A “H₂O donating/methanol accepting” platform for preparation of highly selective Naion-based proton exchange membranes†

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For a proton exchange membrane (PEM), the ratio of its proton conductivity to its fuel permeability usually defines the membrane selectivity. Generally, a highly selective PEM is preferred for application in direct methanol fuel cells. Herein, sulfonated SiO₂@polystyrene core–shell (SiO₂@sPS) nanoparticles were synthesized and then imbedded into a Naion membrane by a blending–casting method. SiO₂@sPS partakes in strong interactions with the Naion polymer, which benefits its dispersion in the membrane matrix. The as-prepared SiO₂@sPS + Naion composite PEM presents a large increase in its proton conductivity owing to the introduction of additional −SO₃H groups and hence has optimized channels for proton transport. Meanwhile, a reduced methanol crossover was also observed for the SiO₂@sPS + Naion composite PEM because of the formation of obstructed transport channels for bulk methanol. Besides this, a deep investigation on further enhancement of the membrane’s performance was conducted by etching the SiO₂ core and hence forming well-dispersed uniform hollow spheres inside the membrane matrix. The intact hollow sulfonated PS spheres (h-sPS) acted as water reservoirs which in turn could gradually release water to hydrate the membrane under high-temperature and low-humidity conditions. Therefore, compared to the SiO₂@sPS + Naion membrane, the h-sPS + Naion one presented a further increased proton conductivity at 100 °C under 40% RH. Meanwhile, h-sPS further suppressed methanol penetration by trapping it inside the hollow spheres. Herein, a “H₂O donating/methanol accepting” mechanism was proposed for the first time, providing a promising platform to alleviate critical disadvantages of Naion membranes and thereby fabricate highly selective Naion-based PEMs.

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) provide a promising alternative to the conventional internal combustion engines owing to their environmental friendliness and high energy conversion efficiency.1,2 They have triggered extensive efforts with a view to driving the traditional society dependent on fossil fuels to move into a new world powered by clean energy technologies. Among PEMFCs, direct methanol fuel cells (DMFCs) stand out by virtue of their distinctive advantages, such as high volumetric and specific energy densities, moderate operation temperature, no requirement of a fuel reformer, low emission and long lifetime. Besides this, the fuel storage problems, typical of hydrogen fed fuel cells, are not a concern for DMFCs, because the liquid nature of methanol is a great convenience in the transportation and storage of fuel for DMFCs. This is very attractive, especially when environmental and economic concerns become a stress in modern society. DMFCs may claim a niche in the market of mobile electrical power generators.

DMFCs employ a proton exchange membrane (PEM) to separate methanol from the oxidant and simultaneously conduct protons from the anode to the cathode to fulfill the conversion of chemical energy into electrical energy. Therefore, the PEM, acting as a vital building component of DMFCs, plays a pivotal role in the DMFCs’ performance. Perfluorosulfonated polymers, e.g. Naion, are the current state-of-the-art commercial PEMs.3 Naion possesses a polytetrafluoroethylene backbone with short perfluoroether side chains bearing terminal −SO₃H groups. The hydrophobic regions bestow excellent thermo-mechanical stability and chemical resistivity upon the Naion membranes, while the hydrophilic domains form well-
interconnected ionic channels which make high proton conductivity possible. All of these properties are requisite for application in DMFCs. Besides this, in consideration of catalyst poisoning and fuel efficiency as well as heat and water management, DMFCs operating under high temperature and low humidity are often desired. However, the typical drawbacks of Nafion membranes, i.e. reduction of proton conductivity above 80 °C and extensive methanol crossover, are detrimental for their practical application in DMFCs. Generally, any methanol crossover will decrease the overall fuel efficiency and simultaneously reduce the cell voltage. An ideal PEM should exhibit a high proton conductivity with a parallel low methanol crossover. However, protons and methanol migrate via similar channels consisting of hydrophilic ionic cluster domains through a Nafion membrane. In most cases, the improvement of the methanol crossover is achieved at the expense of the proton conductivity, or vice versa. Therefore, the current Nafion-based PEMs still perform below the desired real-world application requirements, and the development of PEMs with enhanced transport properties, e.g. high proton conductivity and low methanol permeability, has generated renewed research attention.

Serious efforts have been made to eliminate such a tradeoff relationship between the proton conductivity and methanol permeability of PEMs to render them suitable for real-world DMFC applications, namely: (1) the development of alternative polymeric PEMs whose ionic clusters possess a small percolation size for methanol permeation, such as sulfonated polymeric PEMs whose ionic clusters possess a small percolating domain. As a result, a further increase in the proton conductivity and low methanol permeability, has generated renewed research attention.

