



Flexible proton-conducting glass-based composite membranes for fuel cell application

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ABSTRACT

Based on Nafion[®]/phosphosilicate (NPS) glass and sulfonated poly(ether ether ketone) (SPEEK) polymer, proton-conducting NPS/SPEEK composite membranes are prepared by a simple mechanical ball-milling approach. The chemical structure, morphology, pore structure, and proton conductivity of the NPS/SPEEK composite membranes are investigated. Due to the incorporation of the SPEEK polymer, the obtained composite membranes exhibit sufficient flexibility and remarkably reduced pore volume compared to fragile and highly porous NPS glass. On the other hand, the NPS/SPEEK composite membranes exhibit improved proton conductivities compared with pure SPEEK. Specifically, the composite membranes display quite high proton conductivities of above 10^{-3} S cm⁻¹ in the temperature range from 30 to 80 °C at 90% relative humidity, while pure SPEEK shows moderate proton conductivities of 10^{-3} – 10^{-4} S cm⁻¹ under the same conditions. For a single H₂/O₂ fuel cell equipped with the NPS/SPEEK composite membrane, a peak power density of 322 mW cm⁻² is obtained at 65 °C.

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1. Introduction

Proton-conducting materials have undergone significant developments during the past decades, due to their application as electrolyte membranes in fuel cells and sensors [1–3]. Among them, perfluorosulfonic acid polymer membranes, typically Nafion[®], are characterized by high proton conductivity and good chemical stability, and are widely used in current low-temperature fuel cells (PEMFCs and DMFCs). However, these membranes are very expensive, and they suffer from swelling due to the adsorption of water, which lowers their fuel-cell efficiency.

Sol-gel derived inorganic proton conductors, such as SiO₂ [4,5], Al₂O₃ [6], TiO₂ [6,7], P₂O₅–SiO₂ [8–11], and P₂O₅–TiO₂ [12], may offer very promising alternatives to polymeric membranes because of their low cost and high dimensional stability. Their proton conductivities can reach 10^{-2} – 10^{-1} S cm⁻¹ [7–12], which are comparable to that of Nafion[®], and are thus adequate for fuel-cell applications. Nevertheless, the power densities of fuel cells with inorganic proton-conductive membranes as electrolytes are still not as high as those of fuel cells based on Nafion[®] membrane. Using P₂O₅–SiO₂ and PWA/PMA–P₂O₅–SiO₂ membranes in fuel cells, Nogami et al. [13,14] obtained peak power densities of 6 mW cm⁻² at 50 °C and 41.5 mW cm⁻² at 32 °C, respectively. Tang et al. [15]

achieved a peak power density of 165 mW cm⁻² at 80 °C using an electrolyte membrane made from H₃PW₁₂O₄₀ (HPW)/MCM-41 meso-silica composite powder and a polyimide binder under hot-pressing conditions. Our group has also demonstrated the utility of a Nafion[®]/phosphosilicate (NPS) glass membrane in a fuel cell, and a peak power output of 42.6 mW cm⁻² was obtained [16].

It is believed that a key issue is that sol-gel derived glasses are inflexible and fragile, and thus cannot withstand the pressure required to press them into a membrane–electrode assembly (MEA) for favorable interface contact between the electrolyte and electrode. As a result, a high interface resistance arises, which is responsible for an undesirable power loss. The use of these inorganic proton conductors in fuel cells is thereby hampered, and so endowing them with sufficient flexibility is strongly desired.

Herein, we propose a synthetic strategy whereby a glass-based composite membrane is fabricated by mixing a sol-gel derived glass powder and an organic polymer by a simple mechanical ball-milling method. In the glass-based composite membrane, the inorganic glass component affords high proton conduction and dimensional stability, while the organic component provides sufficient mechanical strength and flexibility. In the present work, the NPS glass with 10 wt% Nafion[®] developed by our group [16], showing high proton conductivity of ca. 10^{-1} S cm⁻¹, was chosen as the glass component of the composite membrane, and sulfonated poly(ether ether ketone) (SPEEK) was utilized as organic polymeric component due to its adequate proton conductivity, low cost, superior mechanical strength, and high thermal and chemical stabilities

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[17]. The NPS glass in powder form was incorporated into the SPEEK polymer so that a large-size, flexible, glass-based composite membrane was fabricated.

Such a composite membrane exhibits efficient proton conduction capability. We showed that a single fuel cell equipped with the composite membrane achieved a peak power density of 322 mW cm^{-2} , which is much higher than the values of $6\text{--}165 \text{ mW cm}^{-2}$ for fuel cells using glass-based electrolytes reported previously [13–15,18].

