

BES001. Fluoropolymers, Electrolytes, Composites and Electrodes

Stephen E. Creager (Primary Contact),
Darryl D. DesMarteau and Dennis W. Smith
Clemson University
Hunter Laboratory
Clemson, SC 29634
Phone: (864) 656-2319
E-mail: screage@clemson.edu

DOE Program Officer: William Millman
Phone: (301) 903-5805
E-mail: william.millman@science.doe.gov

Subcontractors: None

Objectives

- The overall objective of the research program is to provide new electrolyte membranes and electrode materials consisting of integrated catalysts and fluorinated electrolytes for use in PEMFC power sources.
- The research will be pursued in two thrusts, one focused on new proton-conducting fluoropolymer electrolyte membranes for use under high-temperature (95 - 120 °C) and low-humidity (25 - 50% RH) conditions, and another focused on electrolyte integration into fuel-cell electrodes by covalent attachment of electrolytes onto carbon supports.
- The objectives of work in the first thrust area are the discovery, synthesis, characterization, and evaluation of new polymeric proton-conducting electrolyte membranes.
- The objective of work in the second thrust area is to develop methods for accomplishing robust attachment of proton-conducting polymer electrolytes onto carbon supports, and to characterize the resulting materials with special attention to their mixed electronic and ionic conduction and electrochemical properties.

Technical Barriers

- This research seeks to overcome technical barriers to implementation of PEMFC technology associated with low protonic conductivity in polyelectrolyte membranes at high temperatures and low water activities.
- It seeks to develop polymer electrolyte membranes that will overcome this conductivity barrier while also retaining dimensional stability (little to no swelling on contact with liquid water) and durability (lifetimes up to 5000 hours are desired).

- Project-specific technical barriers include limitations from undesired chemical reactivity of trifluorovinyl ether monomers with strong acids which constitutes a barrier to the preparation of polymer electrolytes having high molecular weight, capabilities for crosslinking, and good dimensional stability.

Abstract

Project work focusing on blended fluoropolymer ionomers, mesoporous carbon supports for PEM fuel cell electrode, and grafted electrolytes within pores of mesoporous carbon and nanocomposite mesoporous carbon / zirconia supports is reported. Blended ionomers have conductivity comparable to that of PFSA ionomers with less swelling and improved dimensional stability. Mesoporous carbon supports were prepared by a silica sol templating approach and were shown to have very high pore volume, which is posited to allow for rapid transport into and out of pores. Monomolecular (non-polymeric) electrolytes were grafted inside pores but so far improvements in fuel-cell performance have not been realized. Ongoing work will seek to graft polyelectrolytes inside support pores, which is believed to be necessary to realize improved performance.

Progress Report

- Blended ionomers.** Blends of PFSI and S-PFCB (see Figure 1 for structures) were prepared in various compositions between 70:30 and 50:50 mole ratios of PFSI to S-PFCB. The resulting blends have conductivity comparable to Nafion[®] 112 in the 0-70% RH range, and also lower swelling than the non-blended S-PFCB ionomer. Preliminary studies on blending heteropoly acids (HPAs) and

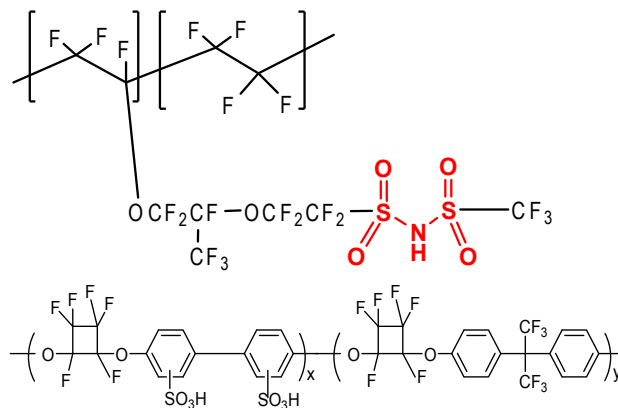


FIGURE 1. Structures of blended ionomers. Top, perfluorosulfonimide ionomer (PFSI); Bottom, sulfonated perfluorocyclobutyl ionomer (S-PFCB).

