

Project ID: FC146

Advanced Materials for Fully-Integrated MEAs in AEMFCs

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Los Alamos National Laboratory

June 8, 2017

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Overview

Timeline

- Project start date: 11/2/2015
- Project end date: 11/2/2018
- Percent complete: 60%

Budget

- Total project funding: \$3,060K
 - DOE share: 98%
 - Contractor share: 2%
- Funding received in FY17: \$1,020K
- Total DOE Funds Spent*: \$1,040K

*As of 4/26/2017

Barriers

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

Project lead

- Los Alamos National Laboratory
 - Yu Seung Kim

Partners

- Sandia National Laboratory
 - Cy Fujimoto
 - Michael Hibbs



- Rensselaer Polytechnic Institute
 - Chul Sung Bae



- Argonne National Laboratory
 - Vojislav Stamenkovic



Relevance

Objective

- Development of improved AEMs, ionomeric binders and integration of catalysts and AEMs into high-performance MEAs.

Technical Target

	Units	LANL Baseline (2015)	DOE Target ⁴ (4Q, 2017)	Current Status (1Q, 2017)
ASR	Ω/cm^2	0.2	≤ 0.1	0.05
AEMFC Performance	mA/cm^2 at 0.6 V	980 (3.0 atm) ¹ 420 (3.0 atm) ²	600 (≤ 1.5 atm)	1,610 (3.0 atm)
AEM Durability	ASR after 500 h run at 600 mA/cm^2	0.8 after 300 h run at 0.3 V	0.1	0.05 after 300 h run at 0.3 V
AEMFC Durability	% voltage loss after 2000 h run at 600 mA/cm^2 at $\geq 60^\circ\text{C}$	60% after 300 h run at 0.3 V at 60°C ³	$< 10\%$ (2Q, 2019)	Not evaluated yet

1: Perfluorinated ionomer; 2: Polyaromatic ionomer; (*Macromolecules* 46, 7826, 2013);
3: *J. Memb. Sci.* 423, 438 (2012); 4: From FCTO MYRDD Plan

Approach: Technical Details

AEM Stability (2015-2016)

- ✓ Polymer backbone stability: Aryl-ether free polymer backbone.
- ✓ Cationic group stability: Alkyl ammonium or resonance stabilized cationic group.

AEMFC Performance (2016-2017)

- Benzene adsorption at HOR potential:
 - (i) Synthesis of ionomers with less-benzene.
 - (ii) Implementation of Pt-Ru alloy catalyst.

AEMFC Durability (2017-2018)

- Time-dependent cation-hydroxide-water co-adsorption
- Investigating other performance degradation mechanism

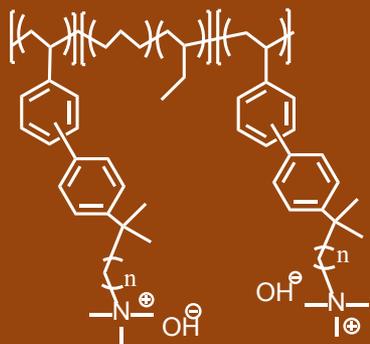
Approach: Milestone & Go-No-Go Decision

Date	Milestone & Go-No-Go	Status# (%)	Comments
Mar. 2016	Down-select AEM	100 (Feb. 2016)	Selected poly(phenyl alkylene) & Diels-Alder poly(phenylene)s
Jun. 2016	Preparation of ionomer binder	100 (Jul. 2016)	Selected guanidinium functional group
Sep. 2016	Assess baseline AMFC performance	100 (Nov. 2016)	Accomplished with testing 20+ MEAs
Dec. 2016	Down-select ionomeric binder	80	Delayed due to the delayed HOR study
Mar. 2017	<i>In-situ</i> AEM ASR measurement; $\leq 0.1 \Omega \text{ cm}^2$ for 500 h at 600 mA/cm ² (G-NG)	80	Obtained $0.05 \Omega \text{ cm}^2$ for 300 h (stopped test due to the gradual fuel cell performance loss)
Jun. 2017	Assess perfluorinated ionomer performance	100 (Mar. 2017)	Completed stability assessment*; Eliminated further development.
SEP. 2017	Integrate MEAs using down-selected AEM and ionomer; Peak power density > 0.6 W/cm² in H₂/O₂ (Milestone)	100 (Apr. 2017)	Obtained 1 W/cm^2 peak power density (used commercial Pt-Ru alloy catalyst)
Dec. 2017	Down-select HOR catalyst	30	Selected PtRu alloy catalyst
Mar. 2018	AMFC performance with down-selected HOR catalyst; Peak power density: 1 W/cm² (Milestone)	90	Obtained 1 W/cm^2 peak power density (used commercial Pt-Ru alloy catalyst)

#as of April 26, 2017, *result shown in Reviewers Only Slide R1.

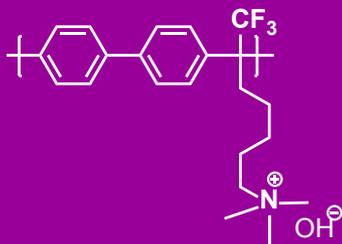
Anion Exchange Membranes Developed from This Project

Styrene-Ethylene-Butylene-Styrene Triblock Copolymer (SEBS series)



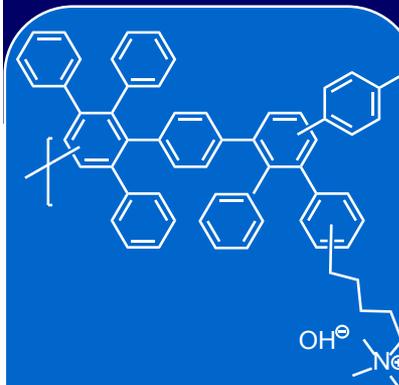
- Developed at RPI (Mohanty & Bae)
- Flexible Elastomeric AEMs

Poly Bi-(or Ter-) Phenyl Alkylene (PBPA series)



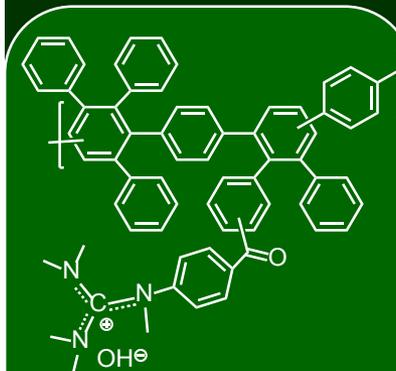
- Developed at RPI (Lee, Park & Bae)
- High M_w Engineering Plastics

Hexamethyl Ammonium Poly(Phenylene) (TMAC6PP series)



- Developed at SNL (Hibbs & Fujimoto)
- Whole Phenylene Backbone by Diels-Alder reaction

Phenyl Guanidinium Poly(Phenylene) (PGP series)

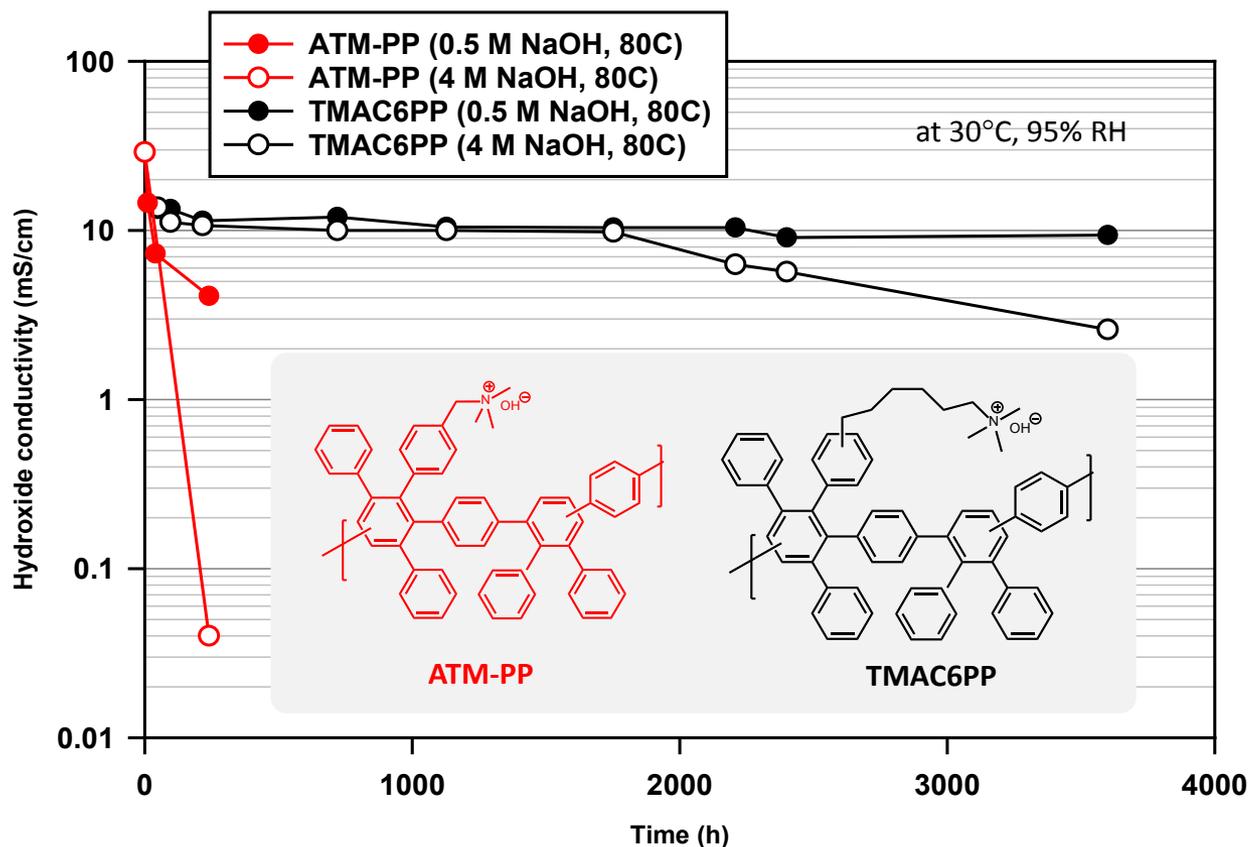


- Developed at SNL & LANL (Fujimoto & Kim)
- Extended-resonance Stabilization

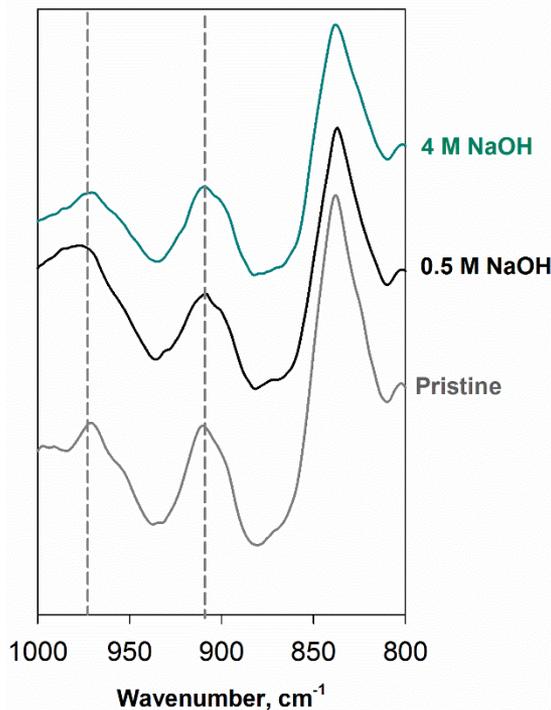
- Down-selected PBPA for AEM applications.
- Down-selected TMAC6PP for MEA study.
- Developing PGP for a potential ionomer candidate.

