
Advanced Materials for Fully-Integrated Membrane Electrode Assemblies in Anion Exchange Membrane Fuel Cells

Yu Seung Kim (Primary Contact), Sandip Maurya,
Eun Joo Park, Dongguo Li, Albert Sung Soo Lee,
Daniel Leonard

Los Alamos National Laboratory (LANL)
MPA-11: Materials Synthesis and Integrated Devices
Los Alamos, NM 87545
Phone: 505-667-5782
Email: yskim@lanl.gov

DOE Manager: David Peterson
Phone: 240-562-1747
Email: David.Peterson@ee.doe.gov

Subcontractors:

- Sandia National Laboratories, Albuquerque, NM
- Rensselaer Polytechnic Institute, Troy, NY

Project Start Date: November 2, 2015

Project End Date: November 1, 2019

Overall Objectives

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

Fiscal Year (FY) 2019 Objectives

- Complete the alkaline stability evaluation of poly(phenylene) AEMs.
- Identify AEMFC degradation mechanisms.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

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

Technical Targets

This project is developing advanced materials for AEMFCs for practical use in power applications. Insights gained from this project will be applied toward the next-stage AEMFC systems. The technical targets for AEMFCs in the Multi-Year Research, Development, and Demonstration Plan are:

- Q2, 2019: 0% chemical degradation for 1,000 h in 4 M NaOH at 80°C.
- Q4, 2019: Identifying AEMFC degradation mechanism.

FY 2019 Accomplishments

- Completed the alkaline stability study of AEMs (no chemical degradation for >1,000 h in 4 M NaOH at 80°C).
- Completed the impact of phenyl adsorption on AEMFC performance.
- Achieved 1.55 W/cm² peak power density from the mitigation strategy of cation hydroxide–water co-adsorption study.
- Identified the possible durability-limiting factor by phenyl oxidation for the first time.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

INTRODUCTION

In the previous project years (FY 2016–2018), we developed alkaline stable AEMs (quaternized Diels-Alder poly(phenylene)s [TMAC6PP] and poly(*m*-terphenylene)s [TPN]) [2–4]. We also developed an advanced ionomer (quaternized poly(fluorene) [FLN]) to demonstrate the AEMFC peak power density of 1.5 W/cm² by reducing undesirable phenyl group adsorption. While we demonstrated excellent alkaline stability of the poly(phenylene) AEMs, we have not shown possible degradation mechanisms in harsher conditions. In FY 2019, we completed the alkaline stability evaluation of TMAC6PP under various accelerated stress conditions to identify the possible degradation mechanisms. We also continue to understand the performance- and durability-limiting factors for AEMFCs. In FY 2019, we focused on cation hydroxide–water co-adsorption, which is a known performance- and durability-limiting factor. Moreover, we identified for the first time that phenyl oxidation of ionomer in the AEMFC cathode is a critical durability-limiting factor.

APPROACH

Alkaline Stability of Quaternized Poly(phenylene) AEMs

We did not observe AEM degradation under normal alkaline stability test conditions, ca. 1 M NaOH at 80°C for 1,000 h. Therefore, in FY 2019, we employed three different accelerated stress test (AST) conditions. In the first method, we placed AEMs at 80°C in 1 M and 4 M NaOH for 11,000 h. In the second method, we put AEMs in a pressure vessel at higher temperatures, ca. 120°C or 160°C, and 4 M and 8 M NaOH. In the third method, we exposed AEMs at higher temperatures, ca. 100°C, under reduced relative humidity (RH). During the stability tests, we investigated the structural change of the AEMs and identified the degradation mechanisms.

AEMFC Performance-Limiting Factor (Cation Hydroxide–Water Co-Adsorption)

We focused the cation hydroxide–water co-adsorption study on the hydrogen oxidation reaction (HOR) catalysts. In FY 2019, we directly detected the co-adsorbed layer on the Pt surface by neutron reflectometry. The co-adsorbed layer thickness and the composition were calculated by the scattering length density modeling. Based on the result, we have synthesized a new ionomer that mitigates the effects of cation hydroxide–water co-adsorption.

AEMFC Durability-Limiting Factor (Phenyl Oxidation)

We characterized the electrolytes that contact with oxygen reduction reaction catalysts under AEMFC operating conditions. By analyzing the electrolyte with ¹H nuclear magnetic resonance spectroscopy (NMR), we identified the degradation component of AEMFCs during cell operations. Density functional theory calculation and surface Fourier-transform infrared spectroscopy were used to understand the ionomer degradation mechanism.

