V.M.18 New Proton Conductive Composite Materials with Co-Continuous Phases Using Functionalized and Crosslinkable VDF/CTFE Fluoropolymers

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Objectives

- Synthesize hydrophilic and proton-conductive inorganic materials.
- Develop the chemistry for preparing cross-linkable functionalized chlorotrifluoroethylene (CTFE)/ vinylidene fluoride (VDF) polymers.
- Develop composite membrane fabrication methods.
- Optimize the membranes' properties based on test results and tune the synthesis of polymers and inorganic additives.
- Develop a new membrane material based on the combination of inorganic proton conductors with a functionalized and cross-linkable CTFE/VDF polymer to be used in proton exchange membrane fuel cells (PEMFCs) at -20 to 120°C and 25-50% relative humidity (RH).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

Technical Targets

The main objective of this project is the development of a highly conductive new composite membrane to be used in PEMFCs at elevated temperatures under conditions of lower RH. The progress we made toward meeting the DOE technical targets for membranes for transportation application is shown in Table 1.

TABLE 1. Progress Towards Meeting Technical Targets for Membranes for Transportation Applications

Characteristic	Units	2010/2015 Targets		2006 Status		
Operating temperature	°C	20	<120	20	<120	
Inlet water vapor partial pressure	kPa	<1.5			139	98
Membrane conductivity	Siemens/cm	0.07	0.1	0.033	0.025	0.0083

Accomplishments

- Synthesized cross-linkable functionalized fluoropolymers using functional borane control radical initiator.
- Synthesized different types (mesoporous, 3-D phase, 2-D phase, and amorphous) proton conductive, hydrophilic inorganic materials.
- Fabricated new inorganic/polymer composites.
- Introduced Nafion® inside the matrix as a model proton conductive substance.
- Determined the most promising inorganic additive.
- Studied the effect of each component of P(VDF-CTFE)/Nafion®/$H_3OZr_2(PO_4)_3$ membranes on conductivity and optimized the membrane composition.
- Optimization of the membrane composition enhanced membrane conductivity at 120°C from 0.0004 and 0.0001 S/cm to 0.025 and 0.0083 S/cm, at 70% and 50% RH, respectively.

- Explored two avenues: introduction of sulfonated silica and sulfonated trimethoxyl phenyl silane (TMPS) into the polymer to obtain desirable membrane conductivity without an addition of Nafion®.

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Introduction

This project addresses one of the main challenges in present-day PEMFC technology: to design a membrane capable of maintaining high conductivity and mechanical integrity when temperature is elevated and water vapor pressure is severely reduced. If this goal is reached, the fuel cell operating pressure can be kept low, which would make the PEMFC much more cost efficient and adaptable to practical operating conditions and facilitate its faster commercialization particularly in automotive applications.

Approach

The unique aspect of our approach is the development of a composite membrane with hydrophilic proton-conductive inorganic material and the polymeric matrix that is able to "bridge" the conduction paths in membrane by functionalized chain ends. A cross-linkable chain-end and side chain functionalized Teflon®-based polymer binds and assembles the inorganic particles into a continuous medium. Three PSU research groups focusing on polymer synthesis, inorganic particle synthesis, membrane synthesis and characterization are involved in a loop of continuous feedback until the final product meets the target requirements.

Results

The main effort was centered on development of the synthesis routes, which can lead to the preparation of perfect telechelic VDF/CTFE copolymers with controllable structures, molecular weight and functionalities at both polymer chain ends. Several process conditions have been examined to find the most suitable fabrication conditions for preparing the PEM composite membranes with high inorganic content. We have successfully prepared telechelic VDF/CTFE polymers exhibiting good compatibility with inorganic surfaces and good crosslinking efficiency. They contain two reactive terminal silane groups [$Si(OC_2H_5)_3$] at both ends of the polymer chain used to form 3-D crosslinked polymer network under heating (during the compress molding process in forming composite membrane). The route of polymer synthesis is shown in Figure 1. The chemistry to prepare telechelic PVDF polymers is centered on a specifically designed functional borane initiator containing a silane group, which was prepared by hydroboration of commercially available vinylsilane. The borane/oxygen mediated control radical polymerization was very effective in random terpolymerization, and the termination by coupling reaction resulted in polymer structure with two terminal silane groups.

