Chem. Mater. **2005,** *17,* 5880−5883

Preparation of Three-Dimensionally Ordered Inorganic/Organic Bi-Continuous Composite Proton Conducting Membranes

Sheng-Li Chen,* Ke-Qi Xu, and Peng Dong

State Key Lab of Heavy Oil Processing and Department of Chemical Engineering, China University of Petroleum, Changping, Beijing 102249, People's Republic of China

Received April 3, 2005
Revised Manuscript Received October 9, 2005

The proton conducting membrane is the key component of polymer electrolyte membrane fuel cells (PEMFCs). The membrane must physically separate the fuel and oxygen, have good proton conductivity, and be chemically robust to oxidation. Nafion (DuPont),[1] a perfluorosulfonic acid polymer, is the most widely used proton conductor in PEMFCs. Nafion is chemically robust in oxidizing environments and has good proton conductivity when hydrated. However, methanol permeation is high in Nafion,[2] decreasing the fuel cell performance when methanol is used as fuel. Operation of Nafion membrane fuel cells has been limited to temperatures below 80 °C, owing to decreased mechanical strength at higher temperature and the need to keep the membrane hydrated.[3] At these temperatures PEMFC electrodes are highly susceptible to poisoning by parts per million concentrations of CO in the hydrogen feed; heat rejection at the low temperature is more cumbersome. High-temperature operation of a PEMFC (above 120 °C) has been investigated to reduce the effect of CO adsorption onto the platinum electrocatalyst.[4,5] Metal oxide/Nafion composites have shown promise to increase the operating temperature regime of PEMFCs.[6,7] It would be desirable to find a less costly proton conducting material than Nafion (presently, \$175/m^2 for 100 μm thick membranes).[8]

Extensive research is currently devoted to the development of new proton conducting membranes to replace Nafion. Low-cost nonperfluorinated ionomer membranes have been prepared and tested, including poly(trifluorostyrene),[9] poly(ether ether ketone),[10] poly(arylene ether sulfone) (PSU),[11] poly(vinylidene difluoride)-*graft*-styrene,[12] acid-doped polybenzimidazole (PBI),[13] and polyphosphazene.[14] With the exception of the acid-doped PBI, all polymer membranes have sulfonic acid group as the ionic group. Water is essential for the proton conductivity with the sulfonic acid membranes; water promotes the dissociation of proton from sulfonic acid and provides the highly mobile hydrated protons. Therefore, all ionic polymer membranes have the drawback of low ionic conductivity at low relative humidity, and only a limited number of systems exist that hold promise for long-term operation above 100 °C.[15]

A second approach is the preparation of composite inorganic/organic membranes. Some researchers have shown that the addition of inorganic materials (particles) into the proton exchange membranes could improve the high-temperature conductivity, mechanical strength, and chemical stability of Nafion membranes improving the fuel cell performance at elevated temperatures.[3,16,17] There are several hypotheses to explain the improved high-temperature fuel cell performance of inorganic/organic membranes; however, it is generally accepted that the mechanical strength and chemical stability are improved from the interaction between the ionic polymer and the surface of the dispersed inorganic particles. Composite membranes were also found to have lower methanol permeability than the plain ionic polymer membranes.[16,18] A wide variety of inorganic materials have been studied for composite materials, including SiO_2,[3,16−19] TiO_2,[18] $H_3PW_{12}O_{40}$, ZrP, ZrO_2,[18,20] $ZrSO_4$, $ZrHPO_4$,[19] Al_2O_3,[21] and heteropolyacids.[22,23]

Two methods of synthesis have been employed to produce inorganic/organic composite membranes. One is the direct addition of inorganic particles into a solution of the ionic polymers followed by recasting of the membrane.[17,18,20] The other is impregnation of cast membranes with solutions of inorganic precursors which are reacted in situ to produce a metal oxide sol gel. Composites of silica, titania, or zirconia with Nafion have been produced from in situ sol−gel synthesis with tetraethoxysilane, monophenyl trimethoxysilane, titanium tetraethylate, and zirconium tetrapropylate.[3,16,18] Silica (SiO_2) is the most commonly tested inorganic filler

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* Corresponding author: Prof. Sheng-Li Chen. Tel.: 86-10-89733783. Fax: 86-10-69724721. E-mail: slchen@cup.edu.cn.

