

Advanced Materials for Fully-Integrated MEAs in AEMFCs

Yu Seung Kim

(yskim@lanl.gov)

Los Alamos National Laboratory

Project ID: **FC146**

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Overview

Timeline

- Project start date: 11/2/2015
- Project end date: 11/2/2018
- Percent complete: 20%

Budget

- Total project funding: \$3,060K
 - DOE share: 98%
 - Contractor share: 2%
- Funding received in FY15: \$1,020K
- Total DOE Funds Spent*: \$550K

*As of 3/31/16

Barriers

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

Project lead

- Los Alamos National Laboratory
 - Yu Seung Kim

Partners

Subcontractors

- Sandia National Laboratory
 - Cy Fujimoto
 - Michael Hibbs
- Rensselaer Polytechnic Institute
 - Chul Sung Bae
- Argonne National Laboratory
 - Vojislav Stamenkovic

Interactions

- | | |
|---|---|
| ▪ Giner Inc. <ul style="list-style-type: none">- Corky Mittelsteadt | ▪ Xergy Inc. <ul style="list-style-type: none">- Bamdad Bahar |
| ▪ Proton Onsite <ul style="list-style-type: none">- Kathy Ayers | ▪ Nanosonic Inc. <ul style="list-style-type: none">- William Harrison |
| ▪ Amsen <ul style="list-style-type: none">- Hongxing Hu | ▪ IRD Fuel Cells, LLC <ul style="list-style-type: none">- Madeleine Odgaard |
| ▪ University of New Mexico <ul style="list-style-type: none">- Alexey Serov | |

Relevance

Objective

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

Go-no-Go decision point (DOE Lab Call Milestone)

- 3/31, 2017 Develop AEMs with an areal specific resistance $\leq 0.1 \Omega \text{ cm}^2$, maintained for 500 hours during at 600 mA/cm^2 at $T > 60^\circ\text{C}$.
- 3/31, 2019 Demonstrate AEMFC initial performance of 0.6 V at 600 mA/cm^2 on H_2/O_2 (maximum pressure of 1.5 atm abs.) in MEA with a total loading of $< 0.1 \text{ mg}_{\text{PGM}}/\text{cm}^2$, and less than 10% voltage degradation over 2,000 hour.

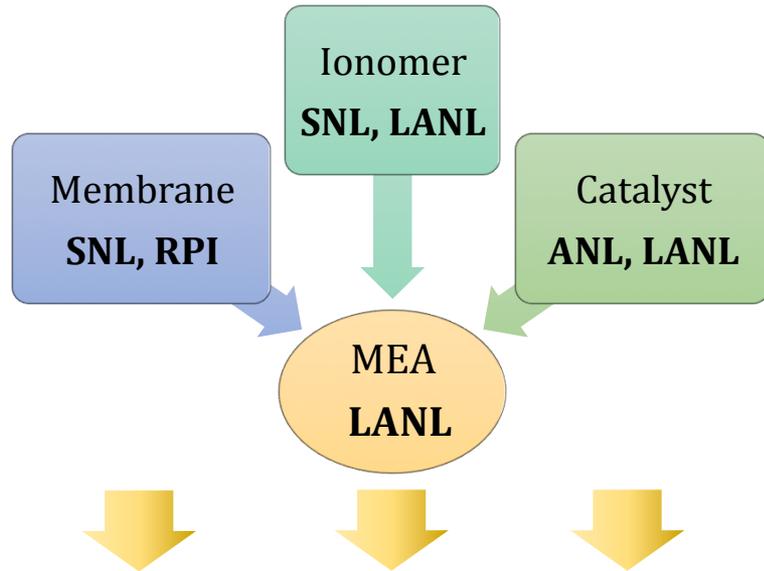
Relevance

- Advanced material development for fully-integrated MEAs in AEMFCs, enabling the fuel cell cost reduction without performance sacrifice.

Technical challenges

- Hydroxide conductivity of AEMs
- Chemical/thermal/mechanical stability of AEMs
- Good performing ionomeric binders
- Optimal catalyst-ionomer interface for fuel cell electrodes
- Integration of high-performing MEAs

Collaborations: Material Development Team



Interactions: Giner Inc. (Industry, DOE FCTO program, water electrolysis), Proton Onsite (Industry, DOE ARPA-E, water electrolysis), Xergy Inc. (Industry, DOE ARPA-E, AEMFC membrane), Nanosonic Inc. (Industry, DOE SBIR, AEMFC membrane), Amsen Technologies LLC (Industry, DOE SBIR, AEMFC MEA), IRD Fuel Cells LLC (Industry, DOE FCTO program, AEMFC MEA), University of New Mexico (Industry, DOE FCTO program, AEMFC anode catalyst)

- **Cy Fujimoto and Michael Hibbs at SNL**
 - Develop poly(phenylene) AEMs & ionomers
 - Supply polyaromatic AEMs
- **Chulsung Bae at RPI**
 - Develop acid-catalyzed poly(biphenyl alkylene) AEMs
 - Supply SEBS triblock copolymers
- **Yu Seung Kim at LANL**
 - Develop hydrocarbon ionomers
 - Develop perfluorinated ionomers
 - Fabricate MEAs
 - Fuel cell performance test
- **Piotr Zelenay at LANL**
 - Supply non-PGM ORR catalysts
- **Vojislav Stamenkovic at ANL**
 - Supply low-PGM HOR catalysts

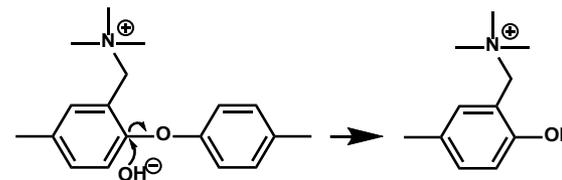
Approach: Technical aspect

AEM

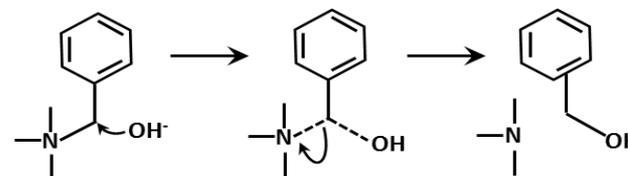
- **General approach:** Preparing AEMs **without ether or electron-withdrawing groups** in the polymer backbone.¹
- Replacing benzyl trimethyl ammonium with **alkylammonium**.²
- **FY 16:** Down-selecting AEM (Slide 6)

Ionomeric binder

- **General approach:** Developing different ionomeric binders for anode and cathode. For anode, **avoid methyl ammonium tethered ionomer** which poisons hydrogen oxidation reaction.³ For cathode, **use methyl ammonium tethered ionomer**.
- **FY 16:** Preparing hydrocarbon ionomers.
- **FY 17:** Preparing perfluorinated ionomers.