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2 Experimental

2.1 Materials

Tetraethylorthosilicate (TEOS), 3-(methacryloyloxy)propyltrimethoxysilane (MPS), N,N'-methylenebisacrylamide (BIS), potassium persulfate and dimethyl sulfoxide-d_6 (D-DMSO) were purchased from Aladdin. Absolute ethanol, ammonia, styrene, 1,2-dichloroethane, acetic anhydride, concentrated sulfuric acid, dimethylformamide (DMF), H_2O_2 solution and HF solution were provided by Sinopharm Chemical Reagent Co., Ltd. Nafion solution (perfluorinated resin solution, 5 wt% in a lower aliphatic alcohol and water mixture) was obtained from Sigma-

However, inorganic materials often suffer from poor compatibility with the Nafion polymer, resulting in an unsatisfactory dispersion of the inorganic components in the Nafion membrane. Hence, non-selective gaps may emerge in the membrane matrix with negative influences on the membrane performance. Although attaching organic components, e.g. polymers, onto the surface of inorganic materials can effectively strengthen the interactions between the additives and the membrane matrix, it usually hides the distinctive benefits of the inorganic components themselves.

In this study, a new platform was developed to prepare highly selective Nafion-based PEMs with the aid of sulfonated organic-inorganic hybrid materials, where the ratio of proton conductivity to methanol permeability defines the membrane selectivity. To be specific, first, sulfonated SiO_2@polystyrene core–shell (SiO_2 (sPS) nanoparticles were synthesized and then imbedded into the Nafion membrane through a traditional blending–casting method. The sulfonated polystyrene (sPS) shell strengthens the interactions between SiO_2 (sPS) and the Nafion matrix via (1) SO_3H (SiO_2 (sPS)) ··· SO_3H (Nafion) hydrogen bonding interactions and (2) hydrophobic interactions between the PS chains and Nafion backbones. Hence, SiO_2 (sPS) nanoparticles are dispersed well in the Nafion membrane. Resultantly, a significant increase in the proton conductivity of the SiO_2 (sPS) + Nafion composite PEM was observed because of the introduction of additional SO_3H groups and hence the ionic cluster channels are optimized for proton transport. Meanwhile, the SiO_2 (sPS) + Nafion composite PEM presented reduced methanol permeability, probably due to the increased tortuosity of the methanol transport channels. Second, to reveal the distinctive advantages of the inorganic component, a template method was further utilized by etching the SiO_2 core to form well-dispersed hollow sPS (h-sPS) spheres inside the membrane matrix in situ. This further enhanced the membrane selectivity owing to the following two advantages. One was that a large amount of free H_2O could be reserved in the h-sPS spheres, which rendered the h-sPS + Nafion composite PEM a stable water environment, resulting in a slower reduction of its proton conductivity under high temperature and/or low humidity. Second, methanol might be impeded by being captured inside the h-sPS spheres. Herein, a “H_2O donating/methanol accepting” mechanism was proposed for the first time, providing another promising approach to alleviate the critical disadvantages of Nafion-based PEMs.
Aldrich. All the other reagents were received from commercial suppliers and used as received unless otherwise stated.

2.2 Preparation of SiO$_2$
First, 20 mL TEOS was added into a mixture of 70 mL H$_2$O, 162.5 mL absolute ethanol and 17.5 mL ammonia. The system was vigorously stirred (400 rpm) at 30 °C for 1 h. Then, a white SiO$_2$ powder was obtained by centrifugation. This was washed with ethanol several times before being vacuum-dried at 70 °C. Finally, 5.2 g SiO$_2$ was produced.

2.3 Preparation of “SiO$_2$@=”
0.5 g of as-prepared SiO$_2$ powder was dispersed homogeneously in 250 mL absolute ethanol by being sonicated for at least 4 h. Subsequently, 15 mL MPS was added into the SiO$_2$/ethanol dispersion. The system was vigorously stirred at 40 °C for 24 h. Then, a white powder was obtained by centrifugation. Lastly, the powder was washed with absolute ethanol several times before being vacuum-dried at 50 °C. The product, MPS-modified SiO$_2$, was marked as “SiO$_2$@=” in the following sections.

2.4 Preparation of SiO$_2$@PS
0.26 g of as-prepared “SiO$_2$@=” powder was dispersed homogeneously in 25 mL absolute ethanol by being sonicated for at least 4 h. Then, a N$_2$ flow was bubbled into the “SiO$_2$@=”/H$_2$O dispersion for 1 h before 1.6 mL styrene and 48 mg BIS were added into the dispersion. After that, 20 mg potassium persulfate was added and then the system was vigorously stirred at 70 °C for 4 h. Subsequently, a white powder was obtained by centrifugation. This was washed with absolute ethanol several times before being vacuum-dried at 60 °C. The product was marked as SiO$_2$@PS in the following sections.