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10.1021/cm050709a CCC: \$30.25 © 2005 American Chemical Society
Published on Web 10/29/2005

for the composite membranes. It is abundant and can be prepared by different routes in several different structural forms.

In previous studies of composite proton conducting membranes the inorganic materials (particles) in the composite membranes were randomly distributed and isolated from each other in the organic polymers. The inorganic materials were a discontinuous phase dispersed in the continuous phase of organic polymer. It has been reported that an organic/organic bi-continuous composite proton conducting membrane demonstrated a low permeation of methanol, a good mechanical strength, and chemical stability.[24,25] Therefore, if both the inorganic materials and the ionic polymer could be continuous in the composite membranes, the performance of composite membranes should be better. The continuous inorganic materials would provide the membrane with greater mechanical strength than the isolated inorganic particles. The bi-continuous phase may also retain water at higher temperature as a result of capillary condensation in the pores of the inorganic matrix.[7]

We report here the synthesis of a three-dimensionally (3-D) ordered SiO_2/sulfonated PSU (SPSU) composite membranes. SPSU was obtained through the sulfonation of PSU, which is a chemically stable and cheap ionomer. An inverse silica opal was formed from self-assembly of monodispersed polystyrene (PS) spheres with a SiO_2 sol. The PS particles were removed from the SiO_2/PS structure producing an ordered porous SiO_2 material. The 3-D ordered SiO_2/SPSU composite membranes were obtained by filling SPSU into the pores of the SiO_2 materials.

Preparation of PS Particles. Uniform PS particles were synthesized through the microemulsion method.[26] A total of 150 mL of H_2O, 18.4 mL of styrene, 0.0833 g of $NaHCO_3$, and 0.080 g of $C_8H_7SO_3Na$ (sodium styrene sulfonate) were measured into a magnetically stirred 300 mL reactor. The reactor was kept at 75 ± 0.1 °C and was stirred at ~250 rpm. Polymerization was initiated by adding 0.083 g of $K_2S_2O_8$ into the reactor. The polymerization was carried out under a nitrogen atmosphere. Polymerization was completed in about 10 h. The PS particles were about 12 wt % suspended in the aqueous solution. The ionic strength of the PS particle suspension was reduced from 587 μS/cm to 16 μS/cm by passing the solution over ion-exchange resin beads. The PS particles were 212 nm as measured by a HITACHI H-800 transmission electron microscope.

Preparation of the Silica Sol. A silica sol was prepared through the hydrolysis and condensation of tetraethylorthosilicate (TEOS) using HCl and ethanol as the catalyst and the mutual solvent, respectively. The mole ratio of TEOS/EtOH/HCl/H_2O was 1:1.3:0.032:2.2. The solution was allowed to react overnight at room temperature. The prepared silica sol suspension was transparent. To obtain the size distribution of the silica particles, the silica solution was diluted with ethanol to 5 wt % SiO_2 sol solution and then measured by a Malvern Zetasizer Nanosizer dynamic light scatterer at 25 °C.

Synthesis of SPSU. The synthesis of SPSU is described elsewhere.[27] It is briefly described as follows. PSU, P-3500, obtained from Solvay Advanced Polymers Co., was dissolved in dichloroethane at room temperature for about 5 h under an Ar atmosphere and stirring conditions. A total of 2.86 mol of trimethysilyl chlorosulfonate per mole of polysulfone monomer were added to the solution to perform the sulfonation. During the reaction, HCl was continuously released out of the reactor. The reaction was carried out for 36 h; the sulfonation reaction was quenched by adding as much as two times as many moles of methanol as moles of the sulfonation agent into the reaction vessel. The products were dried in an ~130 °C oven, and the silicon-containing compounds were removed from the products by the evaporation method.[27] The sulfonation degree could be controlled by varying the mole ratio of the sulfonation agent to the polymer.

