

## V.C.6 Advanced Materials for Fully-Integrated MEAs in AEMFCs

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Project End Date: November 1, 2018

Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) Durability (polymer electrolytes)
- (B) Cost (non-precious metal catalysts)
- (C) Performance (alkaline AEMFCs)

### Technical Targets

This project is investigating technical aspects of AEMFCs for practical use in intermediate (10–50 kW) power applications. Insights gained from this project will be applied towards the next stage of advanced AEMFC systems. The technical targets for AEMFCs in the Multi-Year Research, Development, and Demonstration Plan [1] are listed below.

- Develop AEMs with an area specific resistance  $\leq 0.1 \Omega \text{ cm}^2$ , maintained for 500 hours during testing at  $600 \text{ mA/cm}^2$  at  $T > 60^\circ\text{C}$ . (Q2, 2017)
- Demonstrate AEMFC peak power performance  $> 600 \text{ mW/cm}^2$  on  $\text{H}_2/\text{O}_2$  (maximum pressure of 1.5 atm abs) in MEA with a total loading of  $\leq 0.125 \text{ mg}_{\text{PGM}}/\text{cm}^2$ . (Q4, 2017)

### Overall Objectives

- Synthesize highly conductive and stable hydrocarbon based anion exchange membranes (AEMs).
- Prepare ionomeric electrode binders for the fabrication of fuel cell electrodes.
- Integrate non-precious or low Pt metal loading electrocatalysts into membrane electrode assemblies (MEAs) for alkaline anion exchange membrane fuel cells (AEMFCs).
- Demonstrate high performance of alkaline AEMFCs.
- Demonstrate long-term alkaline AEMFC stability under steady and accelerated stress conditions.

### Fiscal Year (FY) 2016 Objectives

- Down-select highly conductive and alkaline stable AEMs.
- Establish design aspects on ionomeric binding materials for hydrogen oxidation reaction (HOR).
- Prepare and characterize hydrocarbon-based ionomeric binders.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell

### FY 2016 Accomplishments

- Down-selected most promising AEMs through aryl ether-free polymer backbone approach. The selected AEMs were prepared from acid-catalyzed Friedel-Crafts polycondensation without using expensive metal catalysts. The selected AEMs with ion exchange capacity (IEC) of 1.9 meq/g has desired properties that exceed the DOE technical milestone from standalone AEM property measurement.
  - Alkaline stability: no structural change after 720 h in 0.5 M NaOH at  $80^\circ\text{C}$ .
  - Areal resistance:  $0.07 \Omega \text{ cm}^2$  at  $80^\circ\text{C}$ .
  - Tensile elongation at  $50^\circ\text{C}$  and 50% relative humidity:  $>90\%$ .
- Prepared hexamethyl trimethyl ammonium functionalized Diels-Alder poly(phenylene) (DAPP) cathode binders. The prepared cathode binders showed improved AEMFC performance. The cathode binder developed in FY 2016 has properties such as:
  - Ion exchange capacity: 1.8–2.2 meq/g.
  - Alkaline stability: no IEC change and  $<5\%$  conductivity change.
  - Found a major HOR inhibition mechanism. Rotating disk electrode and surface Fourier transform infrared spectroscopy (FTIR) elucidated that

co-adsorbed layer of organic cation, hydroxide, and water adversely impact the HOR of Pt electrodes.

- Prepared phenylguanidinium functionalized DAPP anode binders. The guanidinium functionalized anode binders showed exceptional stability through total resonance structure of phenylguanidinium (no structural change after 1,000 h, 0.5 M NaOH treatment at 80°C).



## INTRODUCTION

Developing high-performing alkaline AEMFCs may effectively reduce fuel cell cost through the use of non-precious metal group electrocatalysts. The purpose of this project is to develop improved AEMs and ionomeric binders in order to integrate into MEAs for advanced alkaline AEMFCs. Over the last decade, significant progress on improving chemical stability of AEMs has been made. In addition, other technical issues such as carbonation, low hydroxide conductivity, low oxygen reduction activity of non-platinum group metal catalysts have been investigated. However, current alkaline AEMFC performance and durability are still inferior to those of the state of the art proton exchange membrane fuel cells. The Los Alamos National Laboratory team has involved AEMFC component development since 2008 and has made an effort to improve material properties associated with the key technical issues of alkaline AEMFCs. In this newly awarded project, we are trying to develop advanced materials for fully integrated AEMFCs.

