

SYNTHESIS OF NOVEL PROTON CONDUCTING MESOPOROUS SILICA (MS) FILMS FOR HIGH TEMPERATURE PEM FUEL CELLS

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ABSTRACT

Transparent free-standing mesoporous silica (MS) films were synthesized from a system of TMOS-Brij-Acid-H₂O. The non-ionic surfactants used included Brij 22 (C₁₂EO₁₀OH), Brij 56 (C₁₆EO₁₀OH), and Brij 76 (C₁₈EO₁₀OH). The acids used include HCl, H₃PO₄, and CF₃SO₃H. The effect of synthesis parameters on the synthesis and the proton conductivity of mesoporous silica were investigated. The Brij 56/CF₃SO₃H based product showed the highest conductivity of 6.5 x 10⁻² S/cm at room temperature.

INTRODUCTION

Proton conducting mesoporous materials offer several important features, such as uniform pore size (in the range of 20 – 500 Å), high specific surface area (≥ 1000 m²/g), large dimensional open channels, and high thermal stability. There have been studies of the proton conductivity of mesoporous silica [1-3]. To make mesoporous silica proton conductive, post-synthesis or co-condensation method can be used to graft acid groups like SO₃H. Margolese et al. [1] reported the direct synthesis of SBA-15 with sulfonic acid groups. Later, Mikhailenko et al. [2] reported sulfonated SBA-15 showed a proton conductivity of 10⁻² S/cm at room temperature. Halla et al. [3] also reported that the synthesis of a novel proton-conducting solid electrolyte, meso-SiO₂-C₁₂E₁₀OH-CF₃SO₃H, and found that the ionic conductivity (at room temperature) varied from 1 x 10⁻⁷ S/cm at low humidity to 1 x 10⁻³ S/cm at high humidity. However, the influence of the synthesis parameters on the synthesis and the proton conductivity were not reported in detail. In this paper, we report the effects of various parameters on the synthesis and the proton conductivity of transparent free-standing mesoporous silica films. The non-ionic surfactants that were used include Brij 22 (C₁₂EO₁₀OH), Brij 56 (C₁₆EO₁₀OH), and Brij 76 (C₁₈EO₁₀OH). The acids employed in this study were HCl, H₃PO₄, and CF₃SO₃H.

EXPERIMENTAL

Materials

Hydrochloric acid (37 wt.%, Mallinckrodt), phosphoric acid (H₃PO₄, 85%, EM), trifluoromethanesulfonic acid (triflic acid, CF₃SO₃H, 98%, Aldrich), tetramethyl orthosilicate (TMOS, 98%, Aldrich), polyoxyethylene 10 lauryl ether (Brij 22, C₁₂EO₁₀OH, Sigma-Aldrich), polyoxyethylene 10 cetyl ether (Brij 56, C₁₆EO₁₀OH, Sigma-Aldrich), and polyoxyethylene 10 stearyl ether (Brij 76, C₁₈EO₁₀OH, Sigma-Aldrich), Pt black (fuel cell grade, E-TEK), carbon layer (ELAT[®], E-TEK Div. of De Nora N. A., Inc), and Nafion[®] 117 (Aldrich) were used as received.

Synthesis of mesoporous silica (MS)

The MS materials were prepared according to a modification of the published procedure [3]. In a typical synthesis, a mixture of 2 g of Brij 22, 2 ml of deionized water and 2

ml of triflic acid (50 wt%) was heated to about 70°C until the solution was homogeneous. It was found that a white monolith was formed if TMOS was added directly. Therefore, the transparent solution was cooled to room temperature, followed by addition of 3.7 g of TMOS dropwise and stirred until a viscous gel was formed (the vessel was kept open to remove the methanol produced from the hydrolysis of TMOS). The molar composition of the final gel was 1 TMOS : (0.065 ~ 0.195) surfactant : (0.015 ~ 0.29) acid : (7.0 ~ 17.5) H₂O, where the surfactant employed included Brij 22, Brij 56, and Brij 76, respectively. The acids included HCl, H₃PO₄, and CF₃SO₃H. The viscous gel was then cast on a Teflon surface and allowed to dry at room temperature. A transparent free-standing continuous film with a thickness of 0.6 mm (FF57, shown in Figure 1) was formed in ~ 2 hours.

