

## V.F.17 Advanced Hydroxide Conducting Membranes

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### Overall Objectives

- Synthesize highly conductive and stable hydrocarbon anion exchange membranes (AEMs)
- Prepare perfluorinated ionomer dispersions for the fabrication of fuel cell electrodes
- Develop non-precious metal electro-catalysts for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR)
- Demonstrate high performing alkaline membrane fuel cells (AMFCs)
- Demonstrate long-term AMFC performance under steady and accelerated stress conditions

### Fiscal Year (FY) 2015 Objectives

- Synthesize highly conductive and alkaline stable AEMs
- Establish design aspects on advanced ionomeric binders
- Predict polarization behaviors through modeling approaches

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) Plan:

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

### Technical Targets

This project is investigating fundamental aspects of AMFCs for practical use in intermediate (10–50 kW) power applications. Insights gained from this project will be applied towards the next stage of advanced AMFC systems. The technical targets for AMFCs in the MYRDD Plan [1] are listed below:

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

### FY 2015 Accomplishments

- Developed synthetic routes to produce thin and tough AEMs having no aryl-ether linkage in the polymer backbones; major significant progress on AEM properties include the following:
  - Areal resistance  $\leq 0.1 \text{ } \Omega\text{-cm}^2$  for FY 2015 AEMs
  - Ex situ alkaline stability  $< 5\%$  degradation after 1–4 M NaOH at  $\geq 80^\circ\text{C}$  for 14–30 days for FY 2015 AEMs
- Demonstrated the excellent alkaline stability of alkyl amide linkage (no apparent degradation after 500 h, 0.5 M NaOH treatment at  $80^\circ\text{C}$ ) that can be used for the preparation of perfluorinated ionomers
- Developed a membrane + electrode model that takes into account the effect of  $\text{CO}_2$  contamination on the AMFC performance; combining with experimental data, benefits of higher temperature operation in the presence of  $\text{CO}_2$  were demonstrated



## INTRODUCTION

Preparation of alkaline stable and highly conductive polymers for AMFCs is one of the urgent technical challenges to elevate the AMFC performance/durability to the next level in the DOE MYRDD plan. In the previous research (2008–2014), we identified the two AEM components that readily degrade under high pH conditions, (1) aryl-ether linkage in the polymer backbone [2], and (2) amide group between polymer backbone and cationic functional group [3]. Based on this research, we focused on developing robust and highly conductive AEMs and ionomeric binders in FY 2015. Moreover, we studied the factors that may impact the MEA performance by a modeling study.

## APPROACH

Our approach to prepare stable and highly conductive AEMs is to synthesize cation group functionalized aryl-ether-free polymers. Three synthetic routes were developed. The first polymer series is the hexamethyl trimethyl ammonium functionalized Diels-Alder poly(phenylene)s (MRH series). In order to synthesize these polymers, the unfunctionalized Diels-Alder poly(phenylene) (DAPP) was prepared according to the procedure of Fujimoto et al. [4]. The DAPP polymer precursor was reacted with 6-bromohexanoyl chloride in the presence of aluminum chloride. The resultant polymer was reacted with trifluoroacetic acid and triethylsilane to reduce the carbonyl group in alkyl aryl ketones, followed by amination by immersing the polymer in trimethylamine solution [5]. The second polymer series is the hexamethyl trialkyl ammonium functionalized poly(biphenyl alkylene)s (AR series) [6]. These polymers were synthesized by newly developed one-pot, acid-catalyzed Friedel-Crafts polycondensations of biphenyl and trifluoromethyl alkyl ketones. Traditional AEM polymer synthesis via nucleophilic aromatic substitution requires a basic medium for polymerization; thus, it prevents monomers from having a potential leaving group such as alkyl halide. However, the use of acidic conditions in the reaction described in this report allows for the condensation polymerization of a monomer containing bromoalkyl side chains without affecting the quaternary ammonium precursor group. The third polymer series is quaternized ammonium functionalized benzyl trimethyl ammonium functionalized polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (SEBS) triblock copolymers. Synthetic methods involving transition metal-catalyzed C-H borylation and Suzuki coupling were utilized to incorporate quaternary ammonium groups to the polystyrene units of SEBS [7].