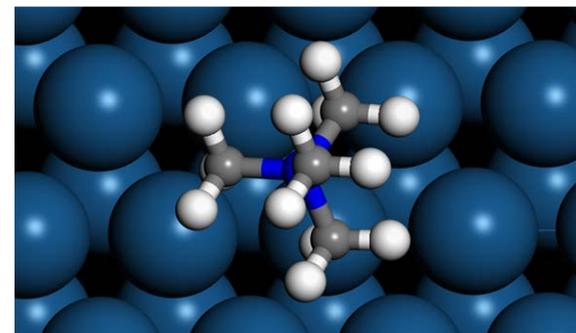


Aryl-ether cleavage reaction



S_N2 degradation of BTMA

TMA⁺ adsorption on Pt surface



HOR inhibition by cation adsorption explained in Slides 12 and 13

Approach: AEM & Ionomer down-selection

No.	Series name	Polymer		IEC (meq./g)	Year	Organization
		Backbone	Cationic group			
1	ATM-PP ^a	Poly(phenylene)	BTMA	1.0 – 2.5	2012	SNL
2	MRH	Poly(phenylene)	Alkyl ammonium	1.8 – 2.5	2015	SNL
3	SPG	Poly(phenylene)	Guanidinium	1.6 – 2.2	2015 - 16	SNL, LANL
4	MRH-2	Poly(phenyl alkylene)	Alkyl ammonium	1.8 – 2.5	2015 – 16	SNL
5	PBPA	Poly(phenyl alkylene)	Alkyl ammonium	1.5 - 2.7	2015 – 16	RPI
6	SEBS	Styrene-ethylene-butane-styrene	BTMA	1.8 - 2.2	2015	RPI
7	N-FA-TMG	Perfluorinated	Guanidinium	0.8	2013	LANL
8	PS ^b	Polystyrene	Ethyl ammonium	2.0	2016	LANL

^a control AEM; ^b Leveraged work with UNM incubator project

No.	Stability	Conductivity	Mechanical Property	Processibility	Gas permeability ^a	Catalyst Interaction ^b	Solvent resistance	Cost ^c	Down-select
1	○	○	○	○	○	△	○	○	Control
2	●	○	●	△	○	○	●	○	Ionomer ^d
3	●	○	△	△	○	●	●	○	Ionomer ^e
4	●	○	○	●	○	△	△	○	New dir. ^f
5	●	●	●	●	△	△	△	●	AEM ^g
6	●	●	●	✘	NA	NA	●	△	
7	△	△	△	△	●	●	●	✘	New dir. ^h
8	NA	△	△	●	○	○	△	●	

^a estimated from chemical structure; ^b from small molecule study; ^c Raw material and synthesis cost

^d Slide 11 & 23; ^e Slide 14 & 24; ^f Slide 20; ^g Slide 8-10, 22; ^h New direction: Slide 21

Approach: Planned milestones and go/no-go decisions

FY '16 AEM Milestone – Completed in February 20, 2016

- Complete synthesis of down-selected AEMs and measure basic properties of AEMs.

FY '16 Ionomer Milestone – 90% Progress as of March 31, 2016

- Prepare baseline materials from wet chemistry and measure the electrochemical properties.

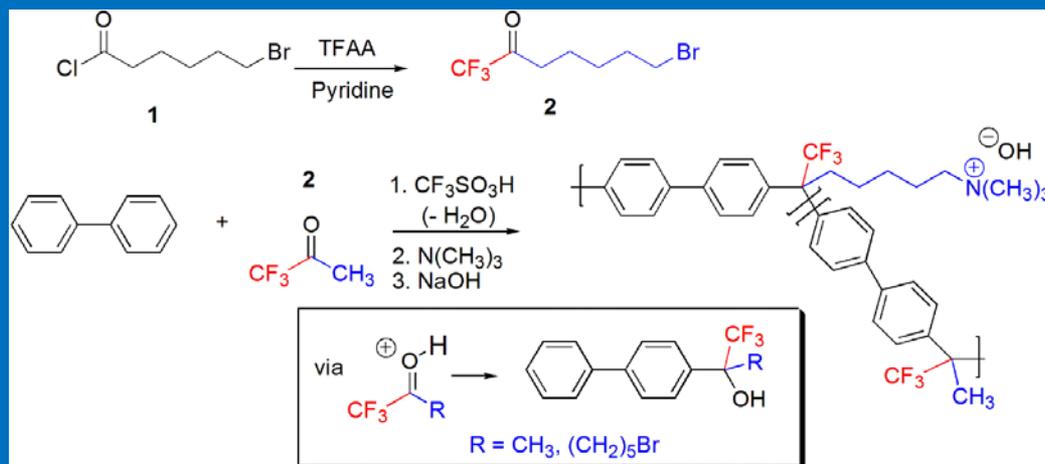
FY '16 MEA Integration Milestone - 50% Progress as of March 31, 2016

- Prepare baseline catalysts and measure the baseline MEA performance.

Go-no-Go Decision Point (March 31, 2017)

- Develop AEMs with an areal specific resistance $\leq 0.1 \Omega \text{ cm}^2$, maintained for 500 hours during at 600 mA/cm^2 at $T > 60^\circ\text{C}$.

Accomplishment: Poly(biphenyl alkylene)



Key features

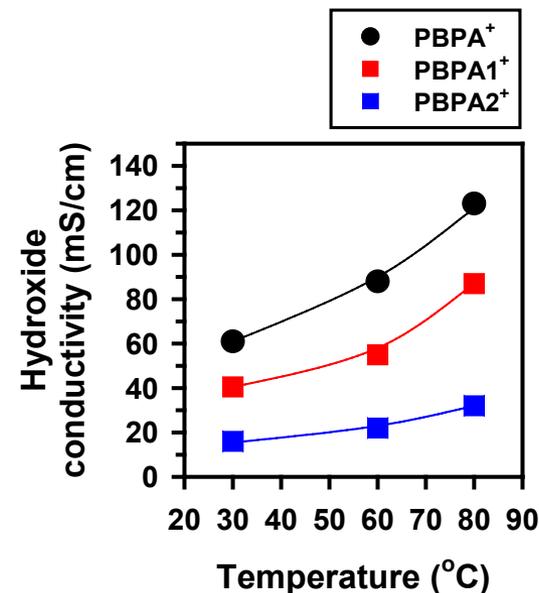
- Hexamethyl ammonium group
- All C-C bond backbone
- No need to use expensive metal catalysts in synthesis
- Easy IEC control

Detail characterization: Backup Slide 22.

Polymer	Monomer ratio (Br: CH ₃)	IEC ^a (meq./g)	Water uptake ^b (%)	M _w ^c (g/mol)
PBPA ⁺	1	2.70	164	110,100
PBPA1 ⁺	0.67	1.94	120	138,600
PBPA2 ⁺	0.33	1.46	81	106,300