Preparation of the 3-D Ordered Inorganic/Organic Composite Membranes. The silica sol and monodispersed PS particles were dispersed into redistilled water. The binary particle suspension contained ~1 wt % PS particles, and the volume ratio of the silica particles to the PS particles in the suspension was around 26:74, which is equal to the volume ratio of the pore to the spherical particles packed in the face-centered cubic (fcc) structure. A glass plate was suspended vertically in the container holding the suspension, and the container was placed in a 60 °C oven. After the water evaporated, a SiO_2/PS film was formed on the glass substrate.

To obtain an inverse SiO_2 opal film, the PS was extracted from the composite material by dissolution in a mixture of 50 vol % tetrahydrofuran (THF) and 50 vol % acetone. Finally, the SiO_2 inverse opal film was immersed into a SPSU−methanol−*N*,*N*-dimethylacetamide solution containing 10 wt % PSPU and then dried at 130 °C. The 3-D ordered inorganic/organic membrane was obtained through repeating the above immersing and drying steps.

Scanning Electron Microscopy (SEM) Examination. PS particles, the PS/SiO_2 film, and the 3-D ordered composite membranes were examined by a HITACHI S-4200 scanning electron microscope. Before the SEM examination, all samples were sputter-coated with 3 nm of gold.

Nitrogen Adsorption Measurements. The surface area and micropore size distribution of the SiO_2 inverse opal film was measured through nitrogen adsorption with ASAP 2020 VOL 1.03 H equipment. The sample mass was 0.1973 g, and the nitrogen adsorption temperature was −195.9 °C.

Ion-Exchange Capacity Measurements. The ion-exchange capacity (IEC) of SPSU was measured through titration. Recast membranes of SPSU were placed in 1 M H_2SO_4 at room temperature overnight and then rinsed with de-ionized water. The protonated membrane was vacuum-dried at ~80 °C for 3 h, weighed, and placed in 1 M NaCl solutions overnight to exchange the H^+ with Na^+. Finally, the proton content in the salt solution was determined by

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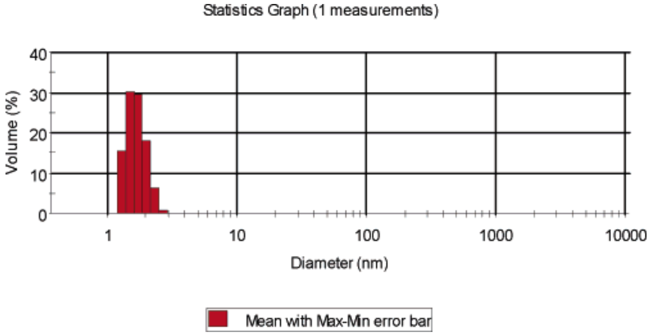

Figure 1. SiO_2 sol size distribution obtained by DLS.

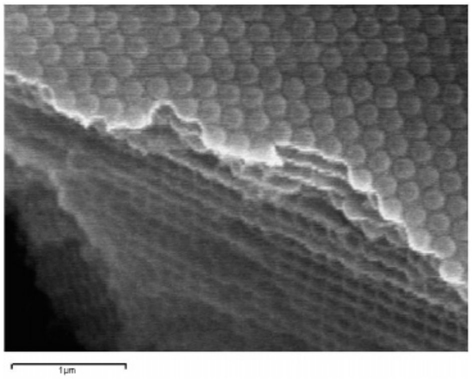

Figure 2. SEM of the SiO_2/PS materials prepared by self-assembly.

titration with a 0.01 N NaOH solution using phenol red as the endpoint indicator.

Conductivity Measurements. Conductivity measurements were performed at 90% relative humidity and 80 °C. Aliquots of water were injected step by step into a container of known volume holding the sample at 80 °C, until the pressure in the barometric container equaled the water vapor pressure at 90% relative humidity and 80 °C. Conductivity measurements were performed using a two-probe method with a CHI604B Potentiostat connected to a PC running electrochemical impedance software.