2. Experimental

2.1. Materials

$\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS, Sinopharm), H_3PO_4 (85% aqueous solution, Sinopharm), Nafion[®] perfluorinated ion-exchange resin (10 wt% solution in a mixture of lower aliphatic alcohols and water, DuPont), and poly(ether ether ketone) (PEEK) (Grade 450-P, Victrex Inc.) were used without further purification.

2.2. Preparation

The NPS glass was prepared by a sol-gel method as reported previously [16]. Briefly, a mixture of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS), deionized water, and hydrochloric acid in a molar ratio of $1:4:4 \times 10^{-3}$ (TEOS:H₂O:HCl) was firstly prepared and stirred for 30 min at room temperature. Then, phosphoric acid solution and Nafion[®] resin in molar ratios of 7:3 (H_3PO_4 :TEOS) and 1:9 (Nafion[®]:TEOS) were slowly added to the above mixture and stirring was continued for 20 min. The obtained transparent solution was then transferred to a Teflon vessel and left to stand at room temperature until gelation occurred. The gel was then hydrothermally treated at 150°C for 24 h under saturated water vapor. After these procedures, an NPS glass monolith was obtained, which was subsequently crushed to powder form using an agate mortar.

PEEK was sulfonated using concentrated sulfuric acid according to a procedure described elsewhere [19]. PEEK powder (5 g) was added to 95–97% sulfuric acid (100 mL) under vigorous stirring and the mixture was stirred for 3 h at 50°C . The polymer was then precipitated by pouring the solution into a large excess of iced water. The precipitated polymer was collected by filtration, washed repeatedly with distilled water until the washings were of neutral pH, and dried overnight. The degree of sulfonation (DS) was determined by titration with NaOH followed by back-titration with HCl.

The composite membranes were prepared by solvent casting. The SPEEK polymer was firstly dissolved in dimethylformamide (DMF) to prepare a 10 wt% solution, and then different amounts of the NPS glass powder were added. To indicate the different weight ratios of NPS glass and SPEEK polymer in the samples, such as 7:3, 6:4, and 5:5, they were designated as 7NPS/3SPEEK, 6NPS/4SPEEK, and 5NPS/5SPEEK, respectively. The resultant mixtures were milled using a planetary ball-mill apparatus (QM-3SP2, NanDa Instrument Plant) for 3 days. Thereafter, the obtained suspensions were cast onto glass plates and then dried at 120°C for 6 h to form (Nafion[®]/phosphosilicate)/SPEEK (NPS/SPEEK) composite membranes ranging from tens to hundreds of micrometers in thickness. A schematic illustration of the preparation of the NPS/SPEEK composite membranes is shown in Fig. 1.

2.3. Characterization

Optical images of samples were captured using a digital camera (DSC-W50, Sony). X-ray diffraction (XRD) patterns were recorded on an X-ray polycrystalline diffractometer (D8-Advance, Bruker). Infrared spectra were recorded on an FTIR spectrometer (Equinox

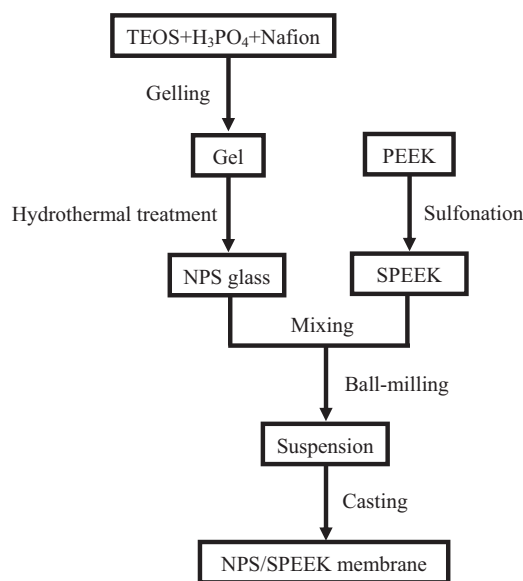


Fig. 1. Preparative procedure for obtaining the NPS/SPEEK composite membranes.

55, Bruker Co.). The porous structure of the samples was analyzed by means of a nitrogen adsorption-desorption apparatus (ASAP 2010 M+C, Micromeritics Inc.) after degassing under vacuum at 120°C . Scanning electron microscopy (SEM) images were obtained on a field-emission SEM (NOVA, NanoSEM 230).