RESULTS

Alkaline Stability of AEMs

In FY 2018, we showed that the TMAC6PP membranes are stable in 0.5 M NaOH at 80°C for at least 3,000 h. In FY 2019, we found that degradation pathways of TMAC6PP under more harsh conditions depend on the testing conditions. The degradation mechanism of TMAC6PP under 4 M NaOH at 80°C after 2,000 h is the β -elimination of cations. However, we also found that even before 3,000 h, Williamson ether synthesis crosslinking reaction can occur with unreacted bromoalkyl group [5]. We proposed a nonaqueous quaternization method to prevent the crosslinking reaction, which may also be utilized in other polymer systems. Under higher temperature or low-RH ASTs, we found that the nucleophilic methyl substitution reaction is predominant. It suggests that high-temperature ASTs may not be a straightforward alternative to low-temperature alkaline stability tests, which is more relevant to the operating conditions of current alkaline membrane-based devices. Table 1 shows the degradation pathways of TMAC6PP AEM.

Table 1. Summary of Degradation Mechanisms of TMAC6PP as a Function of Test Conditions and Duration [5]

Degradation mechanism	Test conditions	Time to occur (h)
Williamson ether synthesis (crosslinking)	80 °C, 4 M NaOH 120 °C, 8 M NaOH	<3,000 h <2 h
β -elimination	80 °C, 0.5 M NaOH 80 °C, 4 M NaOH	>4,000 h >2,000 h
S_N2 methyl substitution	100 °C, 50% RH 160 °C, 8 M NaOH	<250 h <72 h

Cation Hydroxide–Water Co-Adsorption and its Impact on AEMFC Performance

The cation hydroxide–water co-adsorption has been known as a possible AEMFC performance- and durability-limiting factor [6]. In FY 2019, we directly detected the co-adsorbed layer of cation hydroxide–water on Pt using neutron reflectometry. The neutron reflectometry results indicated that the composition of the cation in the co-adsorbed layer is unusually high. For example, the TMAOH-to-water ratio in the co-adsorbed layer was 4.5, 2,800-fold higher than that of the bulk electrolytes [7]. The extremely high cation hydroxide concentration in the co-adsorbed layer may impact the AEMFC performance and durability in three ways. First, the high concentration of cation hydroxide would impact the hydrogen access to the electrocatalyst layer. Second, the cation hydroxide–water co-adsorption would inhibit the water transport of the anode. Under this circumstance, water transport through the anode becomes less, and the hydration of the alkaline membrane can reduce. Third, the chemical stability of the cation group would be affected, and the degradation of the anode ionomer would be accelerated during fuel cell operation.

To reduce the cation hydroxide–water co-adsorption, we have synthesized a new quaternized poly(biphenyl alkylene) ionomer that has a TEA functional group (TEA-*o*-BTN). The microelectrode experiments exhibited that the hydrogen limiting current of TEA-*o*-BTN was approximately 2 times higher than that of quaternized dimethyl poly(biphenylene). Because of reduced cation group co-adsorption and increased hydrogen access to the HOR catalyst surface, the TEA-*o*-BTN based MEAs have shown significantly better performance that reaches 1.55 W/cm² peak power density (Figure 1) [8].

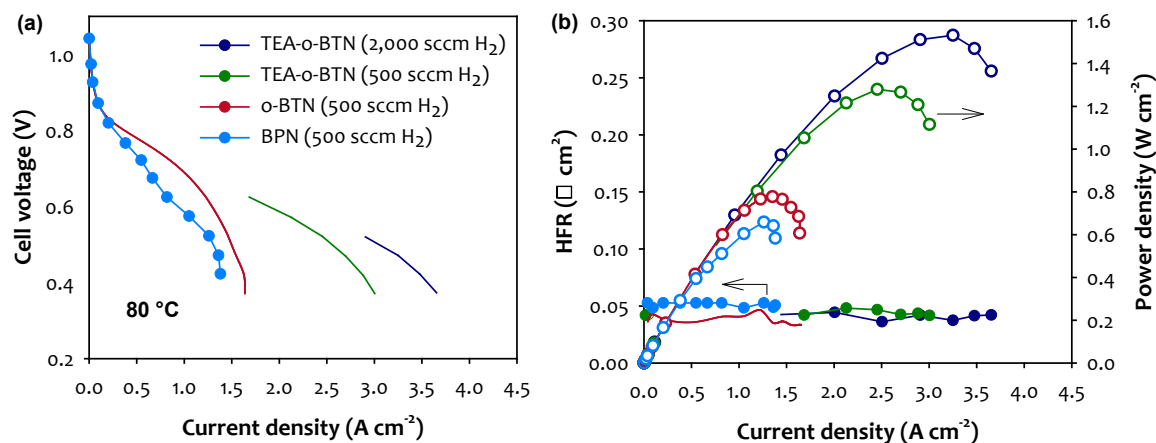


Figure 1. Impact of anode ionomer on AEMFC performance. Performance measured at 80 °C under H₂/O₂ (500/300 sccm, 2,000/1,000 sccm) at 285 kPa backpressure. AEM: *m*-TPN (35 μ m); anode: Pt-Ru/C (0.5 mg_{Pt} cm⁻²); cathode: Pt/C (0.6 mg_{Pt} cm⁻²), humidification: 100%.

