	Tetramethyl guanidine aqueous soln.	Slow (*g*) (2 month, TMG 0.1 M, 25°C)	9
	Benzyl tetra methylammonium	Slow (*g*) (< 100 h, 0.5 M, 80°C)	8
	Sulfone penta methyl guanidinium	Fast (*g*) (< 1 h, 0.5 M, 80°C)	7
	Benzyl penta methyl guanidinium	Moderate (*g*) (24 h 1M, 25°C)	10
	Phenyl penta methyl guanidinium	Stable	10
Electro-catalyst	Platinum/carbon	Stable	13
	CNT/CNP	Stable	13

In-situ AMFC testing

Component	Type	Degradation (time, Temp.)	Slide page
Polymer	Poly(arylene ether)	Moderate (*c*) (55h, 80°C)	6
	Poly(phenylene)	Stable	6
Cation	Benzyl tetramethyl ammonium (AEM)	moderate (*g*) (100h, 80°C)	16
	Benzyl tetramethyl ammonium (ionomer)	Slow (*g*) (< 100h, 80°C)	12
	Phenyl pentamethyl guanidinium (ionomer)	Slow (*g*) (72h, 90°C)	12
AEM-electrode interface	AEM with Mw < 100 K	Unstable (*c*)	6
	AEM with Mw > 100 K	Stable	6
Electro-catalyst	Platinum/carbon	Stable	13
	CNT/CNP	Stable	13
*Water management**	Hydrocarbon ionomer	Fast (*g*)	S
	Perfluorinated ionomer	Moderate (*g*)	

g*: gradual loss; ***c*: catastrophic loss

- **In general, the degradation rate of AMFC materials was faster under *ex-situ* conditions than under *in-situ* test; however other degradations such as membrane-electrode interface or water management issue played greater role in *in-situ* AMFC testing**

Highlight: **Materials developed from this project (appeared in yellow box) showed at least comparable durability to the state-of-the-art AMFC materials**

Project Summary

Relevance: Alkaline membrane fuel cells may enable non-precious metal catalysts and avoid or mitigate the shortcomings of traditional liquid AFCs

Approach: Develop highly stable and conductive anion exchange polymer electrolytes using resonance stabilized guanidinium cations and perfluorinated ionomer

Technical Accomplishments and Progress:

Demonstrated good H_2/O_2 and H_2/air AMFC performance (> 450 and 550 mW/cm^2, respectively) at 80°C

Established several synthetic pathways to prepare stable anion exchange polymer electrolytes and carbon based non-precious metal catalysts

Explored degradation phenomena for polymer backbones, cations and ionomers and ranked the stability both under *ex-situ* and *in-situ* conditions

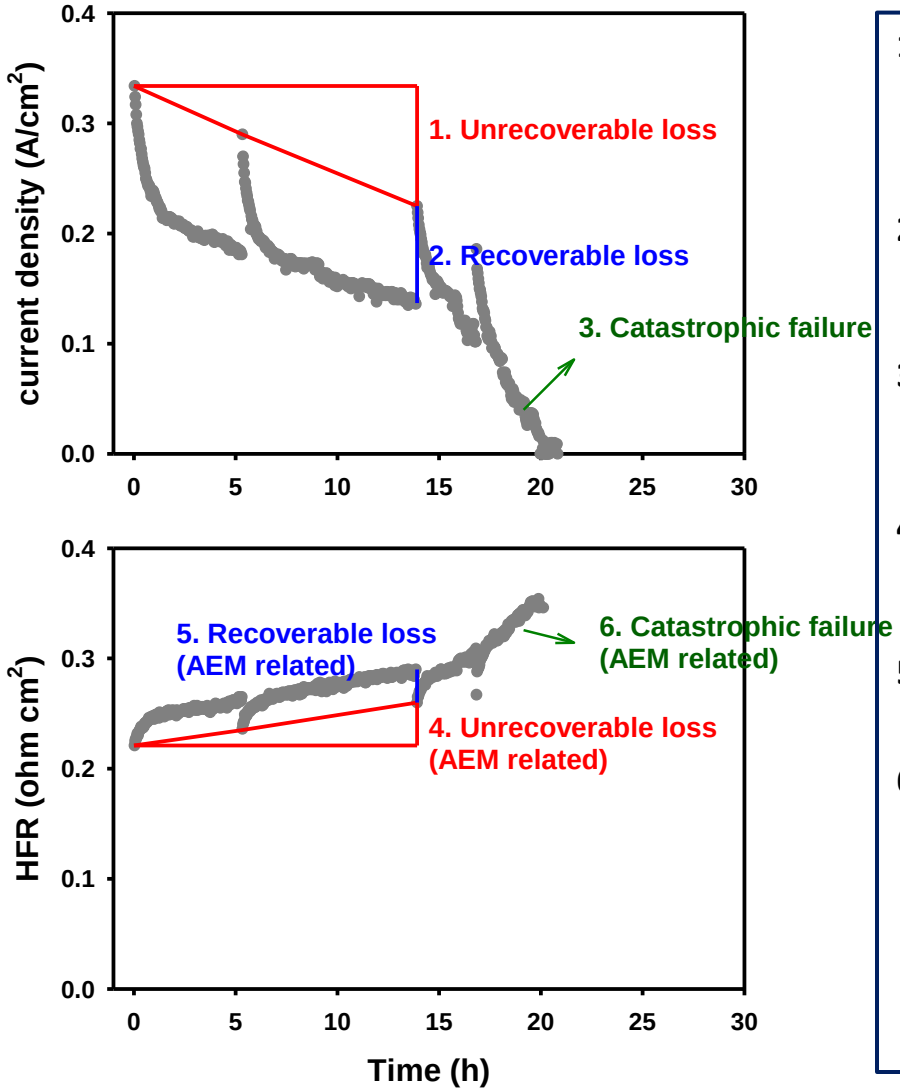
Technology Transfer/Collaborations: Active partnership with Ovonic Fuel Cells and Cellera Inc.; Several patent applications were filed for technology transfer

Proposed Future Research: Catalyst-ionomer interaction and further improvement on stability, conductivity and mechanical properties of polymer electrolytes

Technical Back-Up Slides

Decoupling Degradation from *in-situ* AMFC testing

AMFC extended term test example



General observation & *in-situ* methodology

1. **Unrecoverable loss includes:**
   AEM degradation, ionomer degradation, catalyst degradation and interfacial degradation; AEM and ionomer cation degradation are the major contributors
2. **Recoverable loss includes:**
   AEM dehydration and local flooding depending on operating conditions
3. **Catastrophic failure is mostly due to:**
   AEM backbone failure (this failure accompanied by OCV decrease)
4. **Unrecoverable loss (AEM related) includes:**
   AEM degradation and interfacial degradation: In all cases with few exception, AEM degradation
5. **Recoverable loss (AEM related) is due to:**
   AEM dehydration
6. **Catastrophic failure is mostly due to:**
   AEM backbone failure (this failure accompanied by OCV decrease)

Separated from current density and HFR behavior, the Ionomer degradation rate was measured from Tafel slope change