
Cyclic Olefin Copolymer-Based Alkaline Exchange Polymers and Reinforced Membranes

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- Los Alamos National Laboratory, Los Alamos, NM

Project Start Date: October 1, 2018

Project End Date: March 31, 2021

Overall Objectives

- Develop next-generation high-performance, low-cost anion exchange membranes (AEMs).
- Synthesize a series of quaternary ammonium (QA)-functionalized cyclic olefin copolymers (COCs) having high anion conductivity and high mechanical and chemical stabilities.
- Prepare reinforced composite AEMs by impregnating QA-functionalized COCs into mechanically robust matrix.
- Investigate the interfacial behavior of COC ionomer and catalysts using rotating disk electrode and microelectrode setups.

Fiscal Year (FY) 2019 Objectives

- Optimize COC polymerization in terms of catalytic activity and phenylnorbornene content.
- Synthesize COC AEMs with high anion conductivity, high mechanical properties, and low cost.
- Study compatibility of COC AEMs with various support materials.

- Produce robust ultra-thin composite membranes with COC ionic polymers.
- Provide membrane electrode assembly (MEA) information to improve COC AEM fuel cell performance and durability.

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:

- Cost: decrease production cost of AEMs
- Durability: increase chemical and mechanical durability of AEMs under alkaline operating conditions
- Performance: improve AEM fuel cell performance.

Technical Targets

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Synthesized cyclic olefin polymer with phenyl substituent (COC-Phs) using a metallocene catalyst and optimized the polymerization process. Ethylene and phenylnorbornene (PhNB) were used as monomers, and PhNB incorporation was varied from 16 to 34 mol %. Reaction scale was 1.8–3.6 g.
- Functionalized the COC-Phs with quaternary ammonium group by Friedel-Crafts bromoalkylation followed by amination using trimethylamine (TMA), and enhanced mechanical properties of the COC AEMs by crosslinking.
- Evaluated a crosslinked COC AEM (XL20-COC-TMA-1.7) by measuring ion exchange capacity (IEC), swelling ratio, and ion conductivities.

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

- Small molecule study with benzyltrimethyl ammonium indicated that acidic phenol can form at the oxygen reduction potentials observed in fuel cells.

Table 1. Technical Targets

Characteristic	Conditions	2019 Target (Q4, Go/No-Go)	Project Status (Q2)
Hydroxide conductivity	in-plane, 80 °C	60 mS/cm	57 mS/cm
Alkaline stability	1 M NaOH, 95 °C	500 h, <3%	In progress
Tensile strength at break	50 °C, 50% RH	25 MPa	12 MPa
Elongation at break	50 °C, 50% RH	35%	14%
Swelling ratio	OH ⁻ form, 30 °C	20%	28%
Areal specific resistance	OH ⁻ form, 80 °C	<0.1 Ω cm ²	0.089 Ω cm ²

INTRODUCTION

AEMs in electrochemical devices need to satisfy several key properties: (1) high ion conductivity / low area specific resistance (ASR), (2) robust chemical stability at high pH and temperature (>80°C), (3) good mechanical properties (tensile strength and elongation), (4) conveniently scalable synthesis, and (5) low manufacturing cost. Although numerous AEMs have been reported in the literature, until now there has been no AEM that satisfies all these criteria *simultaneously*. Chemical/alkaline stability of the membrane can be improved by removing labile sites from the chemical structure of polymers. For example, by replacing alkaline labile aryl ether (C_{sp2}-O) bonds in the backbone with all carbon-based bonds, the chemical stability of AEMs has been significantly improved under high pH conditions [1–2]. Manufacturing cost of AEMs is also an important factor because it is directly related to the overall device cost. In this project, we propose QA-functionalized COCs as a new class of chemically stable and low-cost AEMs. Ethylene and norbornene are well-known inexpensive raw chemicals, and COCs consist of only C–C bonds, which are essential for good alkaline stability.

