Project ID: FC146

Advanced Materials for Fully-Integrated MEAs in AEMFCs

PI: Yu Seung Kim

Los Alamos National Laboratory

May 1, 2019

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

Overview

Timeline

- Project start date: 11/2/2015
- Project end date: 9/30/2019
- Percent complete: 98%

Budget

- Total project funding: $3,560K
  - DOE share: 98%
  - Contractor share: 2%
- Funding received in FY19: $500K
- Total DOE Funds Spent*: $3,540K

*As of 3/03/2018

Barriers

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

Project lead

- Los Alamos National Laboratory
  Yu Seung Kim (PI) , Sandip Maurya, Eun Joo Park, Dongguo Li, Albert Sung Soo Lee

Partners

- Sandia National Laboratories
  Cy Fujimoto, Michael Hibbs, Ehren Donel Baca
- Rensselaer Polytechnic Institute
  Chulsung Bae, Jongyeob Jeon
- University of New Mexico
  Ivana Matanovic

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[1] (4Q, 2017)	Current Status (2Q, 2019)
ASR	Ω/cm^2	0.2	≤ 0.1	**0.05**
AEMFC Performance	mA/cm^2 at 0.6 V	420 (382 kPa)[1]	600 (≤ 152 kPa) atm)	**950 (78 kPa)**
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**
AEMFC Durability	% V loss after 2000 h at 0.6 A/cm^2 at ≥ 60°C	60% after 300 h run at 0.3 V at 60°C[3]	< 10%	**12.5% V loss at 0.6 A/cm^2 after 500 h at 80 °C**

[1]From FCTO MYRDD Plan

Approach

Research Focus	Major Founding	Results
AEM **Stability** (2016)	**Polymer backbone degradation[1]**	**Aryl ether-free polyaromatics:** *Demonstrated > 2500 h stability in 4 M NaOH 80 ℃*
AEMFC **Performance** (2017-2019)	**Phenyl group adsorption[2]** **Cation-hydroxide-water co-adsorption[3]**	**Poly(fluorene) ionomers[4]:** **Diethyl ammonium ionomers:** *Demonstrated 1.5 W/cm^2 peak power density*
AEMFC **Durability** (2019)	**Oxidation of phenyl group (in the cathode ionomer)**	*In progress*

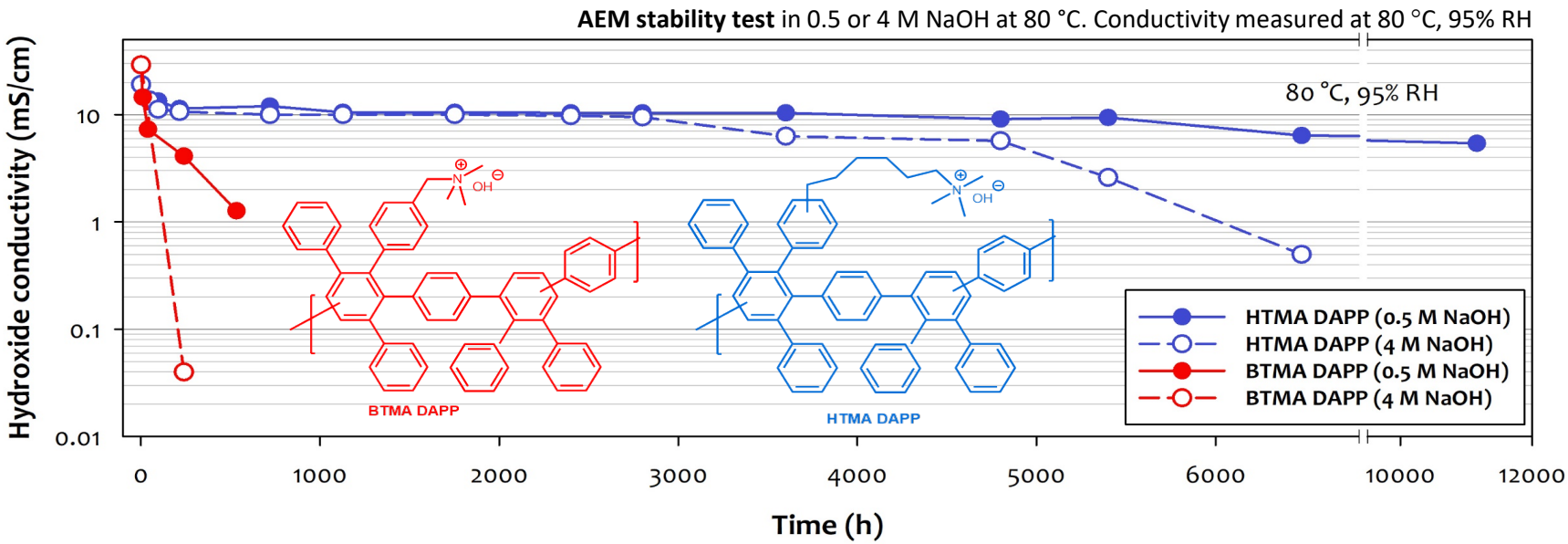
[1]Fujimoto et al. *J. Memb. Sci.* 423-424, 438-449, 2012
[2]Matanovic et al. *J. Phy. Chem. Let*. 8, 4918-4924, 2017
[3]Li et al. *Cur. Opinion in Electrochem.*, 12, 189-195, 2018
[4]S. Murya, S. *Energy & Environ. Sci.* 11, 3283-3291, 2019

Milestone & go-no-go decision

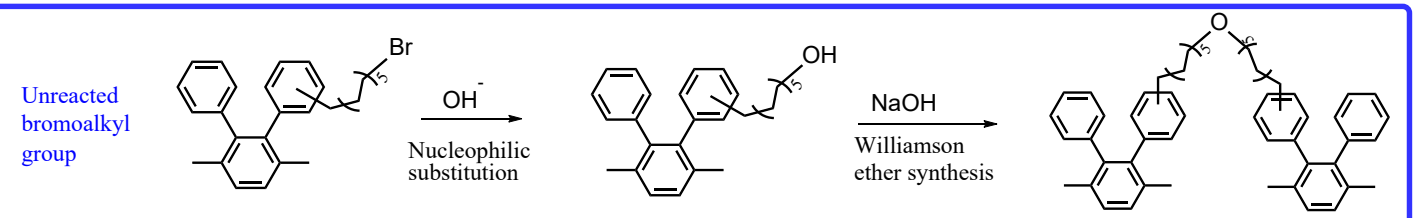
Date	Milestone & Go-No-Go	Status (%)	Result	Comments
Mar. 2016	Down-select AEM	100 (Feb. 2016)	Polyphenylenes	Poly(terphenylene) (RPI) & Diels Alder poly(phenylene) (SNL)
				Delayed due to HOR study
Mar. 2017 **(Go-No Go)**	*In-situ* AEM ASR ≤ 0.1 Ω cm^2 for 500 h at 600 mA/cm^2	100 (Mar 2018)	**0.05 Ω cm^2**	Completed *ex-situ* test on Dec. 2016;
SEP. 2017	Integrate MEAs; Peak power density > 0.6 W/cm^2		**1 W/cm^2**	Best AEMFC performance using polyaromatic ionomer by the time
Dec. 2017	Down-select HOR catalyst		PtRu/C	Least phenyl group adsorbing catalyst
Mar. 2018				Best AEMFC performance using polyaromatic ionomer
		50		
Feb. 2019	Complete AEM degradation mechanism		0% for 1000 h, 4 M NaOH, 80 °C.	Completed 11,000 h test Completed AST at 120 & 160 °C
Sep. 2019				On going