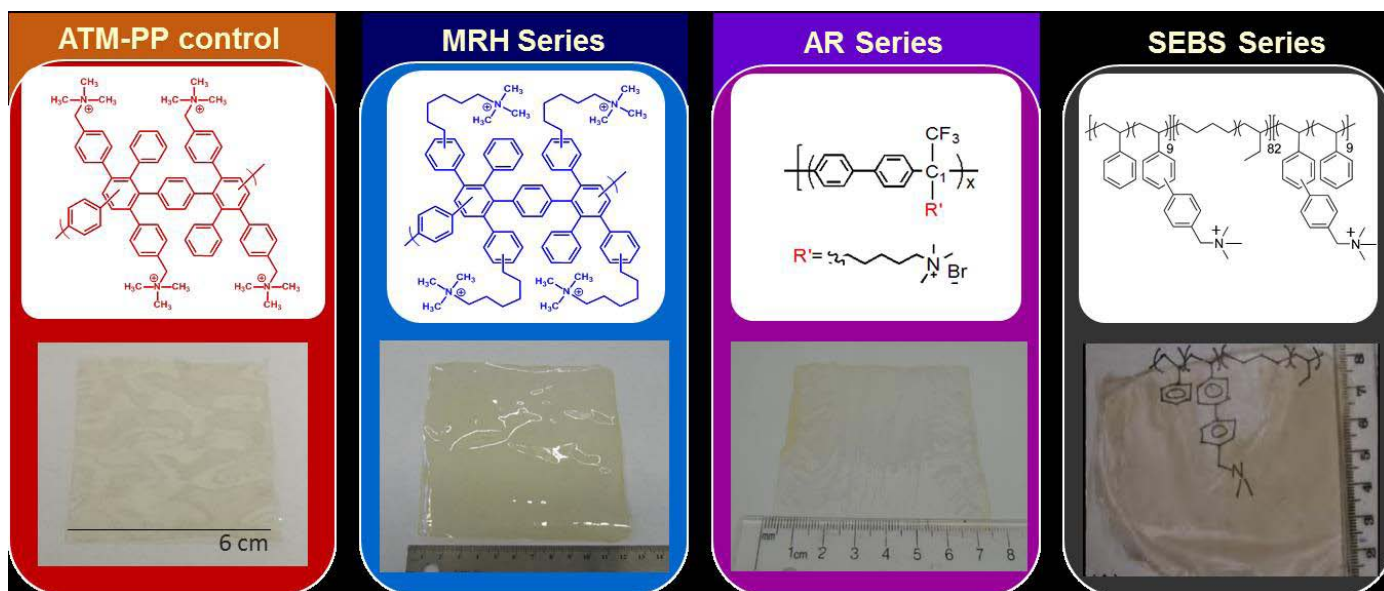
Our approach to develop anion exchange ionomers includes hydrocarbon based poly(phenylene) and perfluorinated anion exchange ionomers. For poly(phenylene) ionomer, we believe that bulky phenylene groups of DAPPs

take advantage of allowing high gas permeability due to the increased free volume. In FY 2015, we compared the electrode performance as a function of ionomer structure to verify this hypothesis. For perfluorinated anion exchange ionomers, we focused on developing stable amide linkage between polymer backbone and cationic functional group. We synthesized multiple perfluorinated amide linkages that include methyl amide, sulfone amide, sulfone methyl amide, alkyl amide and sulfone alkyl amide via condensation reactions. Then, the alkaline stability of the amide linkages was measured under high pH conditions.