Proton conductivities were measured by impedance spectroscopy in a two-electrode geometry at an AC amplitude of 10 mV using an impedance analyzer (SI 1260, Solartron). Gold electrodes were sputtered onto the membranes through a shadow mask with a diameter of 2 mm. Electrical contacts to both electrodes were made with soldered Au wires. Prior to the measurement, the sample was placed in a closed chamber until equilibrium was attained. Data were collected following stepwise changes in the relative humidity or chamber temperature. The proton conductivity, σ (S cm^{-1}), of the samples was calculated from the following formula:

$$\sigma = \frac{l}{AR} \quad (1)$$

where l is the thickness of the membrane, A is the area of the electrode, and R is the membrane resistance determined from the complex impedance plot.

Water uptake and swelling ratio were measured by the difference in weight and length between the dried and wetted membranes. The membranes (5 cm long, 1 cm wide) were dried at 120°C for 24 h, and then their weights and lengths were measured. After that, the membranes were soaked in distilled water at room temperature for 24 h. Then the membranes were taken out and the liquid water on the surface of the wetted membranes was wiped off using tissue paper. The weights and lengths of the wetted membranes were recorded. Water uptake was calculated from the following formula:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where W_{wet} and W_{dry} are the weights of the wetted and dried membranes, respectively.

Also, swelling ratio was calculated from the following formula:

$$\text{Swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\%$$



Fig. 2. Optical image of an NPS/SPEEK composite membrane.

where L_{wet} and L_{dry} are the lengths of the wetted and dried membranes, respectively.

The tensile test of samples was carried out on a mechanical testing machine (MTS, CMT4000). The membranes were cut into normal dog-bone-shape, and stretched at a constant crosshead speed of 5 mm min^{-1} under atmospheric environment.

2.4. H_2/O_2 fuel cell test

Gas-diffusion electrodes (GDEs) with a Pt loading of 0.5 mg cm^{-2} were prepared by spraying Pt/C catalyst ink onto wet-proofed Toray carbon paper. The GDEs were then attached on both sides of the NPS/SPEEK composite membrane to form a sandwich structure. An MEA with circular 0.8 cm diameter active electrodes was then prepared by hot-pressing the sandwich structure under 0.3 MPa at 135°C . For comparison, a fuel cell using the NPS glass as the electrolyte membrane was prepared, for which the MEA was made by attaching the electrodes onto the glass membrane using Nafion[®] solution ($10 \text{ wt}\%$ solution) as an adhesive without hot-pressing procedure. The H_2/O_2 fuel cells were fuelled with hydrogen supplied to the anode and oxygen supplied to the cathode, each at a pressure of 1 atm . The flow rates and humidification of the gases and the temperature of the cell were controlled by a fuel-cell testing system (FC 5100, CHINO Corp.). Polarization curves were collected by an electrochemical interface (SI 1287, Solartron).

3. Results and discussion

3.1. Appearance and chemical structure of the NPS/SPEEK composite membranes

It is known that the proton conductivity of SPEEK strongly depends on the degree of sulfonation (DS) [20]. A high DS with many hydrophilic groups leads to high conductivity, but is associated with a greater susceptibility to swelling and fragility, while a low DS gives low conductivity, but high mechanical and thermal stability [21]. In this study, the DS of SPEEK was set at 0.6 with the aim of achieving a compromise between the requirements of adequate proton conductivity and reasonable stability.

The NPS/SPEEK composite membranes with various weight ratios of NPS glass powder to SPEEK polymer were prepared. Fig. 2 depicts a photograph of a 6NPS/4SPEEK composite membrane, showing sufficient flexibility and a large size of more than 150 cm^2 . The composite membranes had a yellowish, opaque, and glassy appearance, while a pure SPEEK membrane was observed to be

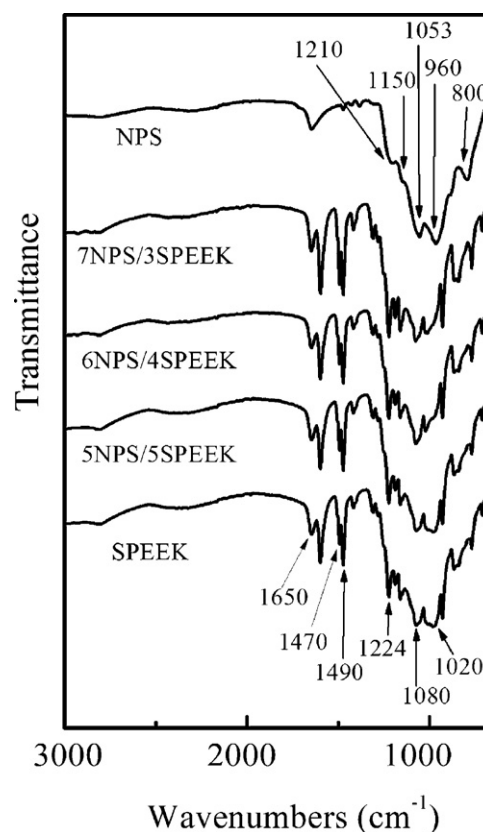


Fig. 3. Infrared spectra of the NPS/SPEEK composites, the NPS glass, and the SPEEK polymer.

yellow and transparent. In addition, the higher the SPEEK content in the NPS/SPEEK composite membranes, the more flexible they become.

