V.N.20 Preparation of Composite Fuel Cell Membranes Containing Electric Field Aligned Inorganic Particles

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Objectives

- To design particles with desirable properties, such as proton conductivity, water retention at elevated temperatures, and methanol barrier properties.
- To use the novel particles in composite fuel cell membranes.
- To control the microstructure of the membranes through the application of AC and DC electric fields during membrane formation.

Technical Barriers

- Through the control of membrane microstructure and by creating novel membrane compositions, the research aims to improve fuel cell membrane properties to reduce technical barriers that limit widespread fuel cell adoption:
- Enhance proton conductivity
- Reduce fuel permeability
- Lower membrane cost
- Increase temperature of operation

Abstract

Electric fields were used to control the structure of polymer composite proton conducting membranes. Under appropriate conditions, functional particles dispersed in the polymer can be aligned into chains in the direction of the applied field. The resulting composite membranes are anisotropically structured with proton conduction greatly enhanced in the alignment direction. Future work will examine the use of these novel structured materials in fuel cells.

Progress Report

Several different types of functional particles were synthesized, including acid-filled mesoporous silica spheres, silica tubes, titania tubes, calcium phosphate rods, calcium carbonate rods, zirconium phosphate rods, sulfonated crosslinked polystyrene spheres, sulfonated poly(ether ether ketone) spheres, and ground Nafion® powder. The particle synthesis work has so far resulted in two publications (Liu et al, *Langmuir*, **2006** and Liu et al, *Chem. Mater.*, **submitted**). Hygroscopic particles, such as those made from silica and titania, were chosen because they are expected to aid in water retention at elevated temperatures when added to polymeric fuel cell membranes. Other particles, such as those made from sulfonated polymers or mesoporous silica filled with tungstophosphoric acid, were chosen for proton conductivity. The particles were suspended in a solvent or a polymer solution and electric fields were applied to induce the particles to rotate, align, and form structured aggregates. A variety of solvents and polymer solutions were examined, including Fomblin (a fluorocarbon oil), toluene, silicone oil, curable polydimethylsiloxane resin, Nafion® in DMF solution, polystyrene in THF solution, teflon suspension in water, poly(vinyl alcohol) in water solution, poly(vinylidene fluoride) in NMP solution. Figure 1 shows the apparatus built to examine the response of particle suspensions to an applied electrical field. A function generator is used for controlling field frequency and waveform. The output of the function generator is sent to a 1000x voltage amplifier. The high voltage signal is connected to micropatterned electrodes on microscope slides and an inverted phase contrast

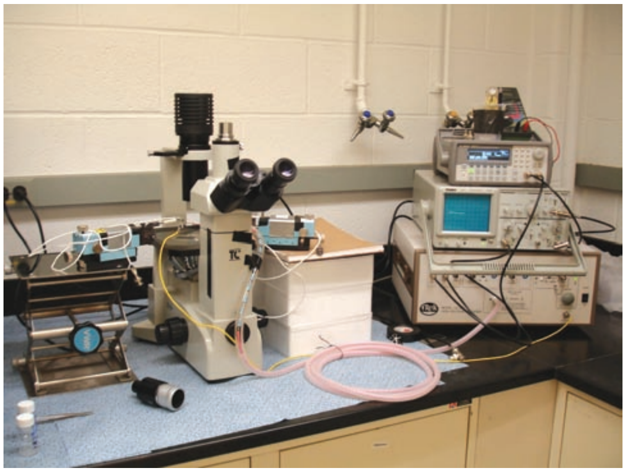

FIGURE 1. Apparatus for observing particle motion due to an applied electric field.

microscope is used for particle observation. A digital camera was connected to the microscope to record images and video of particle motion under the influence of the applied field. For insulating solvents with low dielectric constant, particle response is insensitive to the frequency of the applied field. For conductive solvents, alignment occurs only in a narrow range of voltage and frequency that depends on the solvent and particle examined. For highly conductive polymer solutions such as sulfonated PS dissolved in H_2SO_4 solution, it is often difficult or impossible to find suitable conditions to align particles.