2.5 Preparation of SiO$_2$@sPS
First, a N$_2$ flow was bubbled into 6 mL 1,2-dichloroethane for 0.5 h. Then, the 1,2-dichloroethane solvent was cooled in a 10 wt% CaCl$_2$ ice bath under N$_2$ atmosphere. Third, 2 mL acetic anhydride/concentrated sulphuric acid/1,2-dichloroethane mixture was quickly injected into a N$_2$-pretreated homogenous dispersion of 0.18 g SiO$_2$@PS and 10 mL 1,2-dichloroethane. The whole system was then vigorously stirred at 40 °C for 17 h under a N$_2$ atmosphere. Subsequently, a white powder was obtained by centrifugation. Finally, the powder was washed with a mixture of absolute ethanol and cyclohexane (v : v = 1 : 1) several times before being vacuum-dried at 70 °C. The product, sulfonated SiO$_2$@PS, was marked as SiO$_2$@sPS in the following sections.

2.6 Preparation of SiO$_2$@PS + Nafion composite PEMs
SiO$_2$@PS + Nafion composite PEMs were prepared by a blending–casting method. First, most of the solvent of the as-received Nafion solution was exchanged with DMF with the aid of rotary evaporation. Second, the desired amount of SiO$_2$@sPS nanoparticles was homogeneously dispersed in the Naion/DMF solution by being sonicated for 1 h. The concentration of SiO$_2$@sPS was determined according to the weight of the Naion polymer. Third, the SiO$_2$@sPS/Naion/DMF dispersion was carefully cast onto a rectangular mould in a vacuum oven at 70 °C. The temperature was gradually raised to 120 °C over 6 h. Then, the membrane was further dried under vacuum at 120 °C overnight. Fourth, the membrane was peeled off from the mould, followed by being treated in 3 wt% H$_2$O$_2$ solution at 70 °C for 2 h and then immersed in 1 M H$_2$SO$_4$ solution at 80 °C for another 1 h. Finally, the membrane was rinsed with deionized H$_2$O several times. The membrane thickness was controlled at around 60 ± 10 μm. The composite PEM with 0.5 wt% (1.0 wt%, 2.0 wt%) loading of SiO$_2$@sPS was marked as 0.5 wt% (1.0 wt%, 2.0 wt%) SiO$_2$@sPS + Naion in the following sections. A recast Naion membrane was also prepared for comparison.

2.7 Preparation of the 1.0 wt% h-sPS + Naion composite PEM
The as-prepared 1 wt% SiO$_2$@sPS + Naion composite PEM was immersed in excess 10 wt% HF solution at 30 °C for 24 h to completely dissolve the SiO$_2$. Then, the membrane was immersed in 3 wt% H$_2$O$_2$ solution at 70 °C for 2 h and then boiled in 1 M H$_2$SO$_4$ solution at 80 °C for another 1 h to transform it into the H$^+$ form. Lastly, the membrane, marked as 1.0 wt% h-sPS + Naion, was rinsed with deionized H$_2$O several times and stored in H$_2$O.

2.8 Characterization of SiO$_2$, “SiO$_2$@=”, SiO$_2$@PS, SiO$_2$@sPS and h-sPS
The morphology was observed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). All the samples were coated with gold before the FE-SEM characterization. The transmission electron microscopy (TEM) images were obtained using a JEOL JEM2100 TEM instrument operated under an acceleration voltage of 200 eV. Fourier transform infrared spectroscopy (FTIR) was conducted on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm$^{-1}$ and 64 scans. Thermogravimetric analyses (TGA) were performed under a N$_2$ atmosphere with a PerkinElmer Thermal Analyzer at a heating rate of 20 °C min$^{-1}$. $^1$H NMR (nuclear magnetic resonance) spectra were measured on a Varian Mercury plus 400 M spectrometer with D-DMSO as the solvent and tetramethylsilane as the internal reference.

2.9 Characterization of the PEMs
Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was measured on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm$^{-1}$ and 64 scans. TGA were conducted with a PerkinElmer Thermal Analyzer at a heating rate of 10 °C min$^{-1}$ under a N$_2$ atmosphere. X-ray diffraction (XRD) was performed on a PANalytical X’Pert diffractometer with Cu Kα radiation. The membrane morphology was observed by scanning electron microscopy.
made equipment at 25 and 50 °C.

