

# V.G.14 New Proton Conductive Composite Materials with Co-Continuous Phases Using Functionalized and Crosslinkable VDF/CTFE Fluoropolymers

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## Objectives

- Synthesize different types of hydrophilic inorganic materials with high proton conductivity.
- Develop the synthesis routes for the preparation of a highly conductive polymer based on a styrene grafted and sulfonated vinylidene difluoride-chlorotrifluoroethylene P(VDF-CTFE) copolymer.
- Study the effect of polymer composition on membrane properties.
- Optimize the membranes' properties based on test results and tune the synthesis of polymers.
- 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 (PEM) fuel cells at 120°C and 25-50% relative humidity (RH).

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the

Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (B) Durability
- (E) System Thermal and Water Management
- (F) Air Management

## Technical Targets

The main objective of this project is the development of a highly conductive new composite membrane to be used in PEM fuel cells 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	2007 Status	
			Target	Actual
Inlet water vapor partial pressure	kPa	< 1.5	3.4	100
Membrane conductivity at inlet water vapor partial pressure and Operating temperature: 20°C 30°C 120°C	Siemens/cm	0.07	0.054	0.030

## Accomplishments

- Developed the synthesis routes for the preparation of a highly conductive polymer based on a styrene grafted and sulfonated P(VDF-CTFE) terpolymer.
- Studied the effect of different membrane components on membrane properties by exploring thermal properties of composites.
- Optimized the terpolymer composition (content of CTFE, styrene and level of sulfonation) to improve membrane mechanical properties.
- Improved membrane mechanical properties using an addition of hexafluoropropylene (HFP) and an increase of copolymer molecular weight, reduced swelling by 50% without compromising the conductivity.

- Achieved a conductivity of 54 mS/cm at 30°C, 80% RH and 30 mS/cm at 120°C, 50% RH; 100 mS/cm at 120°C, 70% RH.
- Synthesized highly conductive inorganics such as sulfated zirconia, sulfated titania and phosphosilicate gels for use in composite membrane preparation.
- Characterized inorganic materials by powder X-ray diffraction, scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area and porosity.
- Designed and constructed a measurement system for determining proton conductivity of the inorganic materials at different temperatures and RH.



## Introduction

This project addresses one of the main challenges in present-day PEM fuel cell 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 PEM fuel cell much more cost efficient and adaptable to practical operating conditions and facilitate its faster commercialization particularly in automotive applications.

## Approach

To achieve the project objectives, the approach being employed is to develop 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 P(VDF-CTFE) copolymer with styrene grafted and sulfonated side chains binds and assembles the inorganic particles into a continuous medium. Inorganic proton conductors interact with the ionomer to improve its properties. Inorganic materials having low dependence of the conductivity on RH can be very beneficial for improvement of composite membrane properties.

## Results

In the past year, the main effort was centered on development of the synthesis routes for the preparation of a highly conductive polymer based on a functionalized P(VDF-CTFE) copolymer to obtain a desirable membrane conductivity without an addition of Nafion<sup>®</sup> and on a synthesis of highly conductive inorganic for use in composite membrane preparation. To fabricate a highly conductive polymer, the P(VDF-

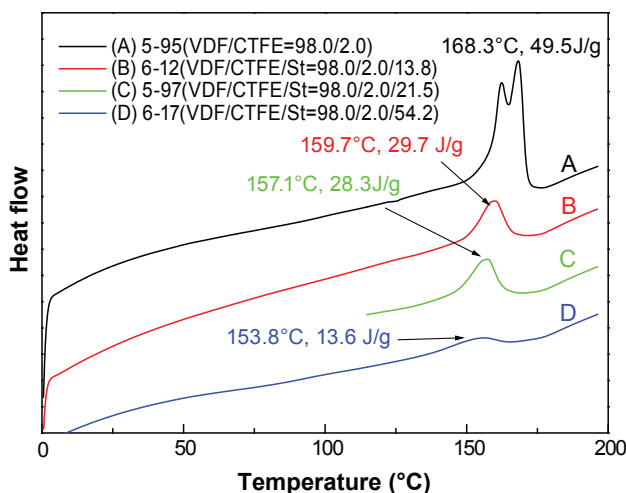
CTFE) copolymer was grafted with styrene (St) via atom transfer radical polymerization (ATRP) followed by partial or the whole sulfonation of phenyl groups. The samples of P(VDF-CTFE-g-St) materials with different composition and corresponding sulfonation products P(VDF-CTFE)-g-St-SSt were prepared and membranes were fabricated using a solution casting technique. At certain level of sulfonation, high conductivity was achieved but the membranes had an excessive swelling and brittleness.

To understand the effect of different membrane components on membrane properties, thermal properties of composites have been investigated using differential scanning calorimetry (DSC). It was found that the increase in CTFE content resulted in the decrease of the melting point and fusion heat, indicating changes in membrane crystallinity (Table 2). The variation of CTFE content in a membrane alternates the membrane crystallinity and, in addition, it can regulate the active sites of the ATRP process, which could change the branch density and branch length of the P(VDF-CTFE)-g-St terpolymer. An increase of styrene content (Figure 1) and the degree of sulfonation had a similar effect on thermal properties, indicating changes in membrane crystallinity as well. Balancing the content of these three components allowed to improve membrane flexibility and to decrease swelling. The high temperature conductivity (120°C) of the highly sulfonated samples (27% sulfonic groups) exceeded conductivity of Nafion<sup>®</sup> at 70% and 50% RH. However, the swelling of these samples was substantially higher than that of Nafion<sup>®</sup>.