The transmission electron microscopy showed that the synthesized PS particles were uniform, with a mean diameter of 212 ± 6 nm. The IEC of the synthesized SPSU was 2.33 mequiv/g, corresponding to 1.27 sulfonic acid groups per monomer. The sulfonation degree of the PSU is greater than that of Nafion-115 (0.91 mequiv/g). The conductivity of SPSU was measured by alternating current impedance and was found to be 0.14 S/cm at 80 °C and 90% relative humidity, which is similar to that of Nafion-115.

The silica sol suspension was transparent, and the size of the silica was measured using dynamic light scattering (DLS) on a Malvern Zetasizer Nanosizer. The particle size distribution of the silica sol is shown in Figure 1; the silica particles are ∼2 nm, much smaller than the PS particles.

An ordered silica scaffold was obtained by self-assembly of the PS particles and the silica sol from the water suspension. The prepared SiO_2/PS materials were highly 3-D ordered with the PS having a fcc arrangement, as shown in Figure 2. The entropy of the system was such that the minimum energy positions correspond to those of a fcc arrangement of PS particles, and the silica particles were placed inside the pores between the ordered PS particles.

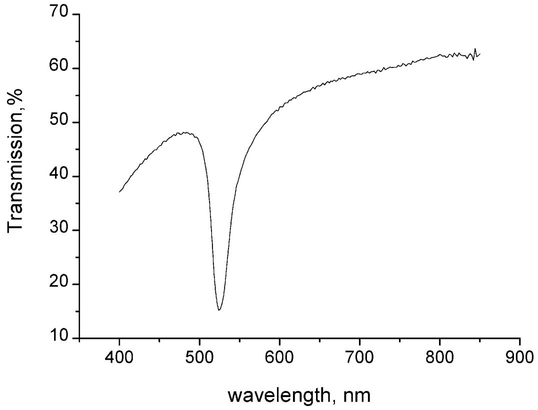

Figure 3. Transmission spectra of SiO_2/PS materials prepared by self-assembly.

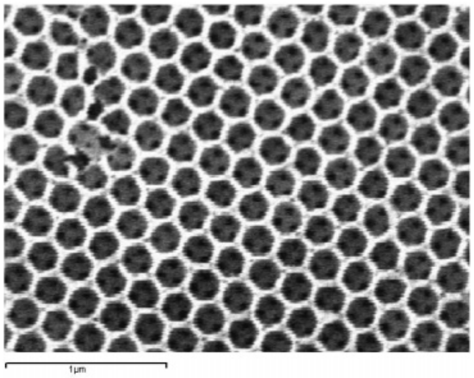

Figure 4. SEM of the inverse opal SiO_2 materials formed by removing PS from SiO_2/PS.

The ordered structure of the SiO_2/PS materials was also evidenced by the photonic band gap of the material. The photonic band was obtained by measuring its optical transmission spectra by an Acton Research Spectrapro-500i, shown in Figure 3. Both SiO_2 and PS are transparent to visible light (400−700 nm). The absorption peak at 523 nm for the SiO_2/PS is a predicted forbidden photonic band gap for the (111) planes of fcc particle packing.[28]

An inverse SiO_2 opal with 3-D ordered pores was obtained by removing PS from the SiO_2/PS materials. The PS was dissolved in a mixture of acetone and THF (1:1 by volume). The SEM image of the 3-D ordered SiO_2 materials is shown in Figure 4. After removal of the PS, there is greater contrast between the SiO_2 framework and the spherical voids. Every particle in the fcc structure has 12 nearest neighbor particles that it touches so that every spherical cavity in the inverse opal has 12 pores connecting to adjacent spherical cavities. Figure 4 shows in detail how three channels communicate with the sphere in the underlying layer.