APPROACH

In this project, we will develop a series of innovative COC AEMs that would overcome the challenges of the state-of-the-art AEM. Specifically, we plan to (1) develop COCs with tunable backbone rigidity (i.e., T_g adjustable polymers), (2) incorporate alkyl chain-tethered QAs of different structures to the polymer by simple post-polymerization functionalization method (i.e., Friedel-Crafts alkylation), (3) impregnate the anionic polymers into a mechanically stable matrix (reinforced AEM), and (4) demonstrate the membranes' performance and durability in fuel cells using Pt-based and precious group metal-free (PGM-free) catalysts. Reinforcement of the AEM will enable production of thinner (e.g., 10–15 μm) membranes, affording lower ASR and better water management in MEAs, particularly with PGM-free catalyst.

RESULTS

Synthesis of COC-Phs

COC-Phs were prepared by copolymerization of PhNB and ethylene. The ethylene unit provides flexibility to the resulting copolymer, while the PhNB gives rigidity to the copolymer. The polymerizations were conducted under inert conditions using a high-pressure reactor using zirconium-based metallocene catalysts that are known for olefin polymerization. The catalysts were activated by modified methylaluminoxane (MMAO). MMAO works as a co-catalyst and scavenger of oxygen and moisture. The Rensselaer Polytechnic Institute team optimized the polymerization in 1.8–3.6 g scale by varying the amounts of monomers, catalyst, and co-catalyst. PhNB incorporation was controlled from 16 to 34 mol % by changing the ratio of the monomers. As the PhNB contents of COC-Ph increase, the glass transition temperature (T_g) of the polymers increases from 43°C to 109°C (Figure 1a). The catalytic activities were 2.87–5.42 × 10⁶ g/mol Zr·h. A representative NMR spectrum indicates the COC-Ph contains 23 mol % of PhNB (COC23), and it is composed of 80% of the endo form and 20% of the exo form (Figure 1b).

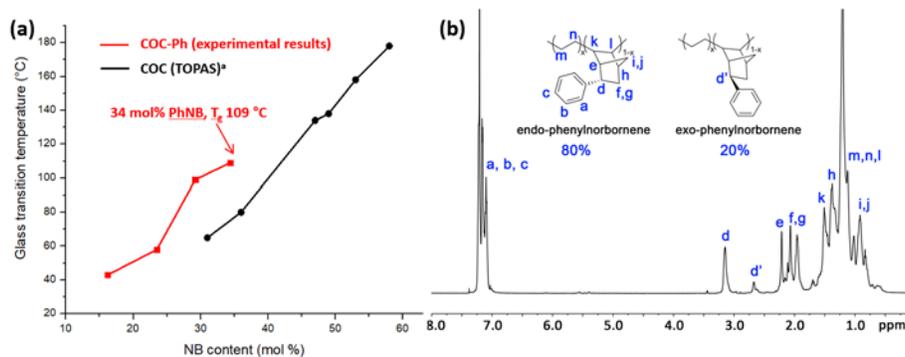
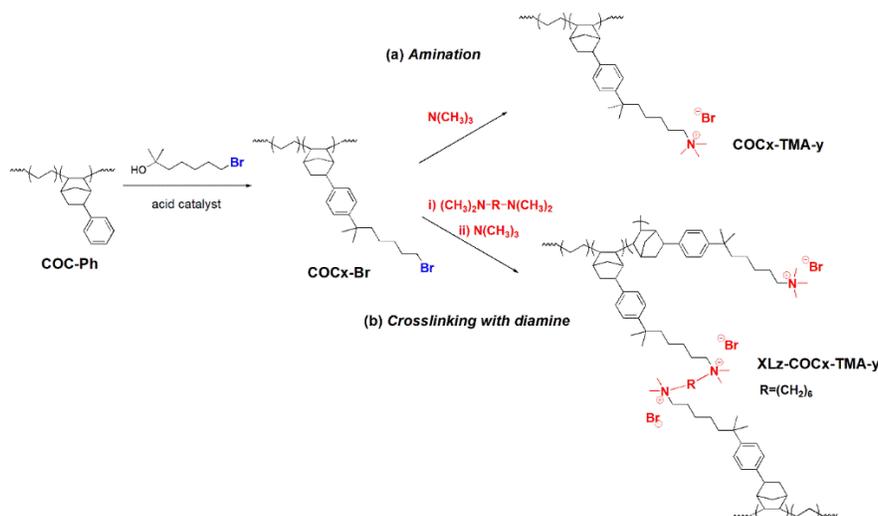


Figure 1. (a) The glass transition temperatures of COC-Phs and COCs with various norbornene contents. COC is a commercial copolymer of norbornene and ethylene, and the COC data is from reference for comparison (*Materials and Design* 31 (2010): 4858). (b) ¹H NMR spectrum of COC23. NMR – nuclear magnetic resonance.