**TABLE 2.** Effect of CTFE Content on VDF-CTFE Copolymer Melting Point and Fusion Heat

Composition (VDF-CTFE)	T <sub>m</sub> (°C)	ΔH (J/g)
99.0/1.0	172.9	49.5
98.0/2.0	168.3	47.9
96.6/3.4	160.6	36.4
95.4/4.6	157.8	29.1
92.8/7.2	152.6	18.0

For further improvement of membrane mechanical properties, two approaches have been investigated; an addition of HFP to P(VDF-CTFE) copolymer and an increase of P(VDF-CTFE) copolymer molecular weight (MW). The addition of 3.4% HFP allowed substantial improvement of membrane plasticity and a 1.5 time decrease in swelling without compromising the conductivity. The MW of the copolymer was increased by five times using a high MW commercial copolymer with 6 mol% of CTFE. The preparation process of proton conductive terpolymers is shown in Figure 2. In order to control the grafting density of the commercial P(VDF-CTFE), we manipulated the



**FIGURE 1.** Effect of Polystyrene Content on the DSC of P(VDF-CTFE)-g-St Terpolymer

content of Cl, converting some CTFE units into TrFE units via hydrogenation reaction. Then, the ATRP and sulfonation reactions were conducted in the same manner as with low MW copolymers, and a series of P(VDF-TrFE-CTFE)-g-SSt-based conductors with varied ion exchange capacity were synthesized. The membranes with increased MW demonstrated 50% less swelling than those with low MW but substantially higher than Nafion<sup>®</sup>.

For further improvement of membrane properties, the inorganic materials known to exhibit high proton conductivity (around  $0.01 \text{ Scm}^{-1}$ ) at low RH [1-5], such as sulfated zirconia, sulfated titania and phosphosilicate gels were synthesized for use in composite membrane preparation. All the samples were characterized

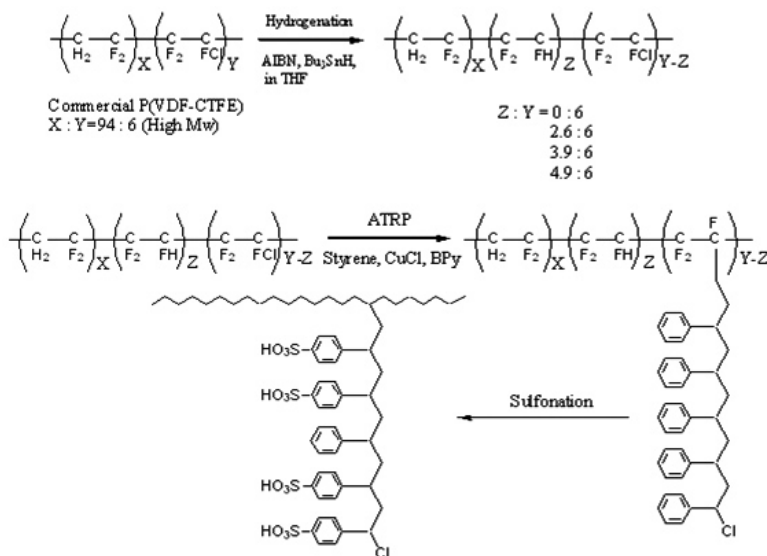
by powder X-ray diffraction and SEM. The BET surface area and porosity of pellets were measured by N<sub>2</sub> adsorption/desorption isotherm analysis. For determining proton conductivity of the inorganic, a measurement system was designed and constructed. The system allowed the conductivity measurements in the temperature range from 25 to 130°C and at 0-100% RH.

## Conclusions and Future Directions

The second year has resulted in fabrication of highly conductive inorganic and a highly conductive styrene grafted and sulfonated P(VDF-CTFE) terpolymer and improvement of its mechanical properties by balancing terpolymer composition. A further modification of the terpolymer will be conducted using inorganic proton conductors which have reduced or no reliance on hydration. In the next year we intend to pursue the following areas:

- Examination of new inorganic additives for conductivity, structure and particle size.
- Development of corresponding fabrication conditions for new types of composite membranes.
- Examination of new composite membranes for conductivity, dimensional swelling, structure, inorganic particle size distribution (SEM, transmission electron microscopy, atomic force microscopy), interaction between ionomer and inorganic moiety (infrared, nuclear magnetic resonance).

We anticipate reaching membrane conductivity at 120°C and 50% RH close to the DOE goal of 100 mS/cm in the next year.



**FIGURE 2.** Synthesis of P(VDF-CTFE)-g-SSt Proton Conductors of High Molecular Weight

## FY 2008 Publications/Presentations

1. M. Chung, Z. Zhang, E. Chalkova, C. Wang, M. Fedkin, S. Komarneni, S. Sharma, and S. Lvov, *Proton Conductive Composite Materials Using Functionalized and Crosslinkable VDF/CFTE Fluoropolymers and Proton Conductive Inorganics*, ECS Trans., 11(1), 35-47 (2007).
2. M. Chung, Z. Zhang, E. Chalkova, C. Wang, M. Fedkin, S. Komarneni, S. Sharma, and S. Lvov, *Proton Conductive Composite Materials Using Functionalized and Crosslinkable VDF/CFTE Fluoropolymers and Proton Conductive Inorganics*, The 212<sup>th</sup> Electrochemical Society Meeting, Washington D.C., October, 2007.

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1. S. Hara and M. Miyayama, *Solid State Ionics*, **168**, 111 (2004).
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