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

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Subcontractors:

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- Rensselaer Polytechnic Institute, Troy, NY

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Project End Date: November 1, 2018

Overall Objectives

- Synthesize highly conductive and chemically stable hydrocarbon-based anion exchange membrane (AEM).
- 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 assembly (MEA).
- Demonstrate the high performance of AEMFCs.
- Demonstrate AEMFC durability under steady and accelerated stress conditions.

Fiscal Year (FY) 2018 Objectives

- Down-select the hydrogen oxidation reaction (HOR) catalyst and ionomer.
- Integrate the high-performance MEAs to obtain AEMFC peak power density >1 W/cm².

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 Plan [1]:

- Durability (polymer electrolytes)
- Cost (non-precious metal catalysts)
- 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 [1] are listed below.

- Q2, 2018: AEMFC power density >1 W/cm².
- Q4, 2018: V loss $<10\%$ for 2,000 h at 600 mA/cm².

FY 2018 Accomplishments

- Demonstrated alkaline stability for hexamethyl ammonium functionalized Diels-Alder poly(phenylene) (TMAC6PP): no structural change after 3,600 h in 0.5 M NaOH at 80°C (most stable AEM).
- Explored inhibition mechanism for alkaline HOR, namely, phenyl group adsorption. Additionally, developed the strategies to minimize phenyl adsorption by using rationally designed ionomeric binders, membranes, and less-phenyl-adsorbing PtRu HOR catalysts.
- Demonstrated stable area specific resistance (ASR) of ~ 0.05 Ω cm² of down-selected AEM for 500 h MEA operation at 0.6 A/cm².
- Designed new poly(fluorene) ionomer that exhibited 1.5 W/cm² (H₂/O₂) and 680 mW/cm² (H₂/CO₂-free air) peak power density of AEMFC.
- Implemented alternative Pd-based HOR catalysts in MEAs, which exhibit ~ 1 W/cm² peak power density.

INTRODUCTION

In previous years (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 three years [4–6]. In FY 2016 and FY 2017, hexamethyl ammonium functionalized Diels-Alder poly(phenylene) (TMAC6PP) and alkyl ammonium functionalized poly(terphenylene)s (TPN) were down-selected. We also developed advanced hydrocarbon ionomeric binders for AEMFC electrodes. Electrochemical and spectroscopic analyses are initiated to elucidate major HOR inhibition mechanisms, which helps to design advanced ionomeric binders for the AEMFC anode. In FY 2018, we completed the alkaline stability of the down-selected TMAC6PP AEM in alkaline medium up to 11,000 h. We exploited the HOR inhibition mechanism at MEA scale and made an effort to mitigate the HOR inhibition by the adoption of bimetallic catalysts and the design of new ionomers. We also demonstrated alternative Pd-based HOR catalysts in the integrated MEAs to prove the high-performance construction of the AEMFCs.

APPROACH

Our general approach to preparing stable and highly conductive AEMs is to synthesize cationic group functionalized aryl ether-free polymers. In addition, the strategy involves changing the commonly used benzyl trimethyl ammonium group with more stable alkylammonium. There are several viable synthetic pathways to accomplish synthesizing such polymer structure. Based on research efforts during FY 2016 and FY 2017, two polymers were down-selected, TMAC6PP (Sandia National Laboratories) and TPN (Rensselaer Polytechnic Institute).

Our general approach to preparing advanced high-performing 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 and Pt-based bimetallic catalysts using various electrolytes to screen the candidate functional groups. Then the selected candidate functional groups will be employed into a polymeric structure and further structural optimization will be made at the MEA level (Los Alamos National Laboratory). For the anode, the less-phenyl-adsorbing catalyst should be used, such as PtRu or PtNi, in combination with less-phenyl-group-containing ionomers. The performance of the AEMFC components is evaluated in both the individual component and the MEA levels.

