

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

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Project End Date: November 1, 2018

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).
- Demonstrate the high performance of anion exchange membrane fuel cells (AEMFCs).
- Demonstrate AEMFC durability under steady and accelerated stress conditions.

Fiscal Year (FY) 2017 Objectives

- Obtain AEM area specific resistance (ASR) $\leq 0.1 \Omega \text{ cm}^2$, maintained for 500 h at 600 mA/cm² at T > 60°C.
- Achieve stable AEM resistance in both ex situ and in situ measurements.
- Obtain AEMFC peak power density > 0.6 W/cm².

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 Plan [1].

- (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 towards the next-stage AEMFC systems. The technical targets for AEMFCs in the Multi-Year Research, Development, and Demonstration Plan [1] are listed below.

- Q2, 2017: AEM ASR $\leq 0.1 \Omega \text{ cm}^2$, maintained for 500 h at 600 mA/cm² at T > 60°C
- Q4, 2017: AEMFC power density > 600 mW/cm²

FY 2017 Accomplishments

- Demonstrated alkaline stability of down-selected hexamethyl trimethyl ammonium functionalized Diels-Alder poly(phenylene) polymers.
 - Alkaline stability: no structural change after 3,600 h in 0.5 M NaOH at 80°C.
- Demonstrated alkaline stability of resonance-stabilized guanidinium functionalized Diels-Alder poly(phenylene) polymers.
 - Alkaline stability: no structural change after 10,000 h in 0.5 M NaOH at 80°C.
- Discovered new inhibition mechanism for alkaline hydrogen oxidation reaction (HOR).
- Achieved 1 W/cm² peak power density of AEMFC using AEM and ionomers made by the LANL team with commercial electrocatalysts.



INTRODUCTION

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 three years [4–6]. In FY 2016, we down-selected hexamethyl ammonium functionalized Diels-Alder poly(phenylene)s (TMAC6PP) and poly(phenyl alkylene)s as AEMs. Also, we started to develop advanced hydrocarbon ionomeric binding

materials for AEMFC electrodes. Electrochemical and spectroscopic analyses were initiated in order to elucidate major HOR inhibition mechanisms, which helps to design advanced ionomeric binders for AEMFC anode. In FY 2017, we focused on alkaline stability of the down-selected AEMs in both ex situ and in situ measurements. We also measured ex situ alkaline stability of resonance-stabilized hydrocarbon binders. For electrode works, we found a new alkaline HOR inhibition mechanism and improved the AEMFC performance.

APPROACH

Our general approach to prepare stable and highly conductive AEMs is to synthesize cationic group functionalized aryl-ether-free polymers. Our strategy also includes changing the 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 Diels-Alder poly(phenylene) precursor developed by Fujimoto et al. [7] (Sandia National Laboratories) or acid-catalyzed Friedel-Crafts polycondensations [4] (Rensselaer Polytechnic Institute). 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. Third, resonance-stabilized cationic group containing polymers can be prepared by Diels-Alder poly(phenylene) frameworks (LANL and Sandia National Laboratories).

Our general approach to prepare 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 using various electrolytes and screened the candidate functional groups (LANL). Then, the selected candidate functional groups were employed into a polymeric structure and further structural optimization was made (LANL). Advanced catalysts will be provided from Argonne National Laboratory and other no-cost collaborators.

RESULTS

Alkaline stability of anion exchange membranes:

Figure 1a compares the hydroxide conductivity change of benzylammonium functionalized Diels-Alder poly(phenylene) (ATM-PP control) and hexamethylammonium functionalized Diels-Alder poly(phenylene) (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 in 0.5 M NaOH conditions and to 1,800 h in 4 M NaOH conditions. Figure 1b shows the Fourier transform infrared spectroscopy spectrum change of TMAC6PP after 3,600 h, 0.5 M NaOH treatment. No changes on the C–N stretching peaks at 910 cm^{-1} and 970 cm^{-1} were observed, indicating that significant improvement of alkaline stability was obtained with the TMAC6PP AEM.