Red: delayed; Blue: exceed milestone criteria

Alkaline stability of the poly(phenylene) AEMs



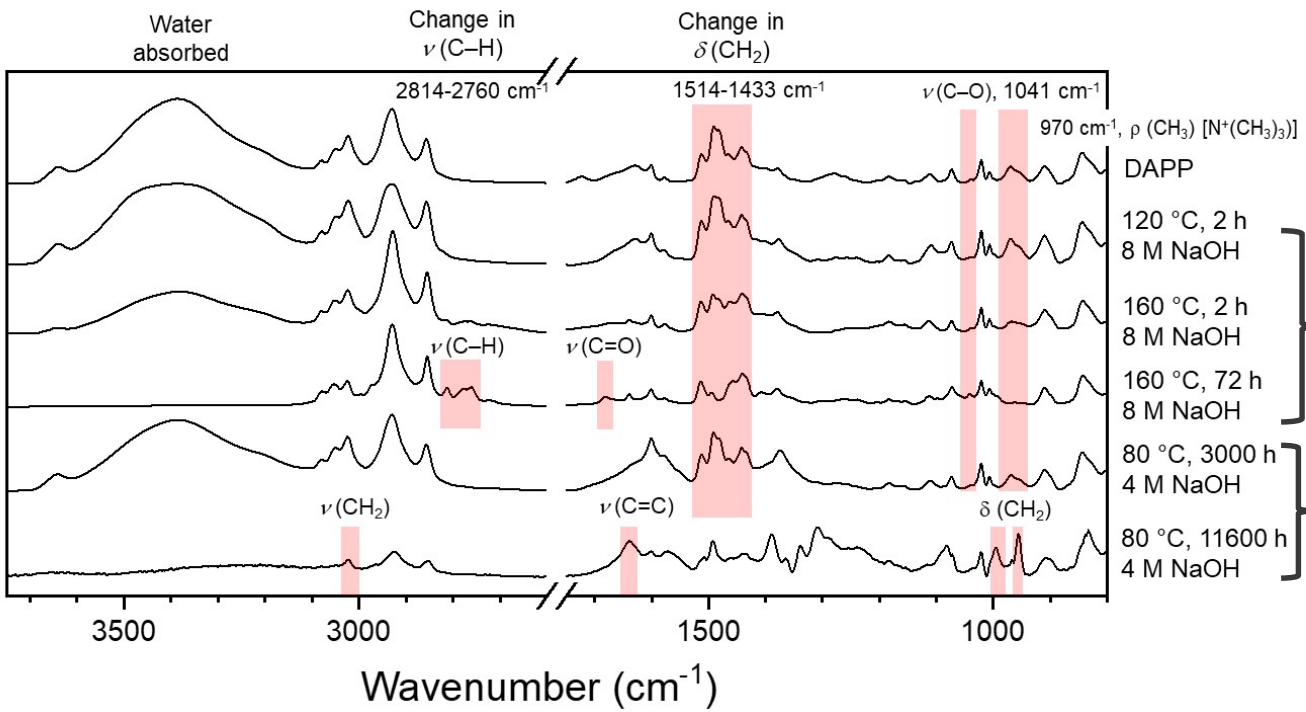
The crosslinking reaction that causes conductivity loss at the early stage.



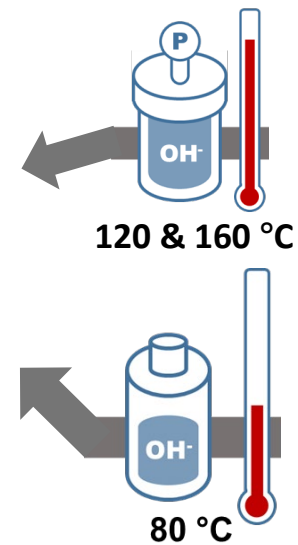
- Identified the cause of conductivity loss at the early stage of the stability test: **crosslinking of unreacted bromoalkyl group**; No other chemical degradation observed during this stage *(see Technical Backup slide 1).*
- After removing the unreacted bromoalkyl group, we obtained poly(phenylene) AEMs without conductivity & structural changes after 4 M NaOH at 80°C to 1,000 h. *(Technical Backup slide 1).*
- Highlight: Known most-alkaline stable AEM (stable in 80 °C, 4 M NaOH to 2,500 h).

AST evaluation on alkaline stability of the poly(phenylene) AEM

FTIR analysis after alkaline stability tests



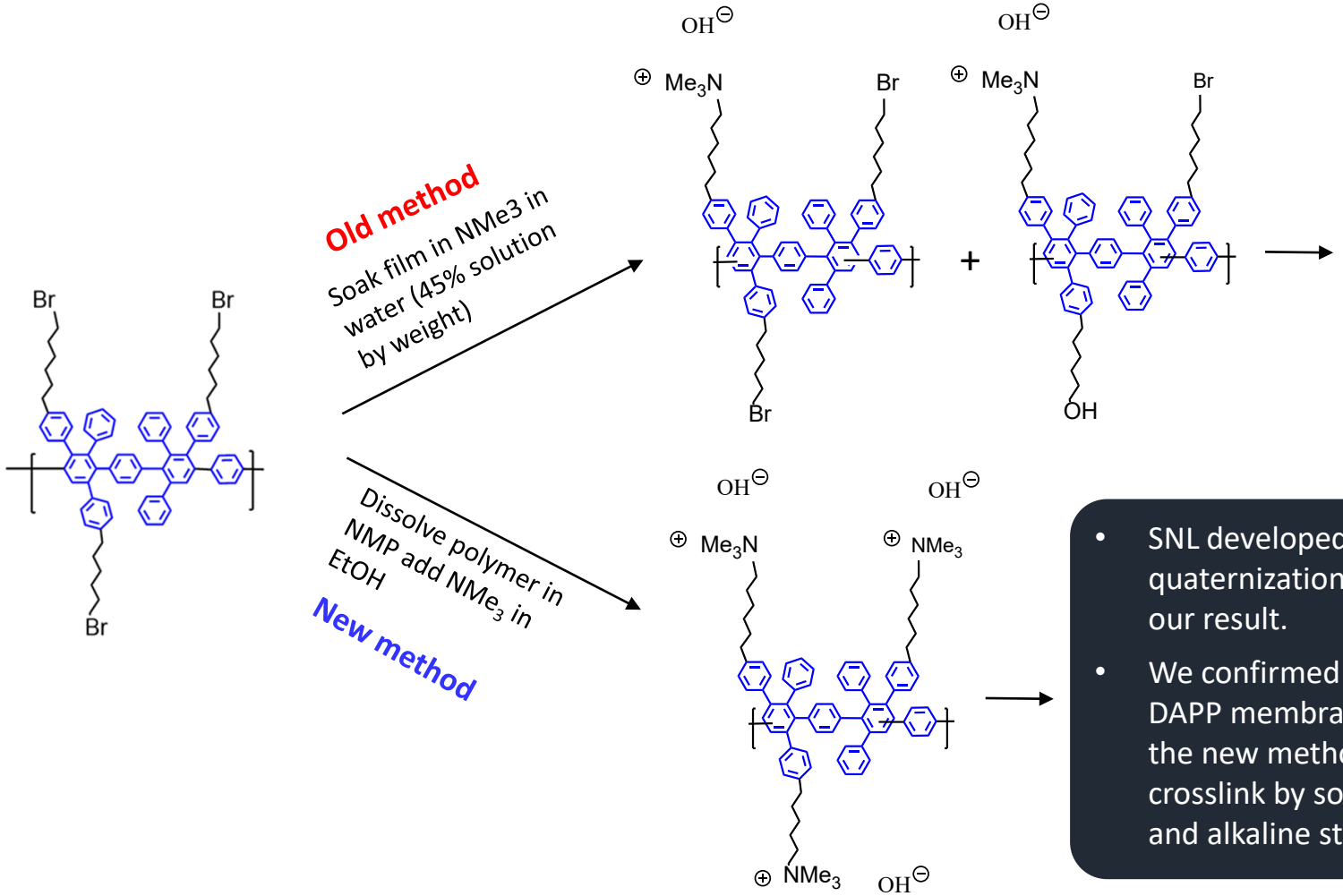
AEM stability test: Immerse HTMA DAPP AEMs in 4 M NaOH at 80 °C or 8 M NaOH at 120 & 160 °C



- Chemical degradation routes of HTMA DAPP are different, depending on testing conditions.
  - 4 M NaOH at 80 °C (2,500 h): S_N2 followed by Williamson ether synthesis (crosslinking)
  - 4 M NaOH at 80 °C (2,500 -11,000 h): Hofmann elimination (E_2 elimination)
  - 8 M NaOH at 120 °C (2 h): Crosslinking + E_2 elimination
  - 8 M NaOH at 160 °C (72 h): S_N2 on alkyl phenyl group *(See details on Technical Backup Slide 2).*
- Note: AEM degradation during the ASTs may not fully reflect the degradation at a mild testing conditions.