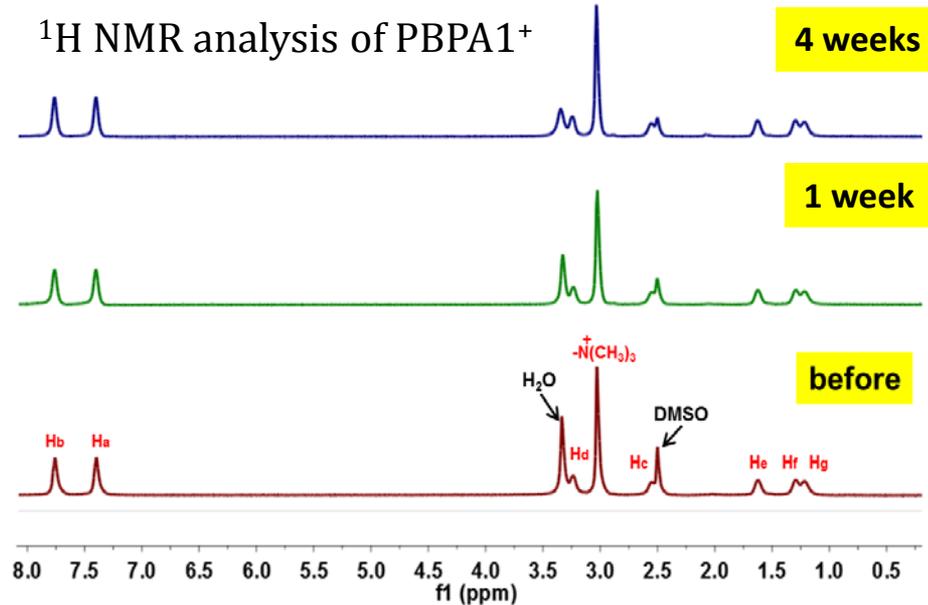
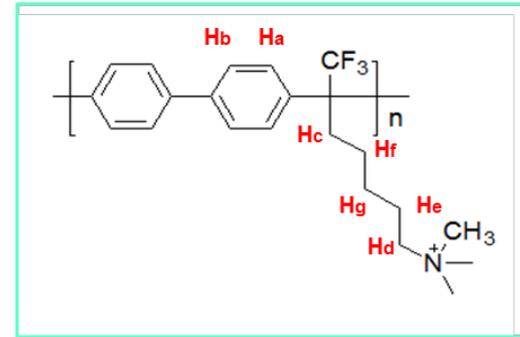
^a titration; ^b measured at 80°C, ^c measured by GPC using Br form

Highlight: Developed new acid-catalyzed synthetic pathway producing highly conductive, high Mw AEMs.



Accomplishment: Stability of poly(biphenyl alkylene)

Ex-situ alkaline stability test by immersing OH⁻ form AEM in 1 M NaOH at 80°C



Sample	IEC (meq./g) by titration		
	Initial	1 week	4 weeks
PBPA ⁺	2.70	2.74	2.65
PBPA1 ⁺	1.94	1.94	1.92
PBPA2 ⁺	1.46	1.47	1.48

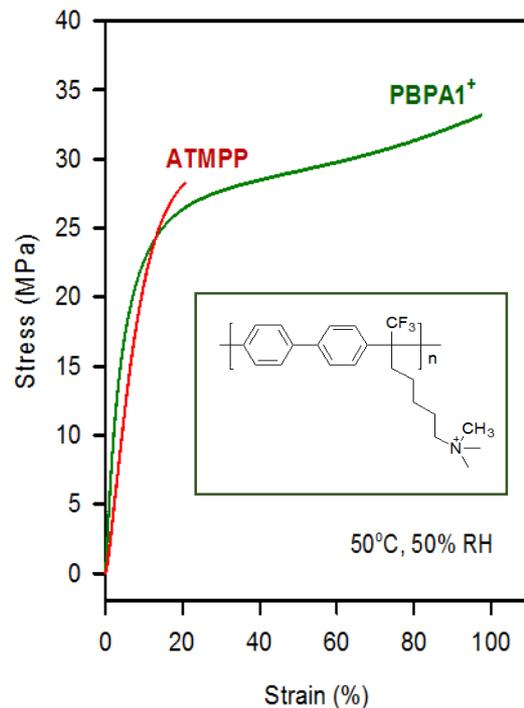
- Ether-free biphenyl alkylene polymer backbone and hexamethyl ammonium cationic functional group provide unprecedented alkaline stability.

Highlight: Alkaline AEM stability (720 h, at 80°C) was achieved.

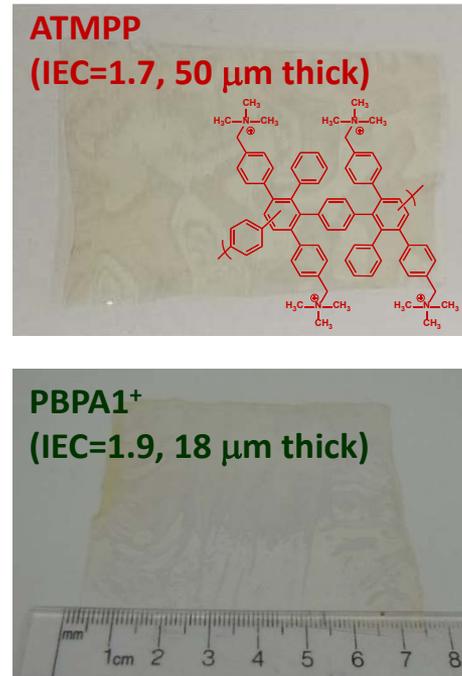
cf. 2017 DOE milestone: > 500 h at > 60°C.

Accomplishment: ASR of poly(biphenyl alkylene)

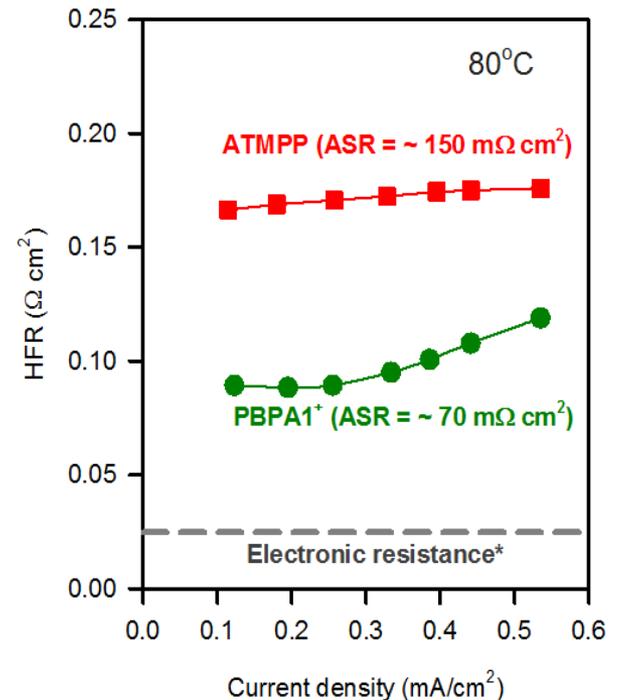
Stress-strain curves



Thin solution cast AEM



ASR from fuel cell operating mode



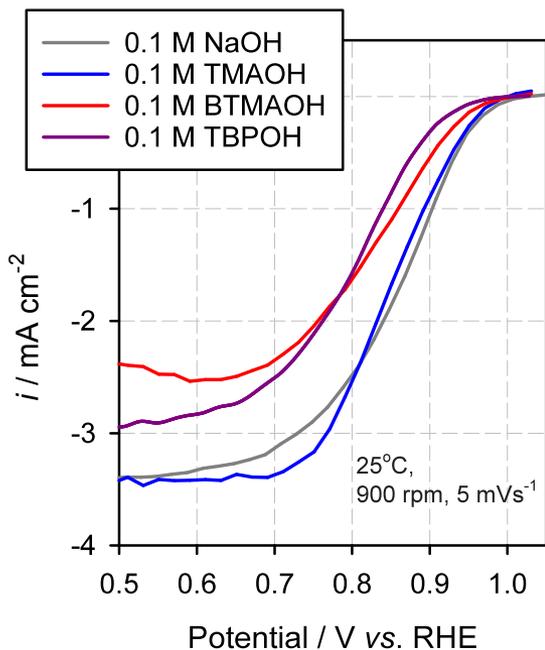
- Excellent toughness of PBPA1⁺ makes it possible to cast thin and robust AEM.