RESULTS

Alkaline Stability of Anion Exchange Membranes

Figure 1a compares the hydroxide conductivity change of benzyltrimethylammonium functionalized Diels-Alder poly(phenylene) (ATM-PP) control and TMAC6PP during ex situ stability test at 0.5 M and 4 M NaOH at 80°C. Note that the conductivity of ATM-PP quickly deteriorated within 200 h, but the conductivity of TMAC6PP was stable to 3,600 h and tends to degrade slowly after 4,000 h in 0.5 M NaOH conditions. The life test further proceeded to 11,000 h when the hydroxide conductivity decreased to 5 mS/cm. The chemical stability of the TMAC6PP during AEMFC operation was also measured. During 300 h of operation at a constant voltage of 0.3 V, it was found that the cell ASR tended to increase due to inevitable carbonation. In FY 2018, we developed a replenishing procedure to remove carbonation during the life test and evaluate the stability of the other down-selected AEM, poly(terphenylene). Figure 1b shows the ASR of the cell using the TPN membrane during AEMFC operation at a constant current of 0.6 A cm⁻² and 80°C. The cell was replenished with NaOH at 210, 350, 480, and 550 h of operation, and polarization curves were recorded along with ASR. It was found that the ASR of the cell using TPN was stable (~0.05 Ω cm²), indicating that the AEM remained stable during the long-term test.

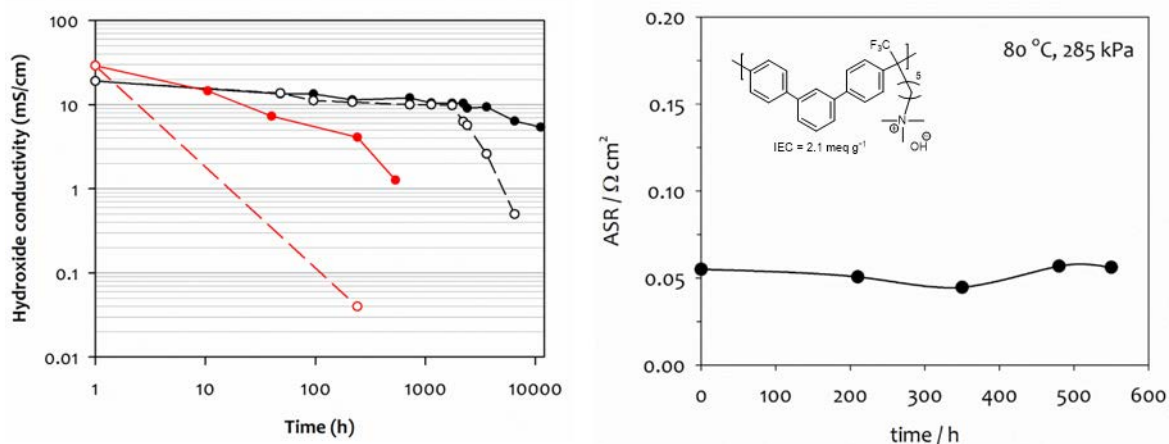


Figure 1. (a) Hydroxide conductivity change of TMAC6PP during ex situ alkaline stability test at 80 °C, (b) hydroxide conductivity change of the TPN membrane during in situ alkaline stability test at 80 °C

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 [7]. We first examined the effect of the catalyst on phenyl group adsorption. It was found that the HOR current density of Pt in 0.1 M benzyltrimethylammonium hydroxide (BTMAOH) showed a peculiar behavior (appearance of inflection point) due to the phenyl group adsorption, the inflection point became less evident with alloying Pt with other transition metal. Less interaction between the phenyl group and catalyst was observed in the order of Mo, Ni, and Ru. The HOR voltammogram of Pt-Ru/C in 0.1 M BTMAOH becomes identical to that of Pt/C in 0.1 M TMAOH (phenyl-group-free solution) with only a slightly lower HOR current density (Figure 2). This result suggests that the phenyl group adsorption may be minimized with Pt-Ru catalysts. Based on this result, we down-selected the Pt-Ru/C catalyst as the HOR catalyst for AEMFCs.