FTIR spectra of the NPS glass, the NPS/SPEEK composites, and pure SPEEK were recorded to confirm their chemical structures, and they are shown in Fig. 3. For the NPS glass, the peaks at 800 and 1053 cm^{-1} may be assigned as the characteristic peaks of Si–O–Si [22], which provide evidence for the formation of the Si–O–Si skeleton by the condensation reaction. An absorption shoulder at 960 cm^{-1} can be assigned to the Si–O stretch of silanol groups, Si–OH [23]. Two peaks at 1210 and 1150 cm^{-1} are attributed to

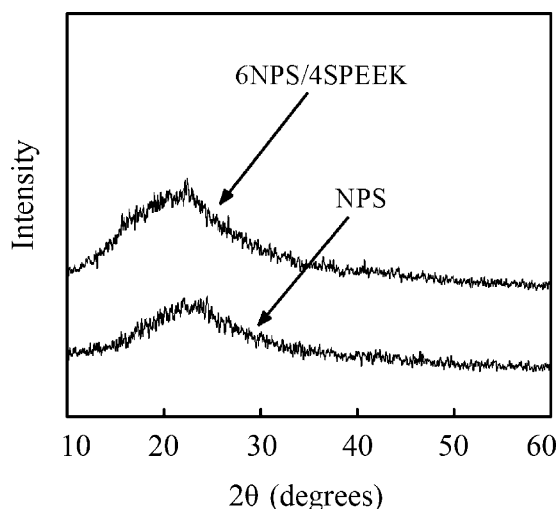


Fig. 4. XRD patterns of the 6NPS/4SPEEK composite and the NPS glass.