Provided the synthesis and alkaline stability of SEBS, PBPA PGP series in the Technical Back-up Slide T1-T3.

Ex-situ Alkaline Stability of TMAC6PP AEM

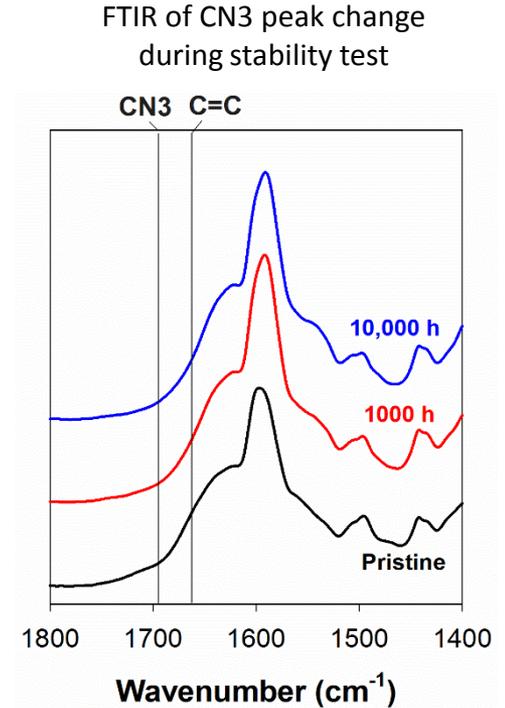
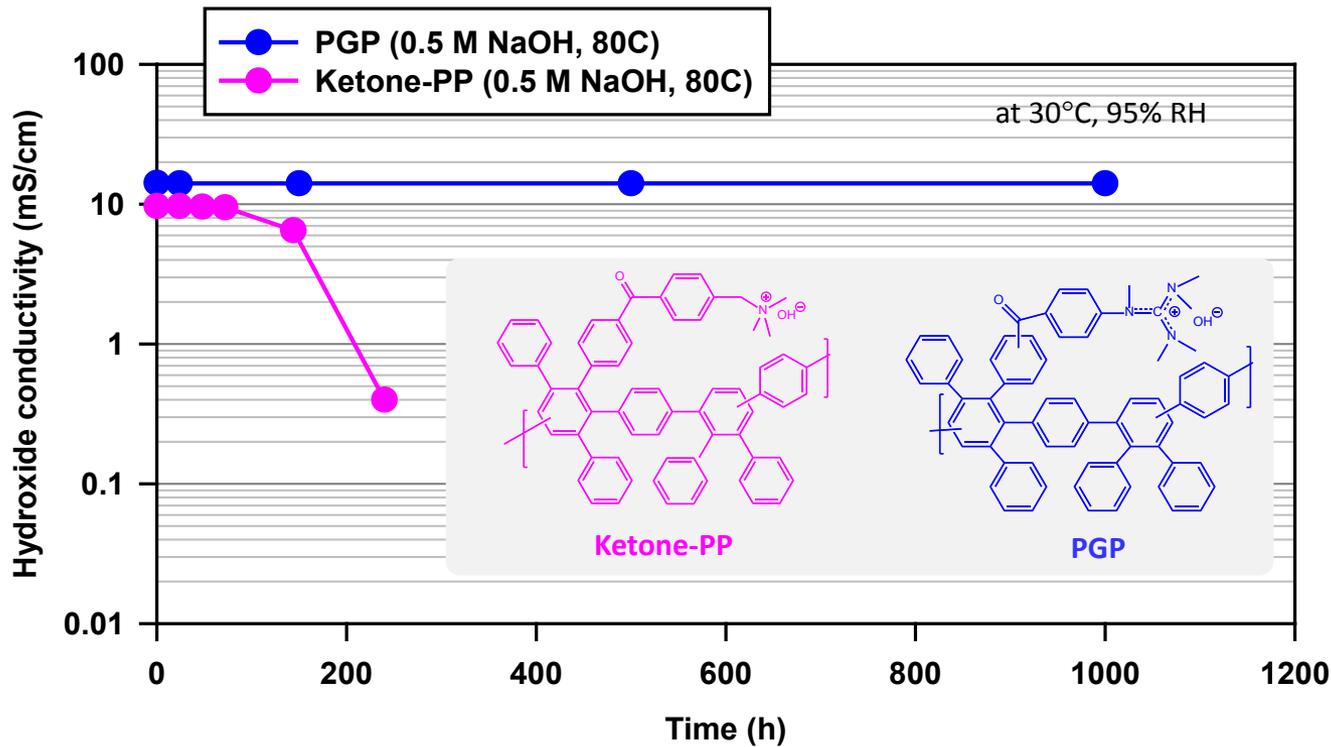


FTIR of TMAC6PP after 3600 h NaOH treatment

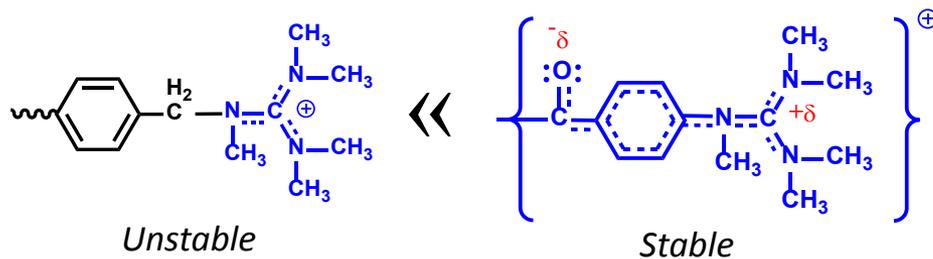


- Highlight:** No conductivity & structural changes for TMAC6PP after 0.5 M NaOH treatment at 80°C for 3600 h.

Ex-situ Alkaline Stability of Phenyl Guanidinium Ionomer

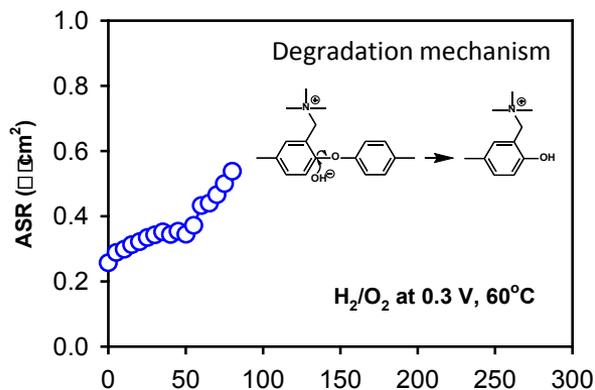
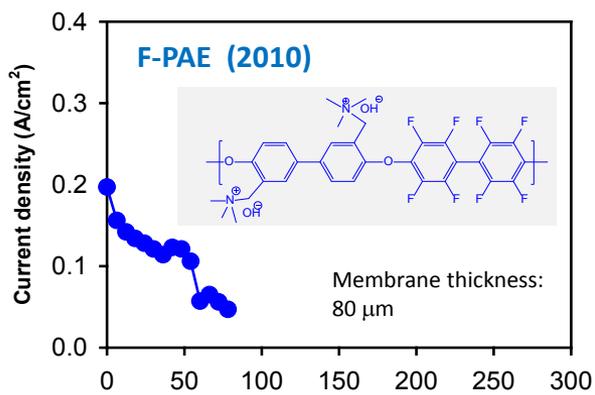


Extended-resonance Stabilization Concept



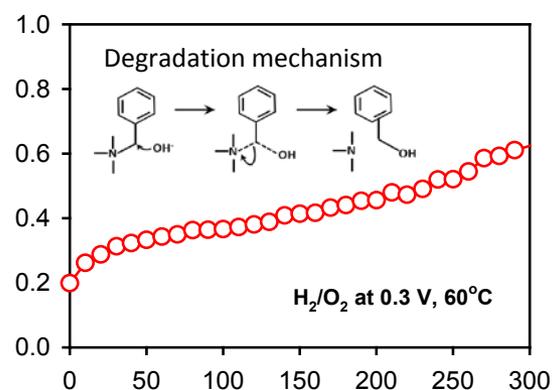
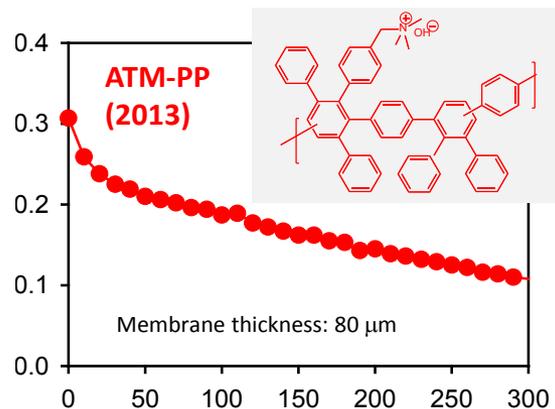
- No chemical structural change after 10,000 h 0.5 M NaOH or 100 h at 80°C, 4 M NaOH* conditions.
- **Highlight:** Developed alkaline-stable ionomer by extended-resonance stabilization.

In-situ Areal Specific Resistance Improvement



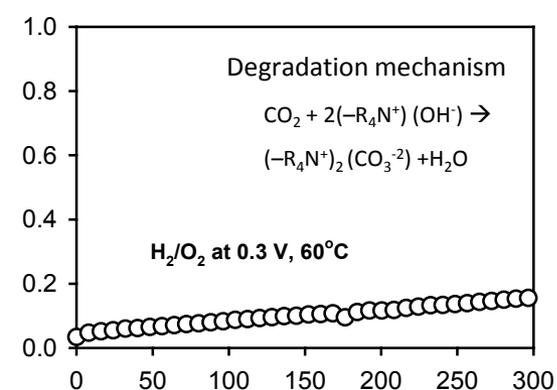
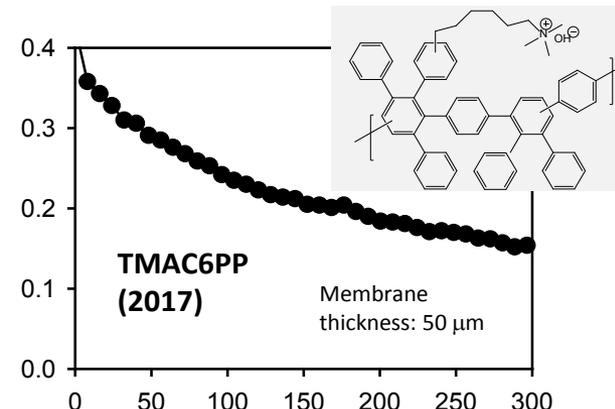
Major Degradation Mode
Polymer backbone
degradation due to aryl-
ether cleavage reaction.