Phenyl Group Adsorption and HOR Inhibition

Rotating disk electrode investigation on alkaline HOR indicated that the HOR activity of Pt-based catalysts is greatly hindered by the phenyl adsorption parallel to the Pt surface. Our results suggested that the phenyl group adsorption may be minimized with Pt-Ru catalysts [9]. Therefore, we down-selected the Pt-Ru/C catalyst as the HOR catalyst for AEMFCs. We designed and synthesized the series of ionomers with biphenyl, *o*-terphenyl, *m*-terphenyl, and *p*-terphenyl polymer backbone and calculated their adsorption energies on Pt and

PtRu catalysts. The adsorption energies for these polymer backbones were -2.87, -1.57, -3.61, and -3.94 eV, respectively, whereas benzene and fluorene's adsorption energies on Pt(111) surface were calculated to be -1.95 and -1.38 eV. The adsorption energies of the ionomer backbone are well correlated with the AEMFC performance (Figure 2) [10]. The AEMFC performance was gradually increased from less than 0.2 for *m*- and *p*- TPN to 1.5 W/cm² for FLN ionomer.

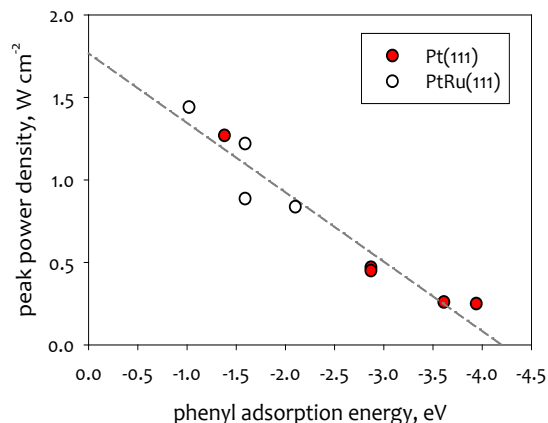


Figure 2. Correlation between phenyl adsorption energy of the backbone fragments of anode ionomer and peak power density of MEAs using the ionomer in the anode

The life of AEMFC is also influenced by the adsorbed phenyl group, which is oxidized to form phenol. The phenol formation in the cathode ionomer of AEMFCs can neutralize the ammonium hydroxide and lowers electrode pH. The possible phenol formation via electrochemical oxidation of the phenyl group was investigated by analyzing the cathode ionomer that was retrieved from an MEA operated at 0.9 V for 75 h. During the 75-h life test, the cell current started to decrease. The ¹H NMR spectrum of the alkyl ammonium functionalized poly(biphenylene)s (BPN) ionomer obtained from the postmortem of the cathode catalyst layer after the durability test detected the phenolic proton peak at 5.75 ppm (Figure 3) [11]. The significance of the phenolic compound interference during the AEMFC operation should be understood in the following aspect. Although the aryl proton conversion rate of BPN after the 75-h operation at 0.9 V is relatively low, the local phenol concentration at the catalyst-ionomer interface would be much higher because most oxidation of the phenyl group occurs at the catalyst-ionomer interface.

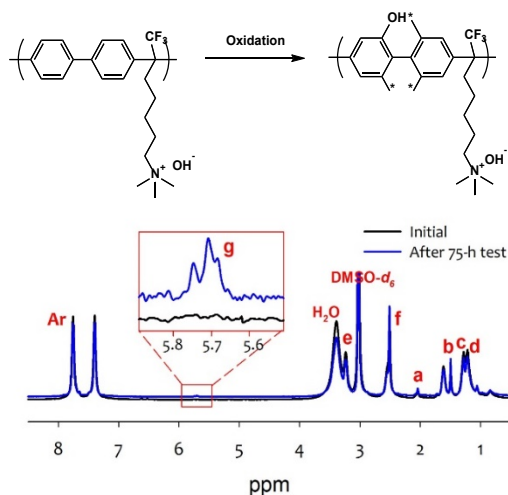


Figure 3. Reaction scheme for electrochemical phenyl oxidation to phenol in a cathode BPN ionomer based on ¹H NMR spectra of BPN ionomer before and after extended-term test at 0.9 V

