Protic Ionic Liquid-Based Hybrid Proton-Conducting Membranes for Anhydrous Proton Exchange Membrane Application

Bencai Lin,[†] Si Cheng,[†] Lihua Qiu,[†] Feng Yan,*[,†,‡] Songmin Shang,[§] and Jianmei Lu*[,†]

[†]*Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, and [‡]Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, P. R. China, and [§]Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong, China*

A new type of proton-conducting hybrid membranes were prepared by in situ cross-linking of a mixture of polymerizable oils containing protic ionic liquids (PILs) and silica nanoparticles or mesoporous silica nanospheres. The resultant hybrid membranes are semitransparent, flexible, and show good thermal stability, good and tunable mechanical properties. Incorporation of proper amount of silica fillers significantly increased the proton conductivity of the membranes, probably due to the ion transport channel or network structures formed in the membranes. However, further addition of silica fillers might block the formed ion transport channels and decrease the conductivity of hybrid membranes. Compared with silica nanoparticles, mesoporous silica nanospheres is more effective in enhancing the conductivity and in preventing the release of ionic liquid component from the composite membranes. Under anhydrous conditions, the produced hybrid membranes show proton conductivity up to the order of 1×10^{-2} S/cm at 160 °C. These properties make this type of PIL-based hybrid membranes suitable for high-temperature polymer electrolyte membrane fuel cells.

Introduction

The polymer electrolyte membranes (PEM), which acts as an electrolyte to transport protons from the anode to the cathode, is one of the key components of polymer electrolyte membrane fuel cells (PEMFCs). More recently, the operation of PEMFCs at elevated temperature (> 100 °C) is receiving much attention because it could enhance reaction kinetics at both electrodes, improve the carbon monoxide tolerance of the platinum catalyst at the anode, and simplify heat and water managements of PEMFCs.[1] However, the most commonly used humidified perfluorosulfonic acid membranes, represented by Nafion, cannot be used at high temperature above 100 °C because of the evaporation of water, which results in a rapid loss of conductivity. In addition, high cost and high fuel crossover of Nafion membranes limit their practical application in fuel cell applications.[1b,c] Therefore, many studies have been carried out to develop alternative membranes with good fuel cell performance and low cost. Recently, several approaches, including synthesis of new types of membranes different than Nafion membranes,[2−4] replacement of water with nonaqueous proton carriers such as phosphoric acid,[5] protic ionic liquids,[6−10] and incorporation of hydrophilic inorganic fillers into the conventional PEMs to enhance the water retention,[11−14] have been pursued to obtain PEMs with high thermal stability and high conductivity at elevated temperature under anhydrous conditions.

Protic ionic liquids (PILs), consisting of combinations of Brønsted acids and bases that could form hydrogen bonds and act as proton carriers, have been considered as effective proton transferring carriers for high-temperature PEMFCs because of their nonvolatility, high proton conductivity, and excellent chemical and thermal and stability properties. Recently, PIL-based PEMs have been extensively studied by several groups.[6−10] This type

*Corresponding author. E-mail: fyan@suda.edu.cn.
(1) (a) Yamada, M.; Honma, I. *J. Phys. Chem. B* **2004,** *108,* 5522–5526. (b) Oetjen, H. F.; Schmidt, V. M.; Stimming, U.; Trila, F. *J. Electrochem. Soc.* **1996,** *143,* 3838–3842. (c) Adjemian, K. T.; Lee, S. J.; Srinivasan, S.; Benziger, J.; Bocarsly, A. B. *J. Electrochem. Soc.* **2002,** *149,* A 256–261.
(2) Khiterer, M.; Loy, D. A.; Cornelius, C. J.; Fujimoto, C. H.; Small, J. H.; Mcintire, T. M.; Shea, K. *Chem. Mater.* **2006,** *18,* 3665–3673.
(3) Tezuka, T.; Tadanaga, K.; Hayashi, A.; Tatsumisago, M. *J. Am. Chem. Soc.* **2006,** *128,* 16470–16471.
(4) Di Vona, M. L.; Sgreccia, E.; Licoccia, S.; Khadhraoui, M.; Denoyel, R.; Knauth, P. *Chem. Mater.* **2008,** *20,* 4327–4334.

