
Lab Call FY19: Electrode Ionomers for High Temperature Fuel Cells

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Subcontractor:
Los Alamos National Laboratory, Los Alamos, NM

Project Start Date: October 1, 2018
Project End Date: September 30, 2020

Overall Objectives

- Demonstrate a high temperature proton exchange membrane fuel cell (HT-PEMFC) performance similar to that of state-of-the-art phosphoric acid poly(benzimidazole) HT-PEMFCs (500 mW/cm² peak power density) with a total platinum group metal (PGM) loading of <0.125 mg_{PGM}/cm².
- Demonstrate a HT-PEMFC with <5% performance decrease after 1,000 h operation at 200°C.

Fiscal Year (FY) 2019 Objectives

- Synthesize 10–20 gram batches of two parent polymers.
- Synthesize phosphonated ionomer based on one parent polymer.
- Synthesize phosphonated ionomer based on a second parent polymer.
- Measure membrane area specific resistance (ASR) using high temperature membrane electrode assembly (MEA) construction.

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:

- Durability
- Cost
- System Thermal and Water Management.

Technical Targets

Sandia National Laboratories (SNL) is conducting research into medium-temperature (the “high-temperature” descriptor in the project title was intended to be applied within the context of PEMFCs) PEMFCs with experimental polymeric materials. The proposed fuel cell will demonstrate progress toward meeting the following DOE fuel cell technical targets:

- Cost: \$40/kW net
- Platinum group metal total loading: 0.13 mg_{PGM}/cm²
- MEA durability: 5,000 h (< 5% decrease in voltage)
- MEA performance: 1,000 mW/cm²

FY 2019 Accomplishments

- Synthesized two poly(phenylene) structures with protected phosphonic acid groups attached.
- Developed a method to deprotect phosphonic acids on poly(phenylene)s with soluble products.
- Synthesized poly(biphenylene) and poly(terphenylene) with pendant fluorinated aryl phosphonic acid groups with proton conductivity of 354 mS/cm at 320°C (0% RH).
- Demonstrated fuel cell with poly(biphenylene) ionomer with power density of 690 W/cm² at 200°C and ASR <0.05 Ohm/cm².

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

INTRODUCTION

HT-PEMFCs offer advantages over low temperature PEMFCs because of their higher operating temperatures. These advantages include higher catalytic activity, higher tolerance to impurities, and easier thermal management. Los Alamos National Laboratory (LANL), in collaboration with SNL, has developed phosphate-quaternary ammonium ion-pair coordinated proton exchange membranes for use in HT-PEMFCs. Fuel cells made with the ion-pair membranes have the potential to be operated at temperatures above 200°C; however there is a tendency for the phosphoric acid to evaporate from the electrodes at temperatures above 180°C. Thus, there is a need to develop an ionomer that can conduct protons at high temperatures and that can be processed into MEAs. Such a polymer also needs to be extremely durable in order to function at low pH, low RH, and high temperature conditions.

APPROACH

Phosphonated polymers have been investigated for the purpose of using the polymer electrolytes under high temperature/low humidity operating conditions [1]. However, despite extensive efforts to prepare phosphonated polymers by attaching phosphonic acid via alkyl, aryl, and perfluoroalkyl groups, as well as direct polymerization using phosphonated monomers [2, 3], no practical fuel cell systems based on phosphonated polymers have been realized. The primary reason for this is that the preparation of phosphonated membranes with high mechanical stability and high conductivity is extremely difficult and the films are often brittle.

On the other hand, phosphonated polymers can be used as the ionomer for ion-pair coordinated membrane fuel cells, an application wherein excellent film-forming properties are not required. In this project, we are developing thermo-oxidatively stable, wholly aromatic phosphonated ionomers for the ion-pair coordinated PEMFCs that further improve fuel cell performance by minimizing electrode flooding and phosphoric acid poisoning and enable the fuel cell to operate up to 300°C using low-PGM or non-PGM oxygen reduction reaction catalysts.