J. Memb. Sci. 423, 438 (2012)



Major Degradation Mode
Nucleophilic substitution of
benzyltrimethyl ammonium
group.

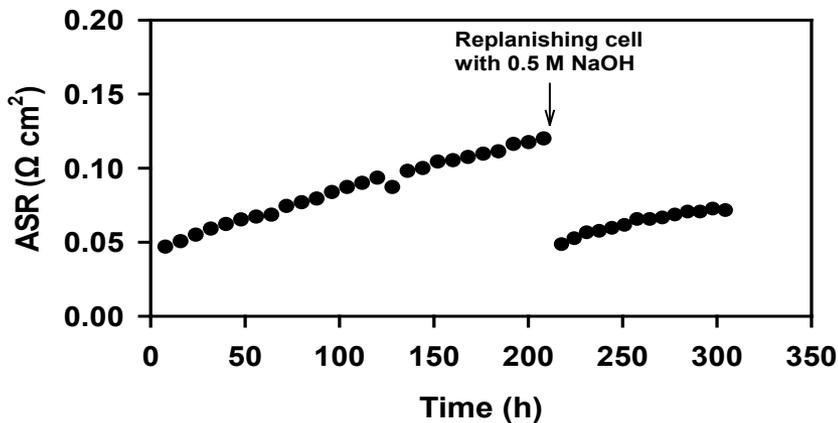
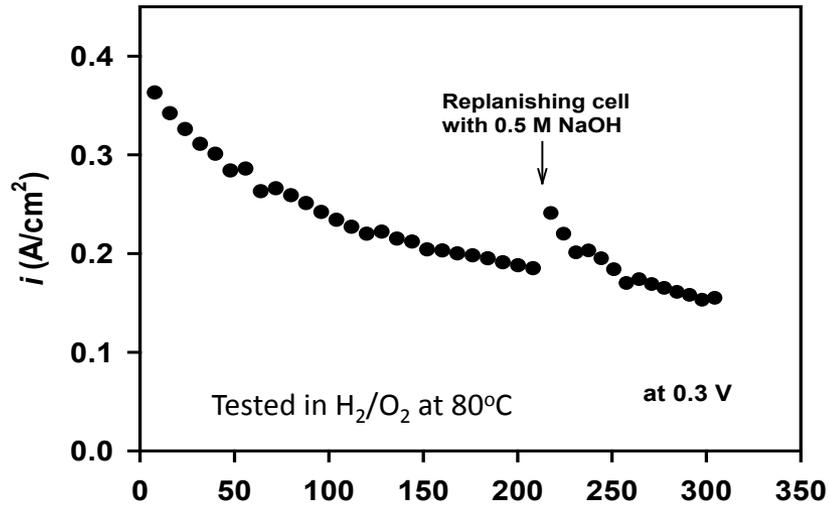
Chem. Mater. 26, 5675 (2014)



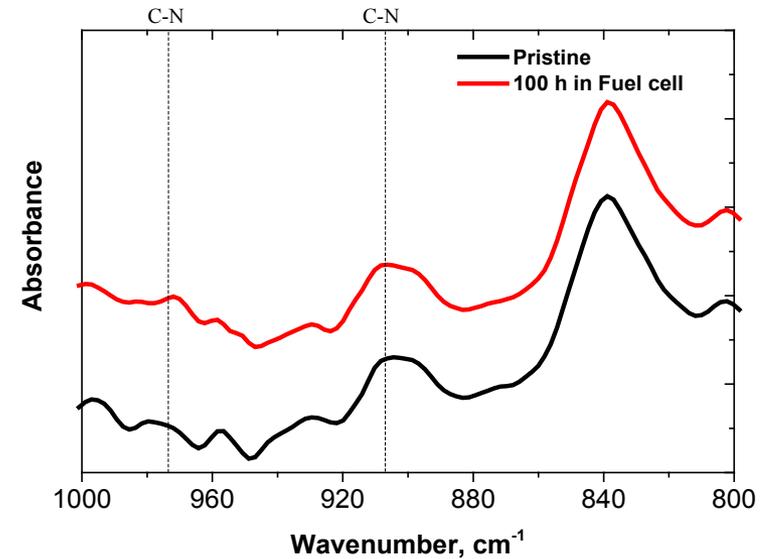
Major Degradation Mode
(bi)-carbonation exchange
reaction (reversible).

Removing Carbonate Ions by Replenishing Cell

AEM: TMAC6PP (thickness: 40 μm), Ionomer: TMAC6PP, Catalyst: Pt/C 0.2 $\text{mg}_{\text{Pt}}/\text{cm}^2$ for both anode and cathode



FT-IR of TMAC6PP AEM after 100 h Test

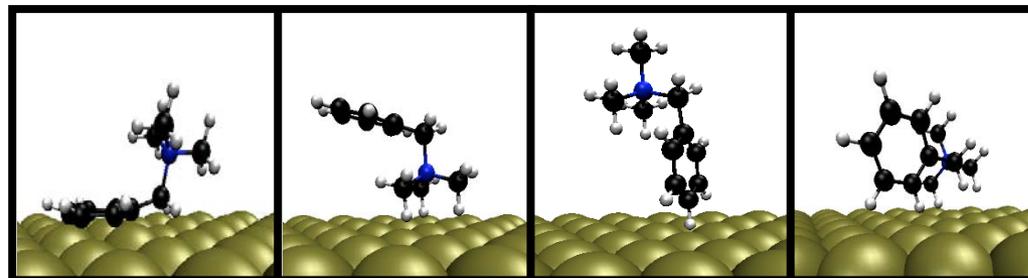


- Maintained low ASR after replenishing cell with 0.5M NaOH.
- No indication of AEM chemical degradation.
- **Highlight:** Achieved 0.05 $\Omega \text{ cm}^2$ ASR for 300 h.
- **Next step:** Improving AEMFC performance

Benzene Adsorption on Pt (New Performance Inhibition Mechanism)