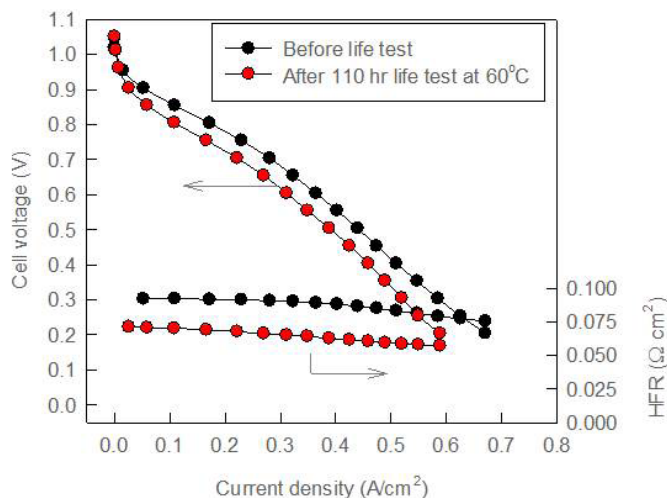
Our approach to developing a two-dimensional non-isothermal AMFC model is to predict the response of an AMFC according to variations of the inlet relative humidity (RH), CO<sub>2</sub> concentration in the cathode inlet, and temperature.

## RESULTS

*Anion Exchange Membranes:* The chemical structures of three series of AEMs and the control benzyl trimethyl ammonium functionalized DAPP (ATM-PP) AEM [2] are shown in Figure 1. We successfully prepared tough and ductile AEMs from the synthetic routes described above. We have achieved areal resistance milestone ( $\leq 0.1 \Omega\text{-cm}^2$ ) with FY 2015 AEMs. The mechanical properties of the AEMs were evaluated by tensile tests under controlled humidity and temperatures (50% RH and 50°C). The FY 2015 Diels-Alder poly(phenylene)-based AEMs, MRH series showed similar mechanical properties with the control ATM-PP. The poly(biphenyl alkylene)-based AEMs, AR series, showed higher strain compared to MRH series probably due to the flexible backbone structure. The SEBS series showed much higher strain (>300%) with low stress, reflecting their elastomer-like block copolymer nature. The water uptake of AEMs is ~120% for MRH and AR series. The SEBS series AEM has higher water uptake ca. 220 wt%. The alkaline stability of the AEMs was evaluated under 80–90°C NaOH or KOH conditions. While the FY 2014 ATM-PP series showed ~14% ion exchange capacity (IEC) decrease after 4 M KOH 90°C conditions, the MRH and AR series AEMs did not show degradation at similar conditions. The SEBS series polymers showed only 3% IEC decrease. This improved stability met the FY 2015 AEM stability milestone, *ca.* <10% IEC loss after 500 h, 0.5 M NaOH at 80°C. The alkaline stability of the FY 2015 AEMs was confirmed with fuel cell test. Figure 2 shows the MEA using SEBS AEM before and after 110 h extended-term test. It was noted that high frequency resistance of the MEA slightly decreased in spite of the cell performance loss after the extended-term test. This indicated that the alkaline stability of the AEM was excellent while there was performance degradation. These polymers have potential to meet the DOE FY 2017 stability targets in the MYRDD Plan. The AEM properties are summarized in Table 1.



**FIGURE 1.** The chemical structures of control and FY 2015 membranes. Tough and ductile membranes were prepared from solution cast procedure. Membranes have the thickness 20–60  $\mu\text{m}$ .



**FIGURE 2.** H<sub>2</sub>/O<sub>2</sub> AMFC performance comparison after 110 h extended-term operation at 60°C. AEM: SEBS series (thickness: 35  $\mu\text{m}$ ), ionomeric binder: MRH series, catalyst: 20 wt% Pt/C Pt loading: 0.2  $\text{mg/cm}^2$ .