Characterization

X-ray diffraction (XRD) patterns were conducted on a Scintag XDS 2000 X-ray diffractometer, using CuK_α radiation. The as-synthesized sample for XRD analysis was prepared by casting the transparent viscous gel on a microscope glass cover. Scanning electron microscopy (SEM) images were recorded on a LEO 1530 VP electron microscope from samples coated with Au/Pd. Energy dispersive X-ray analysis (EDX) was also performed on a LEO 1530 VP electron microscope at 20 kV for 150 seconds.

The conductivities of the MS products were measured according to a reported procedure [2]. The free-standing film was ground to a powder and mixed with deionized water. The resulting paste was placed into a glass tube with a surface area of 1 cm². The glass tube was then clamped between two stainless-steel electrodes. Deionized water was added until a maximum conductivity was obtained. The water content was calculated as a ratio of the water to the sum of the water and the dry solid powder. Using a PC controlled frequency response analyzer–VoltaLab® PGZ301 (Radiometer Analytical S.A.), the AC impedance measurements were conducted over the frequency range of 100 KHz to 1 Hz, using a 10 mV amplitude AC signal throughout the experiments.

RESULTS AND DISCUSSION

Brij 22 template

In a previous report, CF₃SO₃H was employed to make a hexagonal mesoporous silica with Brij 22 [3]. In this study, the acids used included HCl and H₃PO₄ as well as CF₃SO₃H. HCl is a typical acid used for the synthesis of mesoporous silica, while H₃PO₄ is widely used for fuel cell application. CF₃SO₃H was also studied because of its super acidity. Figure 1 shows a typical membrane prepared by CF₃SO₃H. Figure 2 shows the XRD patterns of the as-synthesized membranes with the different acids. The d-spacing of the main reflection of the mesoporous structure was influenced by the acid. In the Brij 22/HCl based system (FF78A), only one broad peak with a d-spacing of 47.0 Å was observed. The Brij 22/H₃PO₄ based film (FF91B) showed an intense (100) reflection with a d-spacing of 48.6 Å. Another weak peak with a d-spacing of 24.3 Å was also observed and could be assigned to the (200) reflection of a hexagonal structure. In the Brij 22/CF₃SO₃H system (FF57), a nearly amorphous product was obtained with a d-spacing of 47.2 Å. No other reflections were observed even after grinding the membrane, which was completely different from the previous report [3]. In that case, the as-synthesized product was a well-ordered hexagonal structure. In our study, the nearly amorphous product could be the result of a much higher CF₃SO₃H/Brij 22 ratio of 2.23 compared with 0.31 [3]. In our experiment, with an HCl/Brij 22 ratio of 0.28 (HCl/TMOS =

0.036), a cubic $Ia3d$ structure was obtained. The pKa values are -7 for HCl, -13.6 for $\text{CF}_3\text{SO}_3\text{H}$, and 2 for H_3PO_4 . The pH values of the final gels were -0.14, 0.34, and 1.18 for HCl, $\text{CF}_3\text{SO}_3\text{H}$, and H_3PO_4 based systems, respectively. The order of the intensity for the (100) reflection of the membranes are $\text{H}_3\text{PO}_4 > \text{HCl} > \text{CF}_3\text{SO}_3\text{H}$. Combined with the appearance of the (200) reflection in the Brij 22/ H_3PO_4 system, it could be concluded that H_3PO_4 might favor the formation of a highly ordered hexagonal mesoporous silica due to the lower reaction rate [4]. Zhao et al. [4] reported that the radius or charge of the anion and the strength of the acid had a significant influence on the reaction rate. Figure 3 shows the XRD patterns of the calcined ground membrane. In the HCl or H_3PO_4 based system, the calcined product showed a very weak broad peak at 40.3 and 46.2 Å for the HCl and H_3PO_4 based products, respectively. After calcination, however, the Brij 22/ $\text{CF}_3\text{SO}_3\text{H}$ product showed four peaks with d-spacings of 71.4, 56.5, 32.9, 21.3 Å, which could be indexed to the (110), (111), (300), and (332) reflections of a well ordered three-dimensional cubic $Pn3m$ mesoporous structure [5]. The unit-cell parameter of 101.0 Å ($a = d_{100}\sqrt{2} = 101.0\text{Å}$) was very similar to that obtained using Brij 56 and HCl (100.7 Å) [5]. The average pore size and wall thickness were 53.0 and 48.0 Å, respectively, suggesting the product had a larger pore size and thinner wall than those of the Brij 56/HCl sample previously reported (30.0 and 71.0 Å, respectively) [5]. In the case of previously reported mesoporous silica prepared with $\text{CF}_3\text{SO}_3\text{H}$ [3], no information was given for the calcined product. Petkov et al. [6] reported a phase transformation from one-dimensional hexagonal to three-dimensional cubic structure during the calcination. In our experiments, the final transparent gel was kept open after adding TMOS, however, there was still some methanol in the transparent gel. Methanol could act as a co-solvent and penetrate into the surfactant micelles and play the role of a co-surfactant [7, 8]. The surfactant packing parameter is $g = V/a_0l$, where V is the total volume of the surfactant chains plus any co-solvent molecules between the chains, a_0 is the effective head group area at the micelle surface, and l is the surfactant chain length [9]. The small g values stabilize more curved structures. During calcination, the surfactant Brij 22, methanol, and occluded acid would be removed. Due to the much lower boiling point, methanol (and trapped acid) would be removed earlier than Brij 22, therefore, the ratio of methanol to Brij 22 decreased gradually. The effective head group area (a_0) and the chain length of the surfactant (l) did not change. However, the total volume (V) would decrease due to the removal of methanol and occluded acid, and therefore the g value decreases, causing from low to high curved phase transformation, such as from hexagonal ($g = 1/2$) to cubic $Pn3m$ ($g = 1/3$ possibly).