The alkaline stability of the TMAC6PP was evaluated during AEMFC operating conditions. Figure 2 shows the

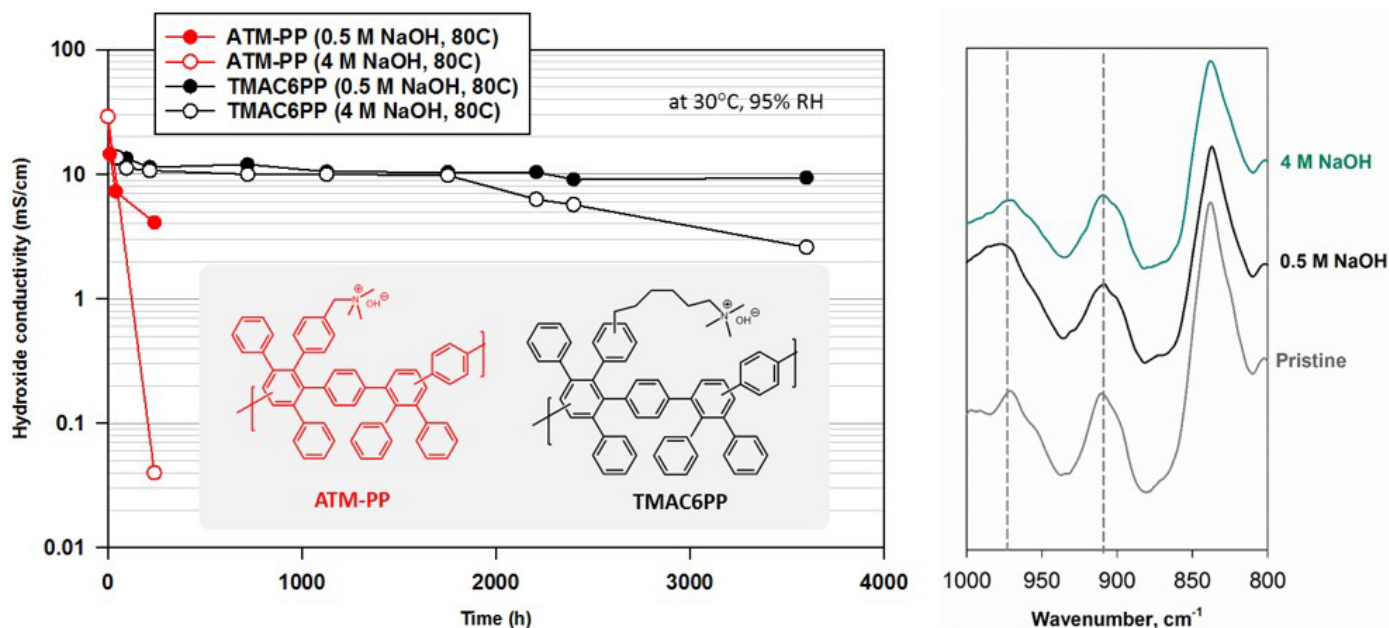


FIGURE 1. (a) Hydroxide conductivity change of TMAC6PP during ex situ alkaline stability test at 80°C; (b) Fourier transform infrared spectroscopy spectrum change after 3,600 h (0.5 M NaOH) and 1,800 h (4 M NaOH)