(5) Weber, J.; Kreuer, K.; Maier, J.; Thomas, A. *Adv. Mater.* **2008,** *20,* 2595–2598.
(6) Ye, H.; Huang, J.; Xu, J.; Kodiweera, N.; Jayakody, J.; Greenbaumb, S. *J. Power Sources* **2008,** *178,* 651–660.
(7) Subianto, S.; Mistry, M. K.; Choudhury, N. R.; Dutta, N. K.; Knott, R. *ACS Appl. Mater. Interfaces* **2009,** *1,* 1173–1182.
(8) Yu, S.; Yan, F.; Zhang, X.; You, J.; Wu, P.; Lu, J.; Xu, Q.; Xia, X.; Ma, G. *Macromolecules* **2008,** *41,* 3389–3392.
(9) Yan, F.; Yu, S.; Zhang, X.; Qiu, L.; Chu, F.; You, J.; Lu, J. *Chem. Mater.* **2009,** *21,* 1480–1484.
(10) Fernicola, A.; Panero, S.; Scrosati, B. *J. Power Sources* **2008,** *178,* 591–595.
(11) Pereira, F.; Vallé, K.; Belleville, P.; Morin, A.; Lambert, S.; Sanchez, C. *Chem. Mater.* **2008,** *20,* 1710–1718.
(12) Tang, H.; Pan, M. *J. Phys. Chem. C* **2008,** *112,* 11556–11568.
(13) Jin, Y.; Qiao, S.; Zhang, L.; Xu, Z.; Smart, S.; Costa, J.; Lu, G. *J. Power Sources* **2008,** *185,* 664–669.
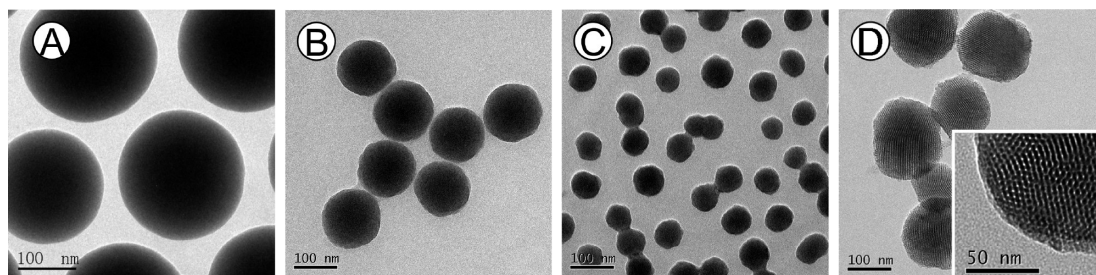(14) Tominaga, Y.; Hong, I. C.; Asai, S.; Sumita, M. *J. Power Sources* **2007,** *171,* 530–534.

Figure 1. TEM images of the silica nanoparticles with the diameter of (A) ~220 nm, (B) ~130 nm, (C) ~60 nm, and (D) mesoporous silica nanospheres (inset shows the MCM-41 structure of the silica nanosphere).

of PEMs exhibits promising proton conductivity, especially at high temperature above 100 °C under anhydrous conditions. However, a major drawback is that the long-term operation of the PIL-based membranes could be affected by a progressive release of the PIL component, resulting in the decline of fuel cell performance.[9,10] To resolve this problem and to increase the lifetime of fuel cell, enhancing the retention of ionic liquid component in PEMs is in great demand.

It is well-known that incorporating inorganic fillers into the polymer membranes can alter and improve the physical and chemical properties of polymers. Hygroscopic inorganic oxide fillers such as silica,[15−17] titania,[18,19] and zeolite[20,21] have been intensively pursued to modify humidified Nafion-type membranes to improve the water retention ability of the membranes at elevated temperature.[22] Among the previous studies, membranes modified with nanosized SiO_2 fillers have exhibited excellent performance and encouraging results. For example, Lee et al.[17] recently reported that the use of hydrophilic silica nanoparticles could improve water uptake and methanol barrier properties of the membranes because of the strong interactions between the inorganic particles and water molecules, and thus increase the proton conductivity and reduce the methanol permeability of the sulfonated copolymer membranes. Pereira[11] and Lu[13] also showed that incorporation of mesoporous silica spheres into the Nanfion membrane could significantly improve the water retention at higher temperatures and lowering relative humidities because of the adsorption of water in mesoporous silica fillers. More recently, Fernicola et al.[10] reported the preparation of ionic liquid-based poly(vinyldenefluoride-*co*-hexafluoropropylene) composite membranes. Addition of fumed silica with the diameter of 0.011 μm into the composite membrane dramatically enhanced the conductivity but was not effective in preventing the release of ionic liquid component from the membranes. However, to understand

the effect of silica fillers on the properties of hybrid membranes, we need a systematic study.

In the present work, we describe the synthesis and characterization of PIL-based silica hybrid membranes. A protic ionic liquid, *N*-ethylimidazolium trifluoromethane-sulfonate ([EIm][TfO]), was chosen as an effective proton carrier at high temperature because of its nonvolatile and high conductivity properties.[9,23] Silica nanoparticles and mesoporous silica nanospheres were synthesized and used as inorganic fillers, respectively. PIL-based hybrid membranes were prepared by in situ polymerization of the mixture of PIL and polymer precursor in which silica fillers were well dispersed. The influence of the silica filler size, morphology, as well as the filler content on the properties of resultant hybrid membranes was systematically investigated with respect to their thermal and mechanical properties and proton conductivity.