Fig. 1. Digital image of a membrane prepared using Brij 22 and $\text{CF}_3\text{SO}_3\text{H}$.

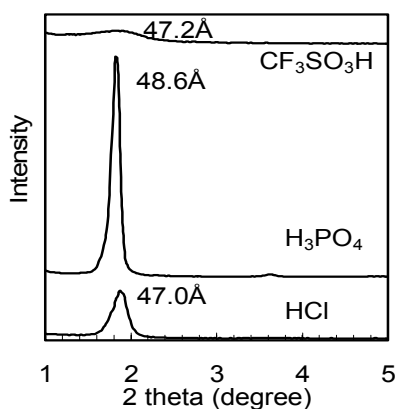


Fig. 2. XRD patterns of as-synthesized films using Brij 22.

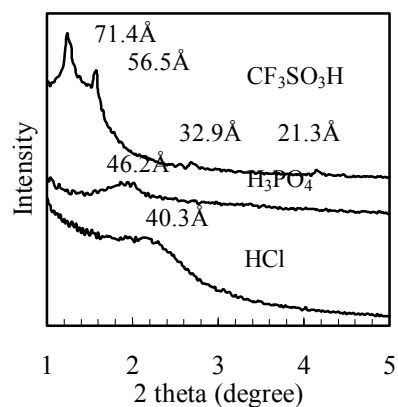


Fig. 3. XRD patterns of calcined films using Brij 22.

Table 1 lists the proton conductivities of the as-synthesized and calcined products at room temperature. For the Brij 22/HCl based product (FF78A), the Cl/Si ratio of 0.02 was detected by EDX. The Brij 22/H₃PO₄ product (FF91B) showed a P/Si molar of 0.25. The S/Si ratio was 0.17 for the Brij 22/CF₃SO₃H product (FF57). The order of the water content in acid was HCl > CF₃SO₃H > H₃PO₄, which was the same as the order of the pH value for the final gel. The maximum conductivity at room temperature for as-made Brij 22/HCl based product (FF78A) was 3.9×10^{-2} S/cm at a water content of 18.8 wt.%, which was comparable with those obtained from sulfonic acid functionalized mesoporous silica [2]. For the Brij 22/H₃PO₄ based material (FF91B), the conductivity was 3.0×10^{-3} S/cm at a water content of 14.6 wt.%. In contrast, the Brij 22/CF₃SO₃H based product (FF57) gave a conductivity of 3.8×10^{-2} S/cm at 15.3 % water content, which was higher than that previously reported for mesoporous silica prepared using Brij 22 and CF₃SO₃H (10^{-3} S/cm) at room temperature [3]. The difference in the proton conductivity could be due to the difference in the amount of the occluded CF₃SO₃H. In a previous report, a hexagonal product was obtained with a CF₃SO₃H/Brij 22 molar ratio of 0.13 in the initial gel. After reproducing this experiment, we found the product contained a S/Si ratio of 0.03 by EDX. However, in our experiment, a CF₃SO₃H/Brij 22 ratio of 2.31 was used and the product showed an S/Si ratio of 0.17 by EDX. Although the Brij 22/H₃PO₄ product showed a higher occluded H₃PO₄ (P/Si = 0.25) contain, the much lower conductivity of the H₃PO₄ based product could be attributed to the much lower acidity of H₃PO₄.