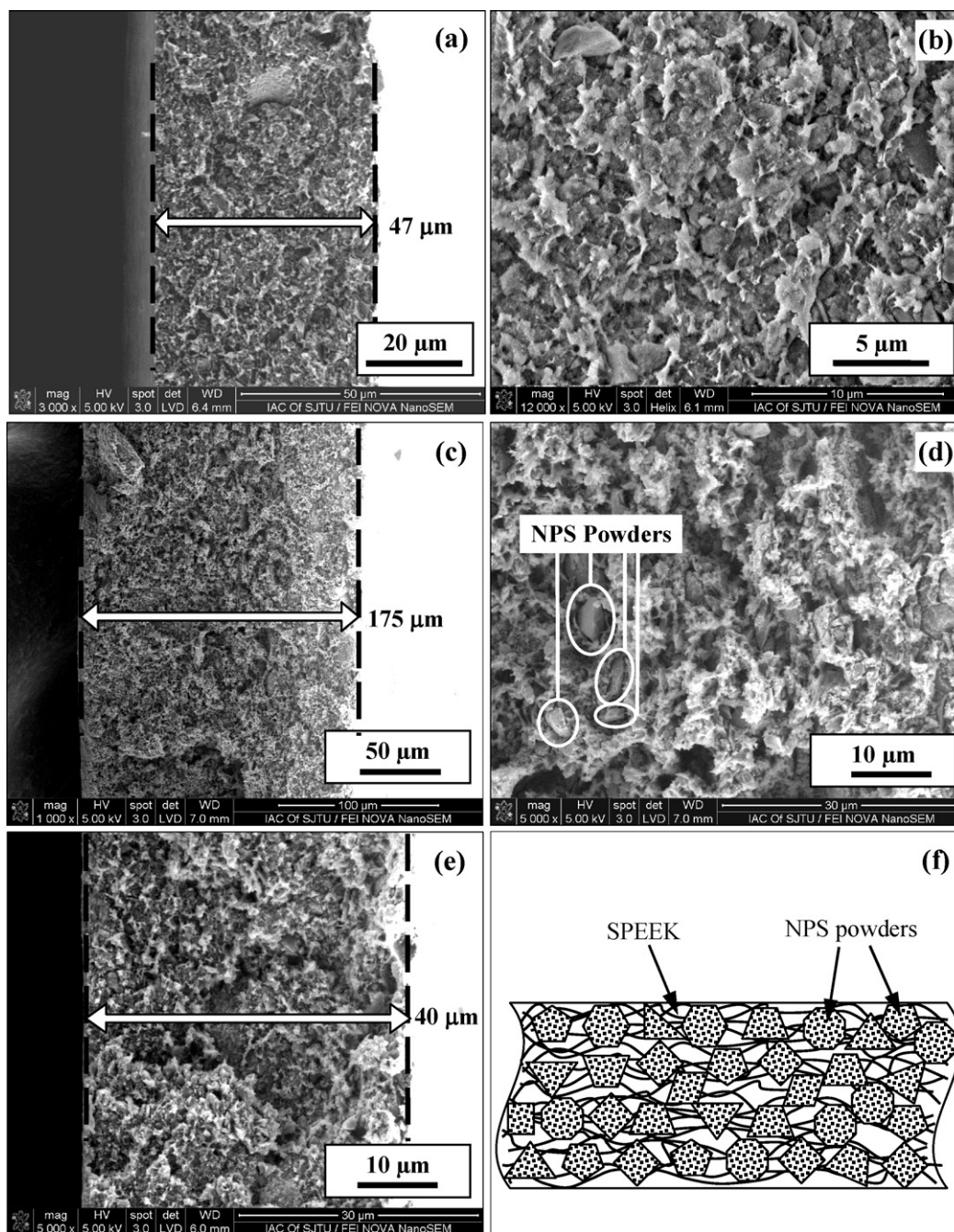


Fig. 5. SEM images of the 5NPS/5SPEEK (a), the 6NPS/4SPEEK (c), and the 7NPS/3SPEEK (e) composite membranes, respectively; (b) and (d) high-magnification SEM images of the 5NPS/5SPEEK and the 6NPS/4SPEEK membranes, respectively; (f) schematic illustration of the NPS/SPEEK composite membranes.

the C–F stretching modes of the perfluorosulfonic acid polymer (Nafion®) [24]. For pure SPEEK and the SPEEK incorporated into the NPS/SPEEK composites, successful sulfonation was verified by the absorptions at 1224, 1080, and 1020 cm^{-1} , attributable to O=S=O vibrations of the sulfonic acid group [25]. The absorption split into two peaks at 1470 and 1490 cm^{-1} may be attributed to C–C stretches of the newly sulfonated aromatic ring [26], and these are also characteristic peaks confirming the structure of SPEEK. The absorption at 1650 cm^{-1} corresponds to the carbonyl group of SPEEK [19].

Fig. 4 shows the XRD patterns of the NPS glass and the 6NPS/4SPEEK composite membrane. A typical amorphous reflection peak ranging from 15 to 30° is observed, suggesting the existence of an amorphous matrix in the NPS glass. PEEK is a

semicrystalline polymer, showing sharp crystalline peaks in the 2 θ range 20–30° [27]. Sulfonation strongly decreases its crystallinity [25]. For the 6NPS/4SPEEK composite membrane, a weak reflection peak at 22.5° overlaying the broad amorphous peak is observed, which may be ascribed to the SPEEK component.

3.2. Morphology and pore structure of the NPS/SPEEK composite membranes

The morphology of the NPS/SPEEK composite membranes was observed by the field-emission SEM. The cross-section SEM images in Fig. 5(a), (c) and (e) reveal that the 5NPS/5SPEEK, 6NPS/4SPEEK, and 7NPS/3SPEEK composite membranes had thicknesses of 47, 175 and 40 μm , respectively. Fig. 5(b) and (d) is