Adsorption Position (side view) of BTMA on Pt(111) at $U = 0$ V



$\Delta E = -2.30$ eV

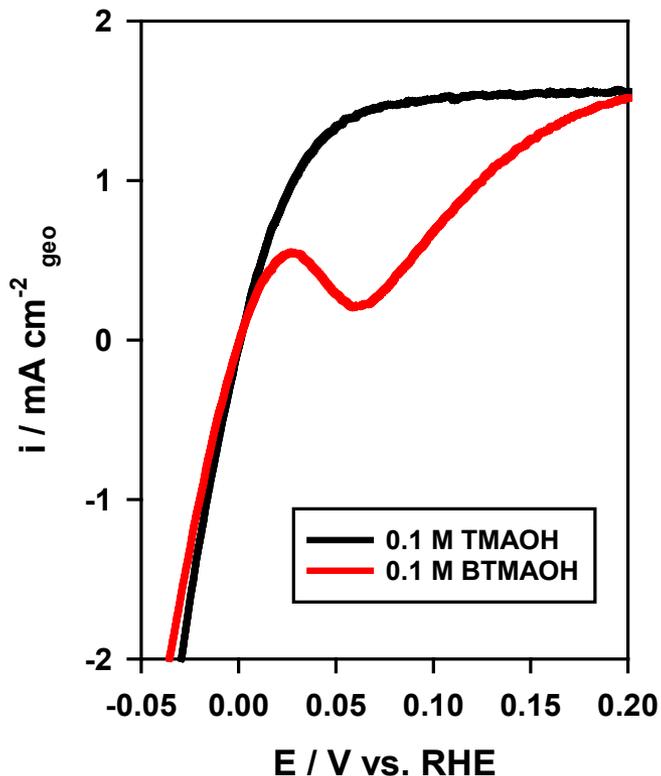
$\Delta E = -2.15$ eV

$\Delta E = -1.51$ eV

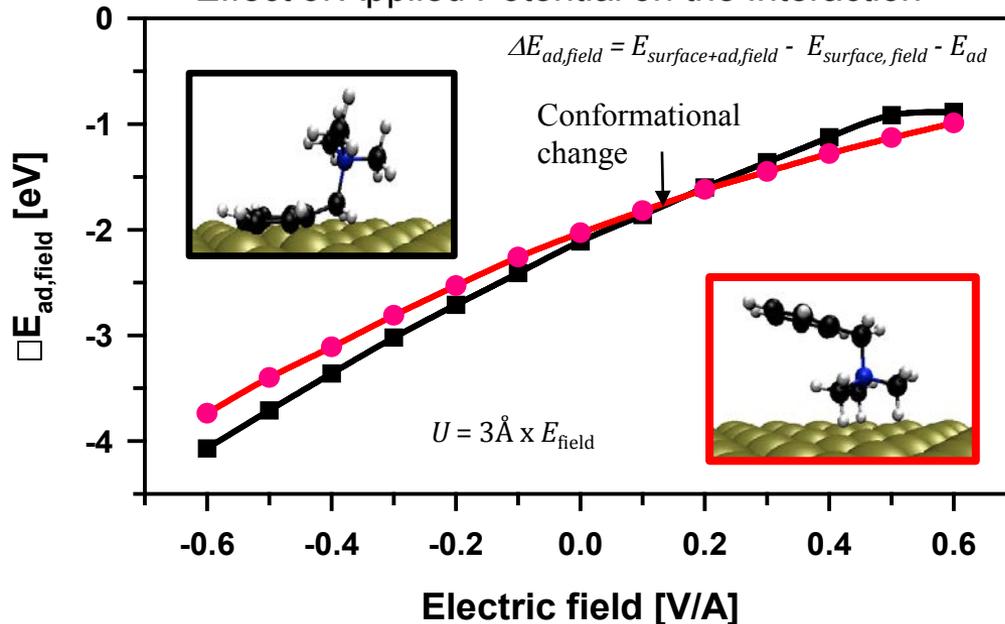
$\Delta E = -2.15$ eV

$$\Delta E_{ad,field} = E_{surface+ad,field} - E_{surface,field} - E_{ad}$$

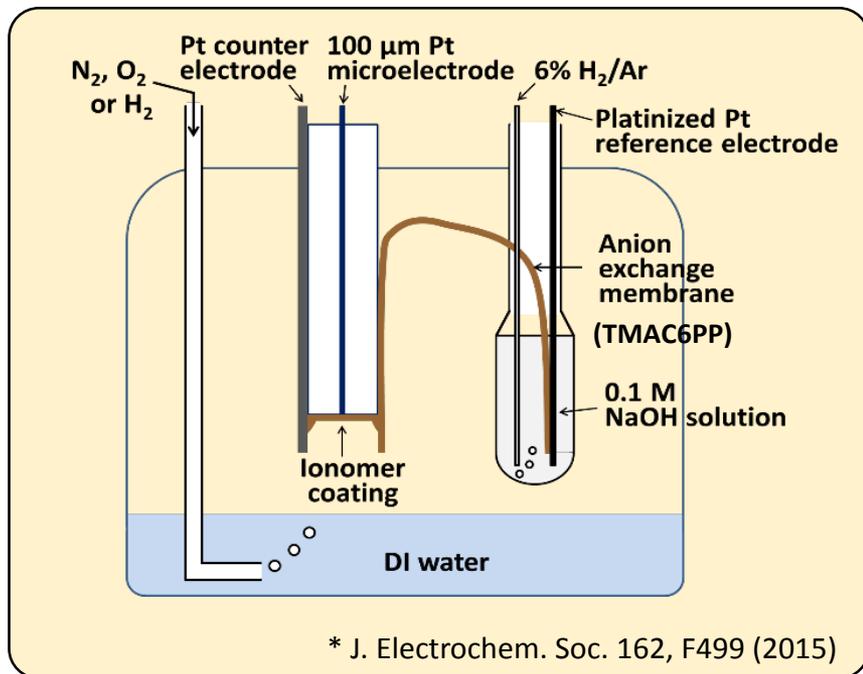
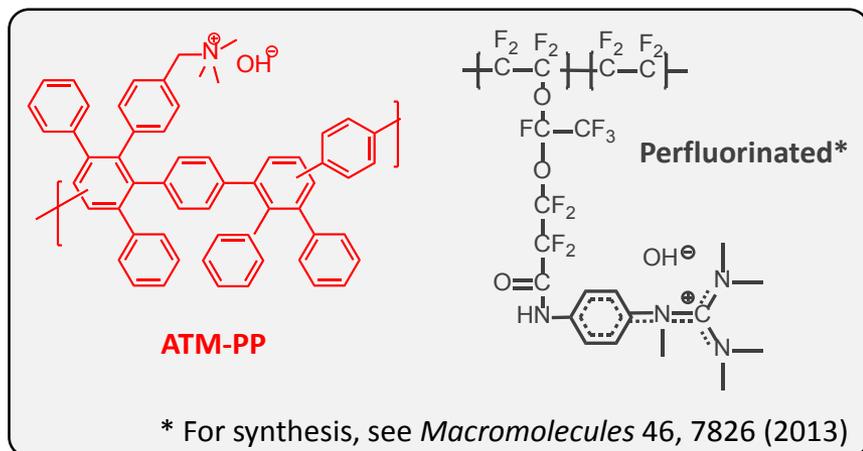
HOR voltammogram (RDE) of Pt/C



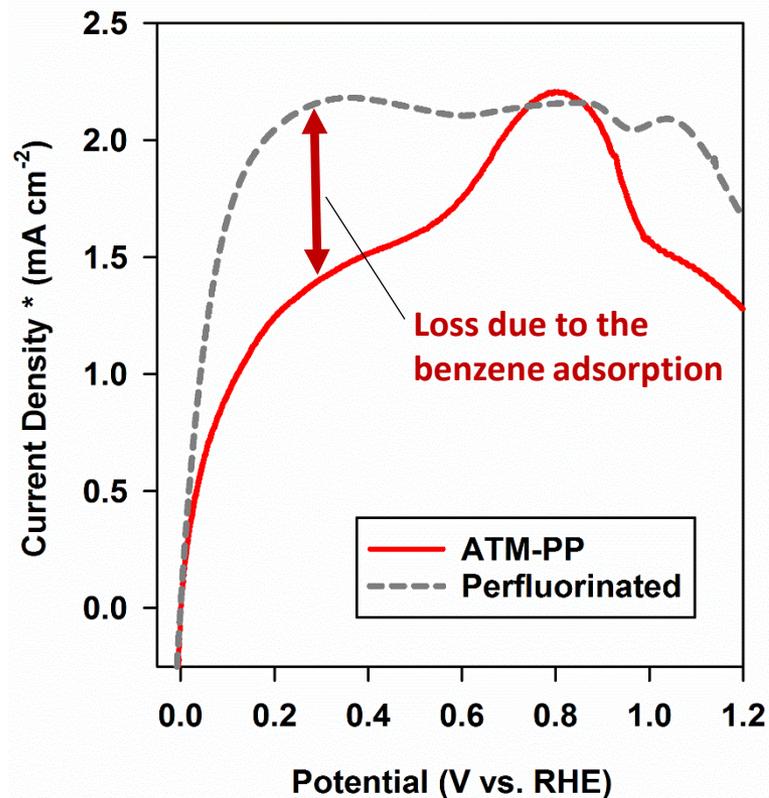
Effect of Applied Potential on the Interaction



Impact of Benzene Ring Containing Ionomer on HOR of Pt



HOR voltammogram of ionomer-coated Pt (after preconditioning at 1.4 V for 20 sec.)

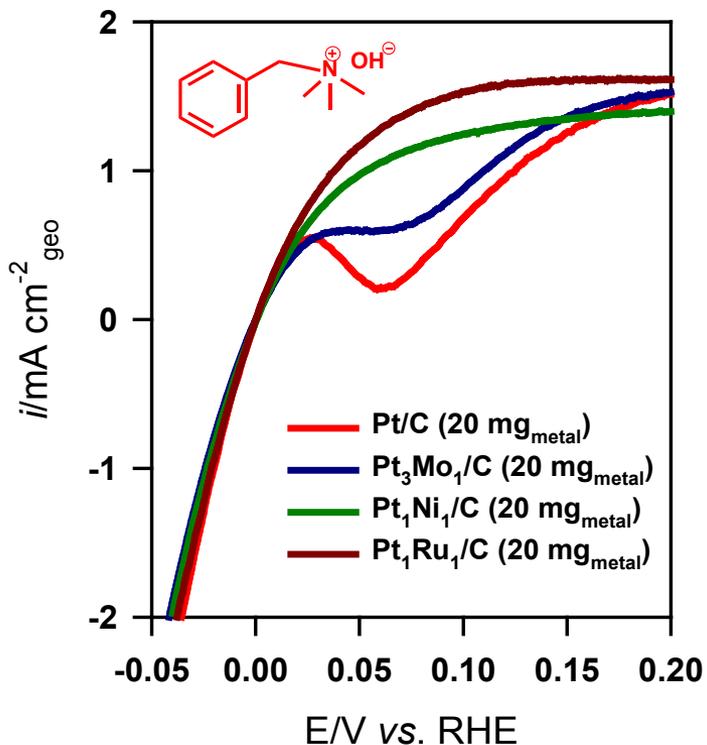


* Film thickness normalized

- Highlight:** First identified benzene adsorption driven HOR inhibition

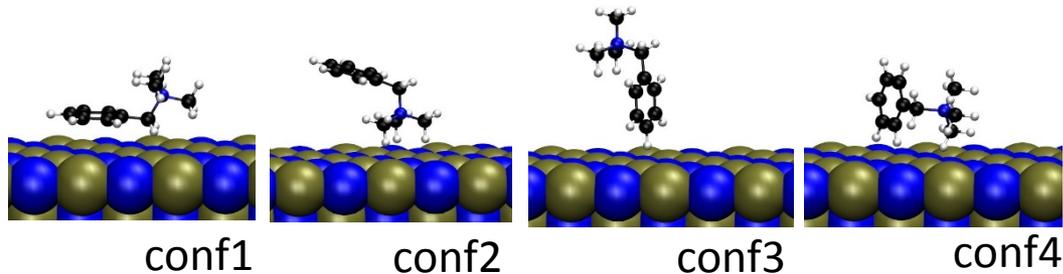
Effect of Alloying Pt with Mo, Ni, and Ru on BTMA Adsorption

Pt alloy HOR Voltammogram in BTMAOH



Adsorption energies of BTMA on Pt, Pt₃Mo, PtNi and PtRu

ΔE (eV)	conf1	conf2	conf3	conf4
Pt(111)	-2.30	-2.15	-1.51	-2.15
Pt ₃ Mo(111)	-1.61	-1.67	-0.99	-1.71
PtNi(111)	-1.45	-1.56	-0.47	-1.52
PtRu(111)	-1.32	-1.42	-0.37	-1.39



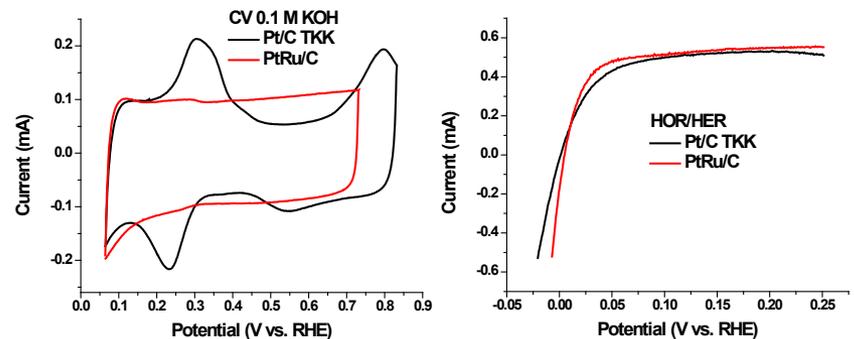
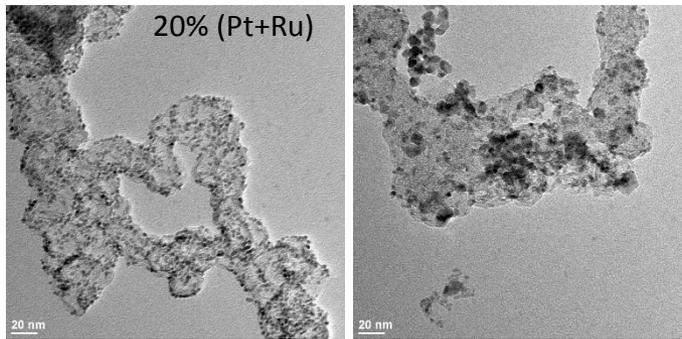
$$\text{PtRu (111)} < \text{PtNi(111)} < \text{Pt}_3\text{Mo(111)} < \text{Pt(111)}$$

- Alloying Pt with Ru decreases the benzene adsorption on Pt surface.
- New direction: Benzene adsorption mitigating strategy: 1. Use Pt/Ru alloying catalyst (ANL); 2. Use phenyl free or less phenyl containing ionomer (LANL, RPI).