Table 1 Proton conductivity of the free-standing films.

Sample	Surf.	Acid	Acid/Si ratio in product	d ₁₀₀ (Å)		Water content (wt%)		Conductivity (x10 ⁻² S/cm) ^b	
				As.	Ca.	As.	Cal.	As.	Cal.
FF78A	C ₁₂	HCl	0.02	47.0	40.3	18.8	39.5	3.89	0.01
FF91B		H ₃ PO ₄	0.25	48.6	46.2	14.6	42.9	0.34	0.01
FF57		CF ₃ SO ₃ H	0.16	47.2	71.4*	15.3	50.3	3.80	1.07
Halla [3]	C ₁₂	CF ₃ SO ₃ H	0.03	42-45	-	-	-	0.10	-
FF90A	C ₁₆	HCl	0.02	57.1	46.2	27.9	46.1	0.05	0.24
FF90B		H ₃ PO ₄	0.25	57.9	a.	26.7	-	0.95	-
FF90C		CF ₃ SO ₃ H	0.23	52.5	a.	23.4	-	6.49	-
FF92A	C ₁₈	HCl	0.08	73.5*	49.5	32.1	51.6	1.18	0.18
FF92B		H ₃ PO ₄	0.23	68.1*	a.	22.9	-	0.65	-
FF56		CF ₃ SO ₃ H	0.10	71.3*	67.4	21.5	53.4	5.01	0.65

As. = as-synthesized; Ca. = calcined; * cubic; a. = amorphous; b. single experiment

For the as-synthesized product, the proton conduction may be mainly due to the occluded acid in the micellar template. After calcination at 500°C, the acid would be removed and the proton conductivity should be close to zero. However, the calcined hexagonal Brij 22/HCl (or H₃PO₄) product still showed a conductivity of 1.0×10^{-4} S/cm, which was higher than that of calcined product obtained using CTMABr (hexagonal *P6mm*, 10^{-10} S/cm) or Brij 56 (cubic *Pm3n*, 10^{-6} S/cm) at full hydration in the literature [10]. From the fact that the calcined product shows some proton conductivity, it can be concluded that the proton conductivity of the mesoporous silica comes from not only the occluded acid but also from other sources, such as the dissociation of the protons from the Si-OH bonds and the proton hopping through water molecules in the mesoporous pores [10]. In the IR spectrum (not shown), the Brij 22/CF₃SO₃H

calcined product (FF57) showed three peaks at 3744, 3446, and 1649 cm^{-1} , corresponding to SiO-H bonds, O-H stretch and O-H bending of hydrogen-bonded water for the cubic phases, respectively [11, 12]. For the calcined product, water was required for the proton conduction. The proton conductivity was observed to increase as the water content increased and then achieved a maximum value. After calcination, the Brij 22/ $\text{CF}_3\text{SO}_3\text{H}$ based product (FF57) gave a proton conductivity up to 1.1×10^{-2} S/cm (at a water content of 50.3 wt.%), which was four orders higher than the calcined cubic $Pm\bar{3}n$ product prepared from a system of Brij 56-HCl- $\text{C}_3\text{H}_7\text{OH-H}_2\text{O}$ [10]. The extremely high conductivity could be due to the presence of the occluded $\text{CF}_3\text{SO}_3\text{H}$ and the interaction between $\text{CF}_3\text{SO}_3\text{H}$ and silanols of mesoporous silica. EDX showed an F/Si ratio of 0.13 for the calcined product, indicating that 25% of trapped $\text{CF}_3\text{SO}_3\text{H}$ was still left after calcination at 500°C for 24 hours. The Si-OH groups of mesoporous silica and the SO and OH groups of $\text{CF}_3\text{SO}_3\text{H}$ could form the hydrogen-bonded species, which was reported by Paze et al. using infrared spectroscopy [13, 14].