In this project, the SNL team will develop high-performance hydrocarbon-based phosphonated polymers using Diels-Alder (SNL) or acid-catalyzed Friedel-Crafts chemistry (LANL). The HT-PEMFC performance using the phosphonated polymers will be demonstrated to prove the possible use of the phosphonated polymers as an ionomeric binder.

RESULTS

Synthesis of Phosphonated Poly(phenylene)s

Several published methods for the addition of phosphonic acid groups were tried initially with little success. The reactions were either too slow or they gave insoluble products due to crosslinking reactions. Eventually, a modified Cabasso approach was used to prepare two different phosphonated Diels-Alder poly(phenylene)s. A very dilute polymer solution (2.5 % or less) was added to triethylphosphite heated to 185°C, and after heating for more than 12 h, the solution was cooled and precipitated in water. The crude polymer was dried and then redissolved in chloroform and reprecipitated in hexanes. Figure 1 shows the basic procedure used.

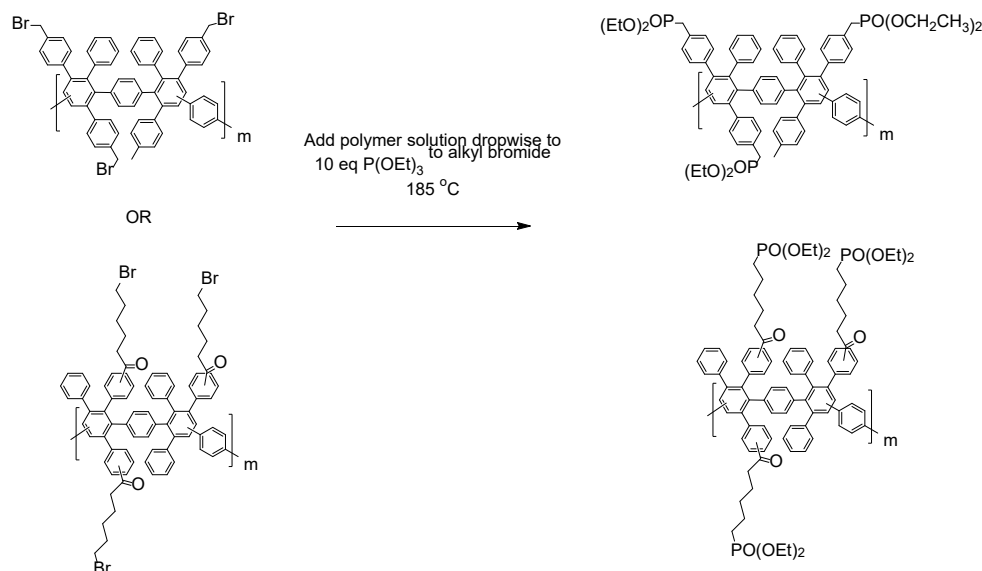


Figure 1. Conversion of bromoalkyl groups to protected phosphoric acids

Two approaches were tried to transform the ester phosphonate to phosphonic acid groups. The first approach required exposing the ethyl phosphonate to concentrated hydrochloric acid at reflux for more than 10 h (Figure 2a). This seemingly straightforward approach involves a corrosive and high-temperature environment and may result in side reactions. When this approach was used, the resultant film could not be redissolved and further analyzed. The second approach begins by dissolving the ethyl phosphonate in a chlorinated solvent then adding bromotrimethyl silane (Figure 2b). The advantage of this approach is the low temperature needed (room temperature).