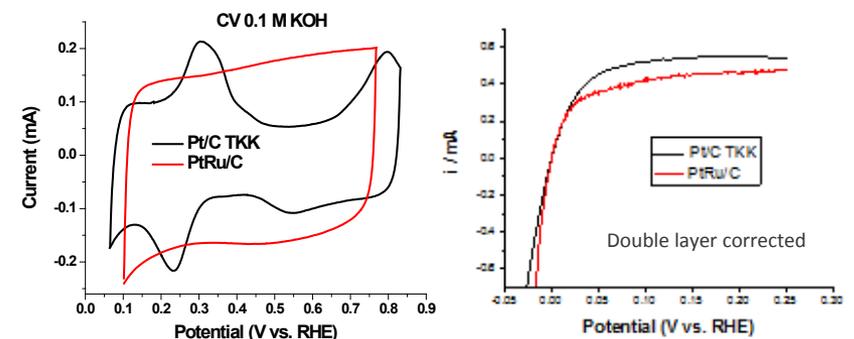
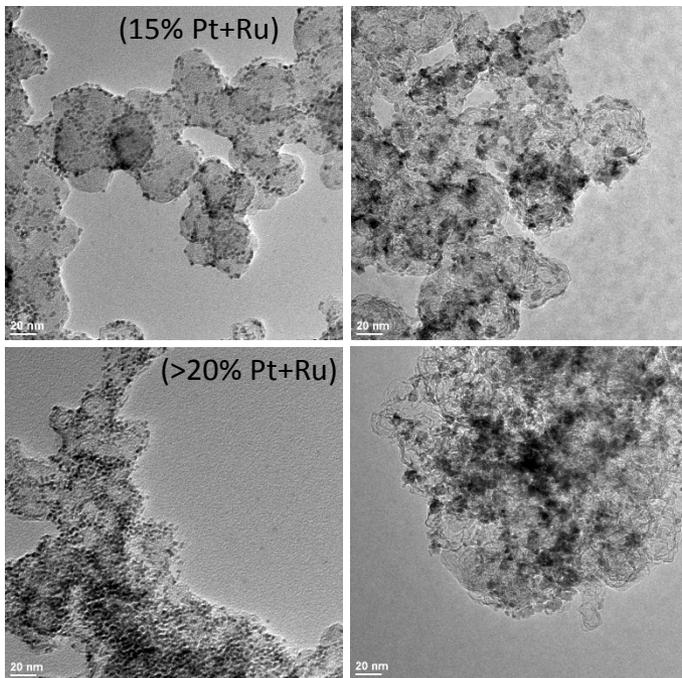
Synthesis and Characterization of Pt₁Ru₈ Nanoparticles

Before annealing After 185°C in air

0.1 g scale synthesis

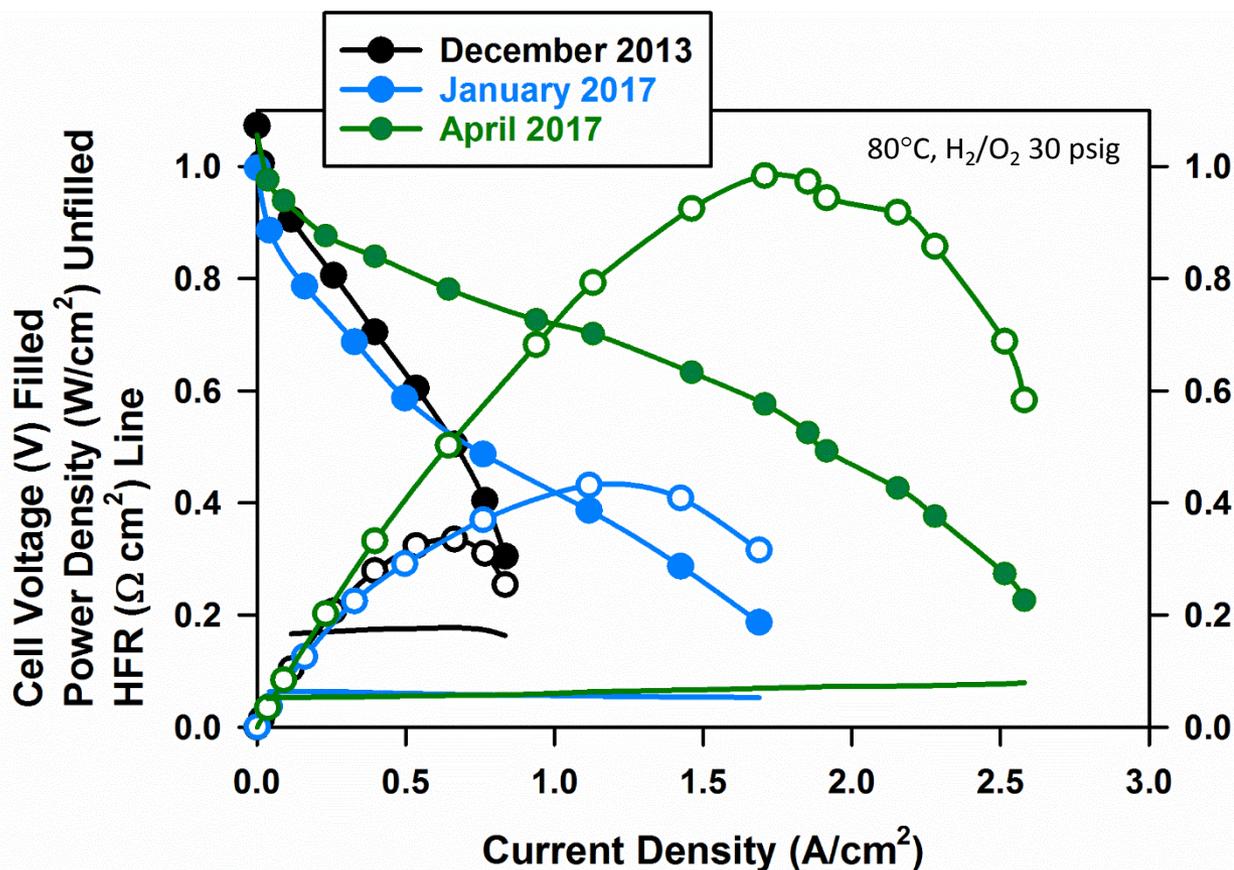


0.6 g scale synthesis



- Synthesized Pt₁Ru₈ nanoparticle (~3 nm).
- Achieved 6X scale up synthesis.
- Demonstrated higher HOR/HER activity than Pt/C.
- Observed particle sintering after annealing.

Achievement: AEMFC Performance



- **Highlight:** Achieved 1 W/cm² peak power density with commercial Pt/Ru catalyst and hydrocarbon AEM/ionomer.
- Next step: Use ANL catalysts with lower PGM loading.

December 2013

AEM: ATM-PP
 Ionomer: ATM-PP
 Catalyst: Pt black 3 mg_{Pt}/cm²
 for both anode and cathode

January 2017

AEM: Poly(terphenyl alkylene)
 (down-selected)[#]
 Ionomer: AS4 (Tokuyama)
 Catalyst: Pt/C 0.6 mg_{Pt}/cm²
 for both anode and cathode

[#] See Technical Backup Slide T2 for synthetic procedure

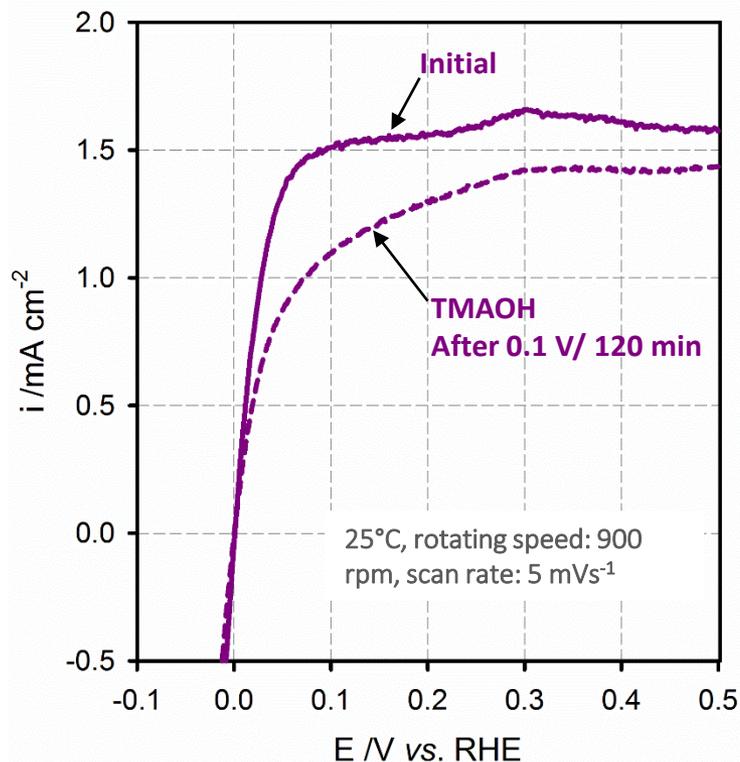
April 2017

AEM: Ter(Phenyl) Alkylene
 (down-selected)
 Ionomer: FLN2-55* (candidate)
 Catalyst: **Pt₂-Ru₁/C** 0.5
 mg_{Pt}/cm² (anode), Pt/C 0.6
 mg_{Pt}/cm² (cathode)

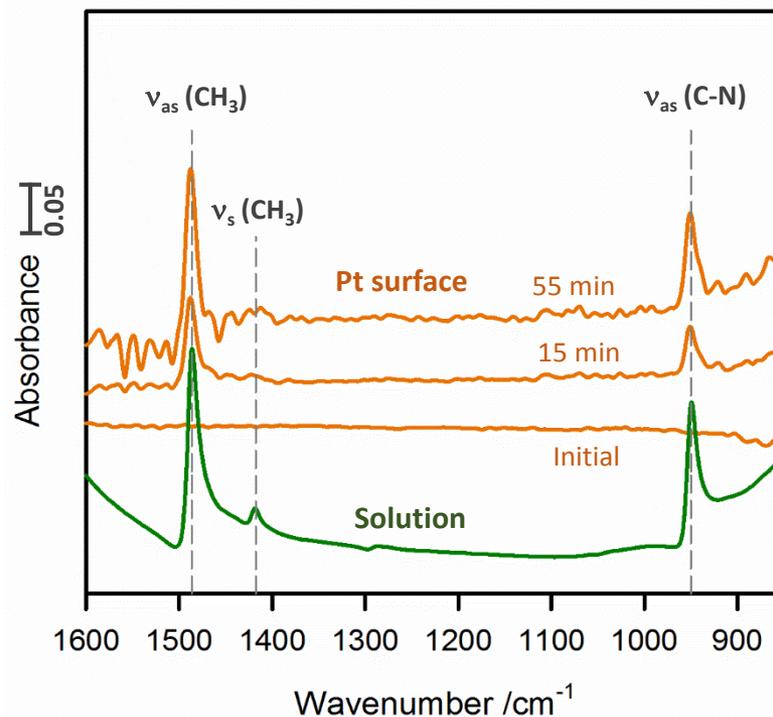
* See Reviewer-only Slide R2 for synthetic procedure

Time-dependent Cationic Group Adsorption

HOR voltammogram of Pt/C in TMAOH



IRRAS spectra change during Chronoamperometry of Pt at 0.1 V vs. RHE

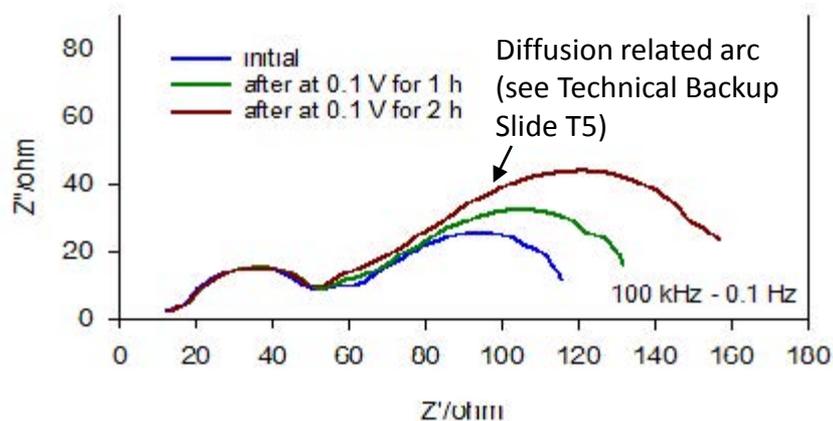


- HOR activity of Pt/C in TMAOH decreases with time as the cationic group adsorption occurs.