Brij 56 template

Table 1 and Figure 4 show the XRD results from membrane prepared using Brij 56 as a surfactant with the different acids. When HCl was used, the d-spacing for the as-synthesized product was 57.1 Å. The H_3PO_4 based as-synthesized product gave an intense peak (57.9 Å) and two possible very weak shoulder peaks (about 54.6 and 52.0 Å), which could be indexed to the (200), (210), and (211) reflections of a $Pm\bar{3}m$ cubic mesoporous structure using Brij 56 [15]. The cubic structure gave a unit-cell parameter of 115.8 Å ($a = d_{200}\sqrt{4} = 115.8$ Å), which was very close to that reported in the literature (121.0 Å) [15]. In the $\text{CF}_3\text{SO}_3\text{H}$ based system, in contrast, the as-synthesized mesoporous silica showed a very strong peak with a d-spacing of 52.5 Å and a weak peak at a d-spacing of 25.8 Å, which might be indexed to the (220) and (442) reflection of a cubic Ia3d phase with a unit cell parameter of 148.5 Å ($a = d_{220}\sqrt{8} = 148.5$ Å). After calcination, unfortunately, the products obtained using H_3PO_4 and $\text{CF}_3\text{SO}_3\text{H}$ were amorphous, suggesting that the products might not be fully condensed. Although, the HCl based calcined product appeared to maintain the lamellar structure based on the thermal stability, the intensity of the peak with a d-spacing of 46.2 Å was very low. It would appear that the products obtained using Brij 56 have a lower thermal stability than the Brij 22 products, which might be attributed to the coiling of the longer chain of Brij 56, leading to a looser packing of the surfactant and therefore a less condensed structure [9].

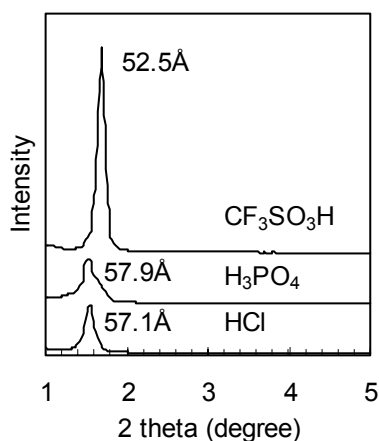


Fig.4 XRD patterns of as-synthesized films using Brij 56.

The proton conductivity of the as-synthesized products was also significantly influenced by the type of acid, listed in Table 1. Using HCl as the acid, the maximum conductivity of the as-synthesized sample (FF90A) was only 5.0×10^{-4} S/cm at a water content of 27.9 wt.%. The Cl/Si ratio of 0.02 was detected by EDX. The calcined product showed a higher conductivity (2.4×10^{-3} S/cm) than that of the as-synthesized, which could be attributed to the fast proton transportation in the empty pores due to the removal of the surfactant. Li et al. [10] reported a proton conductivity of the calcined cubic $Pm\bar{3}n$ product (obtained in the system of TEOS-Brij 56- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ -HCl- H_2O) was about 10^{-5} S/cm, which was two orders lower than that of the product obtained in our experiment. The Brij 56/ H_3PO_4 based as-synthesized product (FF90B) gave a conductivity of 9.5×10^{-3} S/cm (at a 27.6 wt.% water content). The P/Si ratio obtained by EDX was 0.25, which was very similar to the value in the initial gel (0.29). In the Brij56/ $\text{CF}_3\text{SO}_3\text{H}$ system, In contrast, the conductivity for the as-synthesized product (FF90C) was 6.5×10^{-2} (at a water content of 23.4 wt.%), which was much higher than that obtained using HCl or H_3PO_4 as the mineralization agent. EDX showed an S/Si ratio of 0.23. For the Brij56/ $\text{CF}_3\text{SO}_3\text{H}$ as-synthesized product (FF90C), the high proton conductivity could be due to the super acidity of the occluded $\text{CF}_3\text{SO}_3\text{H}$.

In Brij 56/ H_3PO_4 system, a cubic phase was formed, indicating that the occlusion of the weaker acid might favor the formation of a cubic structure followed by a possible $(\text{S}^0\text{H}^+)(\text{X}^-\text{I}^+)$ pathway [4]. Compared to HCl or $\text{CF}_3\text{SO}_3\text{H}$, the much weaker acid H_3PO_4 might favor the pathway assembled by a hydrogen bonding. According to the surfactant packing parameter ($g = V/a_0l$), the occlusion of H_3PO_4 might increase the effective head group area of the Brij 56 and then cause a decrease of the g value, therefore resulting in a more curved phase (cubic).