In the previous research (2008–2013), we identified that aryl-ether linkage of the polymer backbone is not chemically stable under high pH conditions [2,3]. Based on this result, we have developed several aryl-ether free AEMs over the last two years [4–6]. In FY 2016, we further evaluated the AEM properties and down-selected the most promising AEMs for MEA integration. We also started to develop advanced hydrocarbon ionomeric binding materials for AEMFC electrodes. Electrochemical and spectroscopic analyses elucidated a major HOR inhibition mechanism, which helps to design advanced ionomeric binders for AEMFC anode.

## APPROACH

Our general approach to prepare stable and highly conductive AEMs is to synthesize cationic group functionalized aryl-ether-free polymers. In addition, strategy to change most popular benzyl trimethyl ammonium group to more stable alkylammonium. There are several viable synthetic pathways to accomplish synthesizing such polymer structure. First, alkyl ammonium functionalized

poly(phenylene)s can be prepared using DAPP precursor developed by Fujimoto et al. [7] or acid-catalyzed Friedel-Crafts polycondensations [4]. Second, alkyl ammonium functionalized poly(styrene-ethylene-butylene-styrene) block copolymers can be prepared via transition metal-catalyzed C-H borylation and Suzuki coupling reaction.

Our approach to prepare advanced ionomeric binders for AEMFCs is to develop different cationic groups for anode and cathode catalyst layers. For this, we evaluated the catalytic activities of Pt using various electrolytes and screened the candidate functional groups. Then the candidate functional groups have been employed into a polymeric structure and further structural optimization was made. For anode, methyl ammonium should be avoided as the cation adsorption adversely impact the HOR activity of the electrocatalysts. Candidate cationic functional groups for the anode electrolyte include alkyl ammonium, guanidinium, and alkyl phosphonium [8]. For the cathode, methyl ammonium works better than other bulky cationic group.

## RESULTS

*Anion exchange membranes:* The most promising AEM was down-selected from several candidate materials (Table 1). For the AEM, hexamethyl ammonium functionalized poly(biphenyl alkylene) (PBPA) (No. 5 in Table 1) was selected for further study.

While traditional polyaromatic AEMs are synthesized via nucleophilic aromatic substitution in a basic medium, the PBPA polymers were prepared from an acid catalyzed Friedel-Crafts polycondensation (Figure 1a). The chemical structures of the ionic polymers were analyzed by nuclear magnetic resonance (NMR) spectroscopies, which confirmed that the ratio of the two quaternized and unquaternized repeating units of the polymers matched well with the monomer feed ratio. We prepared three PBPA with different IECs (2.70 meq/g, 1.94 meq/g, and 1.46 meq/g). The alkaline stability of PBPA was quantitatively evaluated by measuring the change in IEC after certain periods of time. The <sup>1</sup>H NMR spectral data suggest that the three AEMs maintained their IECs even after immersion in 1 M NaOH solution at 80°C for 720 h; the NMR-based IEC values were 2.65 meq/g, 1.92 meq/g, and 1.48 meq/g, which were close to the initial values (2.60 meq/g, 1.93 meq/g, and 1.46 meq/g, respectively) (Figure 1b). Hydroxide conductivity was also only negligibly different after the same alkaline test, indicating that these membranes exceed the 2017 DOE AEM stability milestone, ca. >500 h stability at T > 60°C. The hydroxide conductivity of PBPA was evaluated with an *in-plane* four-point probe method and *through-plane* MEA method. The hydroxide conductivity increased as IEC and temperature as expected. For example, the AEM with the highest IEC of 2.61 meq/g had the highest conductivity (62 mS/cm), a value almost four times that of the AEM with