Water uptake (WU) was obtained as follows:  

\[ \frac{W_{\text{dry}}}{W_{\text{wet}}} = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100 \]

Differential scanning calorimetry (DSC), carried out using a Mettler-Toledo differential scanning calorimeter thermal analyzer in a N2 atmosphere, was employed to determine the contents of freezable (free) and non-freezable (bonded) water inside the membranes via melting transitions. The tested samples, enclosed in aluminum pans, were first cooled from room temperature to −20 °C and then heated to 40 °C at a heating rate of 5 °C min−1. The ratio of free water (\( R_t \)) to the H2O-saturated PEM was estimated based on its melting enthalpy (\( \Delta H_m \)) as follows:  

\[ R_t = \frac{\Delta H_m}{H_m(\text{ice})} \]

The content of bonded water was obtained by subtracting \( R_t \) from the WU value of corresponding PEM.

Proton conductivity was measured by a four-electrode method utilizing AC impedance spectroscopy between 0.1 MHz and 1 Hz with potentiostat control (CHI660d Model). During the entire measurement, the tested conditions, i.e. humidity and temperature, were controlled by a temperature-and-humidity test chamber. The investigated sample was equilibrated under the desired conditions for 8 h before the measurement.

Methanol permeability was measured with the aid of homemade equipment at 25 and 50 °C (Fig. S1†), and the digital photos of the whole set-up for the methanol permeability measurements are presented in Fig. S2.† First, a dry PEM was put onto the ZnSe crystal of the ATR cell (Nicolet Nexus 470 FTIR spectrometer) and then sandwiched between the crystal and the PTFE mould (Fig. S1†). Second, continuous ATR-FTIR data were acquired as soon as 0.5 mL of a methanol/H2O mixture (the volume ratio of methanol to H2O is 4 : 1) was injected into the PTFE mould through a little hole (Fig. S1 and S2(E and F)). The little hole was blocked during the entire test to avoid any evaporation of methanol. The ATR-FTIR data, with a spectral resolution of 4 cm−1, were taken as a function of diffusion time. The acquisition time interval was 40 s. Third, according to the increase in the peak area of −CH3 stretching vibrations, the Fickian diffusion equation (eqn (1)), put forward by Fieldson and Barbari, was applied to estimate the diffusion coefficients of methanol in the PEMs.

3 Results and discussion

3.1 Characterization of SiO2, “SiO2@=”, SiO2@PS and SiO2@sPS

Fig. 1 depicts the morphologies of SiO2, “SiO2@=”, SiO2@PS and SiO2@sPS by SEM and TEM images. SiO2 presents an excellent spherical structure with a diameter of 330 nm and a mono-dispersed size (Fig. 1(A–D)). As seen in its FTIR spectrum shown in Fig. 2(A), SiO2 possesses the typical IR absorption of the stretching vibration of Si–O–Si linkages at 1101 cm−1. With respect to “SiO2@=”, no obvious FTIR peak typical of C==C groups is detected in its FTIR spectrum, probably because the amount of the C==C precursor MPS modified on the SiO2 surface is quite low (Fig. 2(B)). Based on the TGA results (Fig. 2(C)), compared to SiO2, “SiO2@=” presents a slightly larger weight loss (about 1.6 wt%) at 800 °C because of the decomposition of alkyl chains derived from MPS. Actually, only a small quantity of C==C groups, to subsequently graft PS chains onto the surface of SiO2, is necessary. Hence, no big morphology difference is found between SiO2 and “SiO2@=” based on their SEM and TEM images (Fig. 1(A–G)), and only a slight increase in the particle size is observed in “SiO2@=” due to the modification of MPS. For SiO2@PS, a rough polymer layer with an average thickness of about 38 nm has formed on the surface of SiO2 (Fig. 1(I–L)). Distinctive IR absorptions of PS chains are detected in its FTIR spectrum (Fig. 2(B)). The IR peaks at 3062 and 3028 cm−1 are attributed to the stretching vibrations of the C–H groups belonging to the benzene rings, while the bending vibrations of these C–H groups correspond to the sharp IR peak at 700 cm−1. The benzene rings themselves present three typical IR absorptions at 1452, 1497 and 1658 cm−1. Besides, the IR peaks stemming from the stretching vibrations of the CH2 groups in the PS backbones, below 3000 cm−1, can also be observed in the FTIR spectrum of SiO2@PS (Fig. 2(B)). TGA reveals that about 56 wt% PS is attached onto the surface of SiO2 (Fig. 2(C)).