Using the information gathered from visual observation of the response of particles to applied electric fields, composite membranes were formed in which the structure of the membranes was controlled by application of an appropriate electric field during membrane formation. Initial experiments were carried out using a curable poly(dimethyl siloxane) (PDMS) resin as a model polymer matrix. Crosslinked PDMS is a flexible, durable membrane material that is easy to form and manipulate. However, PDMS has poor gas barrier properties that make it unattractive for use in fuel cells. PDMS was simply used as a model non-proton conducting matrix into which proton conducting particles were dispersed. Figure 2 shows microscopy images of a composite membrane with 5 wt % sulfonated poly(ether ether ketone) (SPEEK) particles dispersed in crosslinked PDMS. In Figure 2a the particles appear randomly distributed without an applied electric field. In Figure 2b, it can be seen that the SPEEK particles form “string of pearl” chains when an AC electric field of 25 Hz frequency and a field strength of 1000 V/cm (Vrms) was applied for 10 minutes prior to curing the PDMS. The structure formation allows for proton conducting channels in the polymer composite. Proton conductivity measurements at room temperature and 100% relative humidity show that a 14 wt% SPEEK/PDMS composite with randomly oriented SPEEK

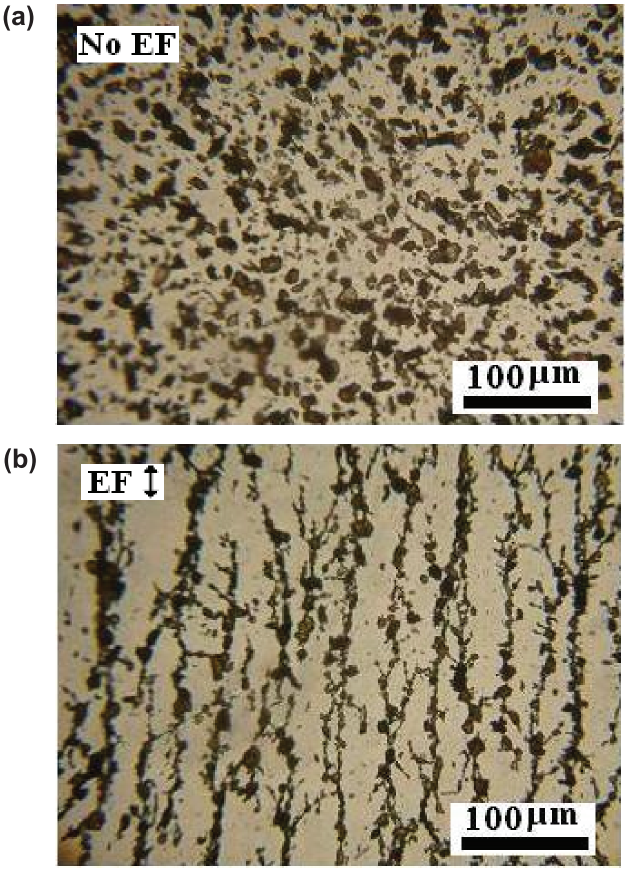

FIGURE 2. SPEEK/PDMS composite formed (a) without and (b) with an applied electric field prior to curing polymer.