Experimental Section

Materials. Styrene, acrylonitrile, divinylbenzene, *N*-ethylimidazole, trifluoromethanesulfonate, benzoin ethylether, tetraethyl orthosilicate (TEOS), aqueous ammonia, ethanol, ethyl ether, hexadecyltrimethylammonium bromide (CTAB), and sodium hydroxide were used as purchased. All of the vinyl monomers were made inhibitor-free by passing the liquid through a column filled with Al_2O_3. Distilled deionized water was used for all experiments.

Synthesis of Spherical Silica Nanoparticles. Monodispersed silica nanoparticles with mean diameter of 60, 130, and 220 nm were prepared by hydrolysis of TEOS in an ethanol medium in the presence of ammonia and water and using a modified procedure originally described by Stöber et al.[24]

Synthesis of Mesoporous Silica Nanospheres. The nanospherical mesoporous silica was synthesized as documented in the previous literature.[25] Briefly, 1.0 g of cationic surfactant CTAB was dissolved in 480 mL H_2O, and to which 3.5 mL of NaOH solution (2 M) was added. The mixed solution was heated to 80 °C, followed by sequentially adding 5 mL of TEOS under vigorous stirring. The white precipitates were collected by centrifugation and dried at room temperature. The surfactant was then removed by calcination in air at 550 °C for 4 h.

(15) Zhou, Y.; Xiang, W.; Chen, S.; Fang, S.; Zhou, X.; Zhang, J.; Lin, Y. *Chem. Commun.* **2009**, 3895–3897.
(16) Tripathi, P.; Shahi, V. K. *J. Phys. Chem. B* **2008**, *112*, 15678–15690.
(17) Kim, J.; Mulmi, S.; Lee, C.; Park, H.; Chung, Y.; Lee, Y. *J. Membr. Sci.* **2006**, *283*, 172–181.
(18) Vona, M. L. D.; Ahmed, Z.; Bellitto, S.; Lenci, A.; Traversa, E.; Licoccia, S. *J. Membr. Sci.* **2007**, *296*, 156–161.
(19) Santiago, E. I.; Isidoro, R. A.; Dresch, M. A.; Matos, B. R.; Linardi, M.; Fonseca, F. C. *Electrochim. Acta* **2009**, *54*, 4111–4117.
(20) Wang, J.; Merino, J.; Aranda, P.; Galvan, J. C.; Hitzky-Ruiz, E. *J. Mater. Chem.* **1999**, *9*, 161–167.
(21) Alonso, R. H.; Estevez, L.; Lian, H.; Kelarakis, A.; Giannelis, E. P. *Polymer* **2009**, *50*, 2402–2410.
(22) Yang, C.; Srinivasan, S.; Bocarsly, A. B.; Tulyani, S.; Benziger, J. B. *J. Membr. Sci.* **2004**, *237*, 145–161.

(23) Fernicola, A.; Panero, S.; Scrosati, B.; Tamada, M.; Ohno, H. *ChemPhysChem* **2007**, *8*, 1103–1107.
(24) (a) Stöber, W.; Fink, A. *J. Colloid Interface Sci.* **1968**, *26*, 62–69. (b) Wang, W.; Gu, B.; Liang, L.; William, A.; Hamilton, W. A. *J. Phys. Chem. B* **2003**, *107*, 12113–12117. (c) Wu, T.; Zhang, Y.; Wang, X.; Liu, S. *Chem. Mater.* **2008**, *20*, 101–109.
(25) Cai, Q.; Luo, Z.; Pang, W.; Fan, Y.; Chen, X.; Cui, F. *Chem. Mater.* **2001**, *13*, 258–263.

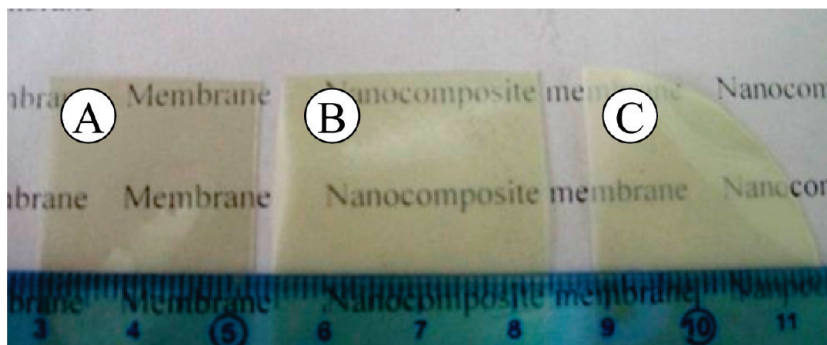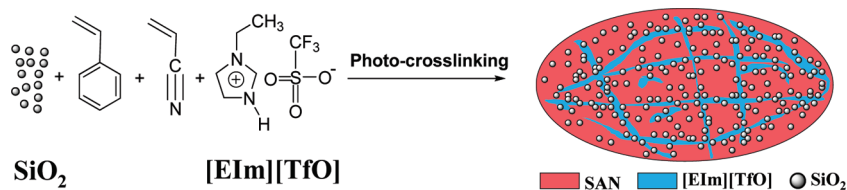**Scheme 1. Reaction Scheme for the Preparation of PIL-Based Hybrid Membranes**