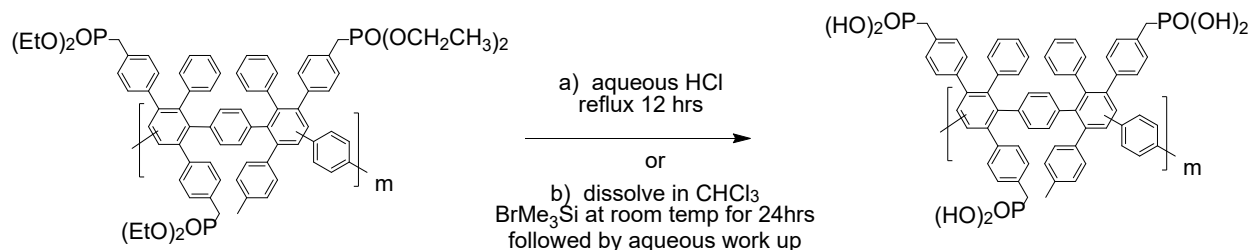


Figure 2. Two possible methods for deprotecting phosphonate esters

Using bromotrimethylsilane to deprotect ethyl phosphonate is a low-temperature reaction; it does take up to 24 hours for the reaction to be complete. To monitor the reaction, ³¹P nuclear magnetic resonance (NMR) spectroscopy was used and the product NMR shows a single (new) peak indicating the fully deprotected phosphonic acid Diels-Alder poly(phenylene).

Synthesis of Acid Catalyzed Phosphonated Poly(biphenylene)s

We prepared phosphonated poly(biphenylene)s using acid catalyzed polymer precursors. We applied the phosphonation using trimethylsilyl phosphite into poly(phenylene)s (Figure 3a). The conversion of para-fluoro group into phosphonic acid was confirmed by ¹⁹F NMR spectra (Figure 3b). The polymer with the ion exchange capacity of 2.2 meq/g was soluble in polar aprotic solvents, such as DMSO and DMAc. We also prepared phosphonated poly(terphenylene)s using the same synthetic scheme. Unlike the poly(biphenylene), the terphenyl-based polymer backbone could grow into high molecular weight due to the rigid structure of *p*-terphenyl used as the aromatic backbone. The polymer with the ion exchange capacity of 1.9 meq/g was not only soluble in polar aprotic solvent but also film forming. The membrane showed the conductivity of ~200 mS/cm at 160°–240°C. The maximum proton conductivity of the membrane was 354 mS/cm at 320°C.

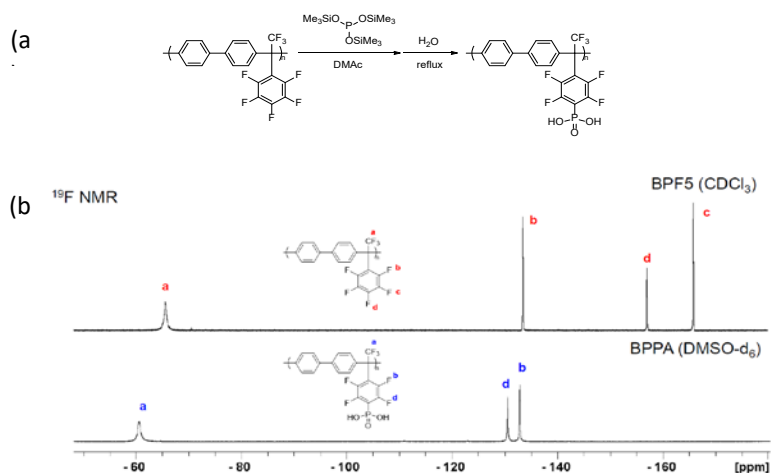


Figure 3. (a) Synthetic scheme of phosphonated poly(biphenylene)s. (b) ^{19}F NMR spectra of the polymer precursor and phosphonated poly(biphenylene)s.

Fuel Cell Performance Evaluation

The HT-PEMFC performance of an MEA using a phosphoric acid doped quaternary ammonium polymer and phosphonated poly(biphenylene) ionomer was measured as a function of temperature (Figure 4). For this test, we used a phosphoric acid doped quaternary ammonium functionalized Diels-Alder poly(phenylene) (PA-doped QAPOH). The fuel cell performance increased as the operating temperature increased from 120°C to 200°C. At 200°C, we obtained the peak power density of 691 mW/cm². The high frequency resistance of the MEA was 0.06 Ω cm², corresponding ASR of 0.03 Ω cm².