Developing preparation route for complete quaternization

Crosslinking reaction occurs because trimethyl amine in water is in equilibrium with amine and ammonium hydroxide: $NMe_3 + H_2O \rightleftharpoons HNMe_3^+ + OH^-$ $K_b = 6.3 \times 10^{-5}$



Crosslinking AEM became insoluble & hydroxide conductivity decrease at 80 °C 4 M NaOH

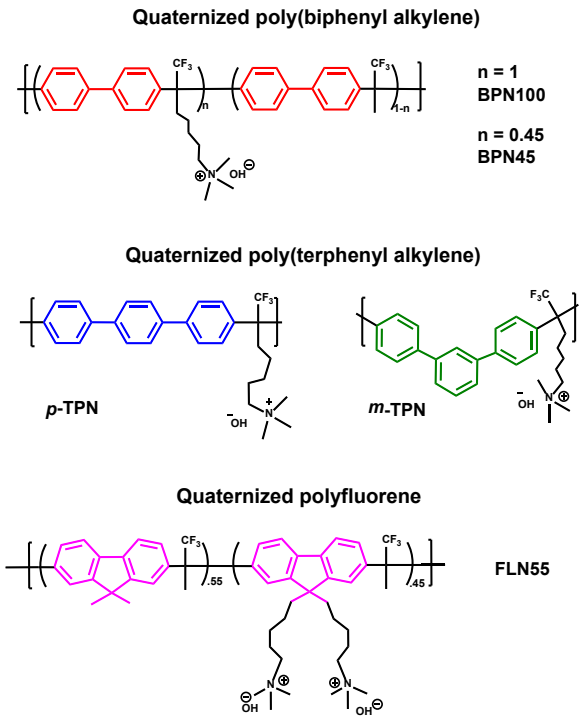
- SNL developed a new quaternization method based on our result.
- We confirmed that quaternary DAPP membrane prepared from the new method does not crosslink by solubility experiment and alkaline stability test.

Impact of phenyl adsorption on AEMFC performance –Complete the study

Adsorption energies (in eV) using optPBE-vdW (UNM)

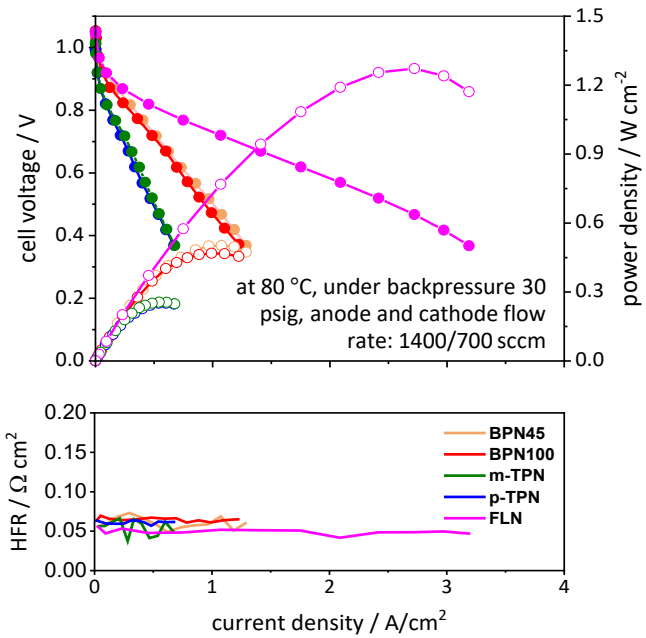
Fragment	E_{ad} (eV)	rank
benzene*	-1.95	3
biphenyl	-2.87	5
o-terphenyl	-1.52	2
m-terphenyl	-3.61	6
p-terphenyl	-3.94	7
fluorene	-1.38	1
biphenyl ether	-2.19	4

Polymer electrolyte synthesis (RPI)



H_2/O_2 AEMFC performance using different ionomers (LANL)

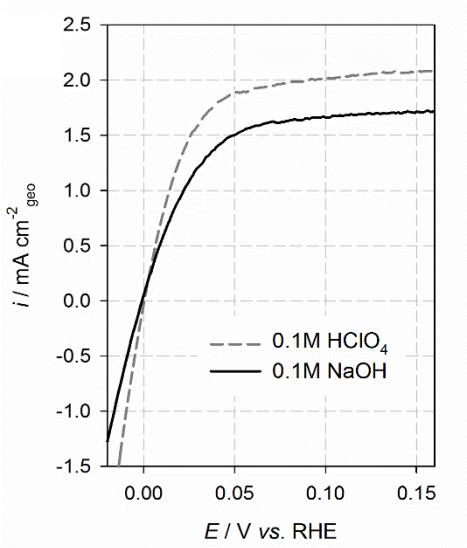
(AEM: *m*-TPN, anode & cathode: Pt/C (0.5 mg_{pt}/cm^2))



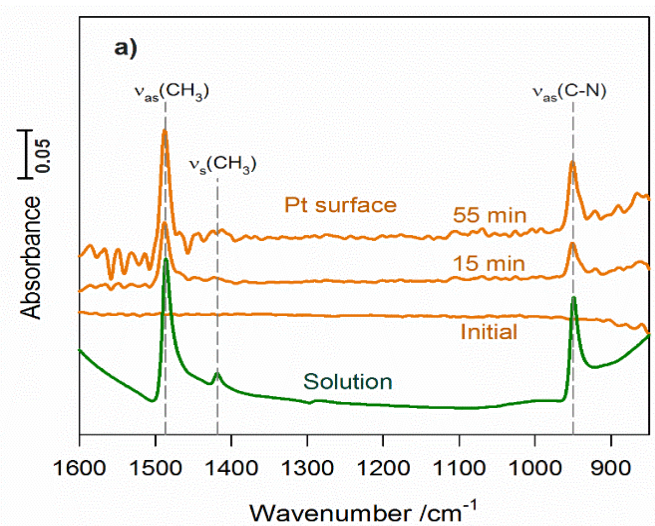
- Density functional theory calculated the phenyl group adsorption on Pt(111) surface using optPBE-vdW.
- Fluorene has the lowest phenyl group adsorption and *p*-terphenyl has the highest phenyl group adsorption.
- The adsorption energy of ionomer backbone is well correlated with the H_2/O_2 AEMFC performance. *(Technical Backup slide 3)*

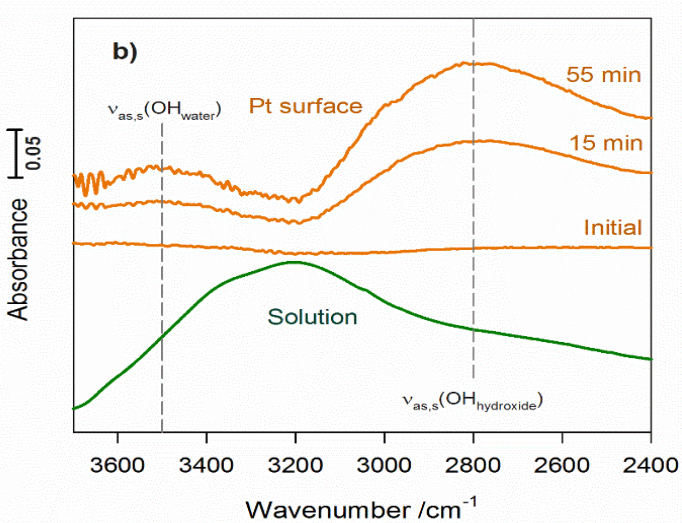
Identify performance limiting factor: Cation co-adsorption

Comparison of HOR voltammogram of Pt/C in acid and alkaline solution



Surface FTIR of Pt in tetramethyl ammonium hydroxide (TMAOH) at 0.1 V vs. RHE as a function of time. (the spectra are compared with that of 0.1 M TMAOH