Highlight: Alkaline AEM ASR of 0.07 $\Omega \text{ cm}^2$ is achieved at 80°C.

cf. 2017 DOE milestone: < 0.1 $\Omega \text{ cm}^2$ at > 60°C.

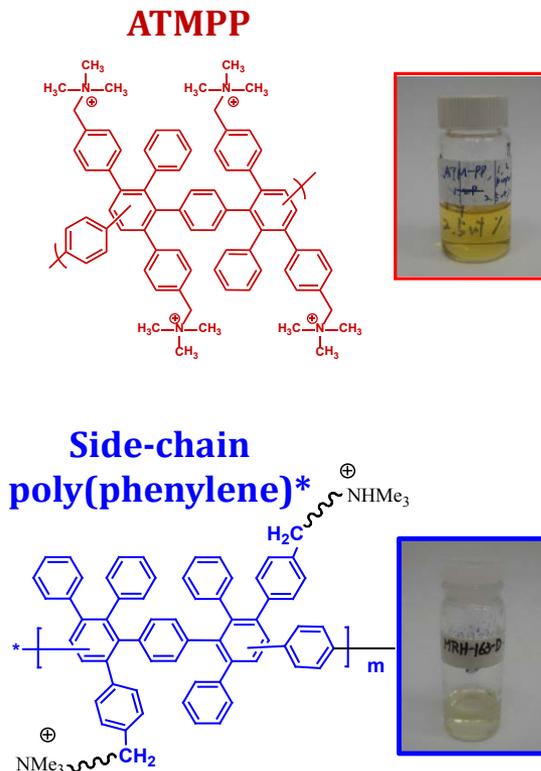
Accomplishment: Side-chain poly(phenylene) cathode binder

ORR voltammogram of Pt/C (RDE)



TMAOH: tetramethyl ammonium OH
 BTMAOH: benzyltrimethylammonium OH
 TBPOH: tetrabutyl ammonium phosphonate OH

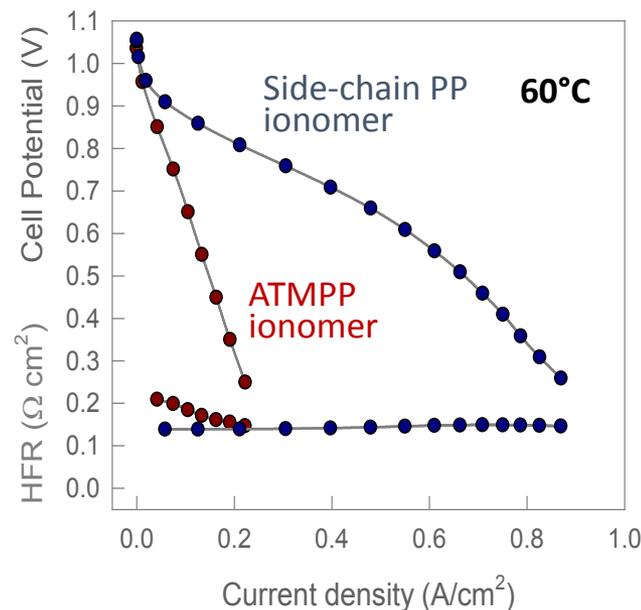
Ionomer dispersion



* Synthetic process: Backup Slide 23

H₂/O₂ AEMFC polarization curves

Catalyst: Pt/C 0.4 mg_{Pt}/cm²;
 AEM: QA-SEBS (40 μm thick); 15 psig backpressure



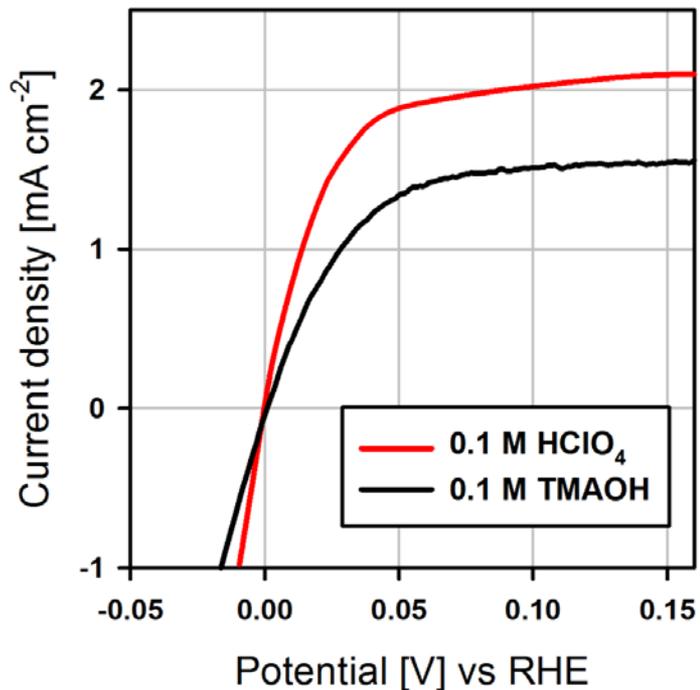
- Prepared ionomer dispersion* using side-chain poly(phenylene).

Highlight: Obtained much improved AEMFC performance.