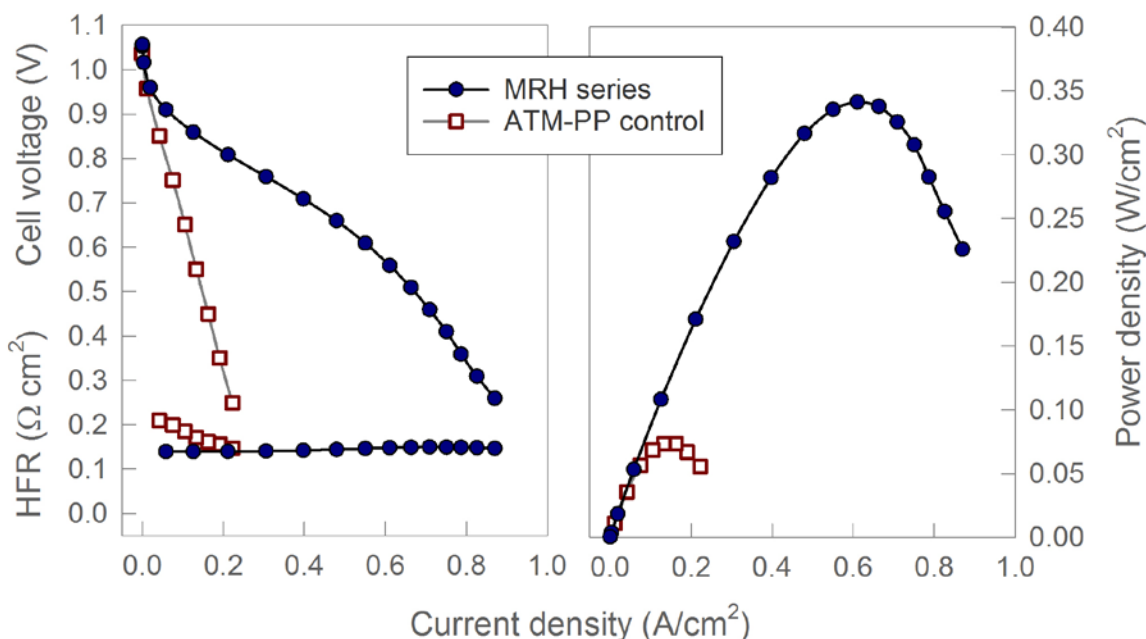
*Anion Exchange Ionomer:* We prepared a series of poly(phenylene) ionomer dispersion using LANL proprietary dispersion technology [8] and tested in AMFCs. AR series ionomers that have linear structure in the polymer backbone showed inferior cell performance compared to the Diels-Alder poly(phenylene)s, which have bulky phenylene group arrangement in the polymer backbone. Comparing with ATM-PP and AR ionomers, the MEA using MRH ionomer showed a superior cell performance, i.e., peak power density of  $\sim 300 \text{ mW/cm}^2$  vs.  $\sim 100 \text{ mW/cm}^2$  for ATM-PP (Figure 3). The superior performance with MRH ionomer is perhaps due to the flexible alkyl chain forming a better interface between electrocatalyst and ionomer.

Finding an alkaline stable linkage for perfluorinated ionomers was the main subject for the FY 2015 perfluorinated ionomer development. All methyl substituted amide ( $\text{C}=\text{ON}(\text{CH}_3)$ ) or sulfone amide ( $\text{SO}_2\text{N}(\text{CH}_3)$ ) turned out to be no good or show very limited improvement in terms of alkaline stability. This is probably because the replacement of hydrogen by a methyl group can destroy the resonance structure of amide group that brings instability under

**TABLE 1.** Summary of the FY 2015 Anion Exchange Membrane Properties

| AEM    | IEC (meq/g) | AEM thickness ( $\mu\text{m}$ ) | Hydroxide conductivity (mS/cm) | Areal resistance ( $\Omega\text{-cm}^2$ ) | Water uptake (wt%) | Stress (MPa) | Strain (%) | IEC loss (%)    |
|--------|-------------|---------------------------------|--------------------------------|---|--------------------|--------------|------------|-----------------|
| ATM-PP | 1.7         | 60                              | 40                             | 0.17                                      | 83                 | 28           | 20         | 14 <sup>a</sup> |
| MRH    | 2.2         | 30                              | 50                             | 0.07                                      | 126                | 28           | 23         | 0 <sup>a</sup>  |
| AR     | 2.0         | 22                              | 50                             | 0.10                                      | 120                | 36           | 50         | 0 <sup>b</sup>  |
| SEBS   | 1.9         | 35                              | 45                             | 0.08                                      | 220                | 4            | >300       | 3 <sup>b</sup>  |

<sup>a</sup> after 4 M KOH, 90°C for 14 days; <sup>b</sup> after 1 M KOH, 80°C for 28 days.