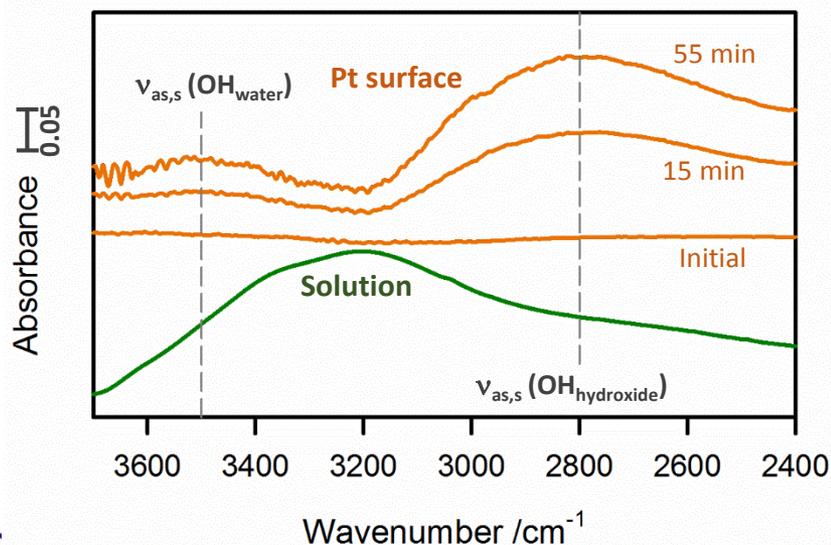
J. Phys. Chem. Lett. 7, 4464 (2016); J. Electrochem. Soc. 163, F1503 (2016)

HOR Degradation Mechanism

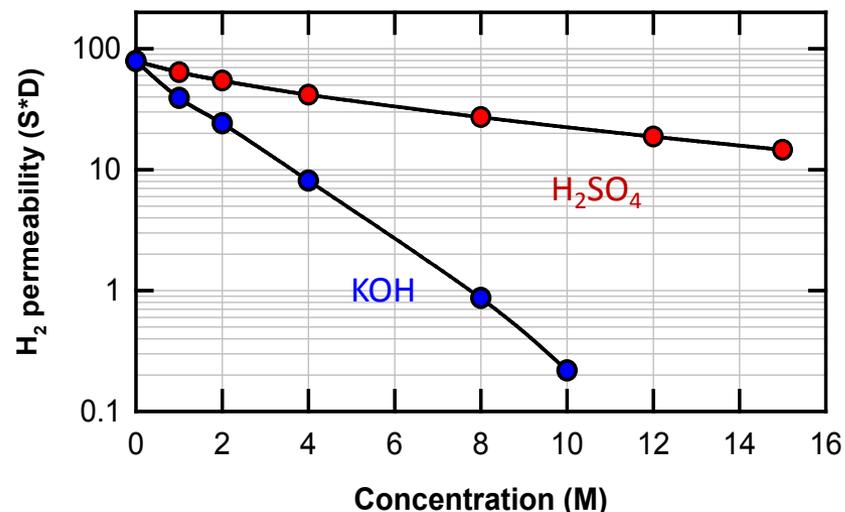
Impedance of Pt/C in 0.1 M TMAOH at OCV



Surface IR Spectra change during Chronoamperometry of Pt at 0.1 V vs. RHE



H₂ Permeability in H₂SO₄ and KOH at 30°C#



J. Electrochem. Soc. 113, 301-305, 1966

- HOR activity loss of Pt is due to the cation-hydroxide-water co-adsorption which blocks the H₂ access through OH⁻ rich adsorbed layer.

Next step: Mitigating strategy for the co-adsorption: Use bulky cations*

- See Reviewers Only Slide R4 for the impact of cationic group structure on the co-adsorption.

Responses to Previous Year Reviewers' Comments

- **It is unclear for what applications AEMFCs will be used.**

AEMFC approaches are at a much earlier stage and much is still unknown about the ultimate limits of AEMFCs. For this year, we have demonstrated 1 W/cm² peak power density with the materials we developed. While we agree that we still have long way to go for a competitive system with PEMFCs, the performance gap between AEMFCs and PEMFCs is getting smaller than the time project started.

- **The project should eliminate the perfluorinated ionomer work or at least ensure that it does not overlap with NREL's work.**

We included the perfluorinated ionomer work because i) the perfluorinated work was originally proposed ii) our early work back in 2012 indicated an excellent AEMFC performance with perfluorinated ionomer. However, our recent results suggested that hydrocarbon materials could perform well. So we decided to eliminate the perfluorinated ionomer work from this project.

- **The approaches to low-PGM loading or non-PGM were not addressed.**

Although the use of non-PGM catalysts is the ultimate goal for AEMFCs, this project focusses on critical issues related to the AEMs and ionomers. DOE is supporting AEMFC catalyst development through other projects. The role of our catalyst partners is to provide high-performing catalysts rather than develop new catalysts.

Collaboration and Partners



AEM & Ionomer Design, Interfacial Electrochemistry, Fuel Cell Testing and Project Management
Yu Seung Kim (Project Lead), Sandipkumar Maurya, Kwan-Soo Lee, Hoon Chung, Ivana Matanovic



AEM & Ionomer Synthesis
Cy Fujimoto (PI), Michael Hibbs



HOR Catalyst Preparation
Vojislav Stamenkovic (PI), Rongyue Wang, Dongguo, Li



AEM & Ionomer Synthesis
Chulsung Bae (PI), Sangtak Noh, Jongyeob Jeon, Junyoung Han, Eun Joo "Sarah" Park

SNL AEMs sent to a large chemical manufacture to test for commercialization.

Other Interactions

- Giner Inc. - Hui Xu
- Shanghai Jiao Tong Univ. - Hong Li
- Proton Onsite - Kathy Ayers
- Nanosonic Inc. - William Harrison
- Amsen - Hongxing Hu
- IRD Fuel Cells, LLC - Madeleine Odgaard
- Univ. of New Mexico - Alexey Serov

Remaining Challenges and Barriers

- **Cationic group-hydroxide-water co-adsorption.**

Design new ionomers which are less adsorbed on catalyst surface.

- **High purity HOR ionomer dispersion.**

Make a homogeneous dispersion with hydroxide form ionomer which has less phenyl groups.

- **AEMFC MEA integration.**

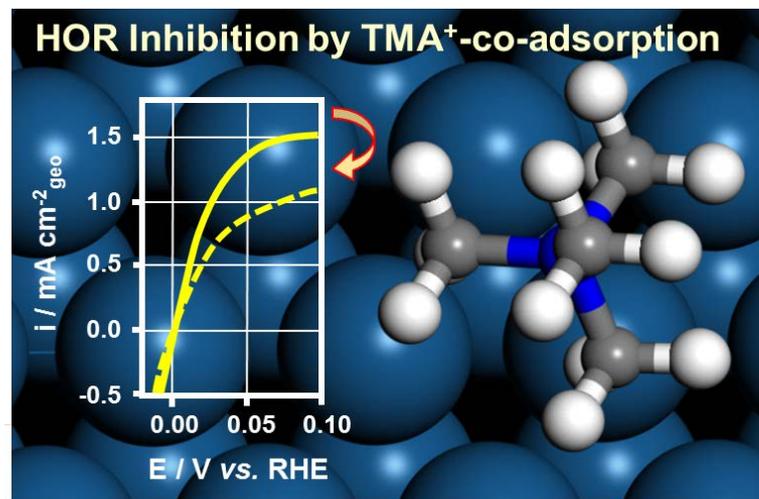
Incorporate high-performing HOR and ORR catalysts with preferably low or non-PGM loading.

- **Scale-up AEM and ionomer synthesis.**

Continues to produce 10-50 g batch membranes by SNL and RPI. We are also looking for industrial partners to produce the AEMs in pilot scale (up to kg).

- **Carbonation issue.**

Plan to purchase CO₂ degassing equipment for supplying carbonate-free water system.



Proposed Future Work

Remainder of FY 2017

AEM synthesis and characterization (SNL, RPI)

- Lab-scale synthesis (10-50g) of AEMs for MEA integration and testing. AEMs include poly(bi(ter)phenyl alkylene)s and Diels-Alder poly(phenylene)s.

Ionomer development (LANL, SNL, RPI)

- Produce small quantity ionomers (1 to 5g) for down-selection to complete 2016 Q4 milestone. Potential candidate ionomers include polyfluorene and polystyrene.

HOR study (LANL, ANL)

- Prepare 200 to 500 mg of PtRu alloy catalyst for HOR reaction.
- Perform RDE, microelectrode, surface FTIR and neutron reflectometry experiments.

FY 2018

MEA integration and optimization (LANL, SNL, ANL, RPI)

- Investigate variables that impact fuel cell performance and durability. Variables include GDL, microporous layer, membrane thickness, I/C ratio, catalyst loading, type of catalyst support, and humidification.

AEMFC performance and durability (LANL)

- Evaluate the performance and durability of the integrated AEMFC MEA.

Technology Transfer Activities

- **RPI:** Contacted several small business companies to produce large scale AEMs during FY 17.
- **SNL:** Co-PI is participating in DOE's Lab Corps program, which has included contacting two large manufacturers to produce poly(phenylene) AEMs. One foreign manufacturer completed the AEM evaluation.
- **LANL:** Participated in a SBIR program to license AEM technology. Also participated in several Small Business Voucher (SBV) projects to transfer AMFC MEA technology.

More than 10 patents on AEM and ionomer materials are available.

- **FY 2017 patent and patent applications**

- **SNL:** "Poly(phenylene alkylene)-based ionomers" US 9,534,097 (2017).
- **SNL & LANL:** "Poly(phenylene)based anion exchange polymers and method thereof" 62/274,592, (2016).
- **LANL:** "Polyol-based compositions comprising cationic group functionalized poly(phenylene) polymers" 15/204,523 (2016).

