

V.N.2 Fluoropolymers, Electrolytes, Composites and Electrodes

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Objectives

- The overall objective of this research is to create and understand the behavior of new fluoropolymer-based electrolytes and electrodes suitable for use in electrochemical energy storage and conversion devices such as batteries and fuel cells.
- This objective is pursued via work in three thrust areas as follows: (1) fluorinated monomers and ionomers for preparing new proton- and hydroxide-ion-conducting ionomers; (2) membrane separators made from these ionomers; and (3) nanocomposite electrodes prepared using these ionomers with carbon aerogels / xerogels to provide mixed electronic / ionic conduction functionality.
- Specific project objectives are as follows:
 - Synthesize and characterize high-ion-exchange-capacity (>1.25 meq/g) TFE-based copolymer and terpolymer ionomers with a broad range of functional groups including sulfonyl fluorides, sulfonic acids, sulfonimides, sulfonamides, and

phosphonates to support proton conduction, and also quaternary ammonium and guanidinium cations to support hydroxide-ion conduction.

- Fabricate and test membrane separators, carbon-based nanocomposite electrodes, and membrane-electrode assemblies by combining fluoroionomers with suitable crosslinking agents and/or mesoporous carbon supports. Work in this objective will include studies aimed at independently measuring ionic and electronic contributions to membrane and thin-film electrode conduction.
- Expected outcomes from the project are new fluoropolymer electrolyte and electrode materials having properties superior to existing materials, and also new knowledge regarding the behavior of such materials in energy storage and conversion applications.

Technical Barriers

- Proton exchange membranes (PEMs). Existing PEMs have low ionic conduction particularly under very hot and dry conditions (e.g. 120°C and 25% RH), as well as poor dimensional stability, high water swelling, and poor durability. Existing fluoroalkyl sulfonic acid ionomers have been in use for over 50 years and have been optimized about as much as they can be. New protogenic groups and new ionomer morphology approaches, e.g. involving crosslinking, are needed to improve properties.
- Crosslinked fluoroionomers. Ionomer crosslinking can mitigate problems from high water swelling / poor dimensional stability, particularly with high-IEC materials; however, few approaches provide crosslinks in a controllable way that could mitigate problems from swelling without introducing undesirable brittleness into membranes.
- Alkaline exchange membranes (AEMs). Alkaline ionomers are not widely used in fuel-cell devices due in part to low ionic conduction but particularly to poor ionomer stability when in contact with hydroxide-ion-containing electrolytes, especially under hot and dry conditions. Fluoropolymer ionomers are widely used in PEM-based devices but are little used to prepare AEMs in part due to concerns about alkali stability.
- Electrodes. High-IEC ionomers are desired in electrodes to promote ionic conduction and thorough wetting of electrode surfaces, however most such materials are water-soluble and therefore unsuitable for PEM and AEM fuel cell use. Ionomer attachment to electrode surfaces could mitigate this problem however existing fluoroionomer materials offer no means for surface attachment.

Abstract

Project work is reported on the preparation and study of new fluorinated trifluorovinyl ether (TFVE) monomers for proposed proton-conducting ionomers, and new partially fluorinated model compounds relevant to proposed hydroxide-ion-conducting ionomers. TFVE monomers having sulfonyl fluoride, sulfonate, phosphonate, and sulfonamide functional groups have been prepared in multigram quantities and are available for project use. A new TFE handling facility is being constructed at Clemson and will be available for project use in summer 2013. Testing of model compounds for alkaline fluoroionomer hydroxide-ion conductors showed that the *N*-methyl sulfonamide, fluorocarbon-sulfonamide, hydrocarbon-sulfonamide, and hydrocarbon-amine linkages are all stable to strongly alkaline media at elevated temperatures, confirming that such linkages can be used to construct robust fluoropolymer-based hydroxide-ion conductors. Aliphatic quaternary ammonium groups decomposed in hot D₂O/KOD media via nucleophilic attack of hydroxide on methyl groups attached to quaternary nitrogen, as was expected from prior work on other aliphatic ammonium salts. Insights from this work are guiding efforts to understand the stability limits of cationic groups in potential fluoropolymer-based hydroxide-ion conductors. In related work, studies on first-generation carbon/zirconia/fluoroionomer nanocomposite materials were completed which provide guidance for studies on next-generation materials, and methods are being refined for studying mixed electronic / ionic conduction in thin-film electrodes prepared from these composite materials.

Progress Report

(1) Fluorinated monomers and ionomers. Fluorocarbon ionomers are being prepared by co-polymerization of one or more trifluorovinyl ether (TFVE) co-monomers with tetrafluoroethylene (TFE) gas. The TFVE monomers shown in Figure 1 have been prepared in multigram quantities and are available for use on the project.

The $-\text{SO}_2\text{F}$, $-\text{SO}_3(\text{Na})$ and $-\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ monomers have long been known and used to prepare proton-conducting fluoroionomers. Ionomers based on the $-\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ monomer in particular have been extensively studied at Clemson. The phosphonate monomers are relatively new.