Figure 2. Photographs of PIL-based polymer hybrid membranes: (A) without silica fillers, (B) containing 4 wt % of 130 nm silica particles and (C) containing 4 wt % of mesoporous silica nanospheres.

Synthesis of *N*-Ethylimidazolium Trifluoromethanesulfonate ([EIm][TfO]). Protic ionic liquid, [EIm][TfO], was synthesized by stirring the mixture of *N*-ethylimidazole with equivalent molar amount of trifluoromethanesulfonic acid at room temperature, as documented in the literature.[9,23] The resultant viscous oil was washed with ethyl ether three times, and then dried in dynamic vacuum at 80 °C for 24 h before use. ^{1}H NMR (400 MHz, DMSO) 8.97 (1H, s, N—CH-N), 7.67 (1H, t, N—CH=C), 7.63 (1H, t, C=CH-N), 3.89 (3H, s, N—CH$_3$).

Preparation of Hybrid Membranes. A mixture of styrene (20 wt %), acrylonitrile (40 wt %), [EIm][TfO] (40 wt %), divinylbenzene (6 wt % to the formulation, based on the weight of monomer), benzoin ethylether (photo initiator), and various amounts of silica fillers (0—16 wt %) was stirred and ultrasonicated to obtain a homogeneous solution, which was then cast into a glass mold and photo-cross-linked by irradiation with UV light of 250 nm wavelength in a glass mold for 30 min at room temperature.

Characterization. Thermal analysis was carried out by Universal Analysis 2000 thermogravimetric analyzer (TGA). Samples were heated from 30 to 500 °C at a heating rate of 10 °C/min under a nitrogen flow. Dynamic mechanical analysis (DMA) measurements of PIL-based hybrid membranes were conducted on a TA DMA Q 800. The samples were heated from 30 to 180 °C at a heating rate of 5 °C/min. The sample chamber was purged with nitrogen at 20 mL/min throughout the test. Transmission electron microscopy (TEM) characterization was performed on a JEOL JEM-2010 electron microscope operating at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were taken with a Hitachi S-4700 microscope with an accelerating voltage of 15 kV.

The resistance of the hybrid membranes was measured by the AC impedance method over the frequency range 1 Hz to 1 MHz using electrochemical workstations (Zahner IM6 EX). A rectangular piece of membrane was sandwiched between two gold electrodes in a glass cell and placed in a programmable oven to measure the temperature dependence of the conductivity. The membranes were dried at 100 °C for 8 h under vacuum and taken out just before conductivity measurement in an effort to keep

the samples dry. Before the measurements at each temperature set point, the samples were held at constant temperature for at least 10 min.

Results and Discussion

Poly(styrene-co-acrylonitrile) (SAN) is one of the most commonly used copolymers, which exhibits the ease of processing, good mechanical properties and chemical resistance. SAN has been recently used as electrolytes for fuel cell[9,26] and dye-sensitized solar cells[27,28] Our recently work has demonstrated that chemical stability of such a cross-linked SAN is even comparative to that of Nafion 117 membranes if tested in Fenton's reagent under the same measuring conditions.[9] Therefore, SAN was chosen as a polymer matrix for the preparation of hybrid polyelectrolyte membranes in this work. Protic ionic liquid, N-ethylimidazolium trifluoromethanesulfonate ([EIm][TfO]), was synthesized and used as anhydrous proton conductor.[9] Figure 1 shows the TEM images of the silica fillers synthesized in this work. Particles with the size of about 60, 130, and 220 nm are monodisperse and spherical (Figure 1A,B and C). Silica nanospheres with cylindrical channels and highly ordered MCM-41 mesoporous structure were also synthesized and used as inorganic fillers for comparison (Figure 1D). The hybrid membranes were prepared via in situ photo cross-linking of a mixture of styrene, acrylonitrile, [EIm][TfO], and various amounts of silica fillers in a glass mold (Scheme 1).