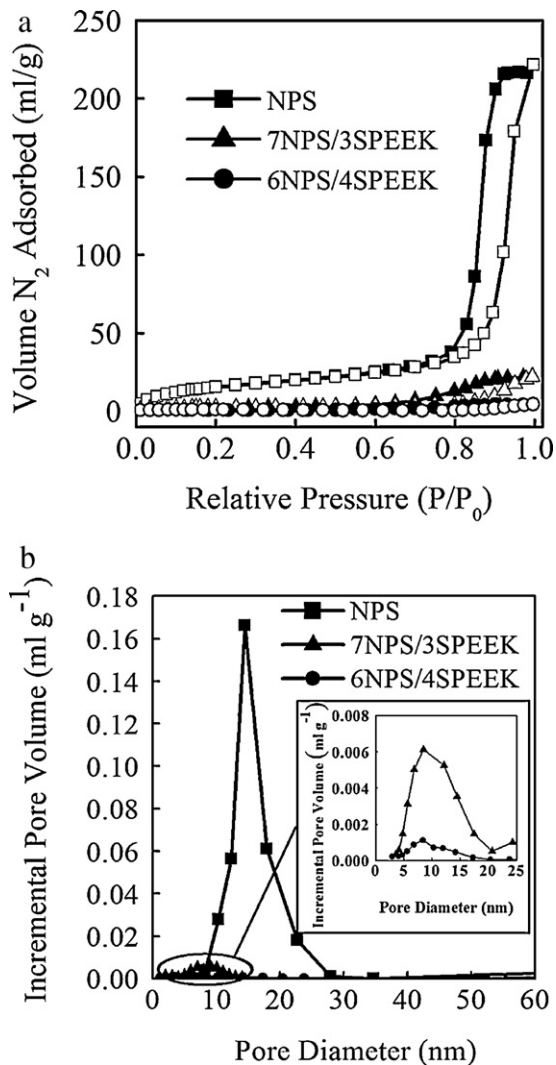


Fig. 6. (a) N_2 adsorption–desorption isotherms of NPS glass and the NPS/SPEEK composite membranes. Empty and filled symbols indicate the adsorption and desorption branches, respectively. (b) Pore-size distribution curves for NPS glass and the NPS/SPEEK composite membranes.

high-magnification SEM images of 5NPS/5SPEEK and 6NPS/4SPEEK membranes, respectively. Fig. 5(d) shows that NPS glass powder particles were entrapped within a continuous matrix, in which no aggregation of the glass particles was observed. As shown schematically in Fig. 5(f), the NPS/SPEEK composite membrane consisted of a SPEEK polymer matrix and dispersed NPS glass powder particles. Such a continuous matrix of SPEEK polymer containing highly dispersed NPS glass particles could endow the composite membrane with good mechanical flexibility, which is crucial for MEA preparation for fuel cells.

The porous structure and accessibility of the NPS glass and the NPS/SPEEK composite membranes were evaluated by N_2 adsorption–desorption measurements. It is known that the width of the hysteresis gives an indication of the accessibility of the pores, and the wider the hysteresis, the more interconnected the pores [7]. As can be seen in Fig. 6(a), the NPS glass had a large hysteresis, which is a typical mesoporous character due to capillary condensation, indicating a high degree of pore interconnection and corresponding gas accessibility, whereas the 7NPS/3SPEEK and 6NPS/4SPEEK composite membranes possessed an extremely small hysteresis, implying restricted interconnection and gas inaccessibility. The pore-size distributions of the samples were determined

by the BJH equation, using the desorption branches of the N_2 adsorption–desorption isotherms. Fig. 6(b) shows that the NPS glass had an average pore diameter of 14.6 nm, and the inset therein reveals that the 7NPS/3SPEEK and 6NPS/4SPEEK composites had average pore diameters of 9 and 6.9 nm, respectively. In addition, the NPSi glass had a pore volume of $0.343\ ml\ g^{-1}$, while the two composites had pore volumes of 0.034 and $0.007\ ml\ g^{-1}$, respectively. Clearly, the NPS glass had higher pore volume and larger pore size, and hence greater gas accessibility in comparison with the NPS/SPEEK composites.

For proton-conducting glass membranes, interconnection between the pores is essential for achieving high proton conductivity [11]. However, interconnected pores may lead to severe fuel leakage. N_2 adsorption–desorption analysis has demonstrated that in the NPS/SPEEK composite membranes the incorporated SPEEK polymer may serve to block pores and to reduce the pore volume and the pore interconnection. In the composite membranes, in which NPS glass particles were encapsulated with SPEEK polymer, as confirmed by SEM analysis, the SPEEK content was evidently sufficient to block the gas accessibility.

3.3. Proton-conducting properties, water uptake and swelling ratio

The proton-conducting properties of the samples were examined by AC impedance spectroscopy. The membrane resistance, R , was obtained from the intercept on the real axis in the high-frequency range, and it was imputed into Eq. (1) to calculate proton conductivity. The obtained proton conductivities were compared with that of the NPS glass reported by our group [16]. Fig. 7(a) shows the proton conductivities of the NPS/SPEEK composites, pure SPEEK, and NPS glass under various relative humidities at 50°C . The conductivities of all of the membranes are seen to increase evidently with increasing relative humidity. This tendency indicates that water plays an important role in proton conduction of these membranes. This is due to the fact that increasing water content provides more proton-jumping sites [23]. In this study, proton conductivities of the pure SPEEK made with DMF casting solvent amount to 10^{-5} – $10^{-4}\ S\ cm^{-1}$ within the relative humidity (RH) range from 70% to 90%. The values are much lower than 10^{-3} – $10^{-2}\ S\ cm^{-1}$ of SPEEK using N,N-dimethylacetamide (DMAC) casting solvent [28], but are comparable to $\sim 10^{-5}\ S\ cm^{-1}$ of SPEEK (0.65 DS) with identical DMF casting solvent [29]. The large discrepancies in conductivity data may be due to chemical interactions of SPEEK with the various solvents [30]. In comparison with DMAC, DMF as a casting solvent has a strong interaction with SPEEK, which leads to its lesser number of available acid groups, and consequently results in the reducing proton conductivity [19].