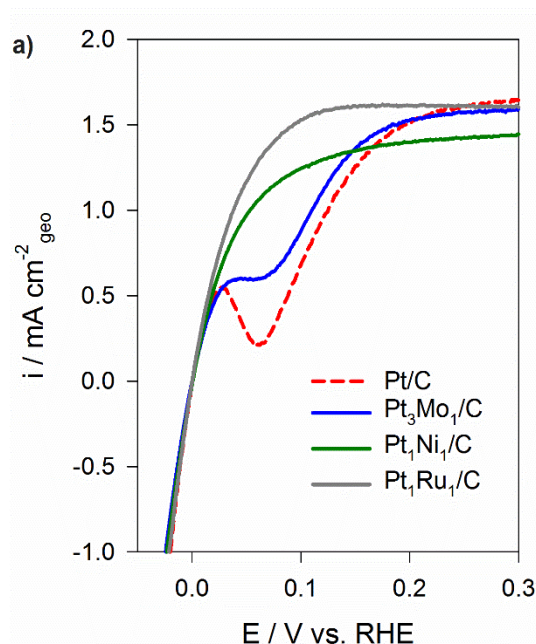


Figure 2. HOR voltammograms of Pt alloy/C catalysts in 0.1 M BTMAOH, measured at 25 °C, rotating speed: 900 rpm, scan rate: 5 mV/s. The graph is reproduced from Maurya et al. [8].

To prevent the phenyl adsorption, we rationally designed and synthesized new ionomeric binders based on poly(fluorene) polymer, that is, FLN [8]. The impact of phenyl group adsorption of FLN and alkyl ammonium functionalized poly(biphenylene) (BPN) ionomer is compared using a microelectrode half-cell. It was found that the HOR voltammogram of the Pt-Ru/C in contact with BPN is significantly suppressed between 0.02 V and 0.7 V, indicating that the phenyl group adsorption substantially inhibits the HOR activity of even low-phenyl-group-adsorbing Pt-Ru/C. In contrast, the HOR voltammogram of the Pt-Ru/C in contact with FLN shows a typical shape like the HOR voltammogram of the catalyst in alkali-metal electrolytes. Based on this result, we down-selected FLN as the electrode ionomer.

AEMFC Performance

Figure 3a shows the progress of AEMFC performance improvement achieved in FY 2018. The AEMFC performance of a control MEA using TMAC6PP was low due to the phenyl group adsorption on the HOR Pt catalyst. The peak power density of the AEMFC is only ~ 300 mW/cm². In FY 2017, the AEMFC performance was improved by using a Pt-Ru catalyst instead of Pt catalyst: ca. the peak power density of ~ 400 mW/cm². When we changed the poly(phenylene) ionomer to FLN, the AEMFC performance improved. The peak power density is $\sim 1,000$ mW/cm². The AEMFC performance further increased with increasing anode flow rate possibly due to the increased hydrogen access to the adsorbed cation layer [9]. The peak power density of the AEMFC reached 1,500 mW/cm² as the anode flow rate increased from 500 sccm to 2,000 sccm. It was also noted that cell high-frequency resistance also improved from ~ 0.07 Ω cm² (FY 2017) to 0.05 Ω cm² (FY 2018). We also examined the fuel cell performance of MEAs using alternative Pd-based HOR catalysts. Figure 3b compares the AEMFC performance of Pt/C, Pt-Ru/C, Pd/C, and Pd/C-CeO₂ anode catalyzed MEAs. Although the performance of the MEAs using the Pt-Ru/C and Pt/C anode catalyzed MEAs is better than Pd-based anode catalyzed MEAs, it was noted that the Pd/C anode catalyzed MEA also reached a peak power density close to 1 W/cm² revealing a benefit associated with the high-hydrogen-absorption characteristics of the Pd/C catalysts.