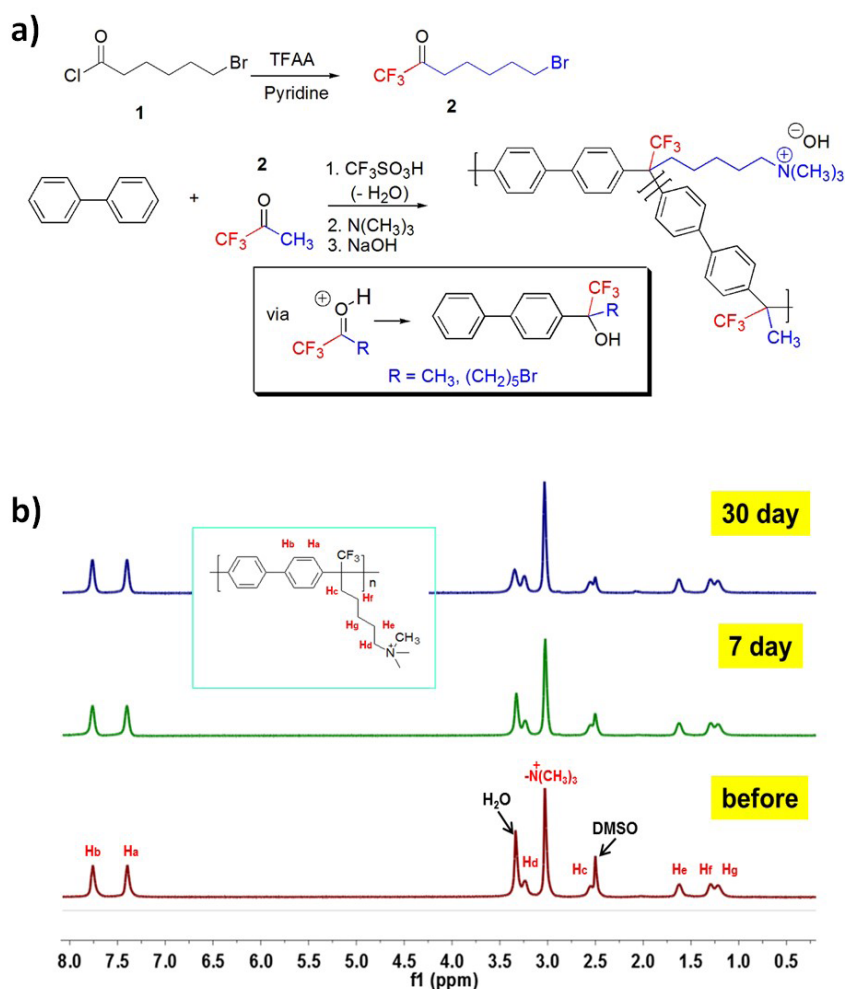
**TABLE 1.** Property Comparison of Anion Exchange Polymer Electrolytes

No.	Polymer		Stability	Conductivity	Mechanical property	Processibility	Cost
	Backbone	Cationic group					
1	Poly(phenylene)	BTMA	○	○	○	○	○
2		Alkyl ammonium	●	○	●	△	○
3		Guanidinium	●	○	△	△	○
4	Poly(phenyl alkylene)	Alkyl ammonium <sup>a</sup>	●	○	○	●	○
5		Alkyl ammonium <sup>b</sup>	●	●	●	●	△
6	Styrene-ethylene-butylene-styrene	BTMA	●	●	●	X	Not available
7	Perfluorinated	Guanidinium	△	△	△	△	●
8	Polystyrene	Ethyl ammonium	Not available	△	△	●	○

<sup>a</sup> DAPP based; <sup>b</sup> Acid catalyzed; ●: excellent, ○: good, △: intermediate, X: poor  
BTMA – Benzyltrimethyl ammonium