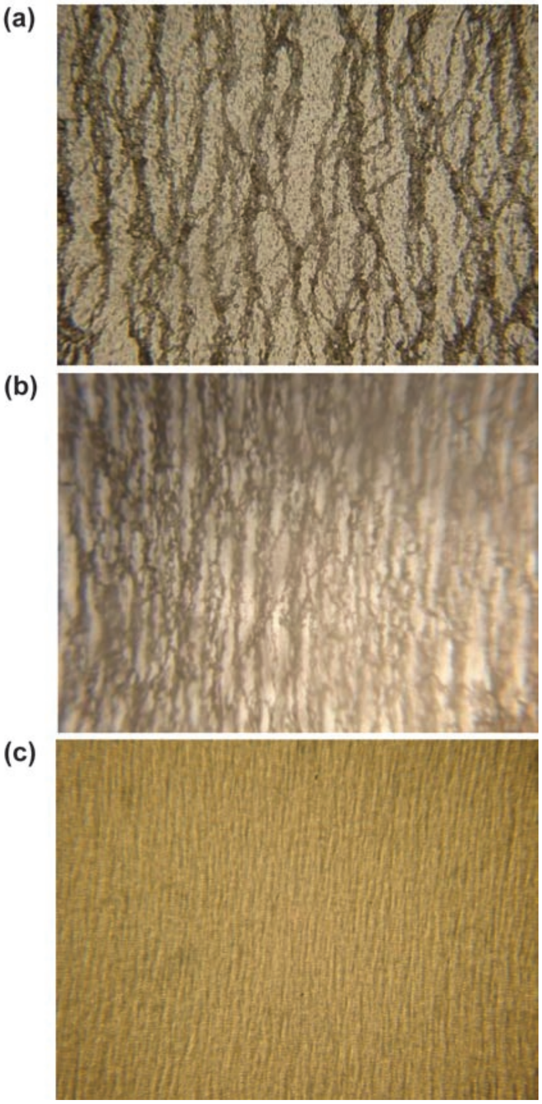

FIGURE 3. (a) 5 wt% Nafion® in PVA, (b) 10 wt% SPEEK in PVA, and (c) 5 wt% sulfonated polystyrene in PVDF. In each case, particles are aligned in the direction of the field applied during solvent casting of the membrane.

particles has a conductivity of 3.38 x 10^{-6} S/m. When the SPEEK particles are aligned as in Figure 2b, the conductivity increases in the direction of alignment more than 1,000 fold to 8.74 x 10^{-3} S/m. Enhancement in conductivity by the applied field was also observed for mesoporous silica particles filled with tungtophosphoric acid (TPA) dispersed in the PDMS resin. For a PDMS composite with 10 wt% TPA filled silica, the proton conductivity at 50°C and 100% relative humidity was 6.5 x 10^{-2} S/m for randomly oriented particles. The conductivity increased to 2.5 x 10^{-1} S/m in the direction of alignment when the particles were aligned into chains by an applied field.

When conductive particles are dispersed in a nonconductive matrix, the resulting composite material will be conductive if the volume fraction of particles is high enough. As the volume fraction is increased, a percolation threshold is reached where the particles become interconnected and continuous conductive pathways form. A series of experiments were conducted on SPEEK/PDMS composites of increasing SPEEK volume fraction to examine the effect of the electric field on the percolation threshold. For randomly oriented SPEEK particles, the percolation threshold was approximately 36 wt% SPEEK. When particles were aligned by the electric field, the percolation threshold was reduced to approximately 10 wt% SPEEK for conductivity measured in the direction of alignment. The results show that the applied electric field can be used to reduce the amount of conductive particles needed in the composite. By lowering the volume fraction of particles dispersed in the polymer, the membrane can have improved mechanical stability.

Electric fields can also be used to control structure of composite membranes formed by solvent casting. Poly(vinyl alcohol) (PVA) and poly(vinylidene fluoride) (PVDF) were chosen for solvent casting experiments because these two polymers have more attractive properties than those of PDMS for fuel cell applications, including better barrier properties and higher chemical stability. Various types of particles were dispersed in PVA and PVDF solutions and electric fields were applied during solvent casting to obtain structured membranes. Figure 3 gives examples of composite PVA and PVDF membranes formed by solvent casting under an applied electric field. Under appropriate conditions, membranes can be formed that are structured with the particles forming chains aligned in the direction of the applied field. As with PDMS based membranes, conductivity can be enhanced in the direction of alignment.

Future Directions

The University of Rochester is currently renovating space to house a fuel cell testing laboratory. The laboratory is scheduled for completion June 1, 2007 and will be able to test both hydrogen fuel cells and direct methanol fuel cells. Promising membrane materials will be used in single fuel cells and performance tested in the new laboratory. It is expected that aligned, structured composite membranes will display improved performance due to enhanced conductivity.

A methanol permeability cell has been constructed and the composite membranes will be tested for methanol permeability. The aim will be to control the membrane structure to enhance proton conductivity while limiting the increase in methanol permeability. Promising membrane materials can be tested as single direct methanol fuel cells. It is expected that composite membranes of controlled structure will display improved fuel cell performance due to reduced fuel crossover.

Publications (Including Patents) Acknowledging the Grant or Contract

1. Liu, D.; Yates, M. Z. "Formation of Rod-Shaped Calcite Crystals by Microemulsion-Based Synthesis" *Langmuir* **2006**, *22*, 5566-5569.

2. Liu, D.; Yates, M. Z. "Fabrication of Size-Tunable TiO_2 Nanotubes Using Rod-Shaped Calcite Templates" *Chemistry of Materials* **2007**, submitted.