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Electrode Ionomers for High Temperature Fuel Cells

Michael Hibbs (Primary Contact), Cy Fujimoto, Ehren Baca
Sandia National Laboratories
P.O. Box 5800, MS 0958
Albuquerque, NM 87185
Phone: 505-284-8790
Email: mhibbs@sandia.gov

DOE Manager: *(will be supplied – no input required)*

Subcontractors:
Los Alamos National Laboratory, Los Alamos, NM

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

Overall Objectives

- Demonstrate a HT-PEMFC performance similar to that of state-of-the-art PA-PBI HT-PEMFCs (500 mW/cm^2 peak power density) with a total PGM loading of < 0.125 mgPGM/cm^2.
- Demonstrate HT-PEMFC with <5% performance decrease after 1000h 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 ASR using high temperature 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 Plan:

- Durability
- Cost
- System Thermal and Water Management

Technical Targets

This project is conducting research into medium-temperature (the “high-temperature descriptor in the project title was intended to be applied within the context of PEM fuel cells) PEM fuel cells with experimental polymeric materials. The proposed fuel cell will demonstrate progress towards meeting the following DOE fuel cell technical targets:

- Cost: $40/kW net
- Platinum group metal total loading: 0.13 mg PGM/cm^2
- MEA durability: 5000 hrs (< 5% decrease in voltage)
- MEA performance: 1,000 mW/cm^2

FY 2019 Accomplishments

- Synthesized two poly(phenylene) structures with protected phosphonic acid groups attached.
- Developed 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^{-1} at 320 ^{o}C.
- Demonstrated fuel cell with poly(biphenylene) ionomer with power density of 690 W/cm^2 at 200 ^{o}C and ASR<0.05 Ohm/cm^2.

Introduction

HT-PEMFCs offer advantages over LT-PEMFCs because of their higher operating temperatures. These advantages include higher catalytic activity, higher tolerance to impurities, and easier thermal management. 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 which can be processed into MEAs. Such a polymer also needs to be extremely durable in order to function at low pH, low RH, 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.

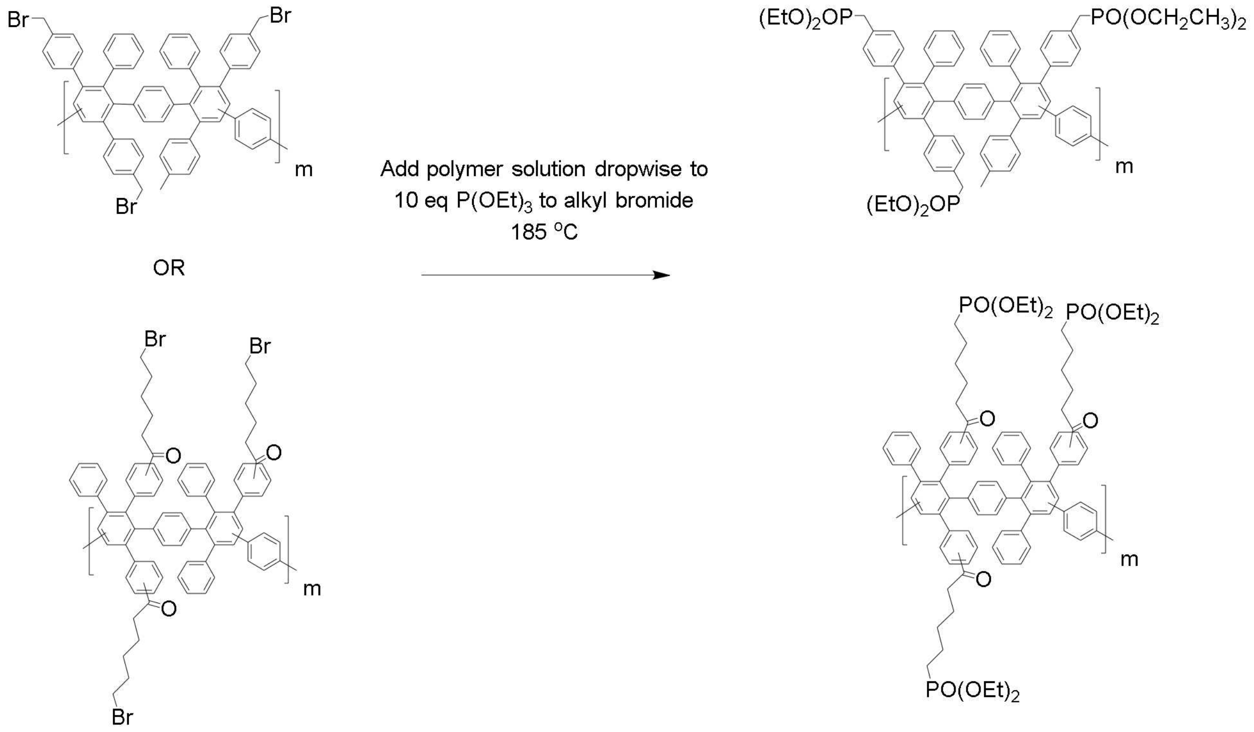
On the other hand, phosphonated polymers can be used as the ionomer for ion-pair coordinated membrane fuel cells, an application wherein excellent film forming properties are not required. In this proposal, we are developing thermo-oxidatively stable wholly aromatic phosphonated ionomers for the ion-pair coordinated polymer electrolyte membrane fuel cells which further improve fuel cell performance by minimizing electrode flooding and PA poisoning and enable the fuel cell to operate up to 300°C using low precious group metal (low-PGM) or non-PGM ORR catalysts.