**FIGURE 3.** Impact of ionomeric binder on  $H_2/O_2$  AMFC performance. Same membrane (MRH-series) with different ionomeric binders (MRH series vs. ATM-PP) were used. Operating temperature:  $80^\circ C$ , catalyst: 20 wt% Pt/C Pt loading:  $0.2 \text{ mg/cm}^2$ .

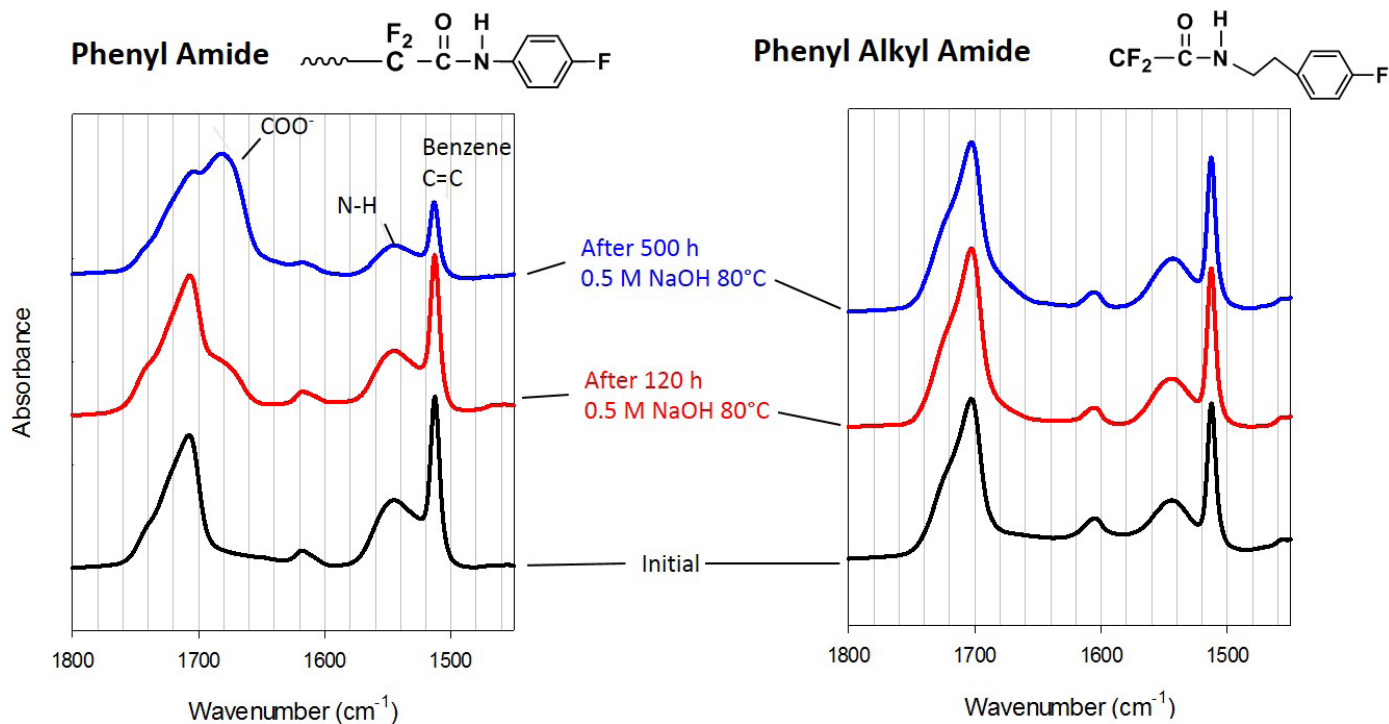
alkaline conditions. The best stability of the amide group was obtained with alkyl amide structure ( $C = ONH(CH_2)_n$ ). Figure 4 compared the amide stability after  $80^\circ C$ , 0.5 M NaOH treatment for 500 h. While perfluorinated amide linkage shows notable peak changes, e.g., increased  $COO^-$  peak at  $1,680 \text{ cm}^{-1}$ , decreased NH peak at  $1,540 \text{ cm}^{-1}$  and decreased benzene  $C = C$  peak at  $1,515 \text{ cm}^{-1}$  due to the hydrolysis of the amide group, the perfluorinated alkyl amide linkage showed no trace of degradation. The exceptional stability of the perfluorinated alkyl amide linkage opens a new strategy to prepare alkaline stable perfluorinated ionomers.