Figure 2 shows the photographs of produced PIL-based polymeric composite membranes without (Figure 2A) and

(26) Silva, A.; Takase, I.; Pereira, R. P.; Rocco, A. *Eur. Polym. J.* **2008**, *44*, 1462–1474.
(27) Wu, J.; Lan, Z.; Wang, D.; Hao, S.; Lin, J.; Huang, Y.; Yin, S.; Sato, T. *Electrochim. Acta* **2006**, *51*, 4243–4249.
(28) Lan, Z.; Wu, J.; Wang, D.; Hao, S.; Lin, J.; Huang, Y. *Solar Energy* **2006**, *80*, 1483–1488.
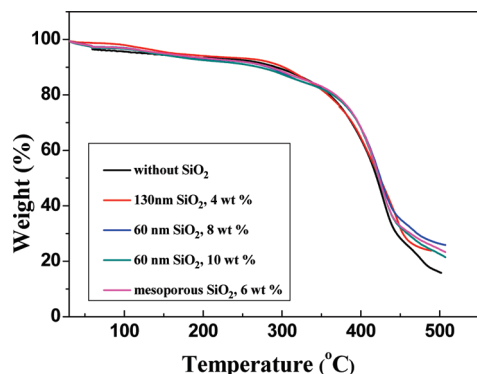
Figure 3. TGA of the [EIm][TfO]/poly(styrene-co-acrylonitrile) composite membranes with different weight ratio of silica fillers.

containing silica fillers (Figure 2B, C). All of the obtained composite membranes are semitransparent, free-standing, flexible and can be easily cut into any desired sizes and shapes. Figure 3 shows the thermal stability of the hybrid membranes examined with a thermogravimetric analyzer. All of the membranes lose less than 13% in weight up to 300 °C, confirming that this type of PIL-based membranes indeed confers a high thermal stability, far beyond the range of interest for application in PEMFCs. However, silica fillers did not dramatically change the decomposition temperature of the composite membranes, indicating that the addition of silica fillers might neither alter nor be involved in the thermal degradation reactions of polymer. Similar results have been observed for sulfonated polymer/silica, epoxy/silica, and poly(dimethylsiloxane)/silica composite membranes.[29−31]

To investigate the effect of the silica fillers on the mechanical properties of the hybrid membranes, dynamic mechanical analysis (DMA) was performed on the composite membranes. Figure 4A shows the tan delta curves of the PIL-based composite membranes obtained from DMA. It can be clearly seen that incorporation of silica nanoparticles increased the glass transition temperature (T_g). With the same content of silica fillers, membrane incorporated with mesoporous silica nanospheres shows the highest T_g value compared to silica nanoparticles. The increase in T_g is possibly due to the strong interfacial interactions between the silica fillers and polymers, which restricted the mobility of the polymer chains.[7,32] Herein, the mesoporous silica nanospheres that have a higher surface area show stronger interfacial interactions between polymers/silica fillers.

Figure 4B shows the storage modulus of the composite membranes. The addition of silica fillers also resulted in an increase in the modulus. At near the room temperature, the PIL-based membrane (without silica fillers) has a lower modulus (1280 MPa) compared to that of hybrid membranes (> 1450 MPa). The storage modulus of all the

samples decreased with temperature increase, reaching the value of 5−11 MPa at 120 °C, which is comparative to that of Nafion 117 under the same experimental condition,[7] indicating good mechanical properties of the hybrid membranes produced in this work.

The proton conductivity of PIL-based composite membranes was measured with an alternating current impedance spectroscopy in a closed cell under anhydrous conditions. Figure 5 shows the reproducible plot of proton conductivity of polymer membranes containing 40 wt % of [EIm][TfO], incorporated with or without 4 wt % of silica nanoparticles or mesoporous silica nanospheres, respectively. The plain membrane (without silica fillers) shows the conductivity of 4.69×10^{-5} S/cm at 40 °C. With the incorporation of silica nanoparticles, the conductivity was considerably improved, reaching the value of 1×10^{-4} S/cm under the same experimental condition. A similar tendency in the proton conductivity was also observed with the temperature increases. All the samples show no decay in conductivity even at the temperature as high as 160 °C, reaching values of 1×10^{-3} S/cm. These results indicate that incorporation of the silica fillers favors the conductivity of the PIL-based composite membrane.

Enhancement in conductivity upon addition of silica fillers has been observed previously in hybrid Nafion membranes because of the enhanced ability of water retention which resulted by the added silica fillers.[33] In this type of anhydrous hybrid membranes, the enhancement of conductivity is probably due to the PIL continuous networks or interconnected channels formed in the membrane, which caused by the distribution of silica fillers and the capillary interaction between the silica fillers. With the same content of the silica fillers in the membrane, the smaller the particle size, the higher conductivity of the membrane is observed. It should be noted that membranes incorporated with mesoporous silica nanospheres show the highest conductivity if compared with that modified with silica nanoparticles. Our understanding is that the mesoporous fillers favor the formation of ionic liquid conductive networks in the membrane because of not only the strong interfacial interactions (such as capillary force) between silica fillers but also the capillary force of mesopores.