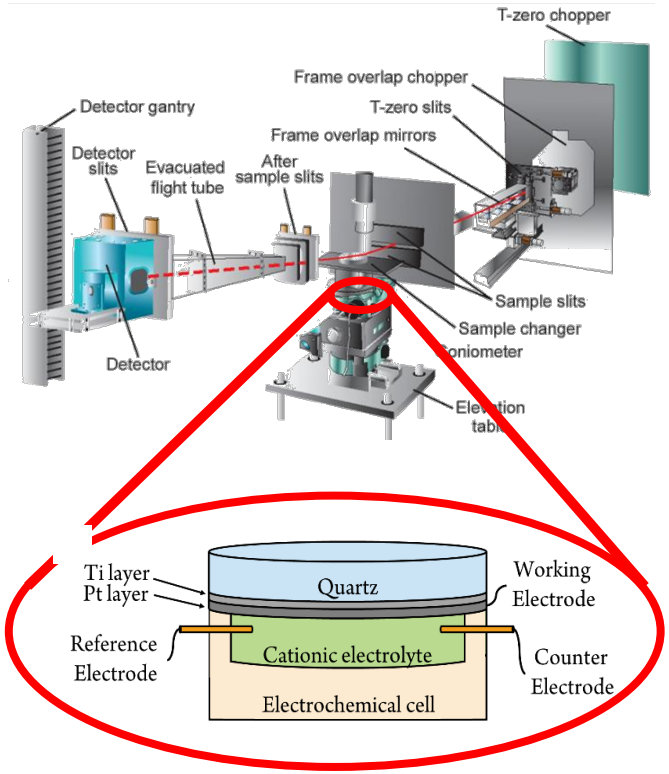


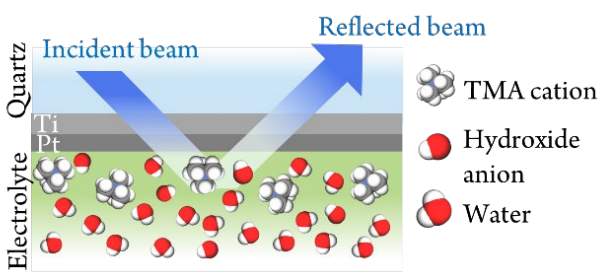


- The low limiting current in the HOR voltammogram cannot be explained by low HOR activity of Pt in alkaline solution.
- We identified that the reason of low H_2 kinetics and low H_2 diffusion access is due to cation-hydroxide-water co-adsorption by surface FTIR.
- Surface FTIR shows that the co-adsorption is cumulative; also the spectrum at the high wave number indicates that the concentration of TMAOH may be high to split water and hydroxide peaks (3,500 and 2,800 cm ^{1})

Characterization of the co-adsorbed layer (neutron reflectometry)

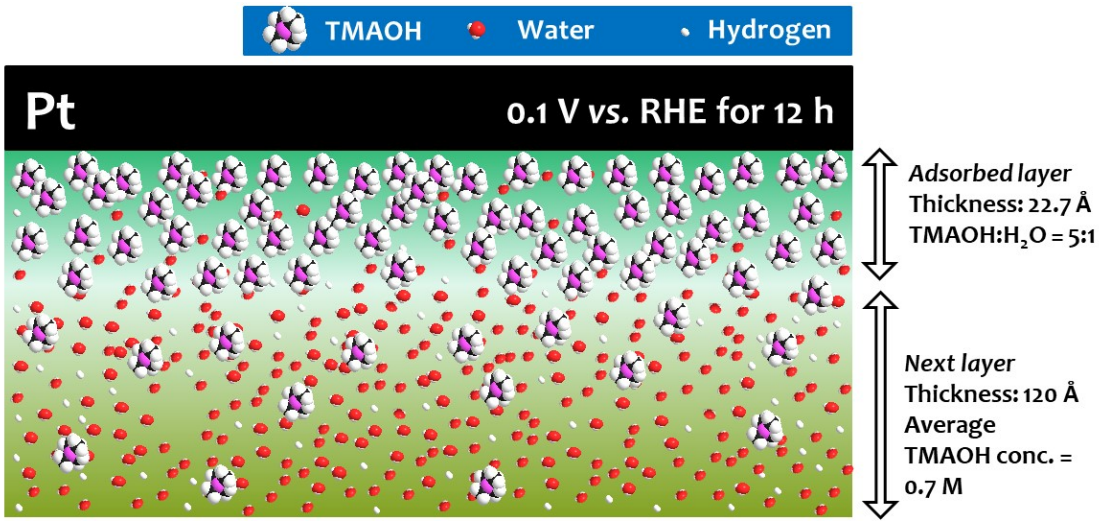
Test set up for neutron reflectometry electrochemical cell*





* The NR experiment was performed at NIST Neutron Center.

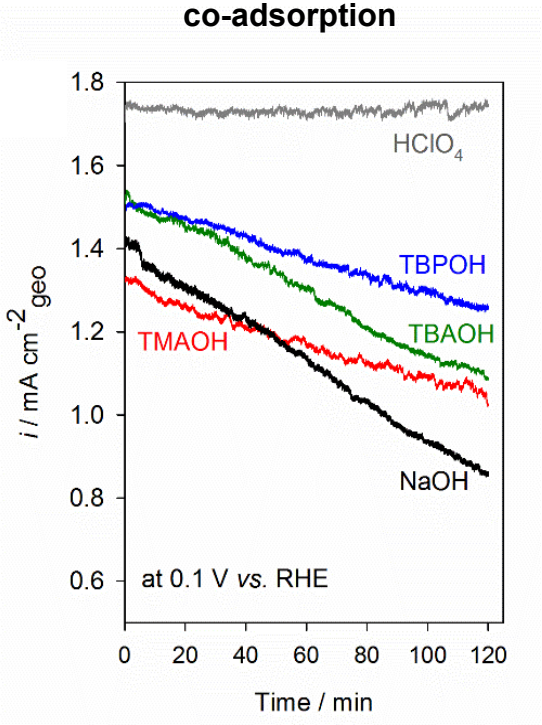
Schematic illustration of co-adsorbed layer structure on Pt after 12 h exposure at 0.1 V vs. RHE



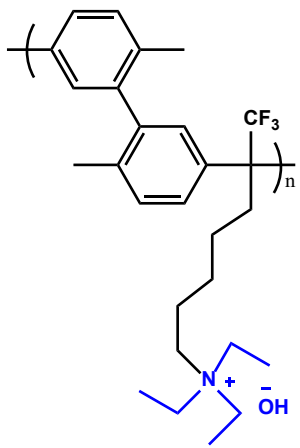
- NR experiments confirmed the cation-hydroxide-water coadsorption on Pt at the HOR potential, ca. 0.1 V vs. RHE.
- The co-adsorbed layer thickness increases with time. The thickness after 12 h exposure the electrode at 0.1 V is 22.7 Å *(see further information on Technical Backup slide #4)*.
- The concentration of the TMAOH in the co-adsorbed layer calculated from scattering length density is extremely high; the ratio of TMAOH to water is 5:1 (previously reported the highest TMAOH to water ratio in the aqueous solution is 1:1).

Development of an HOR ionomers that minimize the cation adsorption

The impact of cationic functional group on the cation-co-adsorption



Synthesis of the ionomer with triethyl ammonium (TEA-BPN)*

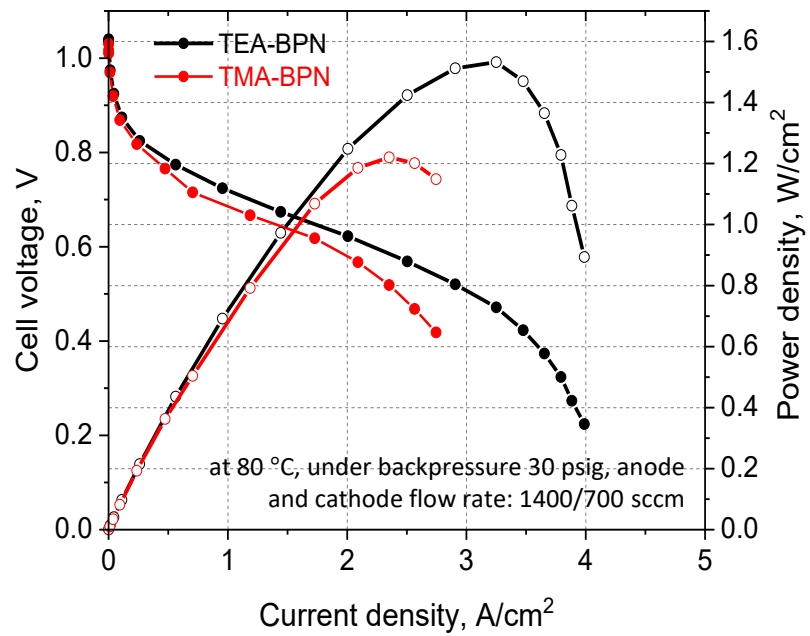


100%: 2.22 mmol/g
75%: 1.85 mmol/g
50%: 1.38 mmol/g

* LANL patent pending

H_2/O_2 AEMFC performance using TEA-BPN

(AEM: *m*-TPN, anode catalyst: Pt-Ru/C (0.5 mg_{pt}/cm^2), cathode catalyst: Pt/C (0.6 mg_{pt}/cm^2), cathode ionomer: TMA-BPN)