Brij 76 template

Figure 5 shows the XRD patterns of the as-synthesized membranes prepared using Brij 76 as a surfactant. In this case, the surfactant Brij 76 appears to favor the formation of a three-dimensional $Pm\bar{3}m$ cubic structure [15], which was not in agreement with the observations reported previously [5]. In our experiments, the molar ratio of Brij 76/TMOS was 0.13, which was much lower than that in the report (0.30). El-Safty et al. reported that 3D mesoporous silicates were relatively easy to form by using Brij 56 compared with Brij 76 [4].

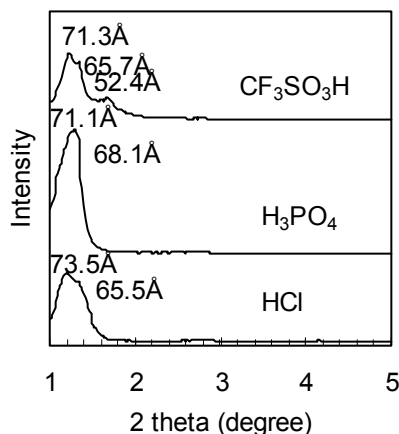


Fig.5 XRD patterns of as-synthesized films using Brij 76.

Both Brij 56 and Brij 76 have similar poly(ethylene oxide) (EO₁₀) head groups and molecular volumes. Brij 76 has a slightly longer aliphatic chain than Brij 56 and a smaller packing parameter value ($g = V/a_0l$), leading to structures with greater curvature [9]. The d-spacing of the (200) reflection increased with an increase in the acidity of the acid. In Brij 76/HCl system, the as-synthesized product showed five peaks with d-spacings of 75.1, 73.5, 65.5, 31.9 and 21.3 Å, which might be indexed to (200), (210), (211), (500) and (632) reflections of a three-dimensional $Pm\bar{3}m$ cubic structure [15]. The unit-cell parameter of 160.4 Å ($a = d_{211}\sqrt{6} = 160.4$ Å) was greater than that obtained using Brij 56 (121.0 Å), which could be due to the fact that Brij 76 has a slightly longer chain than Brij 56. After calcination, only one peak with a d-spacing of 49.5 Å was observed, suggesting that the product was not fully condensed. The Brij 76/H₃PO₄ based product (FF92B) showed only three peaks with d-spacings of 71.1, 68.1, and 31.7 Å, which might be assigned to (210), (211) and (511) reflections of a cubic $Pm\bar{3}m$ phase with a unit-cell parameter of 152.3 Å ($a = d_{211}\sqrt{6} = 166.8$ Å) [15]. However, after calcination, FF90B became amorphous. For the Brij 76/CF₃SO₃H based product, seven peaks with d-spacings of 75.1, 71.3, 65.7, 52.4, 35.0, 31.6, and 20.6 Å were observed and could be indexed to the (200), (210), (211), (220), (331), (500) and (633) reflections of a cubic $Pm\bar{3}m$ phase with a unit-cell parameter of 160.9 Å ($a = d_{211}\sqrt{6} = 160.9$ Å) [15]. The calcined product showed only one reflection with a d-spacing of 67.4 Å, which might be assigned to the (200) reflection of a cubic $Pm\bar{3}m$ structure with a unit cell parameter of 134.8 Å. A Cl/Si ratio of 0.08 was obtained by EDX for Brij 76/HCl product (FF92A). For the Brij 76/H₃PO₄ product (FF92B), EDX showed a P/Si ratio of 0.23. The Brij 76/CF₃SO₃H based product (FF56) showed an S/Si ratio of 0.10 by EDX. Compared to the Brij 76/HCl (or CF₃SO₃H) product, the as-synthesized Brij 76/H₃PO₄ based film showed a larger unit cell parameter (166.8 Å), which might be attributed to the fact that more H₃PO₄ was occluded. Using H₃PO₄, the same cubic $Pm\bar{3}m$ structure was obtained in Brij 56 and Brij 76 systems. The P/Si ratios were 0.25 and 0.23 for the Brij 56/H₃PO₄ and Brij 76/H₃PO₄ based products, respectively. The Brij 76/H₃PO₄ based film showed a much larger unit cell parameter (166.8 Å) than that of the Brij 56/H₃PO₄ based film (115.8 Å), which could be due to the slightly longer chain of Brij 76.