The proton conductivity of PIL-based membranes obtained at elevated temperatures can be used for the estimation of activation energy (E_a) using the following equation[36]

$$\ln \sigma = -\frac{E_a}{RT}$$

where σ is the proton conductivity in S/cm, E_a is the activation energy in kJ/mol, R is the universal gas constant

(29) Su, Y.; Liu, Y.; Sun, Y.; Lai, J.; Guiver, M.; Gao, Y. *J. Power Sources* **2006**, *155*, 111–117.
(30) Liu, Y.; Hsu, C.; Wei, W.; Jeng, R. *Polymer* **2003**, *44*, 5159–5167.
(31) Liu, Y. L.; Li, S. H. *Macromol. Rapid Commun.* **2004**, *25*, 1392–1395.
(32) Wang, L.; Tian, Y.; Ding, H.; Li, J. *Eur. Polym. J.* **2006**, *42*, 2921–2930.

(33) Karthikeyan, C.; Nunes, S.; Prado, L.; Ponce, M.; Silva, H.; Ruffmann, B.; Schulte, K. *J. Membr. Sci.* **2005**, *254*, 139–146.
(34) Pei, H.; Hong, L.; Lee, J. Y. *J. Power Sources* **2006**, *160*, 949–956.
(35) Kim, Y. S.; Hickner, M. A.; Dong, L.; Pivovar, B. S.; McGrath, J. E. *J. Membr. Sci.* **2004**, *243*, 317–326.
(36) Zhou, X.; Weston, E.; Chalkova, E.; Hofmann, M. A.; Ambler, C. M.; Allcock, H. R.; Lvov, S. N. *Electrochim. Acta* **2003**, *48*, 2173–2180.
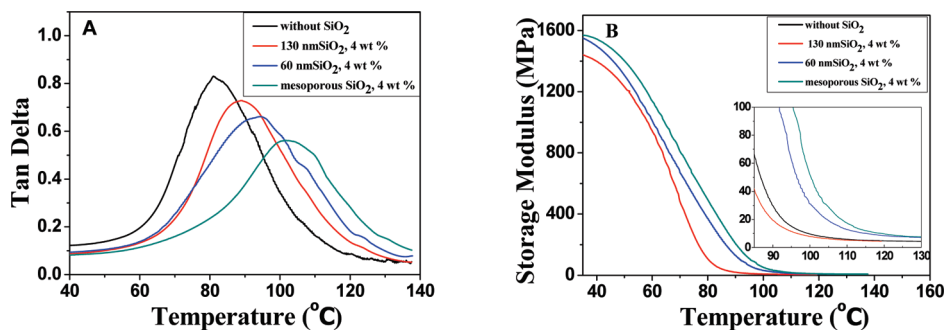
Figure 4. DMA showing (A) the tan delta and (B) storage modulus as a function of temperature for the composite membranes with 4 wt % silica fillers.
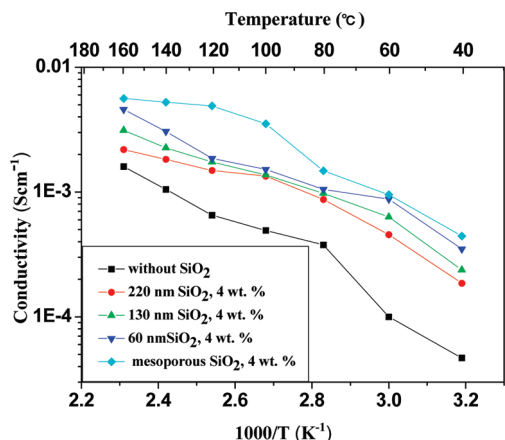

Figure 5. Conductivity Arrhenius plots of the PIL-based hybrid membranes. [EIm][TfO] was 40 wt % in the composite membrane.

Table 1. Energy of Activation (E_a) for Different PIL-Based Hybrid Membranes

membrane	E_a (kJ/mol)
without SiO$_2$	24.13
220 nm SiO$_2$, 4 wt %	21.38
130 nm SiO$_2$, 4 wt %	20.79
60 nm SiO$_2$, 4 wt %	20.04
mesoporous silica, 4 wt %	18.58
Nafion-117[34,35]	11.2−14

(8.314 J/(mol K)), and T is the absolute temperature in K. The calculated E_a values are presented in Table 1. Compared with the plain membrane, addition of silica fillers decreased the E_a values. The changing trend of E_a values is similar to that of proton conductivity which strongly related to the surface/volume ratio of the silica fillers. The higher surface/volume ratio of the silica fillers led to the lower E_a value. In all cases, the membrane containing the mesoporous silica showed the lowest E_a value (18.58 kJ/mol). The E_a values of all the hybrid membranes were higher than that of the Nafion 117 membrane saturated with water (11.2−14 kJ/mol),[34,35] showing that proton transfer needs more energy in the PIL-based hybrid membranes. The proton conduction in ionic liquids has been ascribed to a combination of proton hopping (Grotthuss) and vehicular mechanisms.[37] On the basis of the E_a values it can be concluded that proton transport of this type of PIL-based membranes