Fig. 7(b) demonstrates the temperature dependences of the proton conductivities of the NPS/SPEEK composites and of pure SPEEK measured at 90% RH. It can be seen that the conductivities of all of the membranes increased with increasing temperature. Within the temperature range examined, the NPS/SPEEK composite membranes have quite high proton conductivities of above $10^{-3}\ S\ cm^{-1}$. In particular, the 7NPS/3SPEEK membrane, with the highest content of NPS glass, shows the highest proton conductivity of $0.015\ S\ cm^{-1}$ at 80°C and 90% RH.

Fig. 7(a) and (b) shows the effects of SPEEK content on proton conductivity against temperature and relative humidity, respectively. In such a composite system, the macroscopic conductivity should depend on the conductivities of the individual components and their contents. As shown in Fig. 7(a), the NPS glass has high proton conductivities of 10^{-2} – $10^{-1}\ S\ cm^{-1}$ [16], which are much higher than that of the SPEEK polymer used in this study. As a result, the higher the NPS glass content, the higher the proton conductivity. Indeed, as can be seen in Fig. 7(a) and (b), the 7NPS/3SPEEK

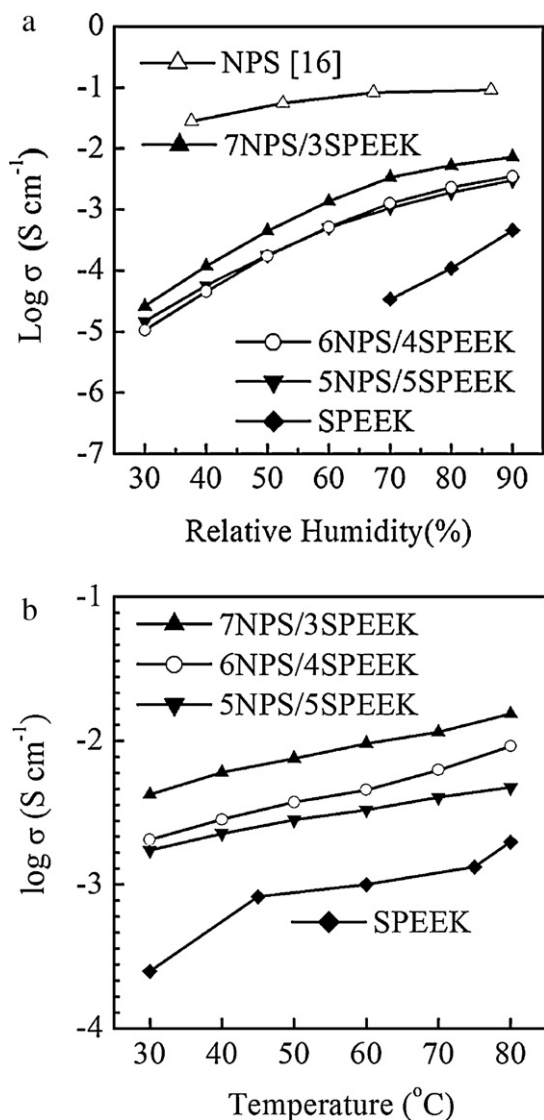


Fig. 7. (a) Proton conductivities of the NPS/SPEEK composites, the pure SPEEK, and the NPS glass plotted against relative humidity at 50 °C. (b) Temperature dependences of the proton conductivities of the NPS/SPEEK composites and the pure SPEEK measured at 90% RH.

composite with the highest content of NPS glass exhibited the highest proton conductivity. It is noteworthy that the SPEEK polymer itself was shown to have reasonable proton-conducting capability, hence its incorporation into the composite membrane did not lead to a notable sacrifice in proton conductivity.