However, after the sulfonation modification, only 23 wt% sPS with a uniform layer thickness of about 25 nm (Fig. 1(M–P)) remains on the surface of SiO2 (Fig. 2(C)). This is because the loosely attached, i.e. un-crosslinked PS chains, have been removed during the sulfonation process. Compared to that of SiO2@PS, the decomposition temperature of the PS shell of SiO2@PS shifts from 392 up to 421 °C (Fig. 2(D)). It is worth noting that the DTG peak around 350 °C corresponds to the desulfonation process of SiO2@PS (Fig. 2(D)). The FTIR spectrum of SiO2@PS also confirms the successful sulfonation modification by displaying two IR peaks at 1036 and 675 cm−1, respectively corresponding to the stretching vibrations of −SO3H and C–S groups (Fig. 2(B)). The degree of sulfonation (DS) of SiO2@sPS is addressed with the aid of 1H NMR. Fig. 2(E) shows the chemical structure of the sPS shell, and Fig. 2(F) presents the 1H NMR spectra of SiO2@PS and SiO2@sPS. For SiO2@PS, the two 1H NMR peaks between 7.6 and 7.8 ppm are attributed to the H atoms belonging to the benzene rings of PS, while the detailed assignment of the 1H NMR peaks of SiO2@sPS is provided in Fig. 2(E and F). Thereby, DS is estimated as DS (%) = 100% \times (c/2)/(a/2 + b/3), where a and c refer to the areas of the 1H NMR peaks labelled as “b” and “c” in Fig. 2(F), respectively. Herein, the DS value of SiO2@sPS is estimated to be about 57% of the PS repeated units.
3.2 Characterization of SiO$_2$@sPS + Nafion composite PEMs

Generally, the hydrophobic backbones (–CF$_2$–)$_n$ and hydrophilic –SO$_3$H groups of Nafion present their symmetric stretching vibrations at 1151 and 1055 cm$^{-1}$, respectively, while their asymmetric stretching vibrations display a superimposed IR peak at 1213 cm$^{-1}$ (Fig. 3(A)). The doublet around 982 and 970 cm$^{-1}$, also typical for the Nafion polymer, corresponds to the stretching vibrations of the –COC– linkages in its side chains.$^4$ When SiO$_2$@sPS was incorporated into the Nafion matrix, the IR peaks at both 1213 and 1151 cm$^{-1}$ shifted evidently in the FTIR spectra of the 0.5, 1 and 2 wt% SiO$_2$@sPS + Nafion membranes. This demonstrates the existence of strong interactions between SiO$_2$@sPS and the Nafion matrix. Such interactions probably come from (1) the hydrogen bonding interactions between –SO$_3$H (SiO$_2$@sPS) and –SO$_3$H (Nafion)$^{45}$ and (2) the hydrophobic interactions between the PS chains and Nafion backbones.$^{46}$ Meanwhile, the IR absorption at 1055 cm$^{-1}$ was strengthened because of the introduction of more –SO$_3$H groups into the membrane matrix. Understandably, with the SiO$_2$@sPS concentration increasing from 0 wt% to 2.0 wt%, the shoulder peak around 1100 cm$^{-1}$, assigned to the stretching vibrations of Si–O–Si linkages, becomes more evident and a similar trend is also observed for the stretching vibrations of the CH(1/2) groups of PS at about 3062 and 3028 cm$^{-1}$.

XRD is a powerful technique to affirm microstructural changes of Nafion-based PEMs.$^{47,48}$ A very broad peak is usually observed in the XRD patterns of Nafion membranes at around 2$\theta$ = 17° (Fig. 3(B)). To be more specific, the amorphous regions of a Nafion membrane mainly contribute to the lower-2$\theta$ part (about 16.1°) of its XRD peak at around 2$\theta$ = 17°, while the higher-2$\theta$ part (about 17.7°) is attributed to its crystalline regions.$^{47,48}$ Compared to that of the recast Nafion, the peak at around 2$\theta$ = 17° shifts slightly to lower 2$\theta$ in the XRD patterns of the SiO$_2$@sPS + Nafion membranes, and the shift degree seems to be proportional to the SiO$_2$@sPS concentration. This indicates that the strong interactions between SiO$_2$@sPS and the Nafion matrix somewhat hinder the crystallization of the Nafion membrane. The TGA results in Fig. 3(C and D) also reveal the existence of interactions between SiO$_2$@sPS and the Nafion matrix. A very slight increase in the decomposition temperatures of the Nafion backbones and side chains can be obtained in SiO$_2$@sPS + Nafion, probably due to strong interactions between SiO$_2$@sPS and Nafion. Many prior studies also found that strong interactions between incorporated additives and the Nafion backbones could effectively enhance the thermal stability of the Nafion backbones.$^{4,46}$ Such interactions probably
reinforce the decomposition reactions of Na\(_2\)fon backbone. To some extent, SiO\(_2\)@sPS suppressing the diffusion of decomposed products during the heating process may also make a contribution to this phenomenon.\(^4\)