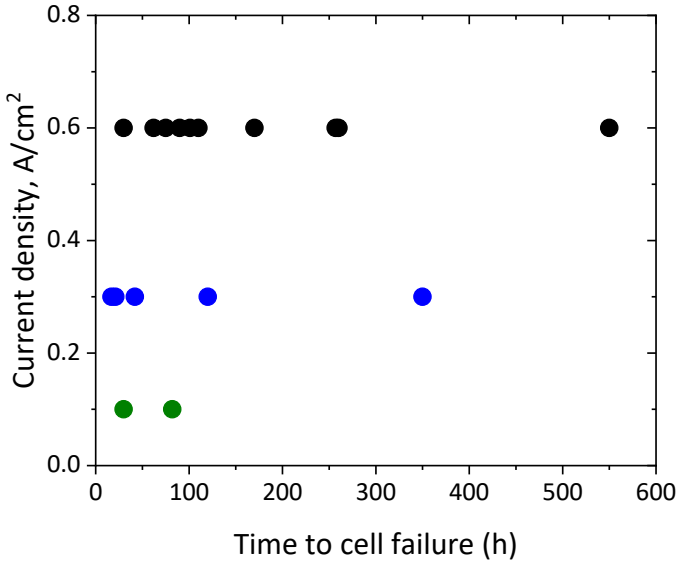


- RDE data suggests that using bulky cations is beneficial to minimize the cation-hydroxide-water co-adsorption. Tetraethylammonium (TEAOH) also showed less adsorbed character (see *in Technical Backup slide #4)*.
- LANL synthesized an ionomer with alkyltriethyl ammonium cationic group (TEA-BPN) via acid catalyzed reaction *(see details in Technical Backup slide #5)*.
- Highlight: Reached to 1.55 W/cm^2 peak power density using TEA functionalized ionomer.

Identify the durability limiting-factor from AEMFC life test

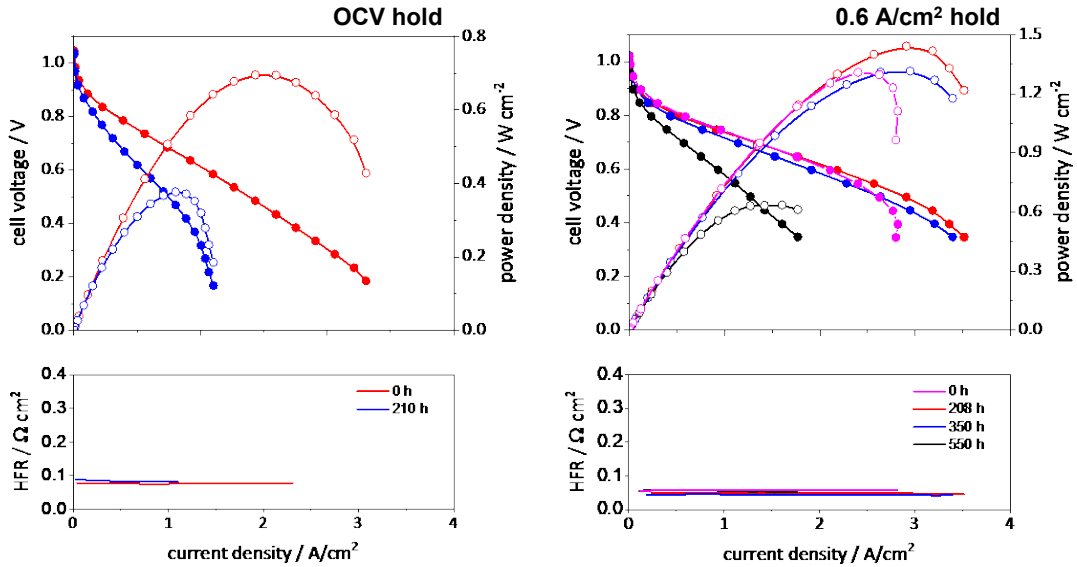
The impact of cell current density of AEMFC life time

Tested at 80 °C and constant current mode.
H_2/O_2 conditions, full humidification.



Polarization curve comparison between OCV and high current density (0.6 A/cm²) conditions.

Tested at 80 °C, H_2/O_2 conditions, full humidification.

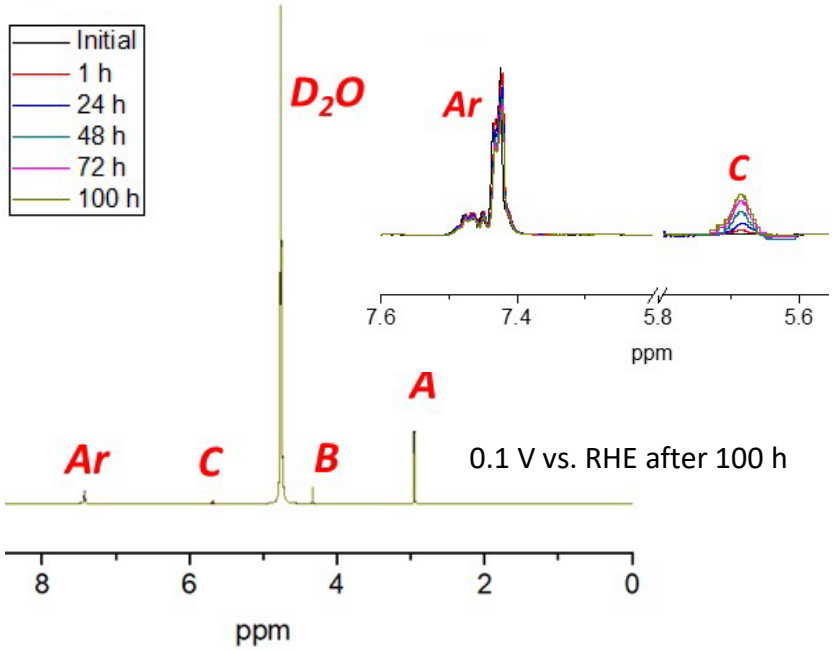


- LANL has performance multiple life tests using down-selected AEMs and ionomers at 80 C. (Total life test duration > 3,000 h)
- The lifetime of AEMFC was determined by various factors such as MEA processing conditions, HOR and ORR catalyst types, gas diffusion layers etc.
- The AEMFC lifetime tested under constant current mode decreases as the test current density decreases.

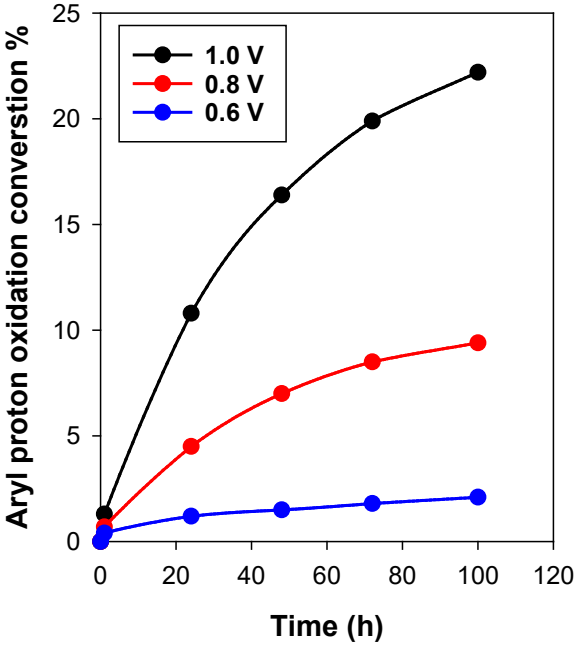
Note: The lower life time with low constant current density condition suggests the AEMFC durability may be predominantly limited by cathode ionomer degradation.

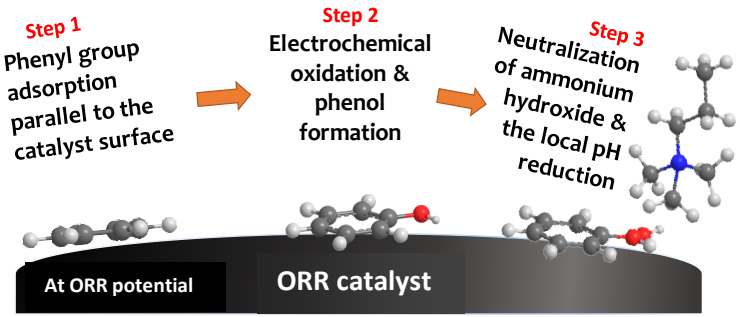
Phenyl oxidation on Pt at 1.0 V vs. RHE (RDE study)

^{1}H NMR analysis of 0.5 M benzyltrimethyl ammonium hydroxide (BTMAOH) solution after the chronoamperometry of Pt at 1.0 V vs. RHE.



