

V.D.3 New Proton Conductive Composite Materials with Co-Continuous Phases Using Functionalized and Crosslinkable VDF/CTFE Fluoropolymers

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Objectives

- Synthesize new cross-linkable polyolefin-based proton conductors with excellent mechanical strength and thermo and chemical stability.
- Synthesize highly conductive inorganic of different structural types with different functional groups for use in composite membrane preparation.
- Test the inorganic in Nafion[®]-based composite membranes to select the most promising materials for the future composite membranes based on the newly developed polymeric materials.
- Develop a new membrane material based on the combination of inorganic proton conductors with a newly developed polyolefin based proton conductors to be used in proton exchange membrane (PEM) fuel cell 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:

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

Technical Targets

This project is conducting fundamental studies on polymer/inorganic composite membranes. Insights gained from these studies will be applied toward the design and synthesis of composite membranes that meet the following DOE 2010 targets for membranes (automotive):

- Membrane conductivity at 120°C and 1.5 kPa water pressure 0.1 S/cm.
- Durability: 5,000 hours.
- Cost: \$5/kWh.

Accomplishments

- Synthesized new cross-linkable polyolefin-based proton conductors with excellent mechanical strength, which are very stable under free radical conditions.
- Synthesized highly conductive inorganic of different structural types with different functional groups such as cylindrical mesoporous silica (SBA-15), mesoporous silica with arrays of hexagonal channels (MCM-41), S-ZrO₂, sulfonic acid functionalized cubic cage mesoporous silica (HOM-1), and P/Si 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, porosity, ion exchange capacity (IEC), and conductivity.
- Achieved a conductivity of 10 mS/cm for S-ZrO₂ at 120°C and 100% RH and 100 mS/cm for phosphosilicate gel with P/Si ratio of 1.5 at 120°C and 70% RH.
- Tested functional inorganic in Nafion[®]-based composite membranes; conducted comparative measurements of swelling, IEC and conductivity of Nafion[®]/inorganic composite membrane with different type of inorganic, different inorganic loading and different fabrication techniques.

- Tested the effect of inorganic on the composite membrane performance in a fuel cell.



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 and stationary applications.

Approach

Our approach addresses the barriers in the development of PEMs such as high-temperature low-RH conductivity and durability and DOE conductivity milestone of 100 mS/cm at 120°C, 50% RH. To overcome this barrier, the approach being employed to develop a composite membrane with hydrophilic proton-conductive inorganic material and the proton conductive polymeric matrix that is able to “bridge” the conduction paths in membrane. The unique aspect of our approach is the use of highly functionalized inorganic additives to benefit from their water retention properties and high conductivity as well.

Results

In the past year, the main effort was centered on the development of a new class of proton conducting materials, synthesis and characterization of highly conductive inorganic and testing the inorganic in composite membranes. Novel cross-linked polyolefin copolymers that contain both crystalline hydrophobic phase and amorphous hydrophilic phase with co-continuous and clear phase separated morphology was synthesized. The major reason of changing the polymer to polyolefin is to improve the chemical and mechanical stability of PEM composites. Polyolefins, such as polyethylene (PE) and polypropylene (PP), are known to be very stable in strong acids and bases, as well as under free radical conditions. Both PE and PP are also semicrystalline thermoplastics with excellent mechanical strength, as well as most hydrophobic materials. This combination could provide a stable polymer matrix with limited swelling and the ability to retain water in the inorganic domains for transporting protons at 120°C. We have developed several powerful methods in the preparation of functional PE and PP polymers, which offer the potential to engineer polyolefin-based

PEM structure (concentration of sulfonic acid groups for increasing conductivity, degree of crosslinking for controlling swelling). The structure of the newly synthesized polyethylene based proton conductor (PE) is shown in Figure1.

Inorganic proton conductors of different structural types with different functional groups, such as alkane sulfonic functionalized cylindrical mesoporous silica (SBA-15), sulfonic acid functionalized mesoporous silica with arrays of hexagonal channels (MCM-41), sulfated zirconia (S-ZrO₂), sulfonic acid functionalized cubic cage mesoporous materials (HOM-1), and phosphosilicate gels with different P/Si molar ratios were synthesized. All the samples were characterized by powder X-ray diffraction and SEM. The BET surface area and porosity of pellets were measured by N₂ adsorption/desorption isotherm analysis. The IEC was measured by titration with NaOH solution after the completion of ion exchange with NaCl. The proton conductivity of the inorganic was measured using previously designed device and measurement method.