The intensity of the XRD peak is actually in proportion to the electron density difference between the ionic cluster domains and the backbone regions of the Na\(_2\)fon membrane.\(^{46,47}\) As depicted in Fig. 3(B), the peak intensity increases in the SiO\(_2\)@sPS + Na\(_2\)fon membranes because of the introduction of more –SO\(_3\)H groups into membrane matrix. These additional –SO\(_3\)H groups can interact with the original –SO\(_3\)H groups of the Na\(_2\)fon polymer via hydrogen bonding interactions. It enlarges the size of the ionic clusters and then increases the electron density difference between the ionic cluster domains and the backbone regions. This is also the reason that the desulfonation process shifts obviously towards lower temperatures in the SiO\(_2\)@sPS + Na\(_2\)fon membranes (Fig. 3[D]).\(^{39,46}\) Hong discovered that a larger ionic cluster possesses a relatively lower desulfonation temperature,\(^{46}\) which was also confirmed by our own previous experimental results.\(^4,37\)

The enlarged ionic clusters and hence optimized ionic channels intensively benefit proton transport in the 0.5 wt% and 1.0 wt% SiO\(_2\)@sPS + Na\(_2\)fon membranes, as the activation energies of proton conduction in Fig. 4(A) illustrate. The activation energy of the recast Na\(_2\)fon is about 14.13 kJ mol\(^{-1}\) under 100% RH, while those of the 0.5 wt% and 1.0 wt% SiO\(_2\)@sPS + Na\(_2\)fon membranes decrease to 8.34 kJ mol\(^{-1}\) and 3.70 kJ mol\(^{-1}\), respectively. Thereby, the 0.5 wt% and 1.0 wt% SiO\(_2\)@sPS + Na\(_2\)fon membranes present a greatly enhanced proton conductivity compared to the recast Na\(_2\)fon, probably resulting from the aggregation of SiO\(_2\)@sPS nanoparticles.

The as-prepared composite PEMs are all transparent, as their digital photos show in Fig. S3.\(^\dagger\) The strong interactions between SiO\(_2\)@sPS and the Na\(_2\)fon matrix bestow a good dispersion of SiO\(_2\)@sPS in the Na\(_2\)fon matrix when the SiO\(_2\)@sPS concentration stays below 2.0 wt%, as shown in the SEM images in Fig. 5. When its concentration increases to 2.0 wt%, some large aggregations of SiO\(_2\)@sPS have emerged in the membrane (Fig. 5[J and L]). This may disrupt the typical hydrophobic/ hydrophilic micro-phase separations of the Na\(_2\)fon membrane.

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**Fig. 3** ATR–FTIR spectra (A), XRD patterns (B) and TGA results (C and D) of the recast Na\(_2\)fon and SiO\(_2\)@sPS + Na\(_2\)fon membranes.

**Fig. 4** Arrhenius plots (A) and temperature-dependent proton conductivities (B) of the recast Na\(_2\)fon and SiO\(_2\)@sPS + Na\(_2\)fon membranes under 100% RH.
which guarantee its good transport properties.\textsuperscript{46,49} Further increasing the incorporated concentration of SiO\textsubscript{2}@sPS is unsuitable and may be bad for the membrane performance.

With respect to another crucial transport property of Na\textsuperscript{+} on membranes, i.e. methanol crossover, SiO\textsubscript{2}@sPS can increase the tunnel zigzagging of diffusion pathways for bulk methanol, leading to the formation of obstructed channels that are detrimental to methanol crossover. Therefore, compared to the recast Na\textsuperscript{+} on membrane, the SiO\textsubscript{2}@sPS + Na\textsuperscript{+} on membranes possess lower methanol permeability at both 25 and 50 °C, as shown in Table 1. Therefore, the SiO\textsubscript{2}@sPS + Na\textsuperscript{+} on membranes present significantly enhanced membrane selectivities.