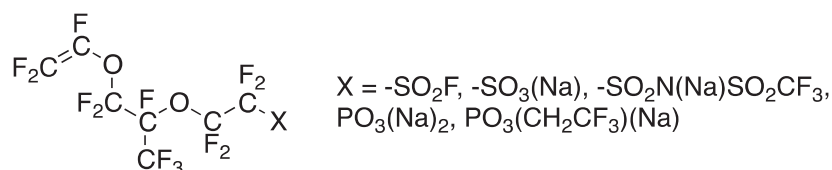


FIGURE 1. Structures of TFVE monomers suitable for co-polymerization with TFE to prepare fluorinated proton-conducting ionomers.

They were recently prepared by DesMarteau and co-workers for use in making all-phosphonate ionomers as part of a separate project, but they have not until now been used to prepare terpolymers containing both protogenic groups (e.g. $-\text{SO}_3(\text{H})$ and $-\text{SO}_2\text{N}(\text{H})\text{SO}_2\text{CF}_3$) and phosphonate-based crosslinking / surface-anchoring agents co-polymerized with TFE. With multi-gram quantities of these monomers in hand we are positioned to start systematically preparing these terpolymer ionomers and studying their properties, particularly their propensity for crosslinking and surface grafting via the phosphonate groups.

TFE is a hazardous and highly explosive gas for which highly specialized handling techniques and facilities are needed. Clemson is in the late stages of completing a new facility under the direction of Joe Thrasher for generating and handling TFE. An opening ceremony is planned for spring/summer 2013. This facility will be used to perform TFE-based co-polymerizations with the monomers in Figure 1 to produce ionomers.

In other work, partially fluorinated model compounds were prepared having structures relevant to proposed alkaline fluoroionomers for accomplishing hydroxide ion transport. Figure 2 presents structures for three such compounds that have been prepared and their stability studied in strongly alkaline media.

The two neutral model compounds ($\text{X} = -\text{H}$ and $-\text{N}(\text{CH}_3)_2$) were dissolved in a solution of 9:1 *d*₆-DMSO:D₂O into which approximately 1.5 M KOH had been dissolved, and the solutions were heated to 60C and 80C for 48 hrs each. No differences in the ¹⁹F or ¹H NMR spectra were observed between the start and finish of heating. We conclude that all of the chemical linkages in these compounds, including the *N*-methyl sulfonamide, the fluorocarbon-sulfonamide, the hydrocarbon-sulfonamide, and the hydrocarbon-amine, are stable to strongly alkaline media at elevated temperatures. Ongoing studies involving

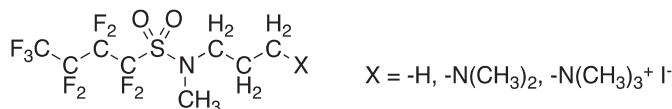


FIGURE 2. Model compounds for studying alkaline stability of chemical linkages in proposed hydroxide-ion-conducting fluoroionomers.

harsher conditions will explore the limits of stability for these linkages. We note that these results refute the commonly-held notion that fluorocarbon ionomers will not be well suited for preparing alkaline exchange membranes due to instability of the fluorocarbons on exposure to hot alkali. There may be stability limits for such materials but they will likely not involve the fluorocarbons or the sulfonamide groups linking anion-exchange groups to the ionomers.

In another stability study, the quaternary ammonium model compound ($X = -N(CH_3)_3^+ I^-$) was dissolved in a solution of KOD in D_2O (without d_6 -DMSO) and heated to 60 and 80 C. In this case it was found that the ^{19}F NMR spectrum did not change but the 1H NMR spectrum did change, in a manner consistent with decomposition by nucleophilic attack of hydroxide at one of the quaternary ammonium methyl groups to produce methanol (actually methoxide) and re-generate the tertiary amine. This decomposition pathway, illustrated in Figure 3, is consistent with known pathways for decomposition of other aliphatic quaternary ammonium ions in strongly alkaline media. Ongoing work is exploring the stability limits of this and other anion-exchange groups, e.g. guanidinium, to strongly alkaline media at elevated temperature, in an effort to understand materials decomposition pathways under such conditions and to down-select appropriate monomers for inclusion in hydroxide-ion-conducting fluoroionomers.

(2) *Membrane separators*. Most project work in this term was focused on monomers and ionomers so there was

relatively little work on membranes. There will be more work in this area as ionomer synthesis work progresses to provide material for membrane and membrane-electrode-assembly fabrication.

3. *Nanocomposite electrodes*. In the past year work was completed on the use of telechelic perfluoro-cyclobutyl-based oligomer ionomers having aryl sulfonic acid groups on the main chain of the polymer and aryl phosphonates on the end groups. These polymers were grafted onto mesoporous carbon supports having large pore volumes (approximately 85% free volume), large internal surface areas (over 500 m^2/g), and integrated zirconia particles that allow for electrolyte attachment via terminal phosphonate groups. A publication describing this work appeared in *Chemical Communications* late in 2012 (see Figure 4).