Aryl proton oxidation conversion as a function of cell potential





- ^{1}H NMR analysis shows that the phenyl group adsorption occurs on the ORR catalyst surface at ORR potentials.
- Note: The formation of phenol is detrimental because it reduces the hydroxide conductivity of ionomer and catalytic activity by lowering local pH.

Responses to previous year reviewers' comments

- **The high performance loss after 500 hours steady-state is very concerning, especially with no specific ideas provided to address the degradation… The top priority should be to identify the durability-limiting factor(s).**
  For the first three years, we have focused on improving AEM stability, developing ionomer and increasing fuel cell performance. Durability study has started from the third year of the project. In the last year, we found that the phenyl oxidation at ORR current is the primary performance loss mechanism. We first demonstrated this performance-limiting factor in this presentation.

- **The project did not have enough data and discussion on low PGM, non-PGM catalysts and CO_2 issue. This project is primarily limited to polymer-development progress that is necessary but not sufficient.**
  This is because we have negotiated the scope of work focusing on AEM & ionomer development and testing at H_2/O_2 conditions. As we have reasonably high fuel cell performance with relatively high loading PGM catalyst at H_2/O_2, those important subjects need to be continued in the following project. If we have an excellent performance with PGM catalysts, there is a high possibility that the fuel cell performance with non-PGM catalysts is also good (see example in a recent publication in *Angewandte Chemie*, 58, 1046, 2018 by William Mustain et al.) We believe that the negative impact of the CO_2 issue may also be mitigated to a certain degree.

Collaboration and Partners

Partners

Los Alamos NATIONAL LABORATORY

Sandia National Laboratories

Rensselaer

THE UNIVERSITY OF NEW MEXICO

Collaboration & Interaction

POCELLTECH

- AEMFC performance evaluation under H_2/air conditions. Obtained 1 W/cm^2 power density using our down-selected membrane.

XERGY

- AEMs developed from this project (RPI) was sent to XERGY for commercialization. The AEMs will be available from Aldrich by the end of this year.

BERKELEY LAB

- Ionomers were sent to Dr. Kusoglu for thin film study.

UNIVERSITY OF SOUTH CAROLINA

- MEAs produced from LANL was sent to Professor William Mustain to evaluate the AEMFC performance.

TECHNION Israel Institute of Technology

- Received Pd based anode catalyst from Dr. Dekel for HOR study.

University of Stuttgart

- Sent AEM samples to Prof. Kreuer to evaluate alkaline stability.

NREL NATIONAL RENEWABLE ENERGY LABORATORY

- Exchanged AEM matrials between NREL and LANL for evaluation.

PAJARITO POWDER FUEL CELL CATALYSTS

- Ni based non-PGM HOR catalysts were received.

NIST Center for Neutron Research

- For cation group adsorption study, we used neutron facility at NIST two times (FY 18).

Proposed future work

Within the project (ending September 30, 2019)

- Verify the AEMFC degradation mechanism (phenyl oxidation) in the *in-situ* durability measurement.
- Identify other unknown possible degradation mechanisms.

After the project

- Develop ionomers stability under electrochemical oxidative conditions.
- Demonstrate > 2,000 h AEMFC durability.
- Develop non-PGM HOR and ORR catalysts.
- Mitigation strategy of carbonation problem.

Any proposed future work is subject to change based on funding levels.

Remaining challenges and barriers

Outside the project

- **AEMFC performance**
  - Development of PGM-free HOR catalysts
  - Development of PGM-free ORR catalysts
  - Development of ionomers with bulky cations for anode electrode
  - Development of ionomers with less phenyl group

- **AEMFC durability**
  - Development alkaline ionomeric binders under electrochemically oxidative conditions.
  - Material and engineering approach to mitigate carbonation problems.
  - Optimized MEA fabrications.

Technology transfer activities

- **RPI:** Established a joint venture to produce large scale production of AEM and ionomers.
- **SNL:** CRADA with an industrial partner.
- **LANL:** Participated in a SBIR program to license AEM & ionomer technology.

- **FY 2018 patent and patent applications**
- **SNL & LANL:** "Poly(phenylene)-based anion exchange polymers and methods thereof. US Patent Appl. 16/039,158 (2019)"
- **LANL:** "Polymer electrolytes for alkaline membrane fuel cells" S133606 (2018)

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.

Approach: Preparing aryl ether-free polyaromatic AEMs (Year 1). Developing high-performing ionomers with minimum interaction with catalysts (Year 2). Demonstrating AEMFC performance of fully-integrated MEAs from materials produced from this project (Year 3). Investigating the durability limiting factor of AEMFC (Year 4 project extension).

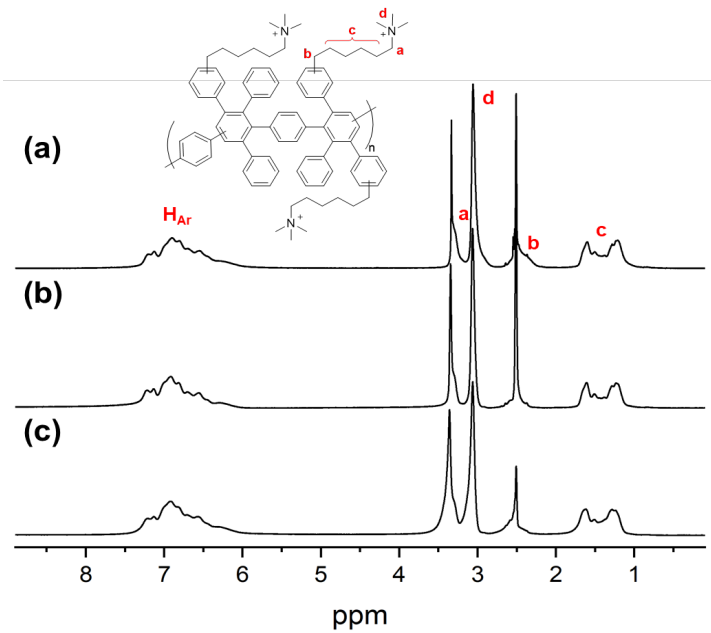
Accomplish-ments (FY 18) Completed to alkaline stability study of AEMs (no chemical degradation for > 1,000 h in 4 M NaOH at 80 °C). Completed the phenyl adsorption study to show gradual AEMFCE performance increase up to 1.5 W/cm^2 peak power density. Elucidated the cation-hydroxide-water co-adsorbed layer by Neutron reflectometry and developed triethyl ammonium functionalized ionomer that allows the AEMFC performance up to 1.5 W/cm^2 peak power density. Identify the possible durability-limiting factor (phenyl oxidation) for the first time (need to complete this study during the rest of the project).

Collaborations: Collaborations with academia, industry and other national labs. In most cases, our team has provided AEMs and ionomers to the collaborators or has obtained potential catalyst materials for MEA testing.

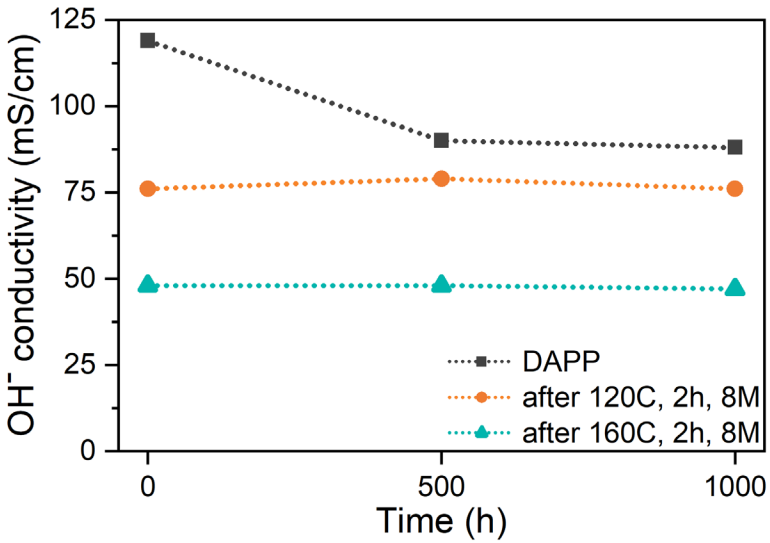
Technical Back-Up Slides

Alkaline stability of the poly(phenylene) AEM

^{1}H NMR spectra of (a) DAPP, (b) DAPP after the alkaline treatment in 4 M NaOH at 80 °C for 500 h, and (c) DAPP after the alkaline treatment in 4 M NaOH at 80 °C for 1000 h in DMSO-d_6.