(37) Noda, A.; Susan, M. A. B. H.; Kudo, K.; Mitsushima, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2003**, *107*, 4024−4033.
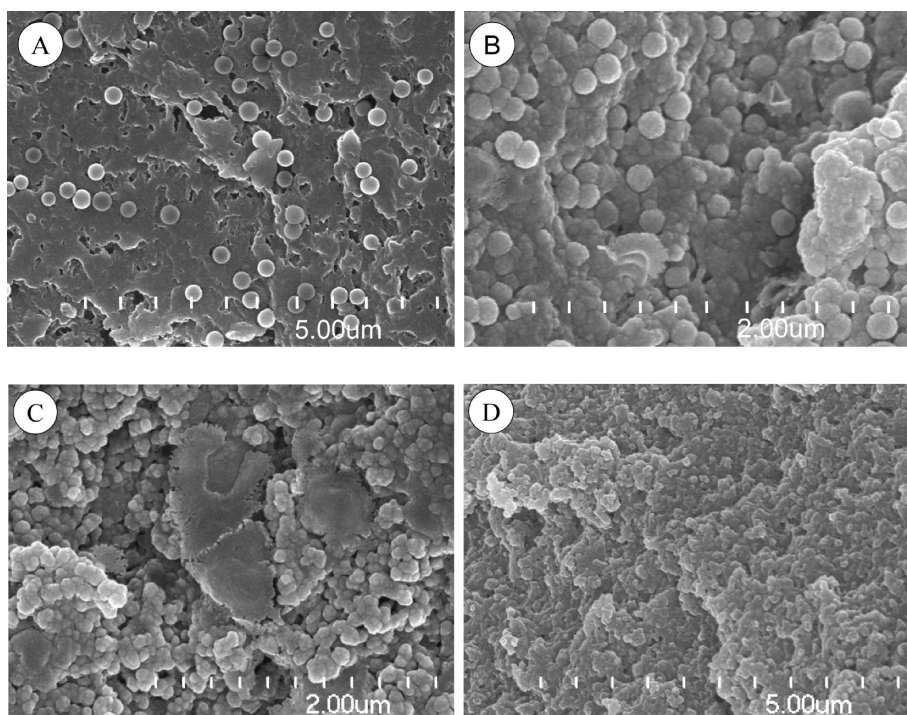
might have occurred by both mechanisms and predominantly by the vehicular mechanism.

Figure 6 shows SEM images of the cross-section of the hybrid membranes. The defects observed in the images were damages of blade cutting. It can be clearly seen that the silica fillers are homogenously embedded in the composite membranes and no agglomerate of the inorganic fillers was observed in any samples. Although we are failed to distinguish the ionic liquid component and polymer regions from SEM images, we believe that such a homogenously distribution of the silica fillers formed PIL continuous networks, which therefore enhanced the conductivity of hybrid membranes.

To further verify the content effect of the inorganic additives on the hybrid membranes, membranes incorporated with various amounts of silica fillers were prepared and characterized. Figure 7 shows the effect of silica filler variation on the conductivity of composite membranes. The conductivity increased with increasing the amount of silica fillers, however, abruptly decreased with the addition of excess silica fillers. As discussed above, the addition of the proper amount of silica fillers favors the formation of PIL continuous networks or interconnected channels in the hybrid membrane, which enhances the conductivity of membranes. However, further addition of excess inorganic fillers might block the formed ion transport channels. In addition, silica fillers themselves are much less conductive than PIL. Therefore, it is not surprising that excess addition of silica fillers declined the membrane conductivity. It can be clearly seen that the higher surface/volume ratio, the lower amount of the silica fillers need to achieve the highest conductivity. For instance, addition of 6 wt % mesoporous silica nanospheres could yield the highest conductivity (1.2×10^{-2} S/cm), whereas 14 wt % 220 nm silica particles is needed to reach the highest conductivity value (9.7×10^{-3} S/cm) of the membrane. This result further supports the assumption that silica fillers with higher surface/volume ratio favor the formation of PIL conductive networks in the membrane.