To compare the properties and behavior of different inorganic materials under fuel cell conditions, we prepared and characterized the composite membranes with these inorganic proton conductors. Nafion[®] was chosen as the reference matrix material for such series because it is the best studied polymer with well-known properties. Three different techniques were used to fabricate Nafion[®]/inorganic composite membranes by: (1) blending of inorganic powders with Nafion[®] solution followed by casting and annealing, (2) in situ forming the inorganic particles from infiltration of precursor solution into Nafion[®] film, and (3) in situ forming the inorganic particles from precursor in Nafion[®] solution followed by casting and heat treatment. Technique (1) was used for the preparation of composite membranes with all inorganic materials, while techniques (2) and (3) were used for the preparation of Nafion[®]/P-Si gel composite membranes only.

The membranes prepared by technique (1) were tested for swelling, IEC, conductivity and fuel cell performance. It was found that the IEC of all Nafion[®]/inorganic composite membranes was higher than that

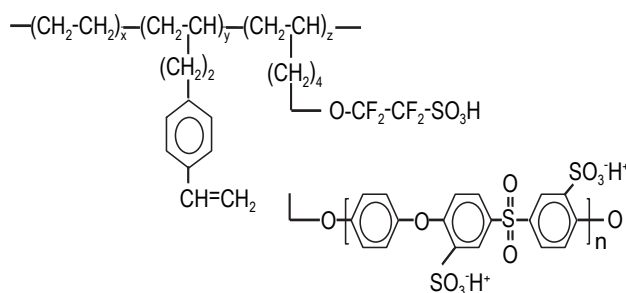


FIGURE 1. New Polyethylene-Based Proton Conductor

of Nafion[®]. The conductivity of composite membranes with 10% of different sulfonated inorganic, was different for different membranes but not higher than the conductivity of recast Nafion[®]. None of these inorganic materials enhanced the conductivity of polymeric matrix. The conductivity measurements of composite membranes were in agreement with their IEC. No correlation between membrane conductivity and swelling was found. The effect of the inorganic content on the membrane conductivity was evaluated on a series of Nafion[®]/SiO₂-SO₃H composite membranes with SiO₂-SO₃H content of 10-120% from the amount of polymeric matrix. The increase in SiO₂-SO₃H content above 10% gradually decreased the membrane conductivity, probably, due to particle agglomeration. No conductivity enhancement was found when doping level was decreased to 3-0.5% (Nafion[®]/3%S-ZrO₂, Nafion[®]/0.5%P-Si, and Nafion[®]/0.5%SBA-15 membranes). It was found that the conductivity of Nafion[®]/phosphosilicate gel composite membranes was affected by surface area of P-Si gel powder.

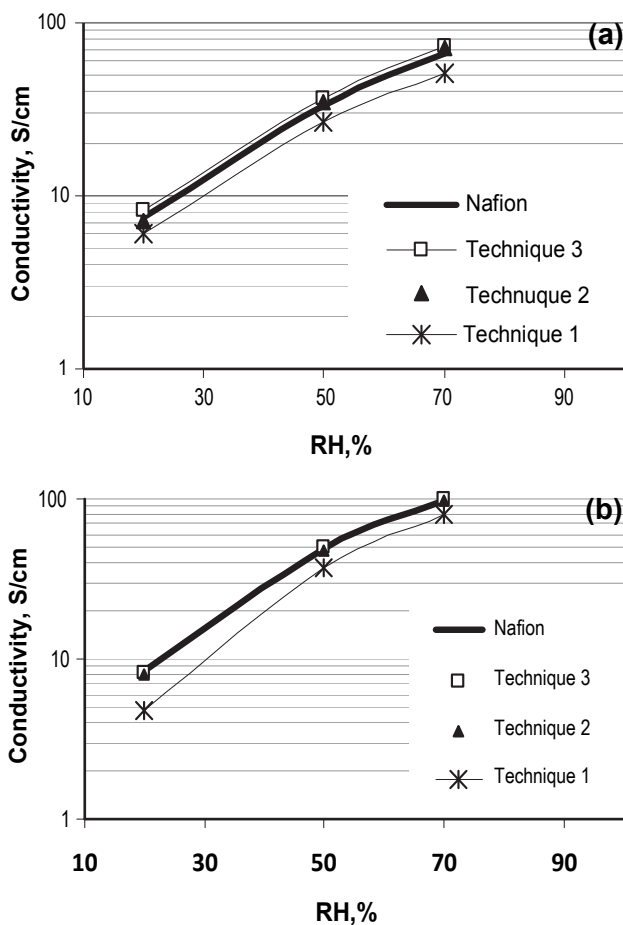


FIGURE 2. Conductivity of Nafion[®]/10% P-Si gel composite membranes prepared using different techniques at 80°C (a) and 120°C (b) and different RH.