### 3.3 Characterization of the 1 wt% h-sPS + Na\textsuperscript{+} on composite PEM

Further enhancement of the membrane performance was explored by creating well-dispersed nano-sized hollow spheres inside the membrane matrix via a template etching method. Considering that the 1.0 wt% SiO\textsubscript{2}@sPS + Na\textsuperscript{+} on membrane possesses a relatively higher proton conductivity, we selected it as the subject for investigation in this section to strengthen the distinctive advantages of our approach. Herein, membrane porosity is achieved by HF solution etching of the acid labile SiO\textsubscript{2} core leaving the chemically stable sPS shell intact. As indicated by the SEM and TEM images (Fig. 6), the spherical hollow structure of h-sPS remains pristine when the SiO\textsubscript{2} core is removed, and its lumen size is similar to the size of the SiO\textsubscript{2} core. Fig. 7(A and B) show the cross-sectional SEM and TEM images of the 1.0 wt% h-sPS + Na\textsuperscript{+} on membrane. Obviously, no SiO\textsubscript{2}@sPS nano-particles are observed now, confirming the successful removal of the SiO\textsubscript{2} core from the composite PEM. This parallels the finding in Fig. 7(C) that the peak at 1100 cm\textsuperscript{-1}, typical for the stretching vibrations of Si–O–Si linkages, disappears in the FTIR spectrum of the 1.0 wt% h-sPS + Na\textsuperscript{+} on membrane. Resultantly, well dispersed h-sPS spheres remain with the generation of nano-sized uniform hollow structures inside the membrane matrix. Such an etching

### Table 1 Methanol permeability of the recast Na\textsuperscript{+} on, 0.5, 1.0, 2.0 wt% SiO\textsubscript{2}@sPS + Na\textsuperscript{+} on and 1.0 wt% h-sPS + Na\textsuperscript{+} on membranes under 80 v/v% methanol/H\textsubscript{2}O (the volume ratio of methanol to H\textsubscript{2}O is 4:1)

<table>
<thead>
<tr>
<th>PEMs</th>
<th>Methanol permeability (P, \times 10^{-1} cm\textsuperscript{2} s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
</tr>
<tr>
<td>Recast Na\textsuperscript{+} on</td>
<td>37.76 ±2.08</td>
</tr>
<tr>
<td>0.5 wt% SiO\textsubscript{2}@sPS + Na\textsuperscript{+} on</td>
<td>12.07 ±0.27</td>
</tr>
<tr>
<td>1.0 wt% SiO\textsubscript{2}@sPS + Na\textsuperscript{+} on</td>
<td>8.99 ±0.15</td>
</tr>
<tr>
<td>2.0 wt% SiO\textsubscript{2}@sPS + Na\textsuperscript{+} on</td>
<td>6.92 ±0.81</td>
</tr>
<tr>
<td>1.0 wt% h-sPS + Na\textsuperscript{+} on</td>
<td>2.31 ±0.27</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The methanol crossover of the recast Na\textsuperscript{+} on membrane is extremely extensive at 50 °C under 80 v/v% methanol/H\textsubscript{2}O. Under these conditions, the methanol permeability cannot be properly measured by the equipment shown in Fig. S1 and S2.
process does not negatively affect the strong interactions between sPS and the Naﬁon matrix, because an increased decomposition temperature of the Naﬁon backbones is still found in the 1.0 wt% h-sPS + Naﬁon membrane (Fig. 7(D and E)).

These newly formed hollow spheres, having a similar role to that of vacuoles in plant cells, would hold more water inside the membrane matrix and hence slow down the rate of water loss of the Naﬁon membrane under higher temperature and low-humidity conditions. In other words, the 1.0 wt% h-sPS + Naﬁon membrane has a stronger water retention capability. Fig. 8 presents the time-dependent proton conductivities of the recast Naﬁon, 1.0 wt% SiO2@sPS + Naﬁon and 1.0 wt% h-sPS + Naﬁon membranes under 40% RH at 100 °C. The recast Naﬁon loses its proton conductivity very quickly. About 60% of its proton conductivity is lost at $t = 580$ min, and the lost proton conductivity reaches up to 80% of its original value at $t = 1860$ min. This is a result of a typical drawback of Naﬁon membranes in that they lose H2O very fast under higher temperature and low-humidity conditions. With regard to the 1.0 wt% SiO2@sPS + Naﬁon membrane, its proton conductivity is more stable during the entire test. About 70% loss of its proton conductivity is found when the dehydration time reaches almost 3000 min. Its enlarged ionic clusters and optimized ionic channels facilitate the proton transport in the 1.0 wt% SiO2@sPS + Naﬁon membrane.

