1 Introduction

The enthusiasm for research on fuel cells is rapidly growing in the recent years considering the urgent demand for clean, renewable and abundant sources of electric power.\textsuperscript{1,2} Direct methanol fuel cell (DMFC), classified as the sixth-type fuel cell,\textsuperscript{3,4} has many advantages over the traditional combustion engine, such as high energy conversion efficiency, low pollutant emissions and enhanced fuel flexibility. Hence, it shows great potential in the environmentally friendly energy-conversion devices for various portable power applications.\textsuperscript{5–8} A vital building block of DMFC is the proton exchange membrane (PEM) because its selectivity \textit{i.e.} the ratio of proton conductivity to methanol permeability is crucial to the performance of DMFC.\textsuperscript{9,10} Generally, any methanol crossover from the anode to the cathode would inevitably reduce the cell potential and hence dramatically decrease the overall fuel efficiency.\textsuperscript{11} An ideal PEM should allow only proton transportation rather than methanol crossover to the cathode.\textsuperscript{12–14} Therefore, it is always a major concern for researchers to achieve a PEM with both enhanced proton conductivity and decreased methanol permeability, especially under the conditions of low-humidity and/or elevated-temperature.\textsuperscript{15} However, since protons and methanol almost transport through the same path (ionic channels) of a PEM,\textsuperscript{16} it is a great challenge to obtain such a highly selective PEM. Sometimes, the decreased methanol crossover could be only obtained at the expense of the proton conductivity.\textsuperscript{17}

Since the rise of graphene oxide (GO) around 2007,\textsuperscript{18} researchers have devoted lots of efforts in developing novel high-performance polymer-based composite materials by taking full advantage of the characteristic and fascinating properties of GOS \textit{i.e.} good thermo-mechanical stability, abundance of oxygen-containing functional groups, barrier effect and amphiphilic nature. The already-obtained knowledge has proven its great potential for the practical applications in the field of PEMs.\textsuperscript{19–21} For example, Nafion is a copolymer possessing a polytetrafluoroethylene backbone upon which the sulfonic acid terminated perfluorovinyl ether monomers are decorated as pendants.\textsuperscript{22} The distinctive chemical structure bestows a series of good properties upon the Nafion-based PEMs, such as excellent chemical resistivity and thermo-mechanical stability, high proton conductivity and good...
durability under dynamic operation conditions.\(^{20-23}\) Therefore, Nafion is one of the most intensively investigated PEM materials currently utilized in DMFCs. With the strong interactions with both the hydrophobic backbone and the hydrophilic ionic cluster of Nafion, the compatibility effect of GO could possibly reorganize the unique bicontinuous microstructure of the Nafion-based PEMs.\(^ {16,17}\) Consequently, it could facilitate the hopping of protons to a significant extent so that high proton conductivity upon the Nafion-based PEMs is bestowed even under elevated-temperature and/or low-humidity conditions.\(^ {16,37}\)

Meanwhile, generally, an increased water retention capability also benefits the enhancement of the proton conductivity.\(^ {16,17,24-26}\) However, GO has a very limited ability to improve the water uptake (WU) of “GO + Nafion” composite membranes because of the amphiphilic nature of GO.\(^ {16,17}\) Usually, an excessive incorporation of GO into Nafion leads to no obvious increase in the WU of a PEM, and sometimes even a slight decrease in the WU could be found.\(^ {17}\) This phenomenon could be explained by the disruption of Nafion’s micellar nature under a non-optimum additive quantity of GO.\(^ {23}\) Considerable efforts have hitherto been devoted in developing a cornucopia of other approaches to improve the WU of a PEM, such as incorporating hygroscopic inorganic additives i.e. SiO\(_2\), TiO\(_2\) and ZrO\(_2\) into the Nafion matrix.\(^ {27-34}\) However, the positive influence of the increase in WU on the proton conductivity is often offset by the fact that these inorganic materials are not proton conductors. For example, the more SiO\(_2\) was incorporated into the Nafion matrix, the lower the proton conductivity of SiO\(_2\)/Nafion composite membranes would be. Interestingly, under this circumstance, the methanol crossover is effectively inhibited due to the promoted tortuosity of the transport channels.\(^ {35-34}\)