In this project, the SNL team will develop high-performance hydrocarbon-based phosphonated polymers using Diels-Alder (SNL) or acid-catalyzed Friedel-Craft 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 ^{o}C, after heating for over 12 h the solution was cooled and precipitated in water. The crude polymer was dried and then re-dissolved in chloroform and re-precipitated in hexanes. Scheme 1 shows the basic procedure used.



Polymers dissolved in NMP at 2.5% by weight

Scheme 1. Conversion of bromoalkyl groups to protected phosphoric acids.

Two approaches were tried to transform the ester phosphonate to phosphonic acid groups. The first apporach required exposuing the ethyl phosphonate to concentrated hydrochloric acid at reflux for over 10 hrs (Figure 1a). This seemingly straighforward approach involves a corrosive and high temperature enviroment and may result in side reactions. When this approach was used the resultant film could not be redissolved and further anaylsed. The second apporach begins by dissolving the ethyl phosphonate in a chloronated solvent then adding bromotrimethyl silane (Figure 1b). The advantage of this approach is the low tempertures needed (room temperature).

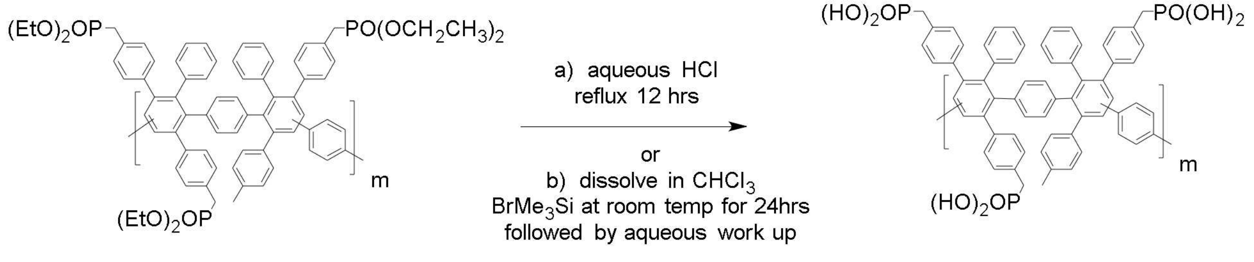


Figure 1. Two possible methods for deprotecting phosphonate esters.

Using Bromotrimethylsilane to deprotect ethyl phosphoate is a low temperature reaction, it does take time for the reaction to be complete. To monitor the reaction, ^{31}P-NMR 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 2a). The conversion of para-fluoro group into phosphonic acid was confirmed by ^{19}F NMR spectra (Figure 2b). The polymer with the IEC of 2.2 meq. g^{-1} 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 IEC of 1.9 meq. g^{-1} 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.

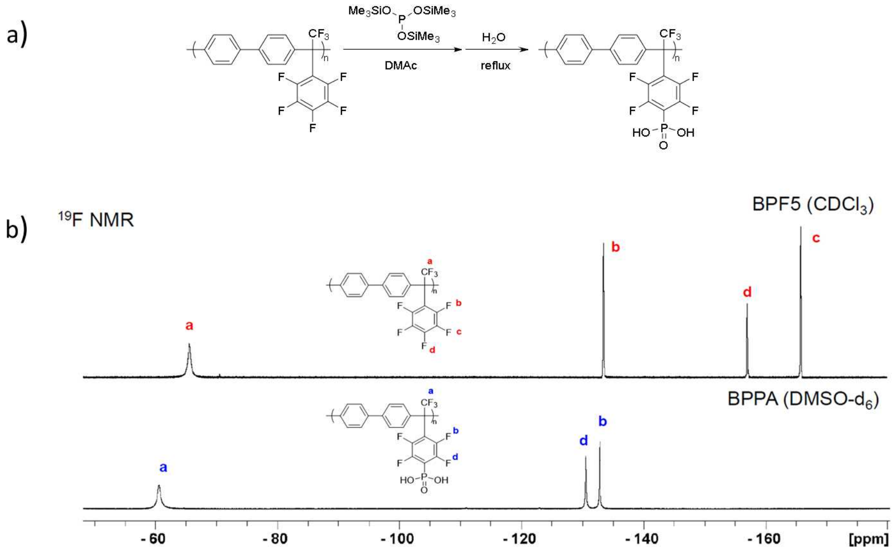


Figure 2. (a) Synthetic scheme of phosphonated poly(biphenylene)s (b) ^{19}F NMR spectra of the polymer precursor and phosphonated poly(biphenylene)s.