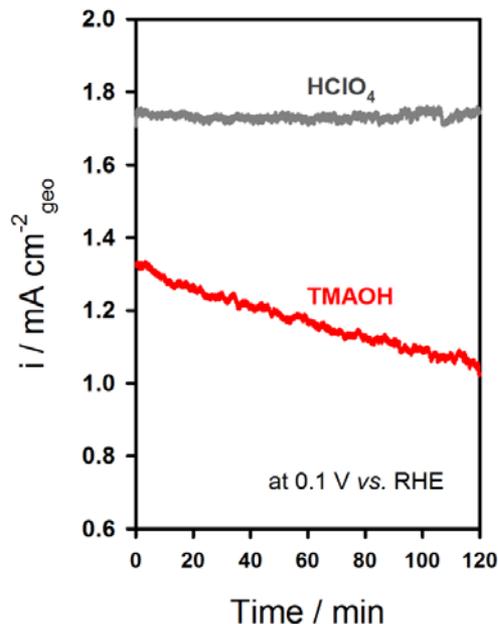
* YS Kim, LANL, Patent pending

Accomplishment: AEMFC HOR study

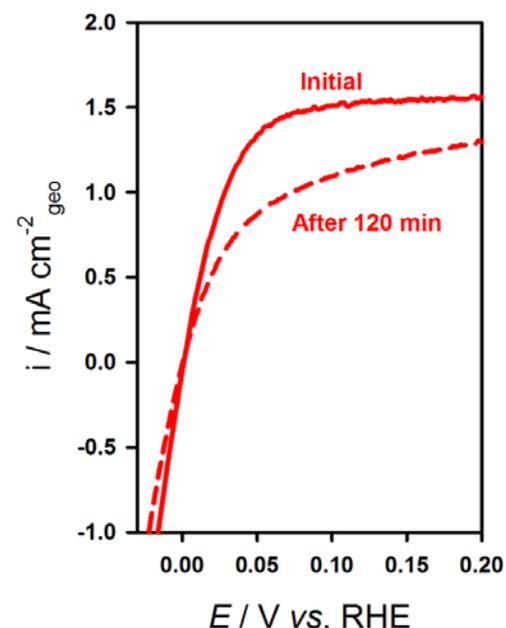
HOR Acid vs. Alkaline electrolytes



Chronoamperometry at 0.1 V



HOR voltammogram after 120 min at 0.1 V

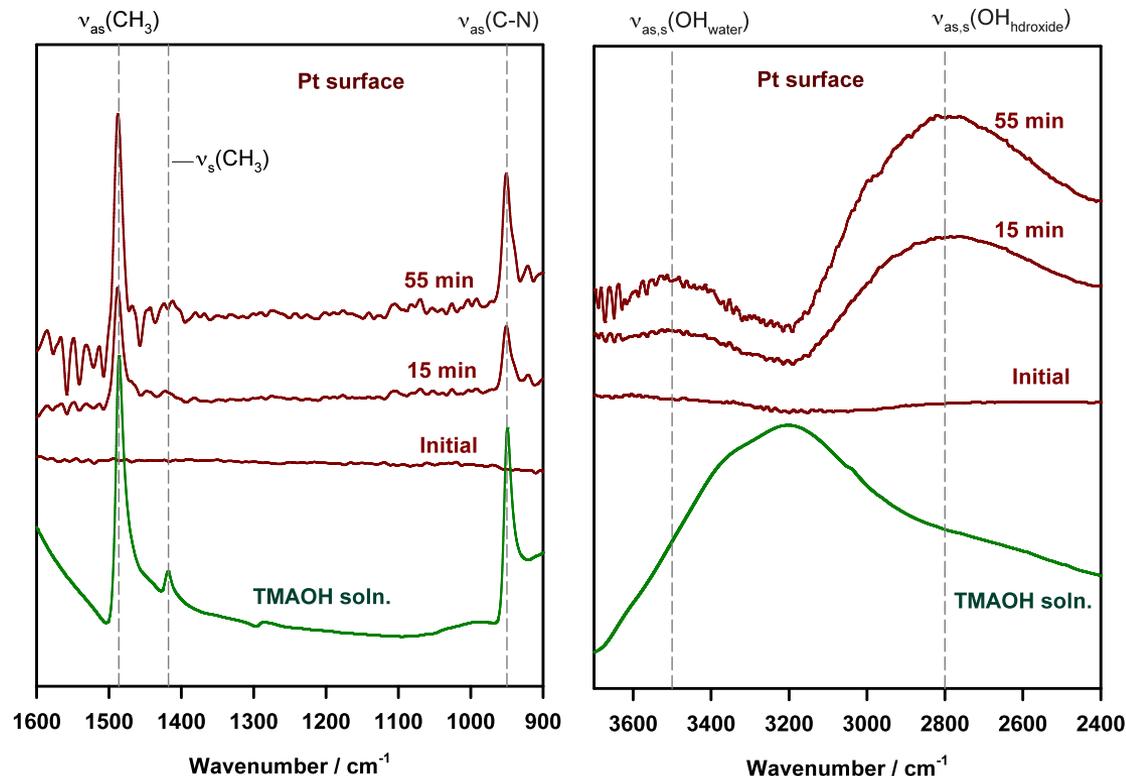


- The HOR activity of Pt catalyst in alkaline solution is much less than that in acidic solution.
- The HOR current keeps decreasing over time when exposed to 0.1 V vs. RHE.

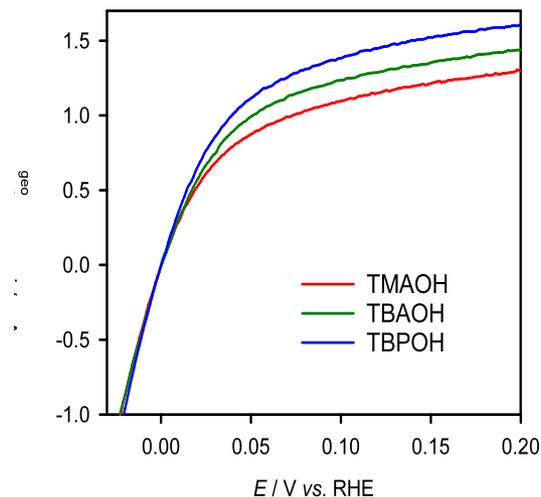
Highlight: Experimental conditions for RDE HOR measurement in organic cation solutions are established.

Accomplishment: HOR inhibition mechanism study

Surface FTIR of the Pt in TMAOH at 0.1 V vs. RHE^a



HOR voltammogram of Pt/C from RDE



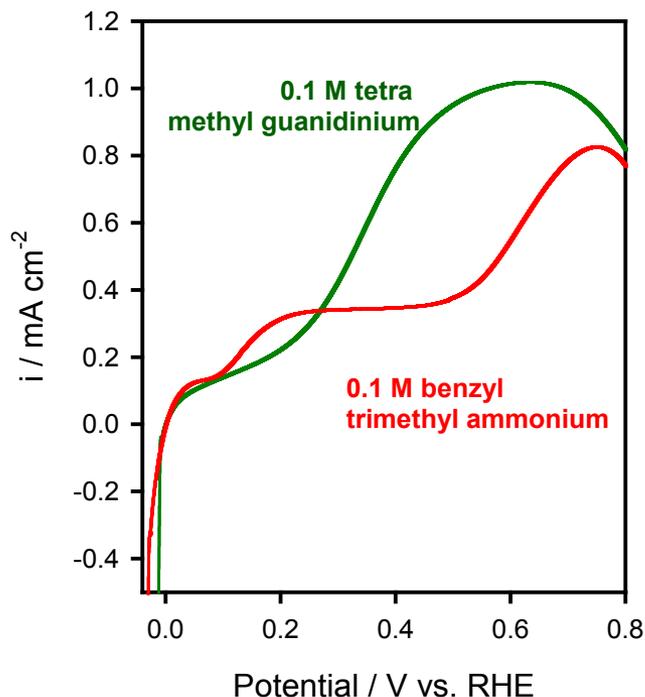
- Observed co-adsorbed layer of TMA⁺, OH* and H₂O*.
- HOR activity depends on the type of organic cations.
- Proposed H₂ diffusion issue through the co-adsorbed layer.^a

Highlight: First observed the co-adsorbed layer by surface FTIR.

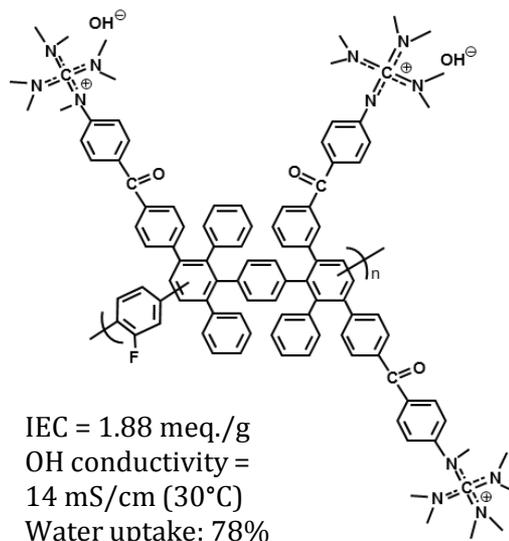
^a H Chung et al. *submitted*, 2016; ^b IT McCrum et al. *J. Phys. Chem. C*. 120, 457, 2016.