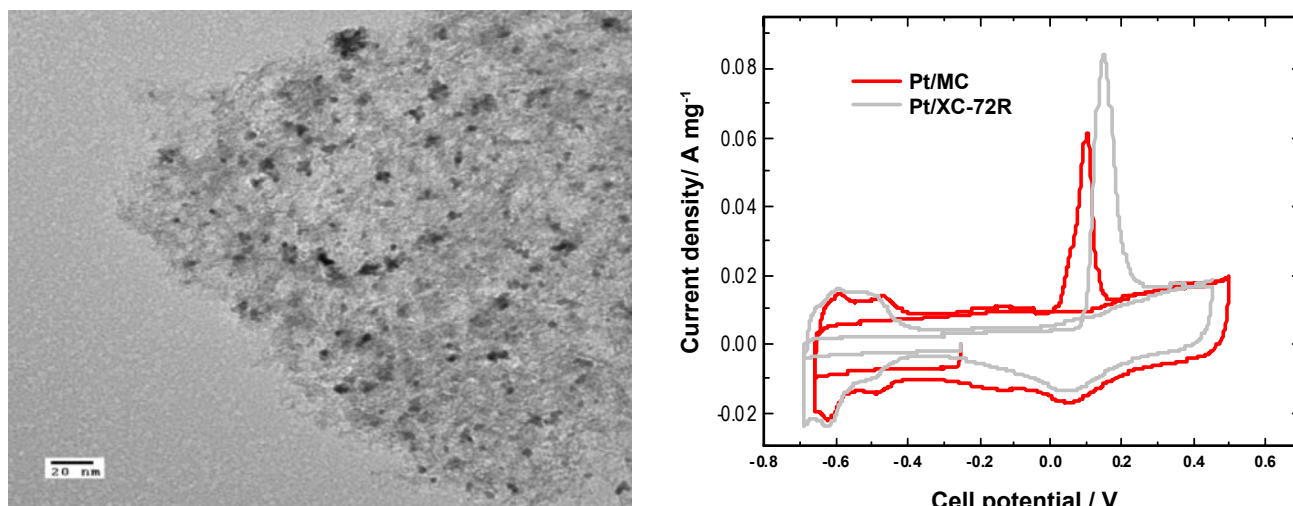


FIGURE 2. Left, TEM of silica-templated mesoporous carbon (MC) support with Pt deposited; right, in-situ CV of CO stripping from Pt on MC (red) and on XC-72R carbon black.

on electrospinning of ionomer blends were also undertaken.

- 2. Mesoporous carbon supports.** Mesoporous carbon (MC) supports for Pt in PEMFC electrodes were prepared by making resorcinol-formaldehyde (RF) carbon aerogels with colloidal silica added, followed by silica removal using caustic. The resulting supports had high surface area and very high pore volume (over 4 cc/g). Platinum deposition was accomplished via formaldehyde reduction of hexachloroplatinate deposited by the incipient wetness method. In-situ CV of electrodes fabricated on glassy carbon supports (Figure 2) showed high Pt surface area and small particle sizes. Membrane-electrode assembly fabrication onto Nafion[®] membranes using conventional conditions (approx. 30 weight percent Nafion[®]) failed due to poor dimensional stability of the composite electrodes. This fact is thought to be due to Nafion[®] being taken up into the support pores, which left none to accomplish electrode binding. Ongoing work will focus on electrode formulations having more Nafion[®], and on covalently grafted ionomers in the pores.
- 3. Mesoporous carbon supports with grafted electrolytes.** Work on grafting small-molecule aryl fluorosulfonimide electrolytes onto mesoporous carbon continued and was completed this year. Grafting of monolayers of acid electrolyte onto mesoporous carbon was demonstrated using aryl diazonium salts. Ion-exchange capacities of the resulting materials were relatively low (less than 0.2 meq/g) and fuel-cell performance of MEAs fabricated using Pt/carbon having grafted aryl fluorosulfonimide electrolytes was not greatly different from that of MEAs prepared using carbon without the grafted electrolyte. We believe this

reflects the relatively small amount of electrolyte that was ultimately grafted.