In more recent work, a method is being developed for independently measuring the electronic and ionic contributions to conductivity in thin-film mixed-conductor electrodes. The method is illustrated in Figure 5. Formulations have been developed for all-electronic and all-ionic thin-film electrodes and the cell design is being optimized to ensure that measured cell resistances report principally on the properties of the thin-film electrodes and not on the contacts to the electrodes. Excellent progress is being made and a validated method is expected to be available by summer 2013.

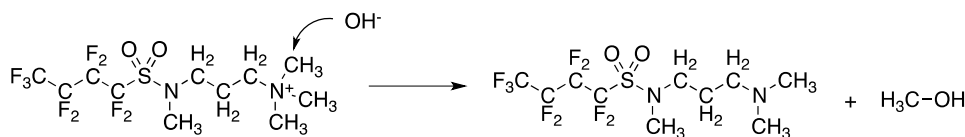


FIGURE 3. Proposed pathway for decomposition of a partially-fluorinated *N*-methyl sulfonamide quaternary ammonium salt in strongly alkaline KOD / D_2O media.

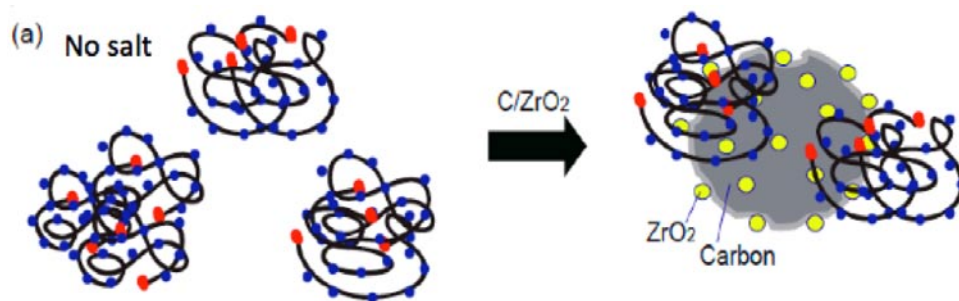


FIGURE 4. Grafting of telechelic oligomer ionomers onto the interior pore surfaces of mesoporous carbon/zirconia composite electrodes. Terminal phosphonate groups provide a means for anchoring polymer chains onto embedded zirconia particles in the carbon matrix.

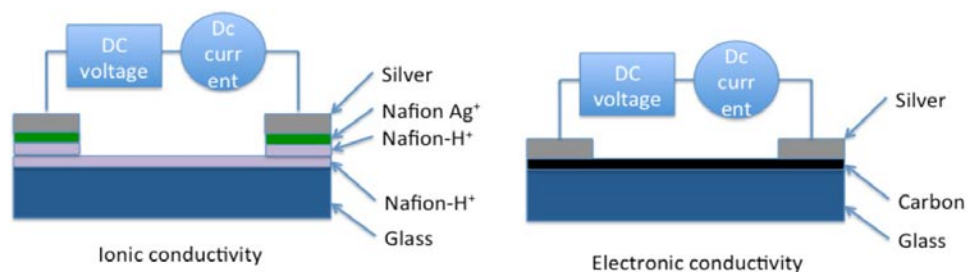


FIGURE 5. Proposed method for independently measuring ionic (left) and electronic (right) contributions to conductivity in thin-film electrodes.

Future Directions

Ongoing work is focused on improving synthesis of TFVE monomers, synthesizing fluorinated terpolymer ionomers having high ion-exchange capacity and desired compositions, continuing to explore alkali stability of model compounds for proposed alkaline exchange membrane ionomers, and continuing to refine and validate methods for studying mixed electronic and ionic conduction in nanocomposite thin-film electrodes. Some work is planned for summer 2013 aimed at preparing carbon / zirconia composites from other carbon sources besides carbon aerogels / xerogels, including carbon black and also graphene. This work will provide a wide range of carbon-based substrates to accommodate grafting of fluorinated ionomers with phosphonate groups incorporated into the polymer structure. As this work progresses, other future work will come into play including fabrication and study of membrane separators and membrane-electrode assemblies.

Publication list (including patents), acknowledging the DOE grant or contract

1. Park, Jiyoung; Jung-Min Oh; Stephen E. Creager; and Dennis W. Smith Jr. "Grafting of Chain-End-Functionalized Perfluorocyclobutyl (PFCB) Aryl Ether Ionomers onto Mesoporous Carbon Supports" *Chemical Communications*, **2012**, 48, 8225-8227
2. Oh, Jung-Min; Amar S. Kumbhar; Olt Geiculescu; and Stephen E. Creager, "Nanoscale ZrO₂ - embedded Mesoporous Carbon Composites: A Potential Route to Functionalized Mesoporous Carbon Composite Materials", *Langmuir*, **2012**, 28, 3259-3270