Nitrogen adsorption measurements for BET and micropore size distribution were made on the inverse SiO_2. The BET surface area was measured to be 745.7 m^2/g, the micropore volume (pore size less than 20 nm) was measured to be 0.386 cm^3/g, and the pore size distribution in Figure 5 shows a preponderance of pores within a diameter of 0.5−1.5 nm. Because the voids left from PS removal are much larger than 2 nm as shown in Figure 4, the above pore volume does not

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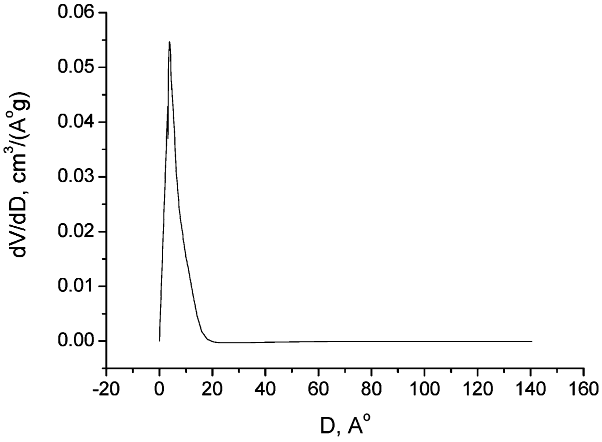

Figure 5. Micropore size distribution of the inverse SiO_2 material.

include the voids left from PS removal. The void fraction of the inverse opal after PS removal should be 74% according to geometry. On the basis of the above data, the total pore volume of the prepared SiO_2 is ~86 vol % or ~2.78 cm^3/g. The large surface area and the preponderance of 0.5−1.5 nm pores indicate that the SiO_2 framework is nanoporous and made of nano-SiO_2 particles.

To obtain a 3-D ordered inorganic/organic composite proton exchange membrane, the pores of the SiO_2 inverse opal were filled with a solution of SPSU−methanol−*N*,*N*-dimethylacetamide, allowing the methanol and *N*,*N*-dimethylacetamide to evaporate. The SPSU filling and the solvent evaporation processes were repeated several times until the mass ratio of SPSU to SiO_2 reached ~70:30. According to the SPSU density (~1.0 g/cm^3) and SiO_2 framework density (~1.19 g/cm^3), the volume ratio of SPSU to SiO_2 framework is ~74:26. The SEM of the composite material is shown in Figure 6. The composite material has the same hexagonal ordering as the original PS/SiO_2 structure. The silica framework has remained intact during the dissolution of the PS and the impregnation with the SPSU. The ionic polymer SPSU has the opal structure while SiO_2 has the inverse opal structure in the composite membrane. Both SiO_2 and the ionic polymer are continuous phases. The ordered and continuous SiO_2 gives the membrane mechanical strength and rigidity, which should improve the lifetime of the membrane and improve the fuel cell performance.[7]

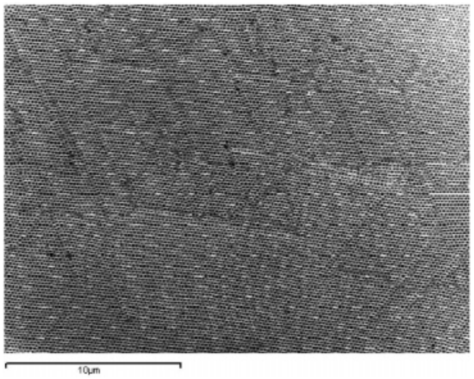

Figure 6. SEM of 3-D ordered SiO_2/SPSU composite membrane.

The high-frequency conductivity of the SPSU/SiO_2 membrane at 80 °C and 90% relative humidity was measured to be 0.102 S/cm. The conductivity of the composite is reduced compared to the polymer itself (0.14 S/cm). This reduction is expected because the proton conductivity is limited to the SPSU phase. The further characterization and fuel cell performance testing of the bi-continuous inorganic/organic composite proton exchange membrane are on going in our lab.

The 3-D ordered inorganic/organic composite proton conducting membrane may also be important for other applications such as water electrolysis, hydrogen separation, sensors, electrocatalytic reaction, chlorine alkaline industry, and other electrochemical devices, which use proton conducting membranes as electrolytes. The synthesis method reported here could be generalized to other inorganic materials and to other ionomers. This procedure should be able to produce tailored materials for a variety of specific applications.

Acknowledgment. The research work was supported by Doctor Program Foundation of the China Education Ministry (Grant 20040425006), by the Foundation of China National Heavy Oil Lab (Grant 2003-07), and by the SRF for ROCS, SEM. The authors are grateful to Prof. Jay Benziger for many helpful discussions and valuable comments.

CM050709A