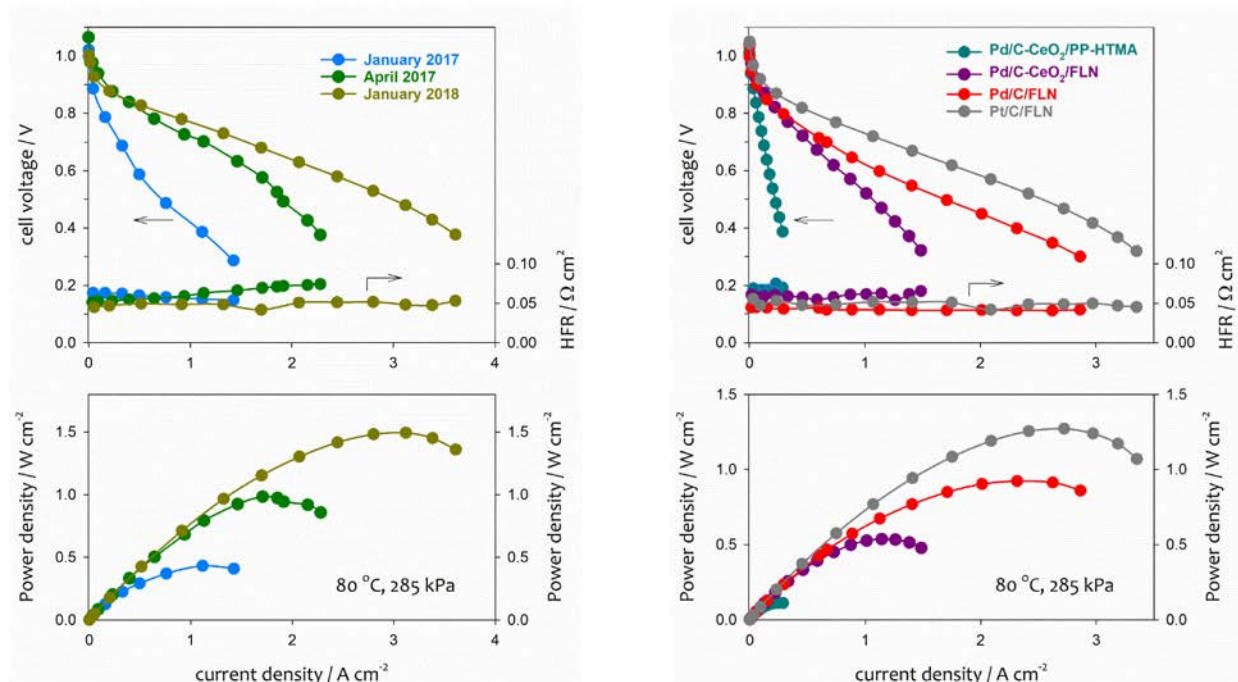


Figure 3. (a) Progress of AEMFC performance improvement; January 2017—AEM: TMAC6PP, anode catalyst: Pt-Ru/C, anode flow rate: 500 sccm; April 2017—AEM: FLN, anode catalyst: Pt-Ru/C, anode flow rate: 500 sccm; January 2018—AEM: FLN, anode catalyst: Pt-Ru/C, anode flow rate: 2,000 sccm. (b) Performance comparison between Pt-based and Pd-based anode catalyzed MEAs. All performance was measured under H₂/O₂ conditions. Cathode catalyst: Pt/C 0.6 mg_{Pt}/cm².

In summary, the major achievement for FY 2018 includes demonstrating high AEMFC performance by the down-selection of bimetallic Pt-Ru catalyst and poly(fluorene) ionomer. We have also tested alternative a Pd-based catalyst to investigate the absorption/adsorption phenomena on the HOR catalysts. In the rest of FY 2019, most of the research will be directed toward solving the durability issues and identifying the durability limiting factors.

CONCLUSIONS AND FUTURE DIRECTIONS

- Demonstrated low ASR (~0.05 Ω cm²) of the down-selected AEM for 11,000 h in ex situ test and >550 h for in situ test.
- The HOR inhibition mechanism was further explored and, based on the study, high AEMFC performance (up to 1,500 mW/cm² peak power density) was obtained.
- Designed new poly(fluorene) ionomer that exhibited the peak power density of 1.5 W/cm² (H₂/O₂) and 680 mW/cm² (H₂/CO₂-free air).
- Plan to evaluate the AEMFC durability after optimizing the MEAs and fuel cell conditions.
- Plan to evaluate the performance of non-platinum-group-metal HOR and oxygen reduction reaction catalysts.

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