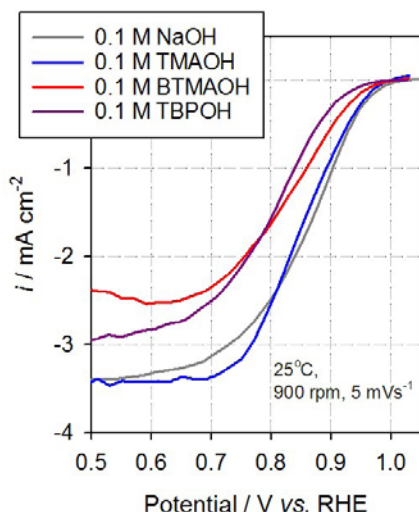
the IEC of 1.45 meq/g at 30°C. The areal resistance of the MEA using 18 μm thick AEM (IEC = 1.9 meq/g) was 0.07 Ωcm<sup>2</sup>, which met the 2017 DOE milestone, ca. <0.1 Ωcm<sup>2</sup> at 60°C. The PBPAs showed excellent mechanical properties compared to the other poly(phenylene) copolymers. For example, the tensile elongation of the AEM with IEC = 1.9 meq/g is over 90% vs. ~20% for quaternized DAPP at 50°C and 50% relative humidity.

*Anion exchange ionomers:* Oxygen reduction reaction (ORR) voltammograms of Pt in 0.1 M NaOH, tetramethyl ammonium hydroxide (TMAOH), BTMAOH and TBPOH indicated that the ORR activity of Pt in NaOH and TMAOH were better than the activity in BTMAOH and TBPOH (Figure 2). Based on this result, we decided to synthesize DAPP with hexamethyltrimethyl ammonium functional group (No. 2 in Table 1) for the cathode binder. In order to synthesize the alkyl ammonium functionalized DAPP, bromo-alkylated poly(phenylene) was first synthesized from the reaction of DAPP precursor with 6-bromohexanoyl chloride in the presence of aluminum chloride. To a bromo-alkylated poly(phenylene) solution in 1,2-dichloroethan, trifluoroacetic acid and triethylsilane were added to reduce the carbonyl groups [9]. The poly(phenylene) ionomer has excellent alkaline stability under high pH conditions. For example, the IEC of the polymer did not change after 14 days in 4 M KOH at 90°C. The ionomer



DMSO - Dimethyl sulfoxide

**FIGURE 1.** (a) Synthetic scheme of PAPB; (b) <sup>1</sup>H NMR spectra during alkaline stability test; testing condition: immersion in 1M NaOH at 80°C.



RHE – Reference hydrogen electrode

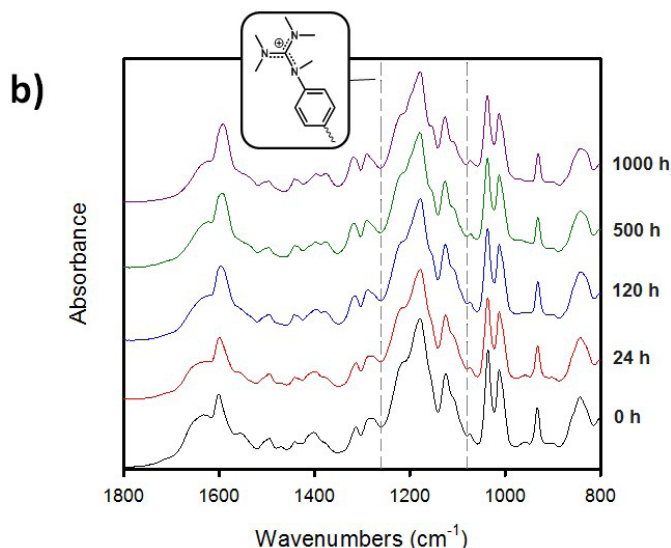
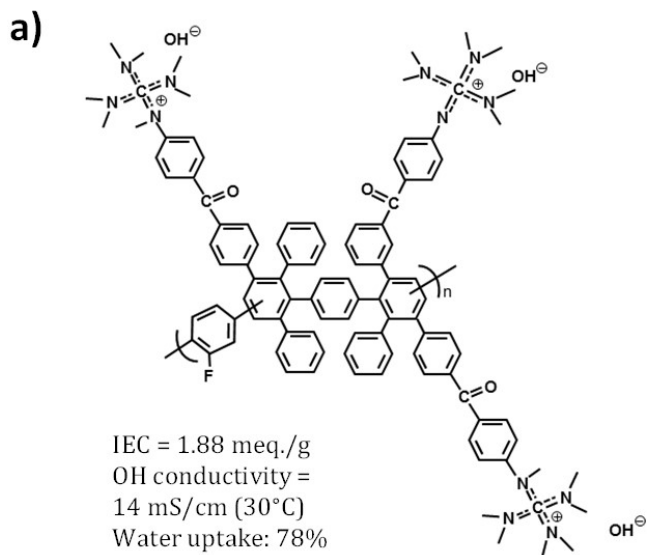
**FIGURE 2.** ORR voltammogram of Pt/C rotating disk electrode in 0.1 M NaOH, TMAOH, BTMAOH, and TBPOH