Several classes of inorganic proton conductors with high water retention capabilities were synthesized for composite membrane fabrication: 3-D, 2-D and amorphous zirconium phosphates, 3-D porous titanosilicate and high surface area mesoporous alumina. Hydrothermal syntheses of 3-D zirconium phosphate $H_3OZr_2(PO_4)_3$ which was used for more detailed studies of composite membranes, was conducted in three steps: (i) synthesis of ammonium zirconium phosphate $NH_4Zr_2(PO_4)_3$, (ii) calcination to hydrogen zirconium phosphate $HZr_2(PO_4)_3$), and (iii) hydration to $H_3O\ Zr_2(PO_4)_3$. A composite membrane fabrication procedure including solution casting of polymer/inorganic additive suspension followed by thermal compressing was developed.

At first, (VDF-CTFE)/Nafion®/inorganic additive membranes were fabricated and tested for proton conductivity. Nafion® was added to VDF/CTFE polymer as a model conductive substance. It was shown that an inorganic phase has a great effect on membrane conductivity. The membranes with the same (VDF-CTFE)/Nafion® ratio and content of inorganic component had very different conductivity depending on the type of inorganic phase. 3-D phase zirconium phosphate was found to be the most beneficial for membrane conductivity. (VDF-CTFE)/Nafion®/$H_3OZr_2(PO_4)_3$ membrane composition was optimized towards each component. This optimization

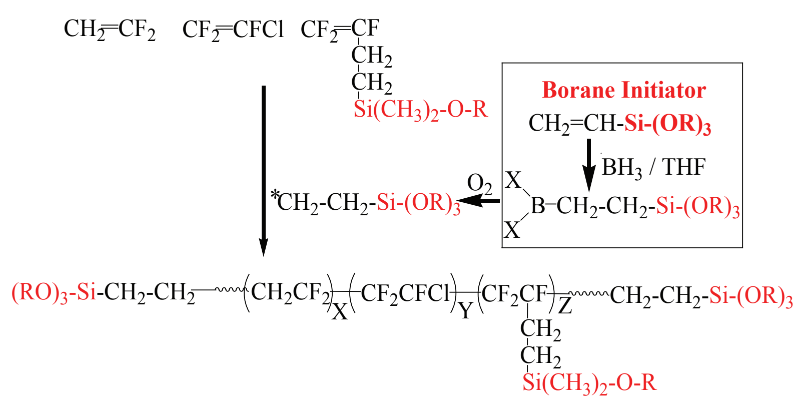

FIGURE 1. Synthesis of Functionalized Fluoropolymers Using Functional Borane Initiator

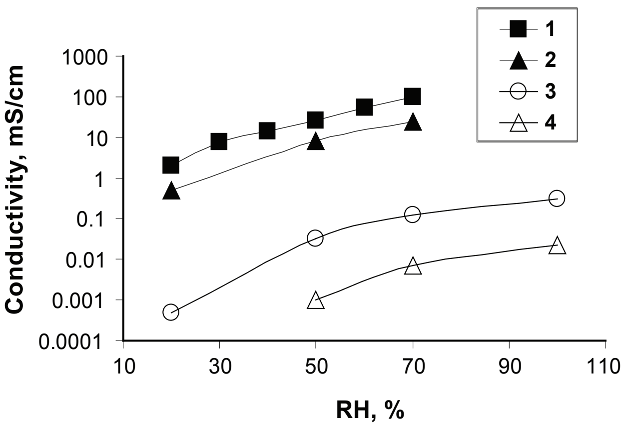

FIGURE 2. Conductivity of New Composite Materials at 120°C compared to Nafion® (1 - Nafion 115; 2 - 20% (VDF-CTFE)/60%Nafion®/20%$H_3OZr_2(PO_4)_3$; 3 - (VDF-CTFE)/Sulfonated TMPS; 4 - 40%(VDF-CTFE)/60%Sulfonated Silica.)