Therefore, motivated by the desire to optimize the use of the above-mentioned two different types of inorganic materials, in the current study, nanohybrid material—sulfonated graphene oxide–silica (S-GO–SiO\(_2\))—was synthesized. Then, we incorporated S-GO–SiO\(_2\) into Nafion matrix to prepare Nafion-based composite PEMs by a solution casting method. Sulfonation could effectively strengthen the interactions between this inorganic material and the Nafion matrix. Meanwhile, it would also improve the proton conductivity by enhancing the membrane’s WUs and optimizing the ionic cluster domains.\(^ {3}\) The surface and cross-sectional morphologies, thermal stability, bicontinuous microstructure, WU, swelling ratio, proton conductivity and methanol permeability of S-GO–SiO\(_2\)/Nafion PEMs were investigated in detail here. Due to the unique properties of S-GO–SiO\(_2\),\(^ {3}\) an increase in proton conductivity by several times than that of the recast Nafion membrane could be observed here in the S-GO–SiO\(_2\)/Nafion composite membranes. Meanwhile, the composite membranes exhibit obvious reduction in methanol permeability probably because of the increased tortuosity of the transport channels. The highly selective composite PEM provides a very promising candidate for the application in DMFC.

Besides, based on our previous work,\(^ {35-38}\) the methanol permeability of PEMs was investigated by the real-time attenuated total reflection Fourier transform infrared (ATR-FTIR) technique. The results have proven the distinctive advantages of this in situ method over the traditional “blot and weigh/measure” immersion techniques,\(^ {35-38}\) especially during the analysis of liquid diffusion in polymers.\(^ {35-44}\) Until now, it has been vastly used in the research on the diffusion of penetrants that are responsive to infrared, including methanol.\(^ {38}\) Here, it could promptly and easily obtain the methanol permeability of PEMs, so it could be a general characterization method with great potential in this field.\(^ {38}\)

### 2 Experimental section

#### 2.1 Materials

Expandable graphite powders were provided by Yingtai Co. (China). N,N′-Dicyclohexylcarbodiimide (DCC), 3-mercaptopropyl trimethoxysilane (MPTMS) and 3-aminopropyltriethoxysilane (APTS) were all purchased from Sigma-Aldrich. Nafion solution (perfluorinated resin solution, 5 wt% in lower aliphatic alcohol and water mixture) was provided by DuPont. Unless otherwise stated, all the other reagents were purchased from commercial suppliers and used as received.

#### 2.2 Preparation of S-GO–SiO\(_2\)

First, GO was produced from graphite powder by a modified Hummers method, as reported in our previous work.\(^ {47}\) Second, 100 mg GO and 50 mg DCC were dispersed in 50 mL APTS and then ultrasonicated for 3 h to obtain a brown and homogeneous mixture. Further, it was vigorously stirred at 70 °C for 24 h. Then, the system was centrifuged and washed with absolute ethanol for several times before being vacuum dried.\(^ {48,49}\) Third, the resultant APTS-functionalized GO was hydrolyzed into GO–SiO\(_2\) at 70 °C for 5 d with the existence of absolute ethanol, water and formic acid (volume ratio 110 : 15 : 1). Then, it was centrifuged and washed with absolute ethanol for several times before being vacuum-dried as well.\(^ {44}\) Lastly, 50 mg GO–SiO\(_2\) dispersed in 3.5 g toluene was kept at 110 °C for 24 h with MPTMS as the sulfonic-acid-group precursor. The mercapto groups attached onto the GO–SiO\(_2\) surface were further oxidized into sulfonic acid groups via being immersed into 30 wt% H\(_2\)O\(_2\) solution at 25 °C for 24 h. Similarly, the product (S-GO–SiO\(_2\)) was carefully filtered and washed with ethanol and water for several times and then vacuum-dried overnight.\(^ {5,50}\)

#### 2.3 Preparation of the S-GO–SiO\(_2\)/Nafion composite membranes

First, about half of the solvent of 4 mL Nafion solution was removed via rotary evaporating at 50 °C and then DMF was added into the resultant concentrated Nafion solution followed by rotary evaporation for another 10 min under 60 °C.\(^ {16}\) Furthermore, a desired amount of the as-prepared S-GO–SiO\(_2\) was added into the Nafion solution. The mixture was stirred and ultrasonicated for 1 h to obtain a homogeneous dispersion. Second, the obtained S-GO–SiO\(_2\)/Nafion mixture was cast into a rectangular model in an amount giving the membrane a thickness of around 60 ± 10 μm. After that, the system was dried in a vacuum oven by gradually raising the temperature...
from 70 to 120 °C for 6 h and further dried under vacuum under 120 °C overnight. Third, the composite PEM was boiled in 3 wt% H2O2 solution under 70 °C for 2 h and then immersed in 1 M H2SO4 solution for 1 h under 80 °C to convert PEM into H+ form. Lastly, the prepared S-GO2/SiO2/Nafion composite membranes were carefully rinsed with H2O for several times before the later characterizations. The composite PEMs with 0.1 (or 0.5, 0.8) wt% S-GO2 particles incorporated into Nafion matrix was marked as “0.1 (or 0.5, 0.8) wt% S-GO2/SiO2/Nafion” composite membranes in the following sections. The content of S-GO2/SiO2 particles was calculated according to the weight of Nafion polymer. The recast Nafion membrane was prepared via the similar method described above.26,38