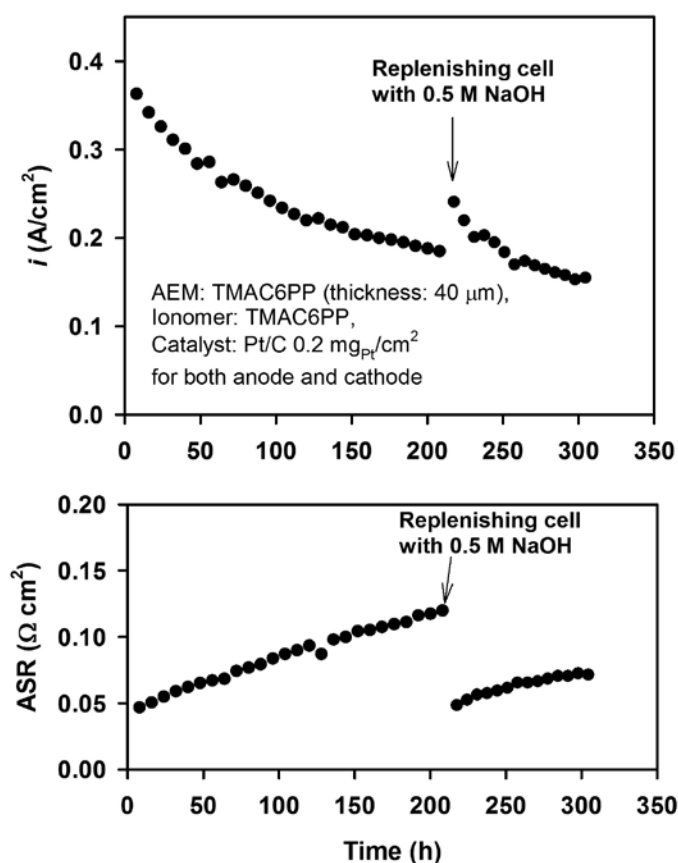


FIGURE 2. AEMFC life test for 300 h with replenishing cell with 0.5 M NaOH at 210 h

cell current density change and AEM ASR during AEMFC operation at 80°C and constant voltage of 0.3 V. The AEM ASR was obtained from cell high-frequency resistance and measured cell electronic resistance [8]. The initial ASR of TMAC6PP was 0.05 $\Omega \text{ cm}^2$, which met the DOE milestone for AEM ASR (<0.1 $\Omega \text{ cm}^2$). The cell current density slowly decreased from 0.37 A/cm^2 – 0.19 A/cm^2 , and the AEM ASR increased from 0.05 to 0.12 $\Omega \text{ cm}^2$ after ~200 h life test. A separate study indicated that the ASR increase is due to the carbonation issue. So we took out the MEAs and replenished the cell with 0.5 M NaOH followed by thorough rinsing with deionized water. After resuming the life test, the AEM ASR recovered to 0.05 $\Omega \text{ cm}^2$, indicating that the ASR increase during the life test was not due to the AEM degradation but due to the carbonation build-up possibly from water humidification. The current density of the cell, however, did not fully recover to the initial value after replenishing the cell, indicating that the AEMFC performance loss may be related to other degradation mechanisms. After 300 h, we stopped the life test. The alkaline stability of the extended-resonance structure was also evaluated. The extended-resonance structure was obtained by a series of connections of phenyl group–ketone–phenyl group–methyl guanidinium via LANL-developed activated fluoro-amine reaction [9].

The extended-resonance group functionalized Diels-Alder poly(phenylene) is a potential candidate for anode ionomeric binder. During in situ 0.5 M NaOH stability test at 80°C, the resonance stabilized Diels-Alder poly(phenylene)s exhibited unprecedented alkaline stability: no degradation after 10,000 h treatment.

HOR inhibition mechanisms and H_2/O_2 AEMFC performance: Rotating disk electrode investigation on alkaline HOR indicated that the HOR activity of Pt-based catalysts is greatly hindered by the benzene adsorption parallel to the Pt surface [10]. We found that this is a major issue for our AEMFC performance as our polymer electrolyte binders have benzene groups in the polymer backbone and side chain. In order to minimize benzene adsorption on the HOR catalyst surface, we further investigated the effect on Pt bimetallic catalysts. The result indicated that Pt–Ru bimetallic catalyst efficiently prevents the benzene adsorption and can improve the HOR activity. Based on this result, Argonne National Laboratory started to synthesize Pt–Ru catalysts. In order to prevent the benzene adsorption, we synthesized new ionomeric binders based on fluorene moiety [11]. Figure 3 shows the AEMFC performance improvement achieved in FY 2017. When the project started, the peak power density of AEMFC using Diels-Alder poly(phenylene)s was only a little over 300 mW/cm^2 . Until January 2017, the AEMFC performance improvement was marginal: peak power density $\approx 400 \text{ mW/cm}^2$. When we changed the HOR catalyst to commercially available Pt–Ru/C catalysts and used new fluorene-based ionomers, the AEMFC performance jumped to 1 W/cm^2 peak power density. The low high-frequency resistance of $\sim 0.07 \Omega \text{ cm}^2$ confirms that the AEMs developed by the LANL team have high enough hydroxide conductivity for high-performing AEMFCs.