Compared the hydroxide conductivity of un-crosslinked sample (DAPP) and pre-crosslinked at 120 and 160 °C after alkaline stability test in 4 M NaOH at 80 °C.



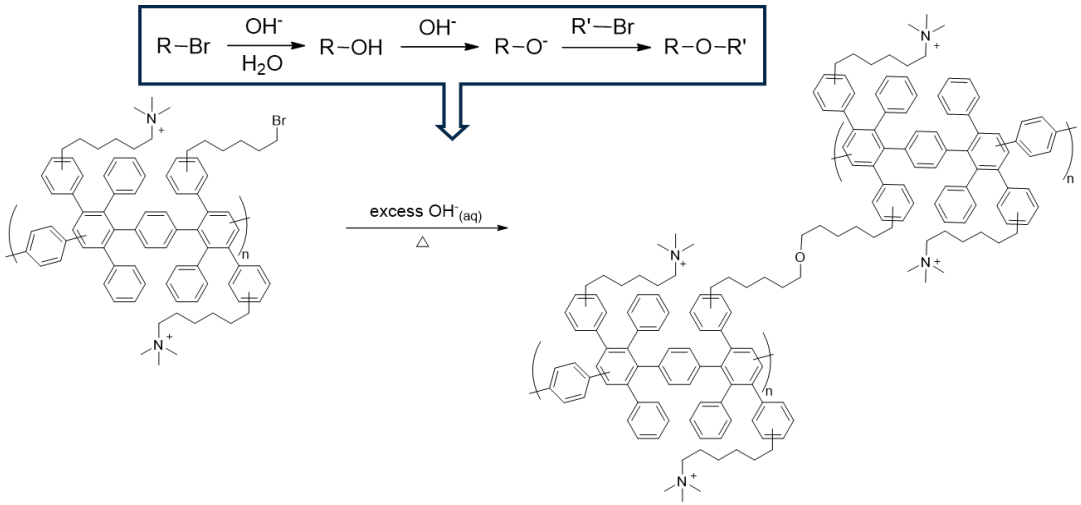
- ^{1}H NMR spectra show that no chemical degradation occurred except the crosslinking reaction during the alkaline stability test in 4 M NaOH, 80 °C for 1000 h.
- The pre-crosslinked DAPP AEM showed no conductivity loss for at least 1,000 h stability test at 4 M NaOH at 80 °C.

Various degradation routes for quaternized polyphenylene AEMs

Crosslinking reaction

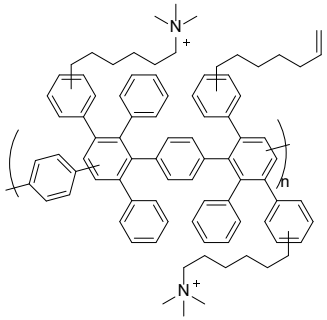
The reaction route describing the crosslinking reaction between unreacted alkyl bromides via substitution followed by Williamson ether synthesis.

This reaction is hard to detect by spectroscopic method and titration but obvious with solubility and water uptake change without IEC change.



E_2 elimination

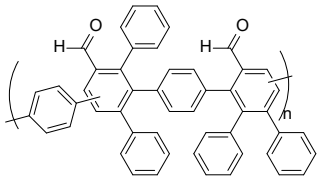
The degradation route of DAPP via β-elimination at low temperature of 80 °C at 4 M NaOH for >11,000 h, occurs after crosslinking of the membrane.



This reaction is detected by υ(C=C) peak evolution at 1630, and 1000 cm^{-1}.

S_N2 aldehyde formation

The degradation route of DAPP via backbone degradation and formation of aromatic aldehyde after the exposure towards extreme accelerated thermal stress for 72 h, likely occurs after crosslinking and cation degradation of the membrane.

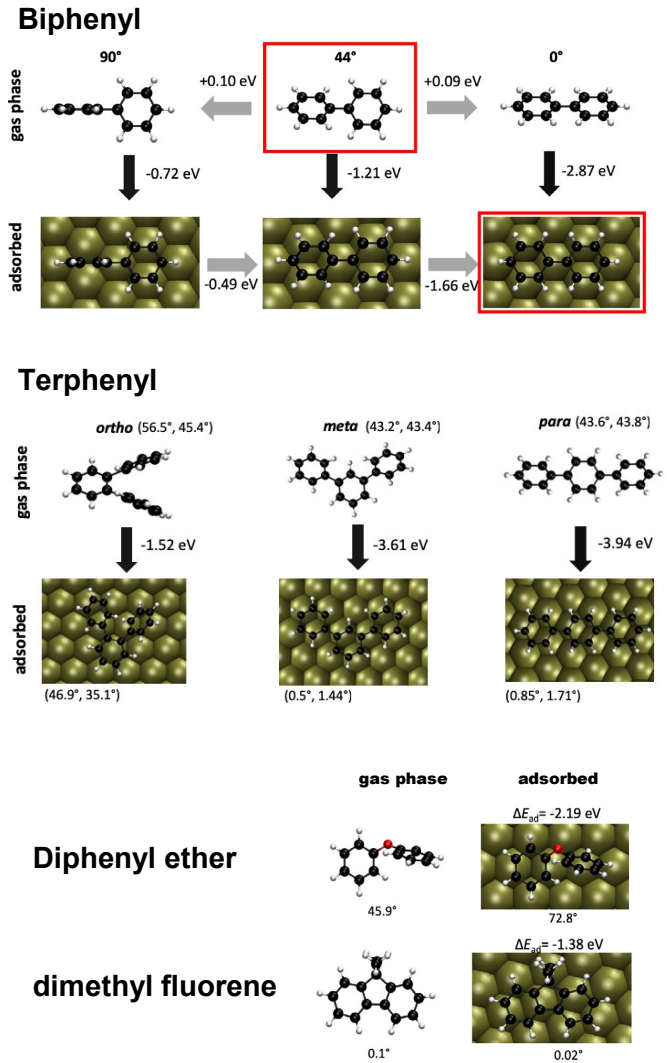


This reaction is detected by υ(C-H) peak evolution from aldehyde at 2750-2800 cm^{-1}. Also υ(C=O) peak evolution at 1680 cm^{-1}.

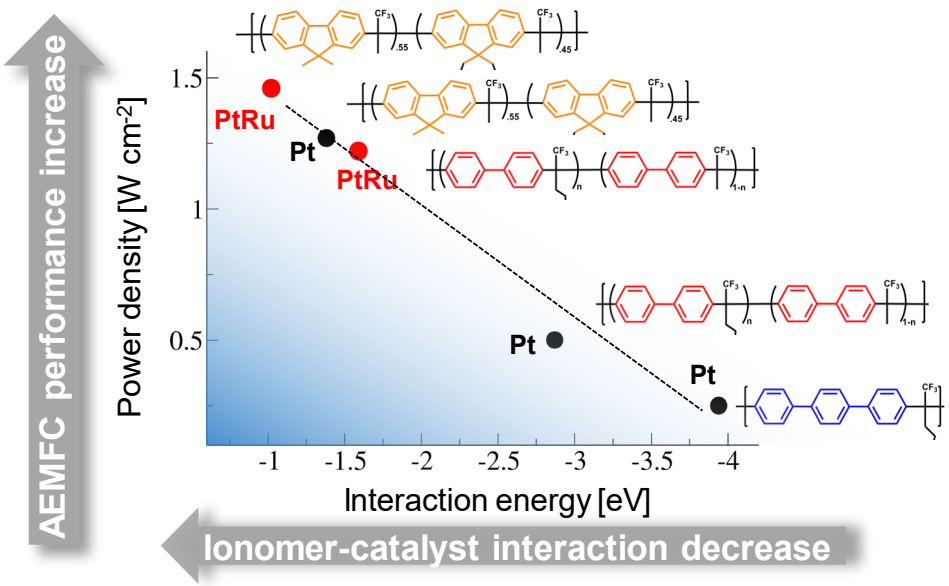
- We have observed at least three different chemical structure changes depending on alkaline stability test conditions.

Correlation between phenyl adsorption and AEMFC peak power density

DFT optimized geometries of ionomer backbone fragments on the Pt(111) surface.