The type of acid influenced the proton conductivity of these products as listed in Table 1. For the as-synthesized products, the order of the water content in acid was HCl > H₃PO₄ > CF₃SO₃H, which was the same as that using Brij 56 as the surfactant. The order of the proton conductivity in acid (CF₃SO₃H > HCl > H₃PO₄) was the same as the order of the acidity. Using HCl, the as-synthesized product (FF92A) showed a conductivity of 1.2×10^{-2} S/cm at a water content of 32.1 wt.%. When H₃PO₄ was used, the conductivity of the as-synthesized product (FF92B) was 6.5×10^{-3} S/cm at 22.9 wt.% water content. In the Brij 76/CF₃SO₃H system (FF56), the as-synthesized product showed a conductivity up to 5.0×10^{-2} S/cm (at a water content of 21.5 wt.%), which could be due to the occlusion of CF₃SO₃H. Due to the removal of the acid upon calcination, the calcined product showed a much lower conductivity. The Brij 76/HCl calcined product showed a conductivity of 1.8×10^{-3} S/cm at a water content of 51.6 wt.%. For the Brij 76/CF₃SO₃H calcined product, a conductivity of 6.5×10^{-3} S/cm was obtained at a water content of 53.4 wt.%. The high conductivity could be due to the presence of the occluded CF₃SO₃H and the formation of the hydrogen bonding between CF₃SO₃H and silanols of mesoporous silica [13, 14]. EDX confirmed the presence of CF₃SO₃H with an F/Si ratio of 0.09, indicating that 30% of trapped CF₃SO₃H was still adsorbed in some form after calcination at 500°C for 24 hours.

CONCLUSIONS

Using three non-ionic Brij surfactants (Brij 22, Brij 56, and Brij 76), transparent free-standing mesoporous silica (MS) films were synthesized from a system of TMOS-Brij-Acid-H₂O, where the acids used were HCl, H₃PO₄, and CF₃SO₃H. Most CF₃SO₃H-based as-synthesized products showed the highest proton conductivity at room temperature. Therefore, the preliminary results for the composite membranes suggest that acid containing mesoporous silicas are promising additives for high temperature proton exchange membrane fuel cell applications.

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REFERENCES

- [1] D. Margolese, J. A. Melero, S. C. Christianse, B. F. Chmelka, G.D. Stucky, *Chem. Mater.* 12(2000) 2448.
- [2] S. Mikhailenko, D. Desplandier-Giscard, C. Danumah, S. Kaliaguine, *Micropor. Mesopor. Mater.* 52 (2002) 29.
- [3] J. D. Halla, M. Mamak, D. E. Williams, G. A. Ozin, *Adv. Funct. Mater.* 13 (2003) 133.
- [4] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* 120 (1998) 6024.
- [5] S. A. El-Safty, T. Hanaoka, *Chem. Mater.* 15 (2003) 2892.
- [6] N. Petkov, S. Mintova, T. Bein, *Stud. Surf. Sci. Catal.* 142B (2002) 1465.
- [7] F. Kleitz, J. Blanchard, B. Zibrowius, F. Schuth, *Langmuir*, 18 (2002) 4963.
- [8] O. I. Lebedev, G. V. tendeloo, O. Collart, P. Cool, E. F. Vansant, *Solid State Sci.* 6 (2004) 489.
- [9] Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* 8 (1996) 1147.
- [10] H. Li, M. Nogami, *Adv. Mater.* 14 (2002) 912.
- [11] M. S. Morey, S. O'Brien, S. Schwarz, G. D. Stucky, *Chem. Mater.* 12 (2000) 898.
- [12] N. Petkov, S. Mintova, B. Jean, T. Metzger, T. Bein, *Mater. Sci. Eng. C* 23 (2003) 827.
- [13] C. Paze, G. T. Palomino, A. Zecchina, *Catal. Lett.* 60 (1999) 139.
- [14] A. de Angelis, C. Flego, P. Ingallina, L. Montanari, M. G. Clerici, C. Perego, *Catal. Today* 65 (2001) 363.
- [15] D. Zhao, P. Yang, N. Melosh, J. Feng, F. Chmelka, G. D. Stucky, *Adv. Mater.* 10 (1998) 1380.