Accomplishment: Guanidinium poly(phenylene) anode binder

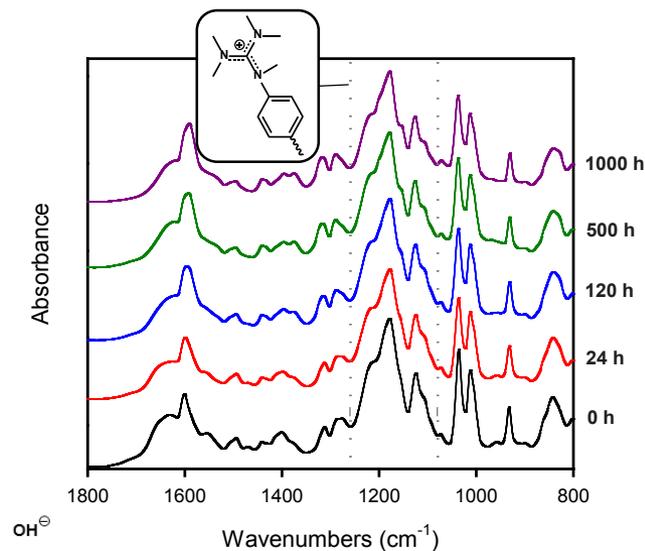
HOR voltammogram of Pt (microelectrode)



Guanidinium poly(phenylene) ionomer*



Ex-situ alkaline stability test



No structural & conductivity change after 1000 h life test at 0.5 M NaOH at 80°C

- Prepared phenyl guanidinium poly(phenylene)s anode binder*

Highlight: Exceptional stability (1000 h, at 80°C) with the resonance stabilized guanidinium poly(phenylene) ionomer.

cf. 2017 DOE milestone: > 500 h at > 60°C.

* Joint IP of SNL and LANL
Synthetic process: Backup slide 24

Remaining Barriers and Challenges

- **Synthesis high-performing anion exchange membranes:** We have synthesized several high-performing anion exchange membranes but excluded from the project due to high cost (e.g. expensive catalysts). We will leave those materials for the risk management purpose.
- **Synthesis of high yield perfluorinated anion exchange ionomers:** This task is delayed due to insufficient solubility of the perfluorinated polymer precursors and low yield. The task was resumed with improved synthetic schemes.
- **Anode ionomer development:** Although we identified the slow HOR reaction of alkaline membrane fuel cell anode, we do not find ideal cationic groups that are inert from the catalyst poisoning. In addition, some cationic groups are difficult to incorporate into polymers.
- **MEA integration using non-PGM anode catalysts:** This task was excluded from the project because there were no highly active non-PGM anode catalysts available. This technical barriers should be dealt with other DOE programs to achieve 2020 DOE milestones.

Proposed Future Researches

Remainder FY2016

AEM development

- Complete structure optimization of poly(biphenyl alkylene)s and poly(phenylene alkylene)s (RPI, SNL, LANL).

Ionomer development

- Cathode: Optimize side-chain poly(phenylene)s (SNL, LANL).
- Anode: Develop two types of ionomers: perfluorinated (LANL) and guanidinium based (SNL, LANL) ionomers.

MEA integration

- Evaluate AEMs and electrode performance.

FY2017

AEM development

- Complete 500 h ASR test (RPI, SNL, LANL).

Ionomer development

- Down-select HOR ionomers (SNL, LANL).

MEA integration

- Demonstrate best-performing AMFC MEAs (LANL).
- Incorporation of low-PGM anode and non-PGM cathode (ANL, LANL)

Technology Transfer Activities

- **RPI:** Contacted several small business companies to produce large scale AEMs during FY 16.
- **SNL:** Co-PI is participating in DOE's Lab Corps program, which has included contacting two large manufacturers to produce poly(phenylene) AEMs.
- **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 2016 patent applications**
 - RPI: "Novel polymers and methods for their manufacture" PCT/US2015/061036
 - 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" S-133,257, 2015.

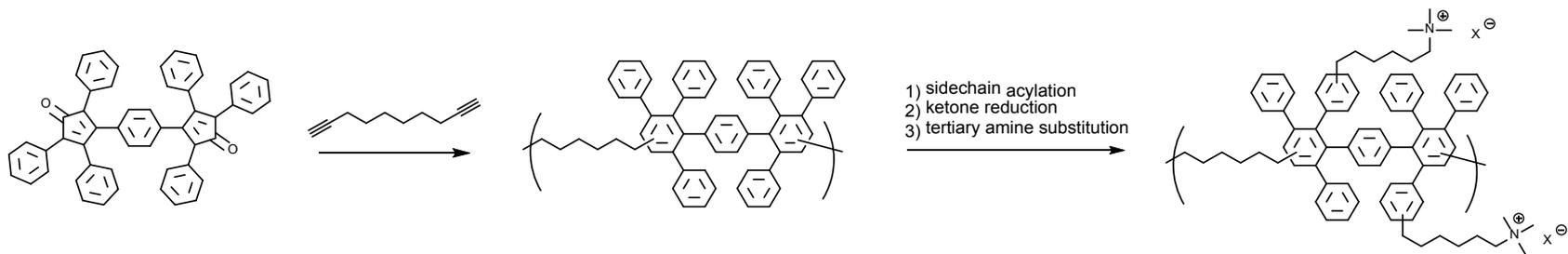
Summary

- Objective:** Development of improved AEMs, ionomeric binders and integration of catalysts and membranes into high-performance MEAs.
- Relevance:** Advanced material development for fully-integrated MEAs in AEMFCs, enabling the fuel cell cost reduction without performance sacrifice.
- Approach:** Preparing AEMs **without ether or electron-withdrawing groups** in the polymer backbone.
Developing different ionomeric binders for anode and cathode. For anode, **avoid methyl ammonium tethered ionomer** which poisons hydrogen oxidation reaction.³ For cathode, **use methyl ammonium tethered ionomer**.
- Accomplishments** Prepared most promising novel AEMs *via* new chemistry. **The prepared AEMs showed exceptional stability with desired film forming properties.**
Investigated ionomer-catalyst interaction using RDE experiments; Initiated novel ionomer synthesis based on the RDE results. Demonstrated the **stability of resonance stabilized poly(phenylene) ionomers.**
- Collaborations:** Strong team comprised of chemical synthesis, MEA integration, electrochemistry and fuel cell testing. Extensive communications with several industrial partners.

Technical Back-Up Slides

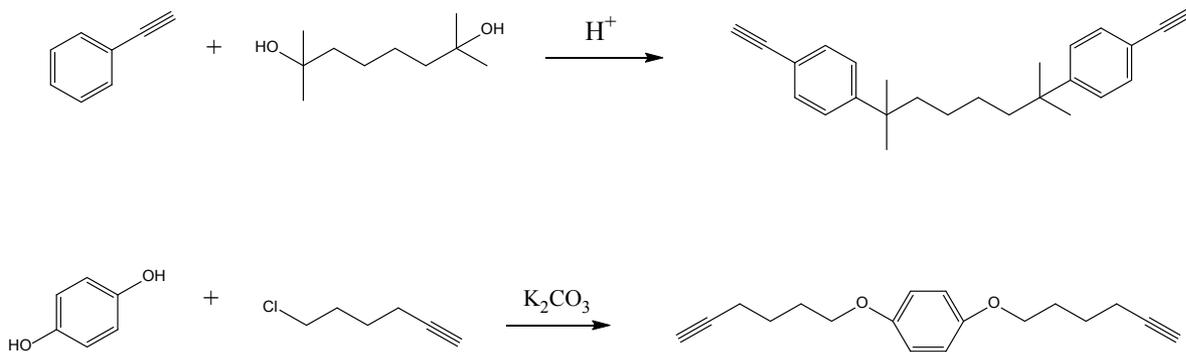
Synthesis of poly(phenyl alkylene) AEM (MRH2)

Goal: Add alkylene segments to DAPP backbone to increase processibility and flexibility.