consented to elevate membrane conductivity at 120°C up to 0.025 and 0.0083 S/cm, at 70% and 50% RH, respectively (Figure 2). To obtain desirable membrane conductivity without an addition of Nafion®, two avenues were explored: introduction of sulfonated silica and sulfonated TMPS into the polymer. Composite membranes were fabricated using solution casting of polymer/sulfonated silica or polymer/sulfonated TMPS suspension followed by thermal compressing. Both types of composite membranes exhibited proton conductivity. Conductivity of membranes with sulfonated TMPS is substantially higher than that of the membrane with sulfonated silica (Figure 2). This material can be used for further modification to meet objectives of this project and achieve the corresponding DOE targets.

Conclusions and Future Directions

The first year has resulted in a great expansion in knowledge with the routes of synthesis telechelic VDF-CTFE copolymers, fabrication of polymer/inorganic additive composite membranes, conductivity measurements, role of each component of the membrane, and their effect on membrane conductivity. In the next year we intend to pursue the following areas:

- Development of new methods to prepare the grafted copolymers, which would include structural sulfonic acid groups with a tunable content. These polymeric materials will not only provide a crosslinkable matrix but also the conductivity paths that will finally displace Nafion® used in composite membranes at the beginning.
- Development of corresponding fabrication conditions for new types of composite membranes.
- Examination of new inorganic additives with higher proton conductivity than previous ones.

We anticipate reaching membrane conductivity of 0.07 S/cm at 80% RH at 25°C in the next year.

FY 2007 Publications/Presentations

1. T. C. Mike Chung, S. Komarneni, E. Chalkova, and S. Lvov, *Proton Conductive Composite Materials with Co-continuous Phases Using Silane Functionalized and Crosslinkable PVDF Polymers*, ECS Transactions, 3(1), 83-90 (2006).

2. S.N. Lvov, M. Chung,S. Komarneni, E. Chalkova, M. V. Fedkin, Z. Zhang, and S. Sharma, *New Proton Conductive Composite Materials with Co-continuous Phases Using Functionalized and Crosslinkable TFE/VDF Fluoropolymers,* The 2006 DOE Hydrogen Program Review Meeting, May 16–19, 2006, Arlington, VA (poster).

3. S.N. Lvov, M.V. Fedkin, E. Chalkova, S. Komarneni, and D.J. Wesolowski, *Surface Chemistry of Inorganic Materials for Composite Membranes in PEM Fuel Cells Operating at Elevated Temperature and Reduced Relative Humidity*, American Chemical Society 232nd National Meeting & Exposition, September 10–14th, 2006, San-Francisco, CA (oral presentation).

4. S. N. Lvov, T.C. Mike Chung, S. Komarneni, E. Chalkova, and M. Fedkin, *New Proton Conductive Composite Materials with Co-continuous Phases Using Functionalized and Crosslinkable TFE/VDF Fluoropolymers*, Oral Presentation at 210th Meeting of The Electrochemical Society, Cancun, Mexico, October 29 – November 3, 2006.

5. S. Lvov, M. Chung, S. Komarneni, Z. Zhang, E. Chalkova, S. Sharma, M. Fedkin, and C. Wang, *New Proton Conductive Composite Materials with Co-continuous Phases Using Functionalized and Crosslinkable VDF/CTFE Fluoropolymers*, The 2007 DOE Hydrogen Program Review Meeting, May 15–18, 2007, Arlington, VA (oral presentation).

6. S.N. Lvov, M. Chung,S. Komarneni, E. Chalkova, M. V. Fedkin, Z. Zhang, and S. Sharma, *New Proton Conductive Composite Materials with Co-c ontinuous Phases Using Functionalized and Crosslinkable TFE/VDF Fluoropolymers*, Quarterly Progress Reports #1,2,3,4, Report periods May 1 to June 30, 2006; July 1 to September 30, 2006; October 1to December 31, 2006; January 1 to March 31, 2007, respectively.