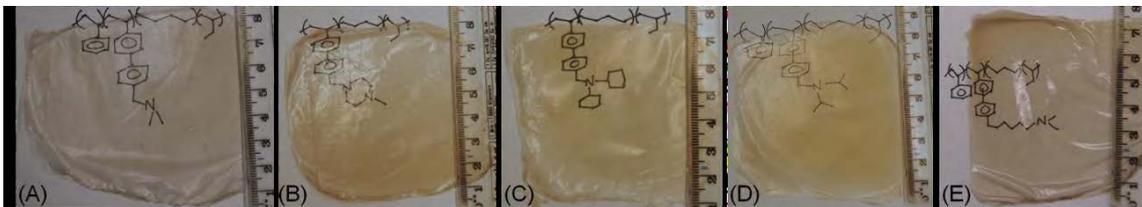
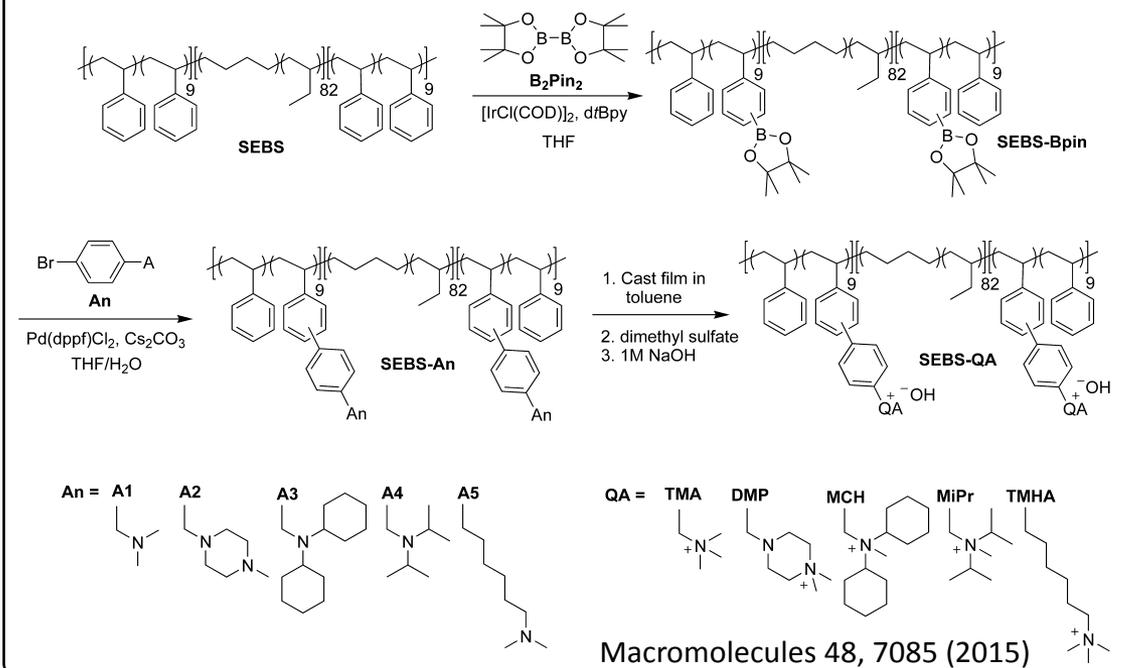
Summary

- Objective:** Development of improved AEMs, ionomeric binders and integration of catalysts and membranes into high-performance MEAs.
- Relevance:** Aiming to make AEMFC system competitive to PEMFCs in terms of performance and durability. Identifying performance barrier and degradation mechanism of AEMFCs can contribute for further developing advanced materials.
- Approach:** Preparing AEMs without ether or electron-withdrawing groups in the polymer backbone (FY 16). Developing high-performing electrodes through catalyst-ionomer interfacial study (FY 17). Demonstrating good AEMFC durability of fully-integrated MEAs from materials developed from this project (FY 18).
- Accomplishments (FY 17)** Completed to prepared AEMs with exceptional stability with desired film forming properties. **Achieved ASR ~ 0.05 Ω cm² which is maintained for 300 h without AEM chemical degradation.** First identified the benzene adsorption that adversely impact the HOR kinetics. **Demonstrated 1 W/cm² peak power density** of AEMFC performance by mitigating the benzene adsorption.
- Collaborations:** Strong team comprised of chemical synthesis, MEA integration, electrochemistry and fuel cell testing. Extensive communications with several industrial partners.

Technical Back-Up Slides

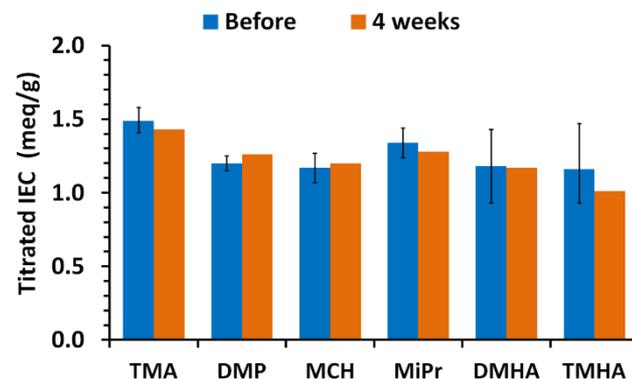
Synthesis and Alkaline Stability of SEBS based AEMs

Synthetic Scheme of quaternary ammonium functionalized SEBS via C-H borylation and Suzuki coupling reactions



Photos of films of (A) SEBS-A1, (B) SEBS-A2, (C) SEBS-A3, (D) SEBS-A4, and (E) SEBS-A5 cast from toluene onto Teflon plates.

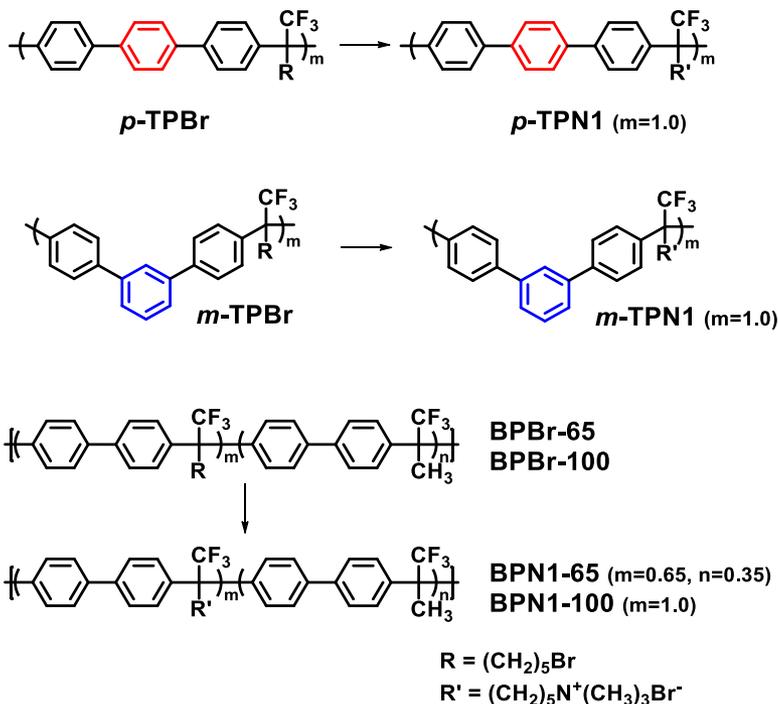
Alkaline stability of SEBS polymers (IEC change after 1M NaOH, 80°C)



- Alkaline stable cationic functional groups are incorporated into commercial SEBS polymers.
- The AEMs show excellent alkaline stability after 4 week treatment at 1 M NaOH, 80°C.

Synthesis and Alkaline Stability of Poly(terphenyl alkylene)s

Chemical structures of para-terphenyl (*p*-TPN1), meta-terphenyl (*m*-TPN1) and biphenyl (BPN1) polymers



IECs (before and after alkaline stability test), water uptake, hydration number and hydroxide conductivity of terphenyl alkylene)s.

Polymer	IEC ^a	IEC ^b	WU (%) ^c	λ (OH ⁻) ^d	σ (mS/cm) ^e	
					30 °C	80 °C
p-TPN1	2.12	2.15	17(65)	17	43	81
m-TPN1	2.15	2.13	25(70)	18	54	112
BPN1-65	1.94	1.93 ^f	34(85)	24	41	88
BPN1-100	2.70	2.80 ^f	61(124)	26	62	122

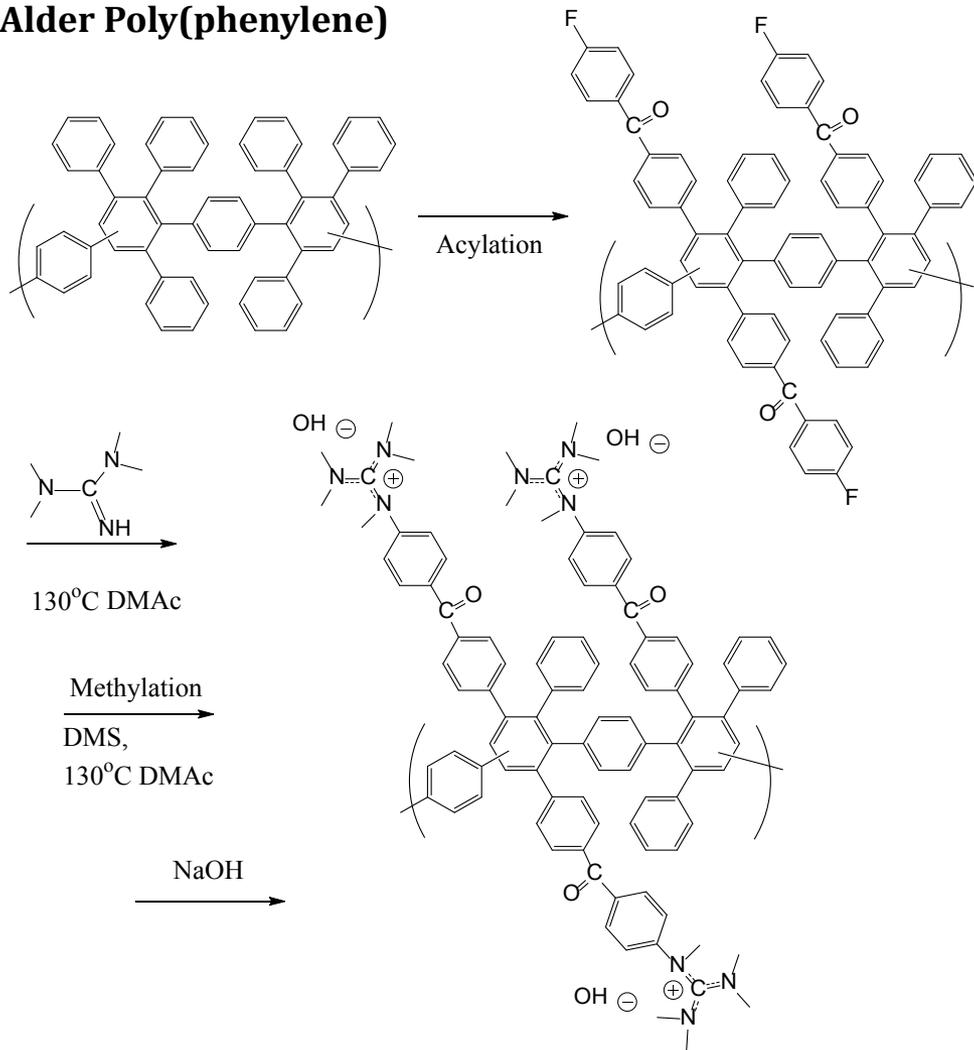
^aIEC values were determined by ¹H NMR analysis (mequiv/g). ^bIECs after alkaline test at 1M NaOH at 95°C for 30 days (mequiv/g). ^cWater uptake was measured in both Cl⁻ and OH⁻ form at 80 °C. The values in brackets represent water uptake in OH⁻ form. ^dBased on water uptake value at 80 °C. ^ehydroxide conductivity. ^fLee et al. ACS Macro Lett. 2015, 4, 814.