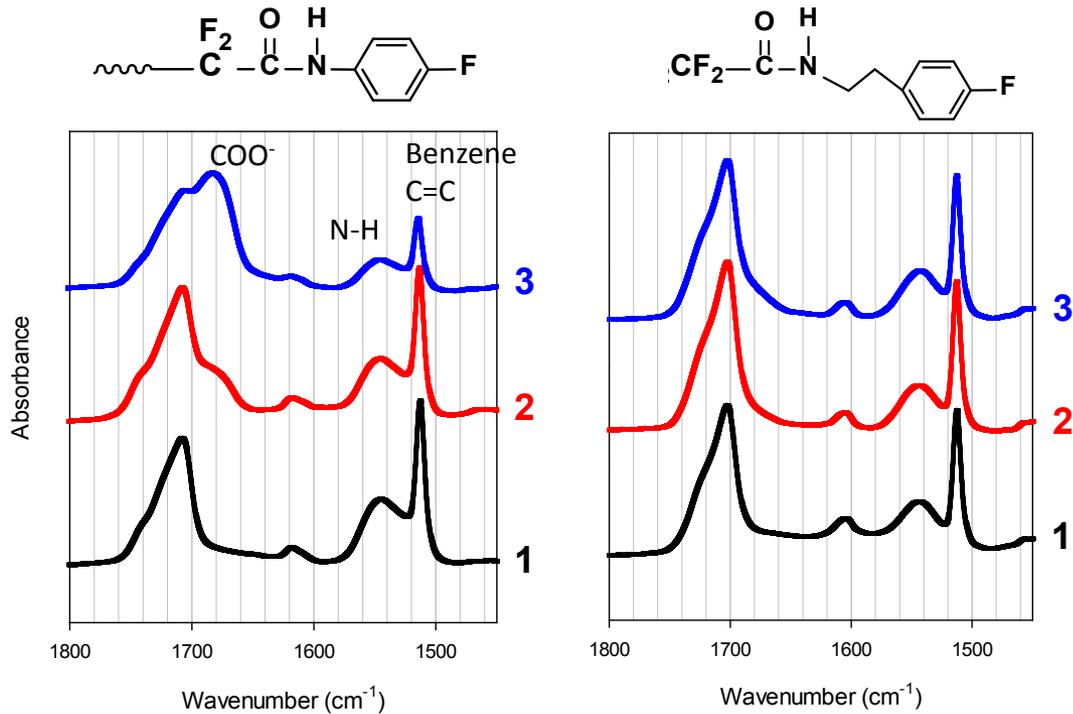


TMAC6PPC6 has been prepared but molecular weights are low ($M_n < 10,000$), probably due to difficulty purifying 1,9-decadiene.

New direction: plan to synthesize alternate monomers with alkylene flexibility:



Approach to prepare perfluorinated ionomers

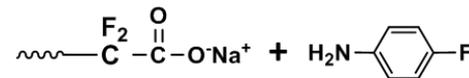


Alkaline testing conditions

0.1M NaOH at 80°C

1. Initial
2. After 120 h
3. After 500 h

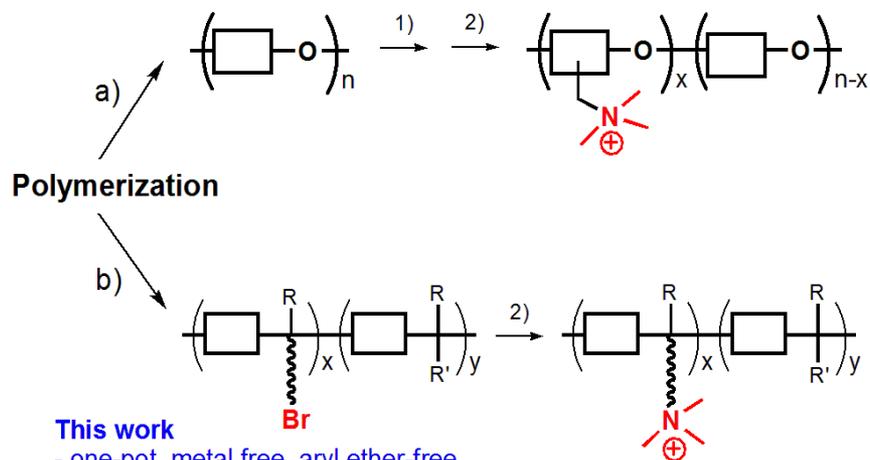
Degradation mechanism for phenyl amide



- LANL perfluorinated anion exchange ionomer, Nafion-FA-TMG showed excellent performance (580 mW/cm² peak power density in 2011)
- However, the amide group between polymer backbone and TMG showed limited alkaline stability (8% loss during 120h in 0.5M NaOH at 80°C).
- FY2015, we found that phenyl alkyl amide is stable compared to the phenyl amide structure and are trying to make perfluorinated ionomers having phenyl alkyl amide linkage. (Progress: 10% as of March 31, 2016)

Approach to prepare perfluorinated ionomers*

Graphical illustrations of synthesis strategy for (a) traditional AEMs and (b) new PBPA series

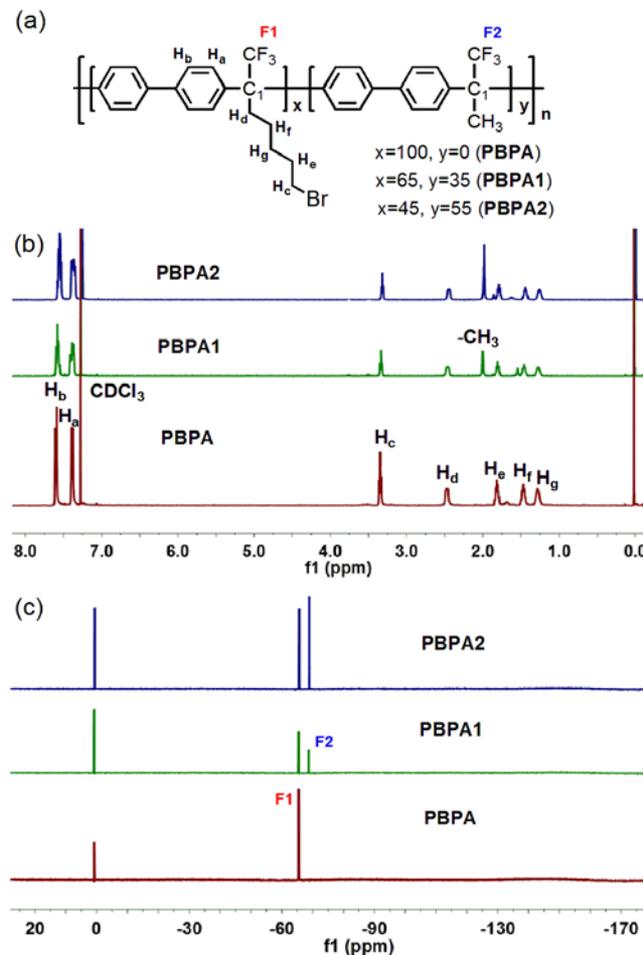


This work

- one-pot, metal free, aryl ether-free
- good yield (>95%)
- high molecular weight (>100,000 kg/mol)
- well-controlled degree of functionalization