CONCLUSIONS AND UPCOMING ACTIVITIES

- Demonstrated >2,000 h alkaline stability of quaternized polyphenylene AEMs in 4 M NaOH at 80°C.
- Elucidated several degradation pathways of quaternized polyphenylene AEMs under different AST conditions.
- Elucidated the cation hydroxide–water co-adsorbed layer by neutron reflectometry and developed TEA-functionalized ionomer that allows the AEMFC performance up to 1.55 W/cm² peak power density.
- Completed the phenyl adsorption study to show a gradual AEMFC performance increase, and achieved up to 1.5 W/cm² peak power density with the least adsorbing ionomer.
- Identified the durability-limiting factor (phenyl oxidation) using fuel cell and rotating disk electrode experiments for the first time.
- Planned to develop a mitigation strategy of phenol formation and verify the AEMFC durability.
- Planned to explore other unknown yet possible degradation mechanisms.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Yu Seung Kim, Kwan-Soo Lee, Cy Fujimoto, “Poly(phenylene)-based Anion Exchange Polymers and Methods Thereof,” US Patent Application Publication, US 16/039,158 (2019).

FY 2019 PUBLICATIONS/PRESENTATIONS

1. R. Wang, D. Li, S. Maurya, Y.S. Kim, Y.A. Wu, Y. Liu, D. Strmcnik, N. Markovic, and V. Stamenkovic, *Nanoscale Horizons*, DOI: 10.1039/C9NH00533A (2019).
2. S. Maurya, A.S. Lee, E.J. Park, D.P. Leonard, S. Noh, C. Bae, and Y.S. Kim, “On the Origin of Permanent Performance Loss of Anion Exchange Membrane Fuel Cells: Electrochemical Oxidation of Phenyl Group,” *J. Power. Sources*, 436 (2019): 226866.
3. S. Noh, J.Y. Jeon, S. Adhikari, Y.S. Kim, and C. Bae, “Molecular Engineering of Hydroxide Conducting Polymers for Anion Exchange Membranes in Electrochemical Energy Conversion Technology,” *Acc. Chem. Res.* 52 (2019): 2745–2755.
4. E.J. Park, S. Maurya, M.R. Hibbs, C.H. Fujimoto, K.D. Kreuer, and Y.S. Kim, “Alkaline Stability of Quaternized Diels-Alder Polyphenylenes,” *Macromolecules*, 52 (2019): 5419–5428.
5. I. Matanovic, S. Maurya, E.J. Park, J.Y. Jeon, C. Bae, and Y.S. Kim, “Adsorption of Polyaromatic Backbone Impacts the Performance of Anion Exchange Membrane Fuel Cells,” *Chem. Mater.* 31 (2019): 4195–4204.
6. C. Fujimoto, E. Sorte, N. Bell, C. Poirier, E.J. Park, S. Maurya, K.S. Lee, and Y.S. Kim, “Acid-Catalyzed Benzoylation Reactions of Diels-Alder Polyphenylenes,” *Polymer*, 158 (2018): 190–197.
7. D. Li, H.T. Chung, S. Maurya, I. Matanovic, and Y.S. Kim, “Impact of Ionomer Adsorption on Alkaline Hydrogen Oxidation Activity and Fuel Cell Performance,” *Curr. Opin. Electrochem.* 12 (2018): 189–195.
8. “The Design Aspect of Polymer Electrolytes for Alkaline Anion Exchange Membrane Fuel Cells,” 22nd International Conference on Solid State Ionics, Pyeong Chang-Gun, Gangwon-Do, South Korea (June 16–21, 2019).
9. Y.S. Kim, “Catalyst-Ionomer Interactions/AMFC Durability,” 2019 Anion Exchange Membrane Workshop, Dallas, TX (May 30, 2019).
10. “Polyaromatic Electrolytes for Alkaline Membrane Fuel Cells,” Polymers for Fuel Cells, Energy Storage, and Conversion, Pacific Grove, CA (February 24–27, 2019).