*Modeling:* The modeling study at different inlet RH from 50% to 100% (without  $CO_2$ ) showed that the performance is enhanced with increasing anode and cathode humidification. Several voltage losses as a function of current density and inlet RH were observed due to the ORR kinetic loss, ohmic loss through the membrane, and water activity gradient across the AEM. The kinetic loss is lower with higher inlet RH values due to water dependence of ORR kinetics in the alkaline media. Sufficient water supply is needed to avoid dehydration at the cathode. The ohmic and water diffusion losses are reduced with higher inlet RH due to more hydrated membrane. With higher  $CO_2$  concentration in the cathode inlet, the current density decays due to the lowered HOR kinetics and hydroxide ion transport. The carbonate formation by  $CO_2$  at the cathode reduces the number of  $OH^-$ , leading to slower HOR in the alkaline media at the anode, as shown by the decrease of current density with increasing  $[CO_2]$  at high potentials.  $OH^-$  depletion also increases the ion

transport resistance through the membrane and catalyst layer ionomer, as indicated by the decreased performance with increasing  $[CO_2]$  at low potentials. The modeling study also shows the effect of operating temperature on polarization curves for the air inlet with  $[CO_2] = 400 \text{ ppm}$ . The increase in the operating temperature does have a positive influence on performance. The improvement is attributed to the enhanced electrochemical kinetics of HOR and ORR, and the increased ionic conductivity and water transport coefficient. The decrease of  $CO_2$  solubility in water with higher temperature slightly improves the performance at higher operating temperature.

## CONCLUSIONS AND FUTURE DIRECTIONS

- A series of aryl-ether-free AEMs were successfully prepared from various synthetic routes. The FY 2015 AEMs showed not only high hydroxide conductivity and good mechanical properties but also exceptional alkaline stability. The AEMs having hexamethyl trimethyl ammonium groups (MRH and AR) showed the optimal properties. Refining the polymer synthetic process for scale-up production is needed. In addition, long-term membrane stability test in MEA configurations should be done to confirm the ex situ stability results. The SEBS series AEMs showed very promising mechanical properties and good compatibility with catalyst layer. Replacing current benzyl ammonium group to more stable cationic group with more economical synthetic pathway is under investigation.



**FIGURE 4.** Fourier transform infrared spectroscopy change of perfluorinated amide and perfluorinated alkyl amide after ex situ alkaline stability test. Membranes were immersed in 0.5 M NaOH at 80°C for the life test.

- Diels-Alder poly(phenylene) with hexamethyl trimethyl ammonium group showed a promising ionomer performance in the preliminary experiments. Further structural optimization is needed for improving electrode performance. It is of great interest to replace the ammonium group with other cationic groups for better electrode kinetics as our preliminary data showed the cationic group in the ionomer greatly impacts the electrocatalyst activity.
- We have investigated the stability of the amide linkage. Alkaline stability test indicates that alkyl amide is most stable under high pH conditions. Based on this result, perfluorinated ionomers having alkyl amide linkage is being synthesized. Development of dispersion technique of the perfluorinated ionomers in liquid fluid is the future work.
- Fuel cell modeling studies showed the adverse impact of low RH and CO<sub>2</sub> on fuel cell performance. Providing actual fuel cell data with variation of modeling parameters is essential for the verification of modeling works.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Anion Exchange Polymer Electrolytes, D.S. Kim, Y.S. Kim, USP 9,048,480 (2015).

2. Poly(Arylene)-based Anion Exchange Membranes, C.B. Bae, Y.S. Kim, USP 9,051,431 (2015).

3. Robust Hydroxide-Conducting Poly(arylenes) for Anion Exchange Membranes and Ionomers, C. Bae, W.-H. Lee (file on November 18, 2014).