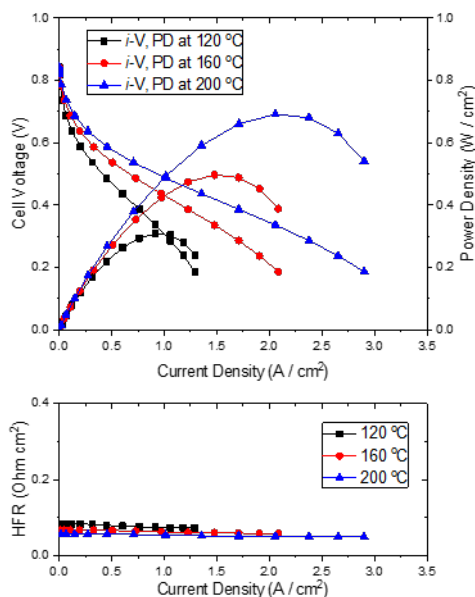


Figure 4. HT-PEMFC performance of an MEA using the phosphonated poly(biphenylene) ionomer. Membrane: PA-doped QAPOH; flow anhydrous gases, H₂/O₂ flow = 500 sccm; A/C backpressure = 10 psi; A/C Pt loadings were 0.75/0.6 mg_{Pt}/cm² using commercial 75 wt % PtRu/60 wt % Pt/C catalysts; MEA fabrication → gas diffusion electrode air brushing on carbon cloth gas diffusion layer.

CONCLUSIONS AND UPCOMING ACTIVITIES

Although we have shown evidence of dealkylation of the ethyl phosphonate to produce the phosphonic acid, the product still has some solubility issues that need to be optimized before it can be utilized as an ionomer. We are working on optimizing polymer concentration and reaction temperature. The sequence and timing of addition were also found to be vitally important to both phosphonation optimization and the deprotection step. In FY 2020, synthesis of phosphonated ionomers will be scaled up to allow for the fabrication of MEAs for HT-PEMFC testing.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. Phosphonated polymers for use as electrolytes in fuel cells, E.J. Park, Y.S. Kim, S133668 (2019).

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Michael R. Hibbs, Cy H. Fujimoto, Ehren D. Baca, Albert S. Lee, and Yu Seung Kim, “High Temperature Fuel Cells with Ion-Pair Membranes and Phosphonated Ionomers,” presented at the North American Membrane Society Annual Meeting, Pittsburgh, PA, May 15, 2019.
2. Michael R. Hibbs, “Electrode Ionomers for High Temperature Fuel Cells,” presented at the DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, April 29, 2019.
3. Albert S. Lee, Yoong-Kee Choe, Ivana Matanovic, and Yu Seung Kim, “Phosphoric Acid Loss Mechanism of High Temperature Proton Exchange Membranes,” presented at the 235th Electrochemical Society Meeting, Dallas, TX, May 26–30, 2019.
4. Albert S. Lee, Yoong-Kee Choe, Ivana Matanovic, and Yu Seung Kim, “The Energetics of Phosphoric Acid Interactions Reveals a New Acid Loss Mechanism,” *Journal of Materials Chemistry A* 7 (2019): 9867–9876.
5. Albert S. Lee, Yoong-Kee Choe, Ivana Matanovic, and Yu Seung Kim, “Phosphoric Acid Loss Mechanism of High Temperature Proton Exchange Membranes,” presented at Polymers for Fuel Cells, Energy Storage, and Conversion Meeting, Pacific Grove, CA, February 24–27, 2019.
6. Yu Seung Kim, “Recent Advances of HT-PEMFCs and AEMFCs,” presented at the Toyota 2018 Fuel Cell Research Workshop Powering Future FCEVs with New Innovations, Torrance, CA, October 9, 2018.

REFERENCES

1. B. Lafitte and P. Jannasch, “On the Prospects for Phosphonated Polymers as Proton-Exchange fuel Cell Membranes,” *Advances in Fuel Cells*, T.S. Zhao, K.-D. Kreuer, T.V. Nguyen, eds. (Oxford: Elsevier Ltd, 2007).
2. V.D. Romanenko and V.P. Kukhar, “Fluorinated Phosphonates: Synthesis and Biomedical Application,” *Chem Rev* 106, no. 9 (2006): 3868–3935.
3. M. Gaboyard, Y. Hervaud, and B. Boutevin, “Synthesis of New Phosphonic Derivatives Bearing Fluorinated Chains,” *J Fluorine Chem* 107, no. 1 (2001): 5–12.