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 3). 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 to 200 °C. At 200 °C, we obtained the peak power density of 691 mW/cm^2. The HFR of the MEA was 0.06 Ω cm^2, corresponding ASR of 0.03 Ω cm^2.

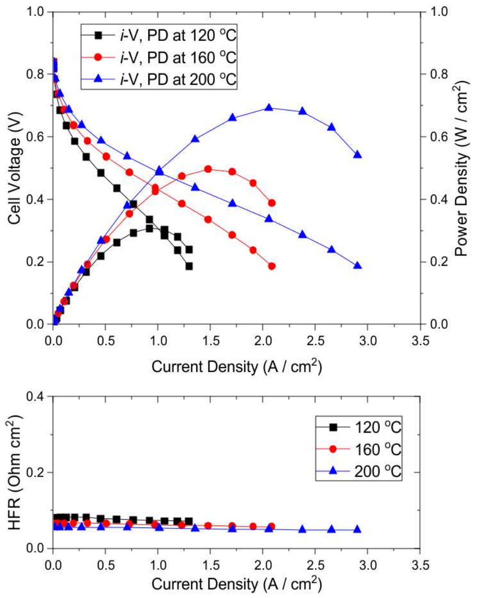


Figure 3. HT-PEMFC performance of an MEA using the phosphonated poly(biphenylene) ionomer. Membrane: PA-doped QAPOH; Flow anhydrous gases, H_2/O_2 flow = 500 sccm; A/C backpressure = 10 psi; A/C Pt loadings were 0.75/0.6 mg_{pt}/cm^2 using commercial 75 wt% PtRu / 60 wt% Pt/C catalysts; MEA fabrication → GDE air brushing on carbon cloth GDL

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 solublity issues that still need to be optimized before it can be utilized as an ionomer. We are working on optimizing polymer concentration, reaction temperature and sequence of addition (which was found to be vitally important in phosphonation optimization) is also important in the deprotection step. In FY20, 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. "High Temperature Fuel Cells with Ion-Pair Membranes and Phosphonated Ionomers" M. R. Hibbs; C. Fujimoto; E. Baca; A. S. Lee; Y. S. Kim, talk presented at the North American Membrane Society annual meeting, Pittsburgh, PA, May 2019.

2. "Electrode Ionomers for High Temperature Fuel Cells" M. R. Hibbs poster presented at the 2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review, Washington DC, April 2019.

3. "Phosphoric Acid Loss Mechanism of High Temperature Proton Exchange Membranes" A. S. Lee; Y. K. Choe; I. Matanovic; Y. S. Kim, talk presented at the 235th ECS Meeting, Dallas, TX, May 26-30, 2019.

4. “The Energetics of Phosphoric Acid Interactions Reveals a New Acid Loss Mechanism”, Albert S. Lee, Yoong-Kee Choe, Ivana Matanovic, Yu Seung Kim, *Journal of Materials Chemistry A*. 7, 9867-9876 (2019).

5. “Phosphoric acid loss mechanism of high temperature proton exchange membranes”. A. S. Lee, Y.-K. Choe, I. Matanovic, Y. S. Kim, Polymers for Fuel Cells, Energy Storage, and Conversion, Feb. 24-27, 2019, Asilomar Conference Ground, Pacific Grove, CA, USA.

6. “Recent Advances of HT-PEMFCs and AEMFCs, Toyota 2018 Fuel Cell Research Workshop Powering Future FCEVs with New Innovations”, Miyako Hybrid Hotel, Torrance, CA, October 9, 2018.

References

1. Lafitte, B.; Jannasch, P., On the Prospects for Phosphonated Polymers as Proton-Exchange fuel Cell Membranes. In *Advances in Fuel Cells*, Zhao, T. S.; Kreuer, K.-D.; Nguyen, T. V., Eds. Elsevier Ltd: Oxford, 2007.

2. Romanenko, V. D.; Kukhar, V. P., Fluorinated phosphonates: Synthesis and biomedical application. *Chem Rev* **2006,** *106* (9), 3868-3935.

3. Gaboyard, M.; Hervaud, Y.; Boutevin, B., Synthesis of new phosphonic derivatives bearing fluorinated chains. *J Fluorine Chem* **2001,** *107* (1), 5-12.

Acronyms

ASR	Area specific resistance
DMAc	N,N-Dimethylacetamide
DMSO	Dimethylsulfoxide
IEC	Ion exchange capacity
LT-PEMFC	Low temperature-proton exchange membrane fuel cell
HT-PEMFC	High temperature-proton exchange membrane fuel cell
MEA	Membrane electrode assembly
PA-PBI	Phosphoric acid poly(benzimidazole)
PGM	Platinum group metal
QA-POH	Biphosphate-Quaternary Ammonium Poly(phenylene)
RH	Relative humidity

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