* Lee et al. ACS Macro Lett. doi:10.1021/acsmacrolett.7b00148

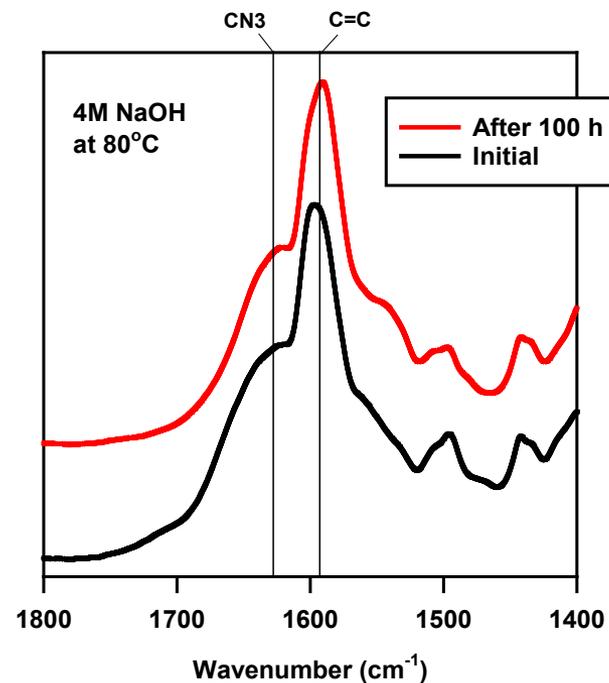
- Chemically and mechanically stable terphenyl-based polymers with pendant quaternary ammonium alkyl groups were synthesized.

Synthesis and Stability of Guanidinium Poly(phenylene)s

Synthetic Scheme of Guanidinium functionalized Diels-Alder Poly(phenylene)

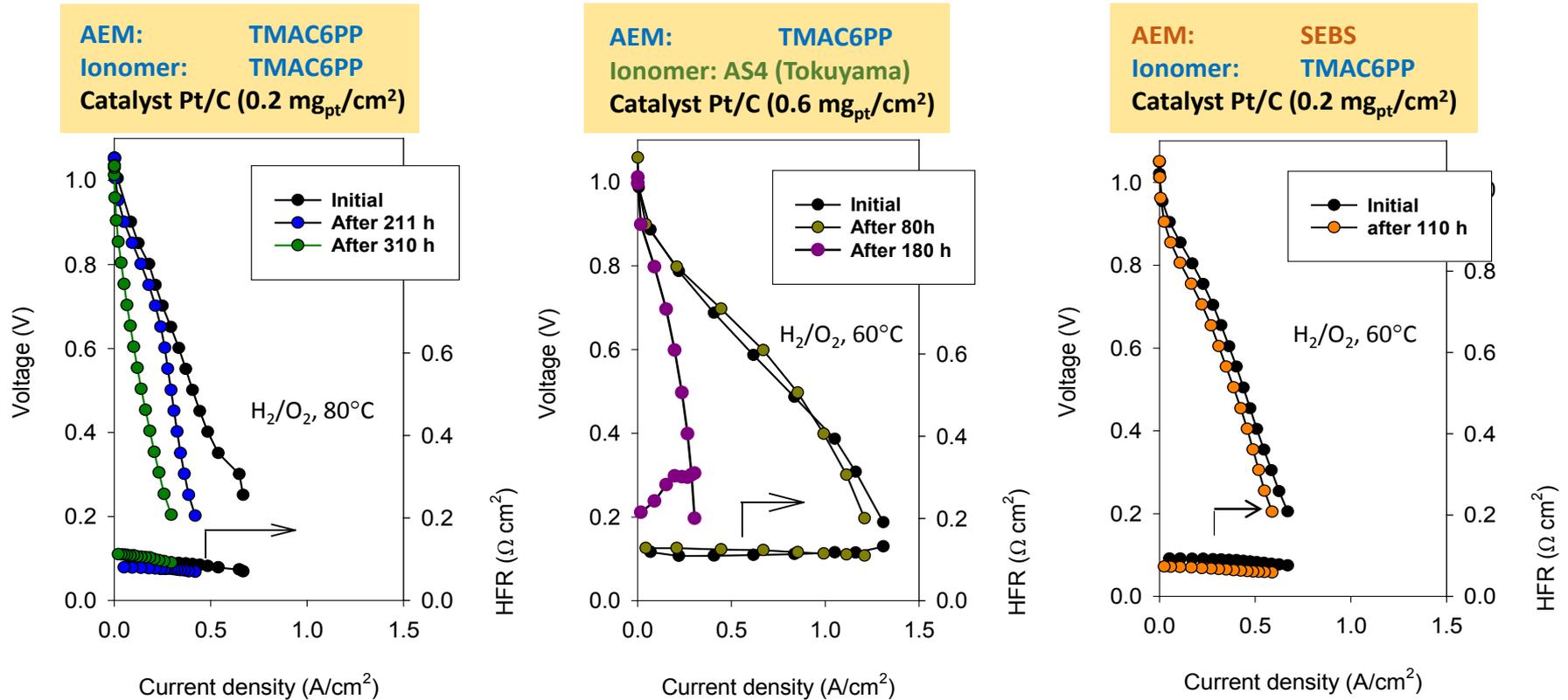


FTIR of CN3 peak after 4M NaOH treatment



- Extended-resonance stabilized guanidinium poly(phenylene) was synthesized and showed alkaline stability under 4M NaOH conditions.

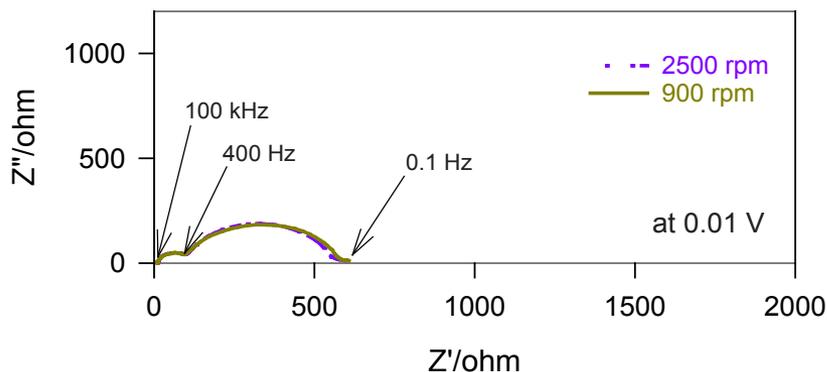
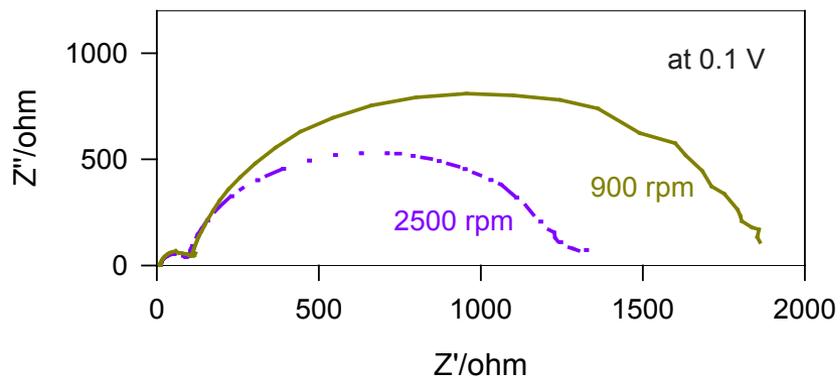
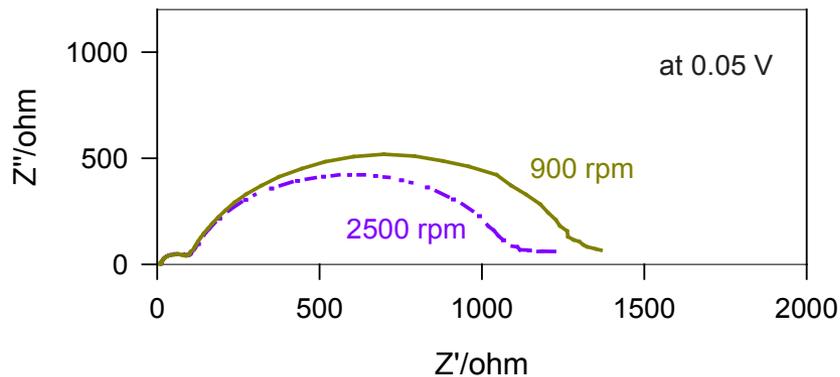
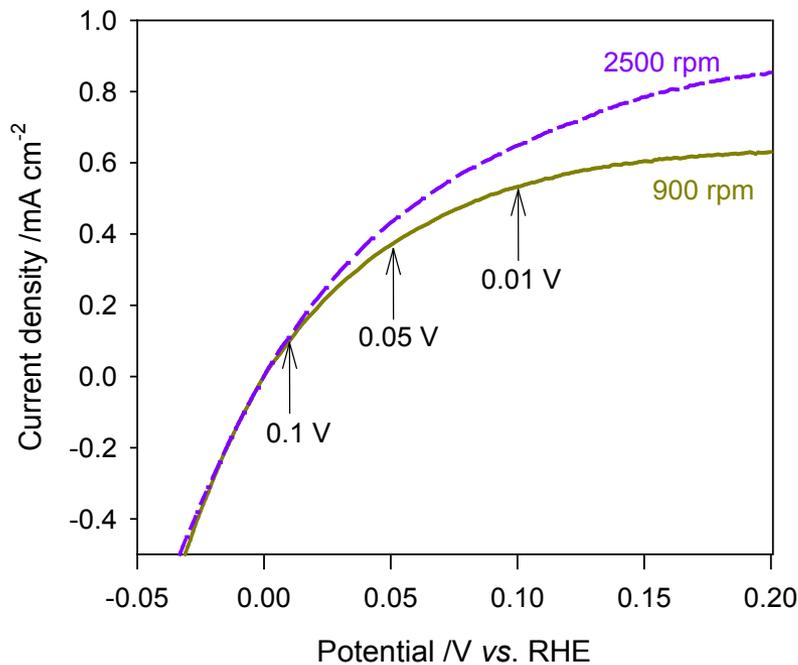
HFR Changes of Various AEMs During Life Test at 0.3 V



- MEAs prepared with TMAC6PP and SEBS showed stable HFRs after replenishing cell with 0.5 M NaOH.
- Often fuel cell performance decreases even when the cell HFR is stable.
- The MEA with TMAC6PP AEM and AS4 ionomer lost performance after 180h with unknown reason, possibly due to the ionomer failure.

RPM Dependency of Low-Frequency Arc of Impedance

HOR of Pt in 0.1 M TMAOH



- Low-frequency arc is related with a diffusion process not with a kinetic process based on the observation that the HOR impedance changes with rpm