We desired access to a simpler chemistry for grafting larger amounts of electrolyte, possible polymeric electrolytes, inside the pores of mesoporous carbon supports. To accomplish this aim, mesoporous carbon supports were prepared using the RF method with both colloidal silica and zirconia added, followed by etching to remove silica but not zirconia. The resulting supports are nanocomposites of carbon containing nanoscale zirconia. Subsequent modification of these supports with the difunctional acid, meta-sulpho-phenyl-phosphonic acid, was accomplished. Titration of the resulting supports confirmed incorporation of sulfonic acid groups. Ongoing work seeks to increase the amount of incorporated acid both by increasing the amount of zirconia in the carbon / zirconia composite, and also by utilizing telechelic S-PFCB polymers having phenyl-phosphonic acid end groups (see Future Directions).

Future Directions

Future work is planned on several fronts. Ionomer blends will continue to be studied with a focus on combinations of low-EW ionomers that can retain water and provide high conductivity, with high-EW ionomers to provide dimensional stability and limit swelling. Crosslinking strategies will be pursued that can stabilize membranes after casting. One such approach will involve new perfluorocyclopentenyl-based ionomers for which a synthesis is shown in Figure 3. The double bond in the PFCP group is a potential site for crosslinking that may be initiated thermally following membrane casting.

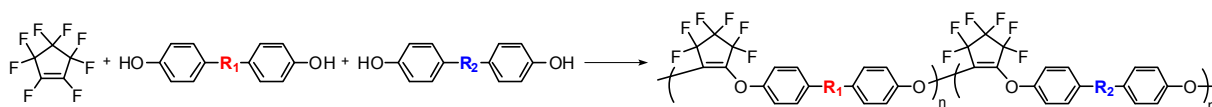


FIGURE 3. General synthesis of perfluorocyclopentenyl (PFCP) polymers.

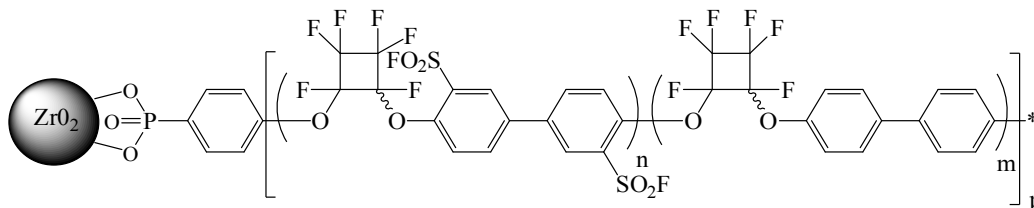


FIGURE 4. Proposed composite structure for zirconia doped sulfonated PFCB aryl ether polymers.

Work on telechelic S-PFCB polymers having terminal phenyl-phosphonic acid groups to provide anchoring sites for zirconia will be pursued to provide a route to nanocomposite carbon / zirconia catalyst supports having high ion-exchange capacities of ionomer integrated into electrolyte pores. Figure 4 presents an illustrative structure of a bound ionomer bound at a terminal phenyl-phosphonic acid group. This work will build upon our prior work demonstrating binding of meta-sulpho-phenyl-phosphonic acid onto zirconia groups in carbon / zirconia composite catalyst supports.

Publications (including patents) acknowledging the grant or contract

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2. Bing Liu and Stephen Creager, "Carbon xerogels as Pt catalyst supports for polymer electrolyte membrane fuel cell applications", *Journal of Power Sources*, 195, 1812-1820 (2010).

3. Bing Liu and Stephen Creager, "Silica-sol-templated mesoporous carbon as catalyst support for polymer electrolyte membrane fuel cell applications" *Electrochimica Acta* 55, 2721-2726 (2010).

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5. Verma R, Tomar N, Creager SE and Smith, DW. Jr.; "Super Hydrophobic Surfaces of Perfluorocyclobutyl (PFCB) Aryl Ether Polymer Doped with Room Temperature Ionic Liquid (RTIL) Prepared by Electrospinning", *Journal of Material Chemistry*, (Submitted).