Ionic Functionalization of COC-Phs

Phenyl groups on the COC backbone were functionalized by Friedel-Crafts bromoalkylation using brominated *tert*-alcohol and an acid catalyst. The bromoalkylated COC (COC23-Br) with a degree of functionalization of 75 % was obtained in the reaction using 1.2 equivalents of *tert*-alcohol per phenyl group. The molecular weight of COC23-Br-1.70 (Br content = 1.70 mmol/g) was M_w 319,000 (dispersity \bar{D} = 6.41). The incorporated alkyl bromide side chains were conveniently converted to quaternary ammonium groups by reaction with trimethylamine (COC23-TMA-1.70 where IEC = 1.70 mequiv./g, Scheme 1a). However, the membrane casting of COC23-TMA-1.70 was unsuccessful because it strongly adhered to the glass plate and dimensional stability of the membrane was poor in water. In order to enhance the mechanical properties of the membrane, 20% of the bromine groups of COC23-Br-1.70 were crosslinked using 1,6-hexanemethylenetetramethylamine during the membrane casting process (Scheme 1b). Subsequent amination of the rest of the bromine groups provided a robust crosslinked COC AEM (XL20-COC23-TMA-1.65, where IEC = 1.65 mequiv./g), and the properties were evaluated by measuring the IEC, anion conductivity, and swelling ratio (Table 1). Hydroxide conductivity of XL20-COC23-TMA-1.65 at 80°C was 57 mS/cm, which is slightly lower than the project target go/no-go criteria. Mechanical properties of XL20-COC23-TMA-1.65 were measured by dynamic mechanical analysis at 50% relative humidity and 50°C. The tensile strength at break was 12 MPa. The Rensselaer Polytechnic Institute team will try to increase the IEC and degree of crosslinking of COC AEMs to improve OH⁻ conductivity and mechanical properties. We believe that reinforcement of COC AEMs using support layers will significantly improve their mechanical properties.



Scheme 1. (a) Synthetic route for QA-functionalized COC AEM (COC_x-TMA-y) and (b) crosslinked COC AEM (x = PhNB content, y = ion exchange capacity, z = degree of crosslinking)

Table 1. IEC, In-Plane Swelling, and Ion Conductivity of XL20-COC23-TMA-1.65

	IEC (mequiv./g)		In-plane swelling (% Cl ⁻)	In-plane swelling (% OH ⁻)	Cl ⁻ σ (mS/cm)			OH ⁻ σ (mS/cm)		
	¹ H NMR	Titration			30 °C	60 °C	80 °C	30 °C	60 °C	80 °C
XL20-COC23-TMA-1.65	1.67	1.65	14%	28%	15	29	37	32	48	57
Q4 Target (Go/No-Go)	– ^a	– ^a	– ^a	20			– ^a			60
Q8 Target	– ^a	– ^a	– ^a	10			– ^a			120

^a Not applicable

Ionomer-Oxygen Reduction Catalyst Interface

The interaction between the oxygen reduction reaction catalyst and the ionomeric binder was investigated. From Los Alamos National Laboratory's alkaline membrane fuel cell project, we have learned that the catalyst-ionomer interaction at the AEM fuel cell electrode may impact the long-term stability. In this project, we have started investigating the possible interaction factors that may impact the AEM fuel cell performance and durability. The possible formation of phenol as a result of the electrochemical oxidation of the phenyl group was investigated by analyzing the cathode ionomer retrieved from an MEA held at 0.9 V for 75 hours at 80°C. The MEA was fabricated using PtRu/C anode catalyst, Pt/C cathode catalyst, the quaternized poly(biphenylene) (BPN) ionomer, and quaternized poly(*m*-terphenylene) AEM. The chemical structures of BPN are shown in Figure 2a. After 75 hours, the cell voltage started to decrease, so we stopped the test. After the test, the replenished cell using 0.1 M NaOH was inoperable. The ¹H NMR spectrum of the BPN ionomer obtained from the postmortem cathode catalyst layer contained a phenolic proton peak at 5.75 ppm (Figure 2b). The NMR analysis indicated that the phenyl group in the ionomer may be oxidized to form a phenolic structure. The phenolic hydrogen is acidic (pK_a = 9.3), and the phenolic hydrogen would neutralize the ammonium hydroxide of the ionomer, adversely impacting the fuel cell performance and durability. Density functional theory calculation suggests that phenyl groups in the polymer backbone have a high energy of adsorption on Pt, thus a negative impact on AEM fuel cell performance [3]. Norbornene and the phenyl group in the side chain of the proposed polymer may also impact the AEM fuel cell performance. Los Alamos National Laboratory will further investigate the electrochemical oxidative degradation of the quaternized COC polymers.