A major achievement for alkaline electrode study during FY 2016 was the HOR inhibition by cation–hydroxide–water co-adsorption [12]. In FY 2017, we completed the elucidation of the inhibition mechanism by electrochemical impedance study. We measured the faradaic impedance of the Pt electrode at 0.01 V, 0.05 V, and 0.1 V vs. reverse hydrogen electrode at two different electrode rotating speeds, ca. 900 rpm and 2500 rpm. The smaller semi-circle with the higher rotating disk electrode rotating speed indicated that the second low-frequency circle was likely originated from a diffusion-controlled process rather than kinetic process. The H_2 diffusion-related HOR inhibition mechanism looks counterintuitive because H_2 is a small molecule and the diffusion of H_2 is fast. A possible explanation is the extremely low solubility and diffusivity of H_2 through the co-adsorbed layer, which has a very high hydroxide population. We are trying to measure the thickness of the co-adsorbed layer and the composition by neutron reflectometry experiments [13]. Further study with different cationic groups indicates that longer alkyl chain tethered ammonium groups tend to adsorb less [14].

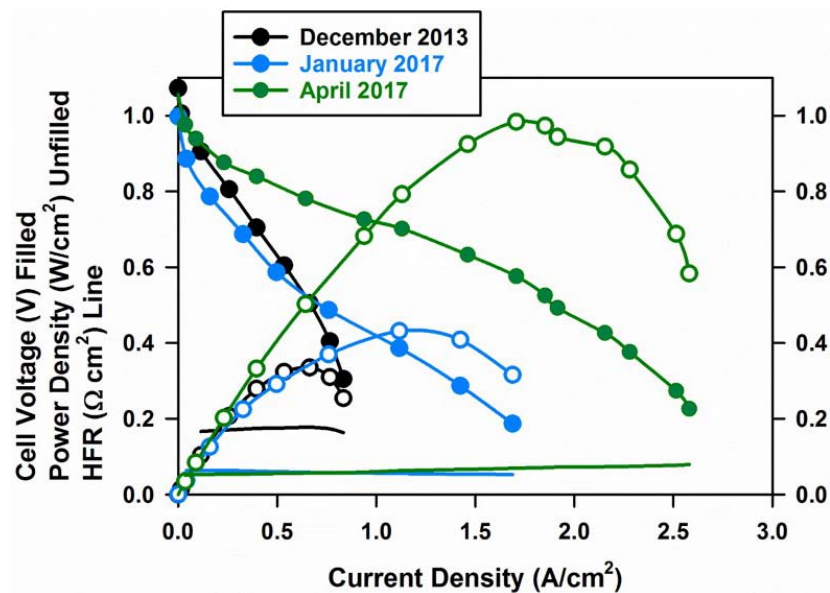


FIGURE 3. Progress of AEMFC performance improvement; AEMFC performance was measured under H_2/O_2 conditions at 30 psig backpressure at 80°C. December 2013 cell, AEM: ATM-PP (80 μm thick), ionomeric binder: ATM-PP, catalyst: Pt black (3 mg_{Pt}/cm^2) for both anode and cathode. January 2017 cell, AEM: Poly(terphenyl alkylene) (30 μm), ionomeric binder: AS 4 (Tokuyama), catalyst: Pt/C (0.6 mg_{Pt}/cm^2) for both anode and cathode. April 2017 cell, AEM: Poly(terphenyl alkylene) (30 μm), ionomeric binder: poly fluorene based, catalyst: Pt-Ru/C (0.5 mg_{Pt}/cm^2) for anode, Pt/C (0.6 mg_{Pt}/cm^2) for cathode.

CONCLUSIONS AND UPCOMING ACTIVITIES

- Down-selected hexamethyl-ammonium functionalized AEM showed low ASR ($\sim 0.05 \Omega cm^2$) and no chemical degradation during 3,600 h ex situ test, >300 h in situ test.
- New HOR inhibition mechanism was explored and based on the study, high AEMFC performance (up to 1 W/cm^2 peak power density) was obtained.
- Time-dependent cation–hydroxide–water co-adsorption behavior was further examined. New ionomeric binders are being synthesized based on this result.
- In FY 2018, further improved fuel cell performance and durability will be demonstrated from the developing AEMs and ionomers.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Yu Seung Kim, Kwan-Soo Lee, Cy Fujimoto, “Poly(phenylene)-based Anion Exchange Polymers and Methods Thereof,” U.S. Patent Application Publication, US 2017/0190831, July 6, 2017.

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