The protic ionic liquid used in this work is water-soluble. Therefore, performance of the PIL-based membranes could be affected by a progressive release of ionic liquid component during operation in the fuel cells. In this work, it is expected that the incorporation of inorganic

Figure 6. SEM images of the cross-sectional profiles of hybrid membranes containing 4 wt % of (A) 220 nm SiO_2 nanoparticles, (B) 130 nm SiO_2 nanoparticles, (C) 60 nm SiO_2 nanoparticles, and (D) mesoporous silica nanospheres.
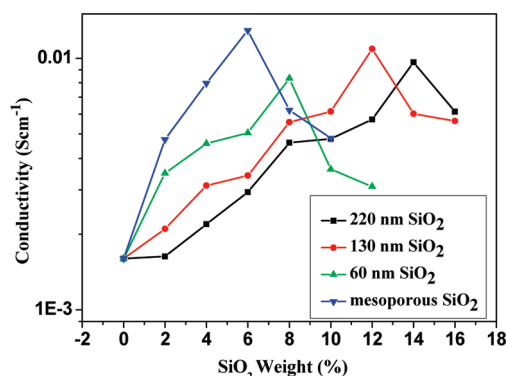

Figure 7. Conductivity of the PIL-based hybrid membranes as a function of the weight fraction of silica fillers at 160 °C. [EIm][TfO] was 40 wt % in the membranes.

Figure 8. (A) Results of ionic liquid retention ability test carried out in distilled water and (B) conductivity Arrhenius plots of various membranes after 50 min of water-extraction treatment.

silica fillers could enhance the PIL retention ability of the membrane. The model was confirmed by determining the weight loss of membrane samples after immersion in distilled water, as shown in Figure 8A. It can be seen that all of the PIL-based membranes with or without silica fillers lost most of their ionic liquids in a short time. The weight loss behavior of the membrane containing 130 nm silica particles is quite similar to that of plain membrane, which lost about 90 wt % ionic liquids from the membrane within 10 min. Incorporation of smaller silica nanoparticles (~60 nm in diameter) could slightly slow the release of ionic liquid component; however, it is still not effective in ionic liquid retention. It is worth noting that there is still about 20 wt % ionic liquids kept in the hybrid membrane modified with mesoporous silica nanospheres, even after being extracted with distilled water for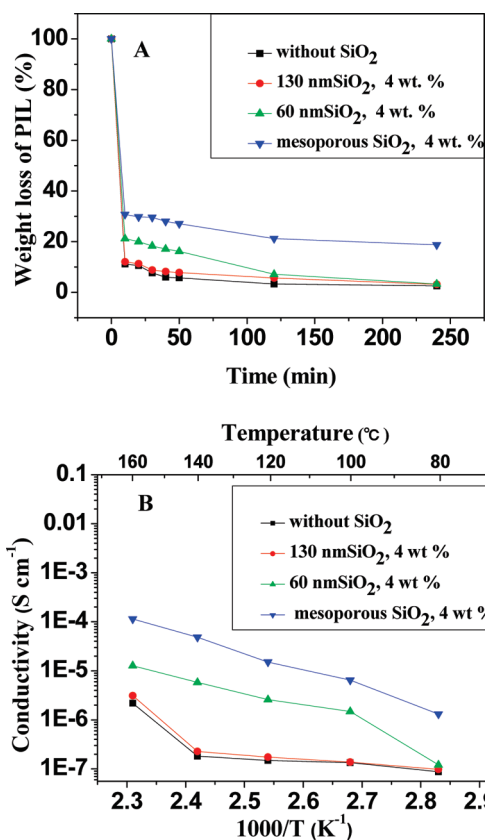 4 h. Compared with silica nanoparticles, we believe that the enhancement of the ionic liquid-holding strength can be ascribed to the capillary forces of mesopores of mesoporous silica nanospheres.

The enhanced ionic liquid-holding ability was further confirmed by conductivity measurements of the water-extracted membranes. Figure 8B shows that the conductivity of the samples dramatically decreased after the extraction of PIL by water. The membrane containing mesoporous silica nanospheres still shows the highest conductivity compared to the plain and other hybrid membranes modified with silica nanoparticles. This result further confirmed that the mesoporous silica nanospheres are more effective in holding ionic liquids than silica nanoparticles.

Conclusions

In summary, PIL/poly(styrene-co-acrylonitrile)/silica hybrid PEMs have been synthesized by incorporating silica nanoparticles or mesoporous silica nanospheres into the membrane. The resultant PIL-based hybrid membranes have quite a good thermal stability and mechanical properties. Under anhydrous conditions, the produced composite membranes have conductivity up to the order of 1×10^{-2} S/cm at 160 °C. The proton conductivity of the hybrid membranes increases with the incorporation of proper amount of silica fillers. This is properly due to the PIL-based continuous networks and ion transport channel structures formed in the membrane samples; however, it decreases with the increase in excess addition of silica fillers. Compared with silica nanoparticles, mesoporous silica nanospheres, which have a higher surface/volume ratio, are more effective in enhancing the conductivity and in preventing the release of ionic liquid component from the composite membranes.

This type of hybrid membranes should have an impact on further investigations in the field of proton conducting membranes for PEMPCs. However, further improvements to retain the PIL component upon cell operation still need to be carefully considered. Design and synthesis of polymer matrices have strong interaction with PIL component might be one of the most effective ways to improve the ionic liquid retention and will be further explored in our future work.