4. Stable Quaternary Ammonium-Containing Styrene Block Copolymers for Anion Exchange Membranes, C. Bae, A.D. Mohanty (file on July 22, 2014).

## FY 2015 PUBLICATIONS/PRESENTATIONS

### Peer-Reviewed Publications

1. "Alkaline Stability of Benzyl Trimethyl Ammonium Functionalized Polyaromatics: a Computational and Experimental Study," Yoong-Kee Choe, Cy Fujimoto, Kwan-Soo Lee, Luke Dalton, Kathy Ayers, Neil Henson, Yu Seung Kim\*, *Chem. Mater.*, 26, (19) 5675–5682 (2014).
2. "Mechanistic Analysis of Ammonium Cation Stability for Anion Exchange Membrane Fuel Cells," *J. Mater. Chem. A*, 2, 17314–17320 (2014).
3. "A Microelectrode Study of Interfacial Reactions at the Platinum-Alkaline Polymer Interface," Sung-Dae Yim, Hoon T. Chung, Jerzy Chlistunoff, Dae-Sik Kim, Cy Fujimoto, Tae-Hyun Yang, Yu Seung Kim\*, *J. Electrochem. Soc.* 162 (6) F499–F506 (2015).
4. "Fuel Cell Membrane Characterizations," Yu Seung Kim\* and Kwan-Soo Lee, *Polymer Reviews* 55, 330–370 (2015).

5. “Fluorine-Based Hydroxide Ion Conducting Polymers for Chemically Stable Anion Exchange Membrane Fuel Cells,” *ACS Macro Lett.* 4, 453–457 (2015).
6. “Robust Hydroxide Ion Conducting Poly(biphenyl alkylene)s for Alkaline Fuel Cell Membranes,” Woo-Hyung Lee, Yu Seung Kim, Chulsung Bae, *ACS Macro Lett.* 4, 814–818 (2015).

### Conference Presentations

1. “Chemical Degradation Mechanisms of Membranes for Alkaline Membrane Fuel Cells,” Y-K. Choe, Neil J. Henson, Yu Seung Kim, Computational Chemistry Symposium in ICCMSE 2015, March 20–23, 2015, Athens, Greece.
2. “Perfluorinated Anion Exchange Membranes,” Y.S. Kim, Advances in Polymers for Fuel Cells, Asilomar Conference Grounds, February 8–11, 2015, Pacific Grove, California.
3. “Synthesis of Highly Ion-Conductive Polymers for Fuel Cells,” Bae, C.B., 2015 Asilomar Conference on Fuel Cell, Asilomar Conference Grounds, February 8–11, 2015, Pacific Grove, California.
4. “Anion Exchange Membranes with Improved Chemical Stability,” Bae, C.B., New York State Center for Future Energy System 2014–2015 Annual Conference, Hilton Garden Inn, Troy, NY, February 26, 2015.
5. “Perfluorinated Ionomers for Alkaline Membrane Fuel Cells,” D.S. Kim, S.D. Yim, K.S. Lee, H. Chung, Y-K. Choe, Y.S. Kim, 226th ECS & SMEQ Joint International Meeting, October 5–10, 2014, Cancun, Mexico.
6. “Degradation Mechanism of Membranes for Alkaline Membrane Fuel Cells,” Y-K. Choe, N. Hanson, Y.S. Kim, 226th ECS & SMEQ Joint International Meeting, October 5–10, 2014, Cancun, Mexico.
7. “Development of Ion-Conducting Polymers for Clean Energy Conversion,” Bae, C.B. Sukant Tripathy Memorial Symposium, University of Massachusetts Lowell, December 5, 2014.

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5. M.R. Hibbs, *Journal of Polymer Science, Part B: Polymer Physics* 51, 1736–1742 (2013).
6. Woo-Hyung Lee, Yu Seung Kim, Chulsung Bae, *ACS Macro Lett.* 4, 814–818 (2015).
7. Angela D. Mohanty, Chang Y. Ryu, Yu Seung Kim, Chulsung Bae, *Macromolecules* 48, 19, 7085–7095 (2015).
8. Y.S. Kim, Patent pending, 2015.