The effect of membrane fabrication technique was evaluated on Nafion[®]/10% phosphosilicate gel membranes. The performance of the membrane prepared by blending of inorganic powders with Nafion[®] (Technique 1) was the lowest. The performance of the membranes prepared by in situ formation of inorganic particles in Nafion[®] (Techniques 2 and 3) was higher and very close to each other (Figure 2). The effect of inorganic phase on membrane performance in fuel cell was much stronger. The resistance of Nafion[®]/10% P-Si gel composite membrane in a fuel cell was 40-50% less, and the limiting current about 40-50% higher than those of pure recast Nafion[®] (Figure 3).

Conclusions and Future Directions

The third year of the project resulted in the development of polyolefin-based polymeric proton conductors with excellent mechanical strength and stability under free radical conditions; intense synthesis

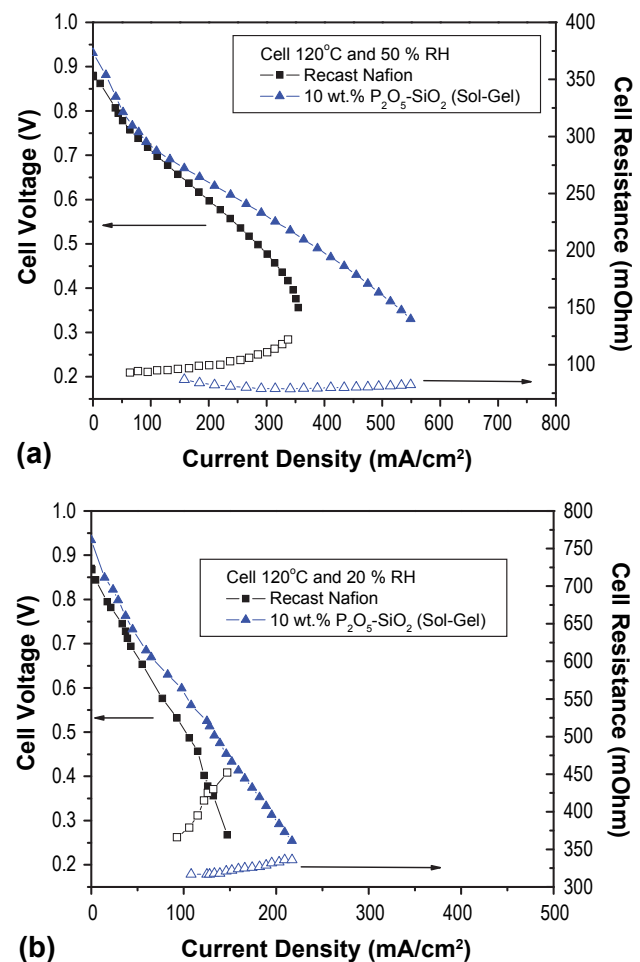


FIGURE 3. Performance and fuel cell resistance of Nafion[®]/10%P-Si gel membranes in H₂/Air fuel cell at 120°C and 50% (a) and 20% (b) RH.

and characterization of different types of functional inorganic; testing the inorganic in Nafion[®]-based composite membranes. These tests allowed us to select the most promising materials for the future composite membranes based on the newly developed polymeric materials.

The next step should be the development of composite sulfonated polyolefin/inorganic membranes. The first candidate for testing should be sulfonated PE/phosphosilica gel membrane fabricated using in situ formation Technique 3 described previously.

FY 2009 Publications/Presentations

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2. C. Wang, E. Chalkova, C. Lute, M. Fedkin, S. Komarneni, T.C.M. Chung, and S. Lvov, *Proton conductive inorganics for composite membranes in PEM fuel cells*, *ECS Trans.*, 16 (2), 1451 (2008).
3. M. Chung, Z. Zhang, E. Chalkova, C. Wang, M. Fedkin, S. Komarneni, and S.N. Lvov, *Recent advance in proton conductive materials using styrene grafted and sulfonated VDF/CTFE fluoropolymers*, *ECS Trans.*, (2008) submitted.
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5. C. Wang, E. Chalkova, C. Lute, M. Fedkin, S. Komarneni, T.C.M. Chung, and S. Lvov, *Proton conductive inorganics for composite membranes in PEM fuel cells*, 14th ECS Meeting, Hawai, October15, 2008.
6. M. Chung, Z. Zhang, E. Chalkova, C. Wang, M. Fedkin, S. Komarneni, and S. N. Lvov, *Recent advance in proton conductive materials using styrene grafted and sulfonated VDF/CTFE fluoropolymers*, 13th ECS Meeting Phoenix, May 18, 2008.
7. C. Wang, E. Chalkova, M. Fedkin, S. Komarneni, T.C.M. Chung, and Serguei N. Lvov, *Conductivity studies of inorganic proton conductors for composite membranes in PEM fuel cells*, 13th ECS Meeting Phoenix, May 18, 2008.