Correlation between phenyl adsorption (DFT results) and AEMFC performance (experimental)

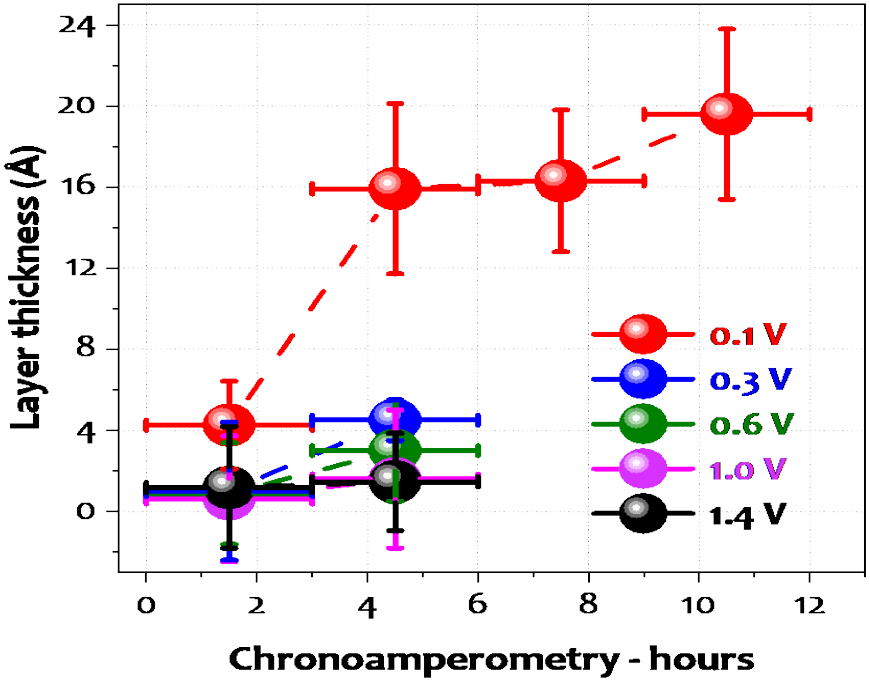


- UNM calculated the adsorption energy on Pt(111) and Pt-Ru(111) using various ionomer backbone fragments.
- LANL tested AEMFC performance to show the correlation between the phenyl group adsorption energy and AEMFC peak power density.

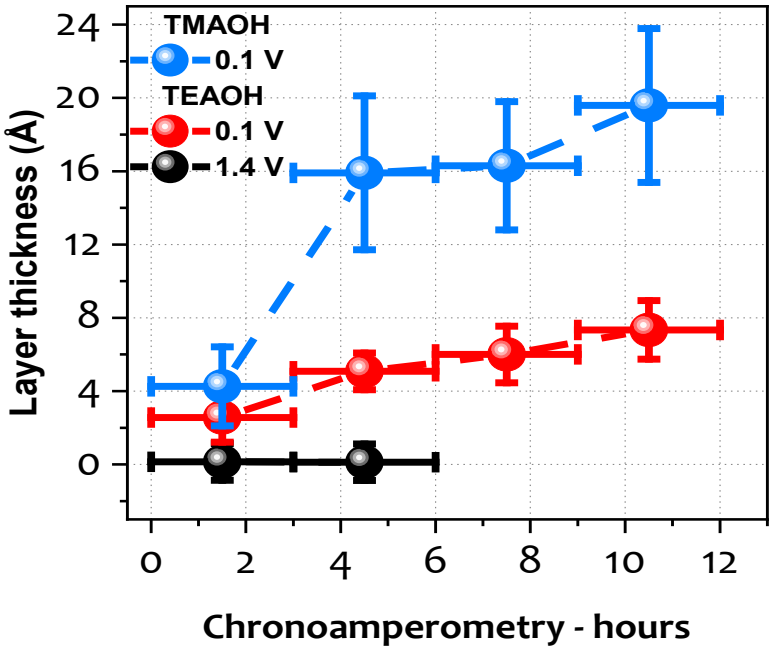
Note: The phenyl adsorption energy of the ionomer backbone is probably one of the most critical design parameters.

Impact of cell potential and type of cations on cation co-adsorption (NR)

The impact of cell potential on tetramethyl ammonium hydroxide (TMAOH) adsorption on Pt surface.

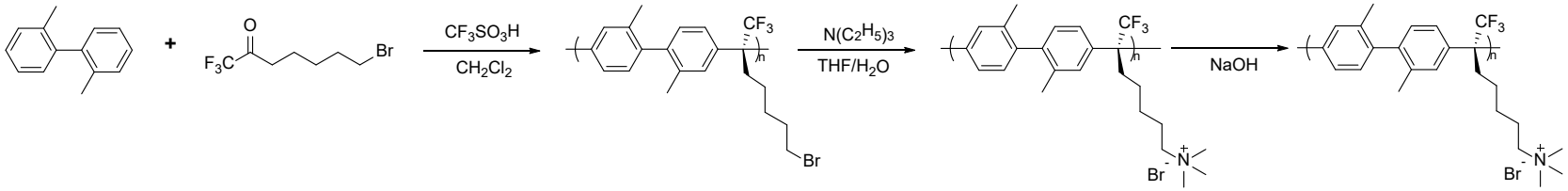


Comparison of co-adsorption layer thickness between TMAOH and tetraethylammonium hydroxide (TEAOH).

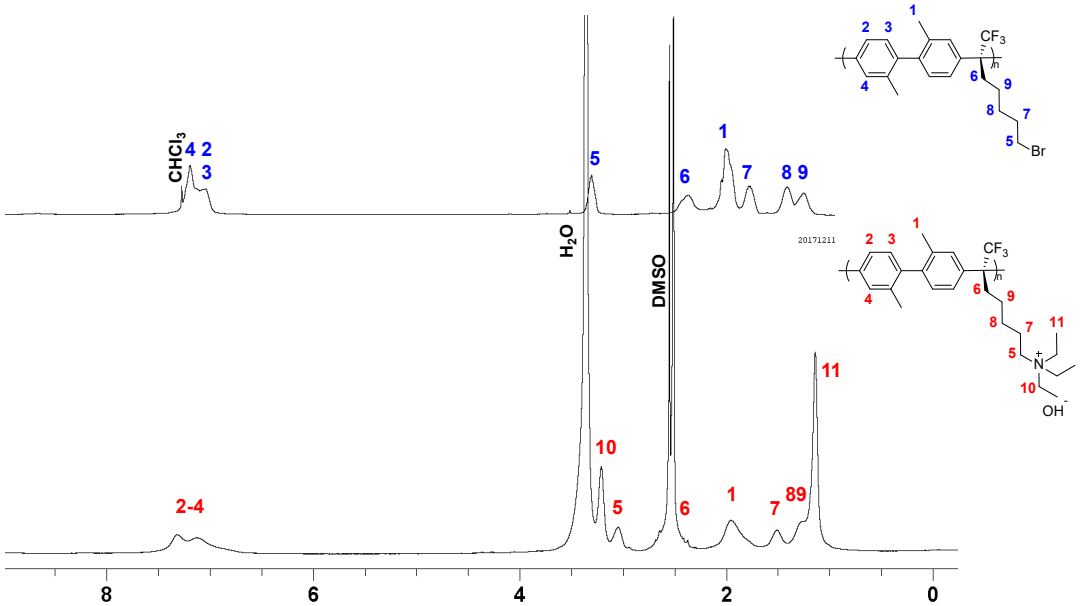


- The neutron reflectometry (NR) data show that cation-hydroxide-water co-adsorption is cumulative and potential dependent.
- Significant cation adsorption occurs at a low potential, ca. 0.1 V vs. RHE; minimal adsorption was observed at 1.0 V or 1.4 V.
- The co-adsorbed layer thickness of TEA-hydroxide-water was much less compared to that of TMA-hydroxide-water.

Synthesis and chracterization of TEA-BPN



^{1}H NMR spectra



- Pentamethylene triethylammonium functionalized poly(biphenylene) (IEC = 2.22 mmol/g) was successfully synthesized via acid catalyzed polymerization.
- The hydroxide form of polymer is soluble alcohols but insoluble in water.

Solubility (OH^- form)	H_2O	MeOH	EtOH	*i*-PrOH	EtOH: *i*-PrOH (1:1)	Ethylene glycol	THF	DMSO
	−	+△	+△	±	+△	+△	−	± (gelled)

+: soluble at rt; −: insoluble; ±: partially soluble/swollen; +△: soluble when heated and sonicated