11. E.J. Park, S. Maurya, M. Hibbs, C. Fujimoto, and Y.S. Kim, "Caveat of High Temperature Accelerated Stability Test for Anion Exchange Membranes," I02-1575, 235th ECS Meeting, Dallas, TX (May 26–30, 2019).
12. S. Maurya, S. Noh, I. Matanovic, E.J. Park, U. Martinez, C. Bae, and Y.S. Kim, "Poly(fluorene) Ionomers with Least Phenyl Adsorption for Alkaline Membrane Fuel Cells," *Polymers for Fuel Cells, Energy Storage, and Conversion*, Pacific Grove, CA (February 24–27, 2019).
13. E.J. Park, S. Maurya, M.R. Hibbs, C.H. Fujimoto, Y.S. Kim, "Caveat of High Temperature Accelerated Stability Test of Anion Exchange Membranes," *Polymers for Fuel Cells, Energy Storage, and Conversion*, Pacific Grove, CA (Feb. 24–27, 2019).
14. S. Maurya, I. Matanovic, H.T. Chung, E.J. Park, C.W. Narvaez Villarrubia, S. Noh, J. Han, C. Bae, C. Fujimoto, M. Hibbs, and Y.S. Kim, "Polyaromatic Ionomers for High Performance Alkaline Membrane Fuel Cells," Abstract No. I01E-1572, AiMES2018, Cancun, Mexico (September 30–October 4, 2018).
15. "Recent Advances of HT-PEMFCs and AEMFCs," Toyota 2018 Fuel Cell Research Workshop Powering Future FCEVs with New Innovations, Torrance, CA (October 9, 2018).

REFERENCES

1. Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan (2014). http://energy.gov/sites/prod/files/2014/12/f19/fcto_myrrdd_fuel_cells.pdf.
2. W.H. Lee, E.J. Park, J. Han, D.W. Shin, Y.S. Kim, and C. Bae, "Poly(terphenylene) Anion Exchange Membranes: The Effect of Backbone Structure on Morphology and Membrane Property," *ACS Macro Letters* 6, no. 5 (2017): 566–570.
3. S. Maurya, C.H. Fujimoto, M.R. Hibbs, C. Narvaez Villarrubia, and Y.S. Kim, "Toward Improved Alkaline Membrane Fuel Cell Performance Using Quaternized Aryl-Ether Free Polyaromatics," *Chemistry of Materials* 30, no. 7 (2018): 2188–2192.
4. S. Maurya, S. Noh, I. Matanovic, E.J. Park, C. Narvaez Villarrubia, U. Martinez, J. Han, C. Bae, and Y.S. Kim, "Rational Design of Polyaromatic Ionomers for Alkaline Membrane Fuel Cells with $>1 \text{ W cm}^{-2}$ Power Density," *Energy & Environmental Science* 11, no. 11 (2018): 3283–3291.
5. E.J. Park, S. Maurya, M.R. Hibbs, C.H. Fujimoto, K.-D. Kreuer, and Y.S. Kim, "Alkaline Stability of Quaternized Diels–Alder Polyphenylenes," *Macromolecules* 52, no. 14 (2019): 5419–5428.
6. H.T. Chung, U. Martinez, I. Matanovic, and Y.S. Kim, "Cation-Hydroxide-Water Coadsorption Inhibits the Alkaline Hydrogen Oxidation Reaction," *J. Phys. Chem. Lett.* 7 (2016): 4464–4469.
7. C.W. Narvaez Villarrubia, A. Serov, J.H. Dumont, P. Attanassov, and Y.S. Kim, "Investigating Non-Precious Metal Catalyst-Electrolyte Interface in Anodes for Alkaline Fuel Cells," Abstract Number 1621, 232nd ECS Meeting, National Harbor, MD (Oct. 1–5, 2017).
8. E.J. Park, S. Maurya, A.S. Lee, D.P. Leonard, D. Li, J.Y. Jeon, C. Bae, and Y.S. Kim, "How Does a Small Structural Change of Anode Ionomer Make a Big Difference in Alkaline Membrane Fuel Cell Performance?" *J. Mater. Chem. A*. submitted (2019).
9. I. Matanovic, H.T. Chung, and Y.S. Kim, "Benzene Adsorption: A Significant Inhibitor for the Hydrogen Oxidation Reaction in Alkaline Conditions," *J. Phys. Chem. Lett.* 8 (2017): 4918–4924.
10. I. Matanovic, S. Maurya, E.J. Park, J.Y. Jeon, C. Bae, and Y.S. Kim, "Adsorption of Polyaromatic Backbone Impacts the Performance of Anion Exchange Membrane Fuel Cells," *Chemistry of Materials* 31, no. 11 (2019): 4195–4204.
11. D. Li, I. Matanovic, A.S. Lee, E.J. Park, C. Fujimoto, H.T. Chung, and Y.S. Kim, "Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer," *ACS Applied Materials and Interfaces* 11, no. 10 (2019): 9696–9701.