Generally, proton transport through PEMs obey the Grotthuss mechanism (“hopping” mechanism) and the vehicle mechanism. The former refers to the proton hopping from one proton donor to a neighboring proton acceptor via hydrogen bonds, which is directly related to the interconnection conditions of the ionic cluster channels inside the PEM matrix. The latter refers to the diffusion of protonated water molecules, such as $\text{H}_3\text{O}^+$ and $\text{H}_5\text{O}_2^+$, where the high water retention capability of the PEM plays an indispensable role. Further enhancement of the proton conductivity is obtained in the 1.0 wt% h-sPS + Naﬁon membrane. The 1.0 wt% h-sPS + Naﬁon membrane not only inherits the advantages of the 1.0 wt% SiO2@sPS + Naﬁon membrane, but also is able to hold more water inside the h-sPS spheres,3,15,36 which is beneﬁcial for the proton transfer via both the Grotthuss mechanism and the vehicle mechanism. This consideration is demonstrated by the WU measurement shown in Table 2. The 1.0 wt% SiO2@sPS + Naﬁon membrane possesses a higher WU value compared to the recast Naﬁon due to the hydrophilicity of SiO2@sPS, and the 1 wt% h-sPS + Naﬁon membrane presents a further increase in WU owing to the hollow structure of h-sPS spheres.

Detailed information of the water state, i.e. the fraction of free water or freezeable water that does not interact with $-\text{SO}_3\text{H}$
groups, and the fraction of bonded water or non-freezable water, is revealed by DSC analyses (Fig. 9 and Table 2). The 1.0 wt% SiO$_2$@sPS + Nafion membrane has a comparable fraction of free water to the recast Nafion, and its enhanced water retention capability mainly lies in the increased amount of bonded water interacting with the additional –SO$_3$H groups. The increased amount of bonded water ensures continuous water networks, imparting a higher proton conductivity under higher temperature and low-humidity conditions (Fig. 8). For the 1.0 wt% h-sPS + Nafion membrane, the fractions of both of these two types of water increase. H$_2$O-filled h-sPS spheres, acting as water reservoirs, can hydrate the membrane in turn by releasing H$_2$O gradually, which guarantees the high proton conductivity of the 1.0 wt% h-sPS + Nafion membrane under high-temperature and low-humidity conditions. With respect to the Nafion-based PEMs modified by various other sulfonated materials, an optimized proton conductivity is usually observed under high-humidity and moderate-temperature conditions (Fig. 10, Table S1†). Especially under severe conditions, the hollow sphere structure further strengthens this distinctive advantage. Hence an increase in the proton conductivity even by orders of magnitude is found. Probably, the strong interactions between h-sPS and the ionic clusters of Nafion benefit the effective use of H$_2$O released by h-sPS to contribute to the high proton conductivity. Besides this, in terms of the proton conductivity under relatively high humidity, the 1.0 wt% SiO$_2$@sPS + Nafion membrane also presents obvious advantages over the other Nafion-based PEMs modified by optimized sulfonated materials with optimized incorporation contents (Fig. 10, Table S1†).

Besides this, h-sPS can further suppress the penetration of methanol by trapping it inside the hollow spheres. As shown in Table 1, the 1.0 wt% h-sPS + Nafion membrane presents a much lower methanol permeability compared with the 1.0 wt% SiO$_2$@sPS + Nafion one. A schematic illustration is provided in Fig. 11. Herein, a “H$_2$O donating/methanol accepting” mechanism is proposed to explain the further enhancement of the membrane performance of h-sPS + Nafion. This provides another promising approach to alleviate the critical disadvantages of Nafion membranes and hence prepare high-performance Nafion-based PEMs.

4 Conclusions
Imbedding SiO$_2$@sPS nanoparticles into a Nafion matrix can effectively increase the selectivity of the as-prepared SiO$_2$@sPS + Nafion composite PEMs. First, the additional –SO$_3$H groups enlarge the ionic clusters and hence benefit proton conduction. The SiO$_2$@sPS + Nafion membrane has a larger amount of bonded water, ensuring continuous water networks and hence contributing to its high proton conductivity. Second, SiO$_2$@sPS increases the tunnel zigzagging of the diffusion pathways for bulk methanol, enhancing the methanol resistance of the SiO$_2$@sPS + Nafion membrane.

Besides this, etching the SiO$_2$ core leads to the formation of well-dispersed uniform hollow spheres inside the membrane matrix. The intact h-sPS spheres can reserve more free water which in turn is gradually released to hydrate the membrane.
under high-temperature and low-humidity conditions. Therefore, a further increase in the proton conductivity of the h-sPS + Nafion membrane is found. Moreover, by trapping methanol inside the h-sPS spheres, its methanol resistance is further enhanced. Herein, a “H₂O donating/methanol accepting” platform is first proposed. It may provide another promising approach to alleviate the critical disadvantages of Nafion membranes and hence prepare highly selective PEMs.

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Notes and references