dispersion using ethylene glycol was prepared to evaluate the ionomer performance [10].

A major achievement for alkaline ionomer development during FY 2016 is the identification of the HOR inhibition mechanism by cation-hydroxide-water co-adsorption. We have performed HOR voltammograms of Pt in various organic cation solutions. The experiments reveal that the HOR activity of Pt substantially decreased in alkaline electrolytes. Surface FTIR elucidated that such HOR activity loss is related with co-adsorption of organic cation, hydroxide and water on Pt surface. Electrochemical impedance analysis further indicates that the hydrogen diffusion through the co-adsorbed layer is significantly reduced. The HOR inhibition is strongly dependent on the type of cations. HOR voltammograms of Pt/C in 0.1 M TMAOH, tetrabutylammonium hydroxide and TBPOH indicates that the HOR activity loss of Pt increased with TMAOH cations. Further study indicates that phenylguanidinium allowed less cation adsorption compared to BTMAOH and imidazolium. Based on these results, we attempted to synthesize phenyl guanidinium functionalized DAPP ionomer (No. 3 in Table 1) for AEMFC anode binder (Figure 3a). The guanidinium functionalized polymer was synthesized by active fluorine-amine reaction we developed in 2011 [11]. The synthesized ionomer has IEC of 1.88 meq/g and hydroxide conductivity of 14 mS/cm at 30°C. The alkaline stability of the ionomer was excellent; no structural and conductivity change after 1,000-h life test at 0.5 M NaOH at 80°C (Figure 3b).

## CONCLUSIONS AND FUTURE DIRECTIONS

- A series of aryl-ether-free AEMs were prepared from various synthetic routes. Acid catalyzed PBPA was down selected for AEMs. The selected AEMs met the DOE



**FIGURE 3.** (a) Chemical structure of guanidinium functionalized poly(phenylene)ionomer; (b) FTIR change of the ionomer during 0.5 M NaOH at 80°C treatment

2017 conductivity milestone when measured with either standalone or MEA configuration. The alkaline stability of the PBPA AEM was excellent and met the DOE 2017 stability milestone but needs further evaluation in MEA configuration.

- The ORR activity of Pt in BTMAOH was low. Instead of BTMAOH, hexamethyltrimethyl ammonium cationic group was incorporated into DAPP to improve ORR activities of AEMFCs. The hexamethyltrimethyl ammonium functionalized poly(phenylene) was successfully synthesized from multi-step synthetic process. Preliminary data indicated that the hexamethyltrimethyl functionalized poly(phenylene) outperformed to the previous BTMAOH functionalized



poly(phenylene). Further performance evaluation will be made during FY 2017.

- The HOR activity of Pt was greatly affected by the cationic group. Unlike the cathode ionomer, tetramethyl ammonium cationic group easily adsorbed onto the Pt surface and lowered the HOR activity. Based on this result, we successfully synthesized guanidinium functionalized DAPP via activated fluorine-amine reaction. Further performance evaluation for this polymer will be made during FY 2017. In addition, alternative ionomeric binding materials will be developed for further performance improvement.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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