Water uptake and swelling ratio of the membranes are important parameters in the study of PEMFCs. Proton conductivity depends on water content of the membrane. However, very high water uptake may lead to excessive swelling, resulting in fragility and mechanical instability of membranes. Water uptake and swelling ratio of the pure SPEEK and the 6NPS/4SPEEK membranes were measured. The experimental results show that the pure SPEEK membrane has water uptake of 30% and swelling ratio of 5.1%, while the 6NPS/4SPEEK membrane possesses water uptake of 9.8% and very small swelling ratio of 0.5%. Clearly, the incorporation of the NPS glass powders within the composite membrane plays a very important role for restraining the swelling of membrane body, and the NPS glass powders may serve as nano-scale reinforcements and fixtures.

Good mechanical strength is essential for fuel cell application. It was determined that the 6NPS/4SPEEK membrane has a tensile

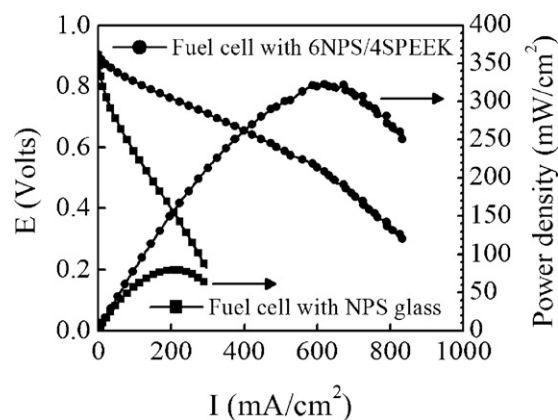


Fig. 8. *I*-*V* and power density curves of both fuel cells operated at 65 °C, which are based on the 6NPS/4SPEEK membrane, and the NPS glass, respectively.

strength of 18 MPa, and a breaking elongation of 1.4% showing a typical brittle behavior. The tensile strength value is much smaller than 51 MPa of the pure SPEEK membrane, but is comparable to 15.5 MPa of a recasted Nafion membrane [31].

3.4. H₂/O₂ fuel cell testing

From among the NPS/SPEEK composites, the 6NPS/4SPEEK membrane was selected to prepare a single fuel cell. The 6NPS/4SPEEK membrane used had a thickness of ca. 30 μm. For comparison, a fuel cell using the NPS glass was also prepared. Both fuel cells were tested by feeding humidified H₂ and O₂ to the anode and cathode, respectively, at 65 °C. The gas flow rates of H₂ and O₂ were 30 sccm and 60 sccm, respectively. A polarization curve was recorded to assess the overall performance of the fuel cell, as shown in Fig. 8. Power density was simultaneously derived from the *I*-*V* curve. The fuel cell based on the 6NPS/4SPEEK membrane has an open-circuit voltage of 0.93 V. A small drop of the cell voltage under an initial small load current was indicative of a low activation potential loss. The flexible NPS/SPEEK composite membrane could endure sufficient hot-pressing to assemble the MEA, so that good interfacial contacts between the electrolyte membrane and the GDE with Pt/C catalyst were formed. The peak power density of the fuel cell reached 322 mW cm⁻², which is much higher than the values of 6–163 mW cm⁻² previously reported for fuel cells utilizing glass-based electrolytes [13–16,18]. To the best of our knowledge, this value is the highest output power obtained for a fuel cell with a glass-based electrolyte. In comparison, the fuel cell based on the NPS glass without the hot-pressing procedure, due to the fact that hot-pressing would crush the NPS glass, released a peak power density of 80 mW cm⁻², as shown in Fig. 8. This value is much lower than that of the fuel cell with the 6NPS/4SPEEK composite membrane. The large discrepancy in output power may be due to the difference of interface resistance between the electrolyte membrane and electrodes for both fuel cells. The NPS glass has high proton conductivities of 10⁻²–10⁻¹ S cm⁻¹, giving a low electrolyte resistance. However, the high interface resistance arisen between the NPS glass and electrodes due to poor interface contact without hot-pressing procedure may result in the remarkable reduction in output power.

4. Conclusion

Proton-conducting composite membranes based on NPS glass and SPEEK polymer have been successfully prepared by a simple mechanical ball-milling approach. The large-size NPS/SPEEK composite membranes were found to be flexible, and they showed very

promising proton conductivities of above $10^{-3} \text{ S cm}^{-1}$ under 90% relative humidity. The incorporated SPEEK polymer remarkably reduced the pore volume of the composite membranes. A single H_2/O_2 fuel cell equipped with the composite membrane released a peak power density of 322 mW cm^{-2} . Based on the promising output power, such low-cost, flexible composite membranes may possibly be used as novel proton-exchange membranes in fuel cells. Another possible application of this kind of membrane might be in hydrogen and humidity sensors.

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