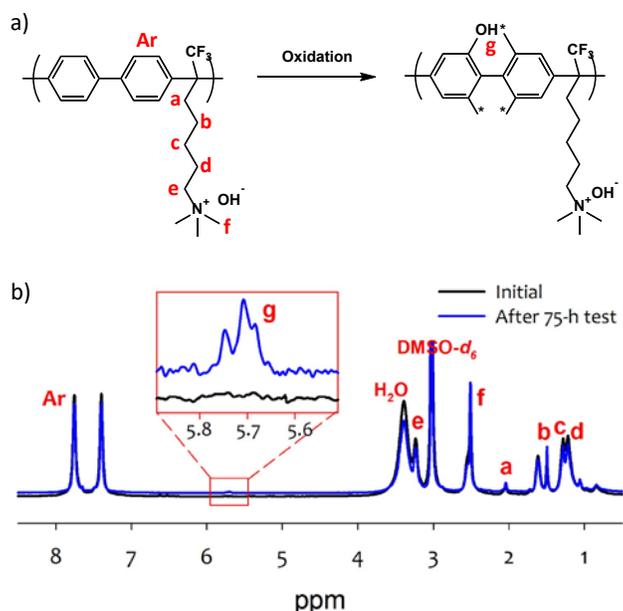


Figure 2. (a) Reaction scheme for electrochemical phenyl oxidation to phenol in a cathode BPN ionomer on the basis of (b) ¹H NMR spectra of BPN ionomer before and after extended-term test at 0.9 V

CONCLUSIONS AND UPCOMING ACTIVITIES

- COC-Phs were successfully synthesized using a [(ethylenebis(indenyl))ZrCl₂] catalyst with various PhNB incorporation from 16.2 to 34.4 mol %. The T_gs of the COC-Phs were proportional to the PhNB contents. The reaction scale was 1.77–3.61 g.
- The COC-Phs were functionalized by Friedel-Crafts bromoalkylation, followed by amination using trimethylamine, and the membrane was crosslinked by 1,6-hexanediamine to enhance mechanical properties.
- Crosslinked COC AEM (XL20-COC-TMA-1.7) was evaluated by measuring IEC, swelling ratio, and ionic conductivities of the Cl⁻ and OH⁻ forms.
- IEC and degree of crosslinking of COC AEMs will be increased to improve OH⁻ conductivity and mechanical properties.
- Chemical durability tests will be performed in Q3.
- COC AEMs with different cation groups will be synthesized and evaluated.
- Ionic polymers will be sent to Xergy for pore-filling reinforcement (ePTFE substrates).
- Ionomer phenyl oxidation occurs for the cathode binder. The phenyl oxidation generates phenol, which neutralizes the ammonium hydroxide group; thus, the AEMFC performance decreases.
- Ionomer degradation of the anode side will be studied.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Sandip Maurya, Albert S. Lee, Dongguo Li, Eun Joo Park, Daniel P. Leonard, Sangtaik Noh, Chulsung Bae, and Yu Seung 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.
2. Ivana Matanovic, Sandip Maurya, Eun Joo Park, Jong Yeob Jeon, Chulsung Bae, and Yu Seung Kim, “Adsorption of Polyaromatic Backbone Impacts the Performance of Anion Exchange Membrane Fuel Cells,” *Chem. Mater.* 31 (2019): 4195–4202.

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1. W.-H. Lee, Y.S. Kim, and C. Bae, “Robust Hydroxide Ion Conducting Poly(biphenyl alkylene)s for Alkaline Fuel Cell Membranes,” *ACS Macro Letters* 4 (2015): 814–818.
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 (2017): 566–570.
3. 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): 4195–4202.