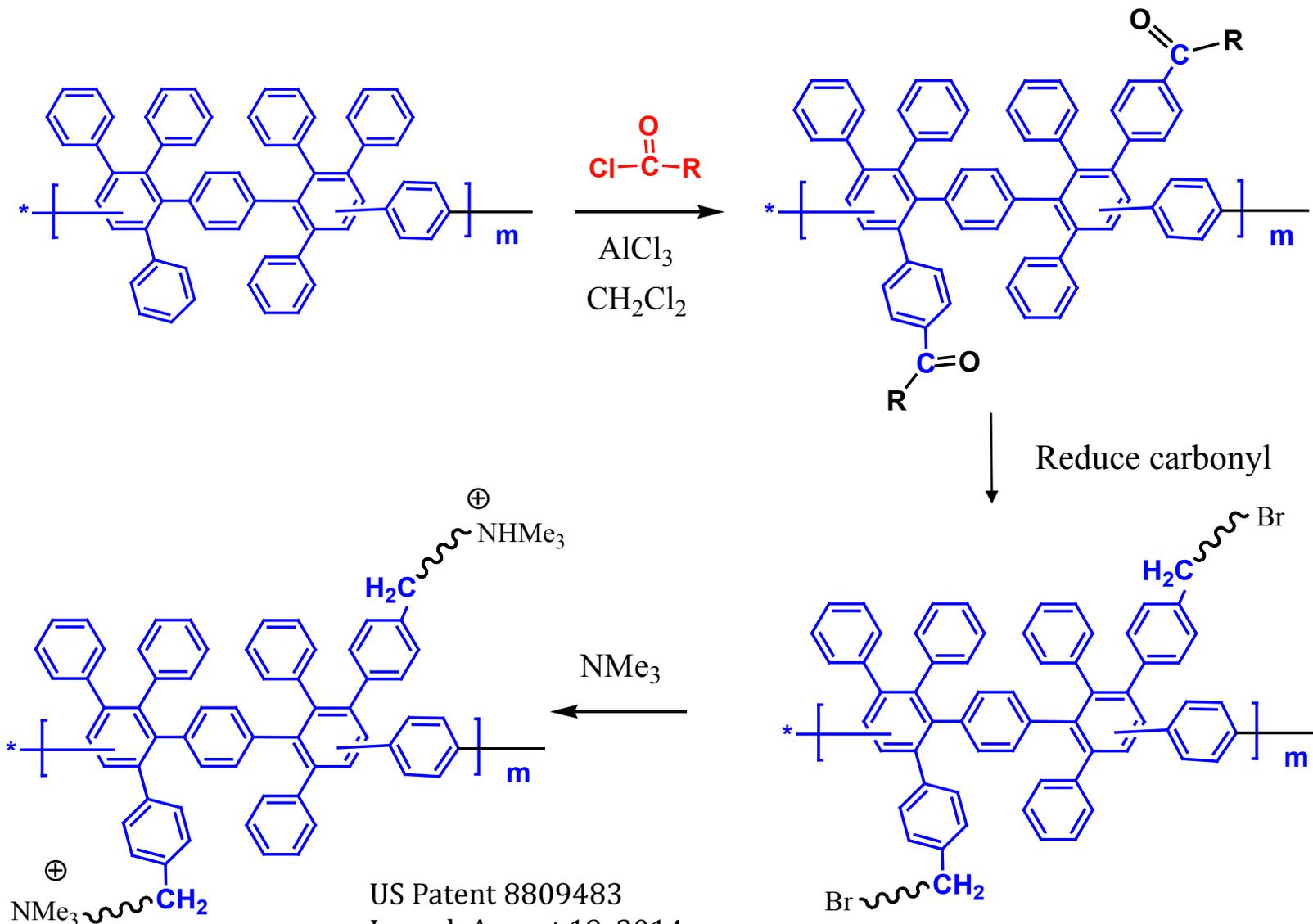
- 1) chloromethylation of aromatic rings or bromination of benzylmethyl groups
- 2) quaternization

Structure of bromoalkylated precursor polymers (a), and their (b) ^1H NMR (c) ^{19}F NMR spectra.



* WH Lee et al. *ACS Macro Letters* 4, 814, 2015

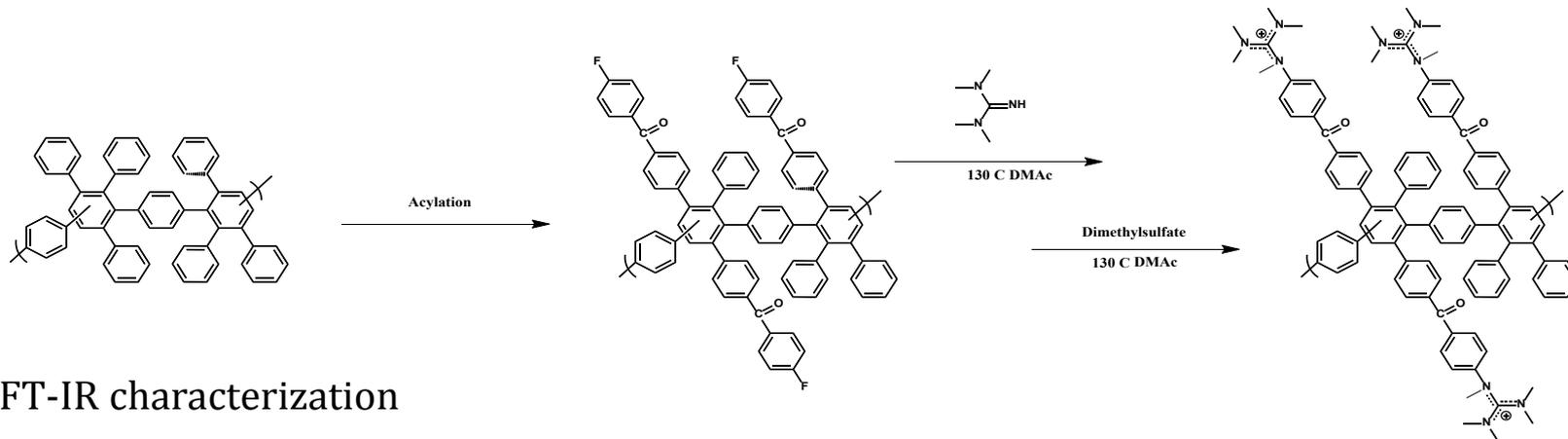
Synthetic process for side-chain poly(phenylene)s



US Patent 8809483
Issued: August 19, 2014
Inventor: Michael R. Hibbs
Sandia National Laboratory

Synthesis of Guanidinium Functionalized Poly(Phenylene)s

Synthesis and characterization of guanidinium functionalized poly(phenylene)s



FT-IR characterization