2.4 Characterizations of (S)-GO–SiO2

The FT-IR (Fourier transform infrared spectroscopy) spectra were collected on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm⁻¹ and 64 scans. The TGA (thermogravimetric analysis) measurements were conducted under N2 atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 10 °C min⁻¹. The Raman spectra were collected by a Renishaw inVia Reflex micor-Raman spectrometer with 633 nm laser excitation. In addition, the XRD patterns (X-ray diffraction) were obtained by utilizing a PANalytical X’pert diffractometer with Cu Kα radiation. The morphology was observed with both FE-SEM (field emission scanning electron microscopy, Hitachi, S-4800) and AFM (atomic force microscopy, Multimode Nano 4, tapping mode) techniques. The samples were coated with gold before the FE-SEM observation. Besides, the EDX (energy dispersive X-ray fluorescence spectrometer) analysis was also carried on the FE-SEM (Hitachi, S-4800) equipment.

2.5 Characterizations of S-GO–SiO2/Nafion composite membranes

Both the surface and the cross-sectional morphologies of the S-GO–SiO2/Nafion composite membranes were obtained with a SEM (XL 30 ESEM-TMP PHILIP). All the samples were coated with gold before the SEM observation. The cross-sectional TEM (transmission electron microscopy) images of the S-GO–SiO2/Nafion composite membranes were recorded on a JEOL JEM2100 TEM instrument operated under an acceleration voltage of 200 keV. The surface AFM measurement was conducted by a Multimode Nano 4 in the tapping mode. The FT-IR spectra were measured on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm⁻¹ and 64 scans. The TGA analyses were carried on atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 10 °C min⁻¹ under N2.

The WU (water uptake), measured by the following procedures,28 was used to investigate the water retention capability of each PEM. Wdry was first obtained after PEMs dried at 80 °C for 24 h. Then, they were saturated with H2O by being immersed in deionized water at room temperature for 24 h. Moreover, they were taken out followed by being quickly sandwiched between two pieces of filter paper to remove the water on the membrane surface. PEMs were immediately put into a sealed weighing bottle and weighted (Wwet).2 Thereby, WU could be calculated by the following equation:

\[
WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100.
\]

Meanwhile, the membrane area of the dry one (Adry) and wet (A wet) one was also obtained during the measurement of Wdry and Wwet, respectively. The membrane swelling ratio in H2O could be calculated as:

\[
\text{Swelling ratio(\%)} = \frac{A_{\text{wet}} - A_{\text{dry}}}{A_{\text{dry}}} \times 100.
\]

The membrane swelling ratio in MeOH was measured via a similar method. Every swelling ratio is the average value calculated from two individual measurements.

The proton conductivities of PEMs were measured with the aid of a four-electrode method utilizing AC impedance spectroscopy between 0.1 MHz and 1 Hz with potentiostat control (CH1660d Model).16,38 The investigated conditions, including humidity and temperature, were always controlled by a temperature and humidity test chamber during the entire measurements. All PEMs were placed under the desired humidity and temperature for 8 h before the measurements.16,38 Every proton conductivity present here was the average value calculated from four individual measurements.

The methanol permeability of the recast Nafion membrane and the composite PEMs was measured under 25 and 50 °C with home-made equipment as reported in our previous paper (Fig. S1†).39 Briefly, the dry PEM was first put onto the surface of the ZnSe crystal in the ATR cell (Nicolet Nexus 470 FTIR spectrometer). Then, it was sandwiched between the ZnSe crystal and the PTFE mould (Fig. S1†). Second, the continuous IR spectra were collected as soon as 0.5 mL of 80 v/v% methanol–H2O solution was injected into the PTFE mould. Using a macro program, the IR spectra, based on 4 cm⁻¹ spectral resolution, were taken as a function of the diffusion time. The acquisition time interval is controlled at 40 s. Third, based on the increase in the peak area corresponding to the –CH3 stretching vibration, the Fickian diffusion equation (eqn (1)) put forward by Fieldson and Babari30 is used to estimate the diffusion coefficients of methanol in the PEMs.35

\[
\frac{A_t}{A_e} = 1 - \frac{8\gamma}{\pi[1 - \exp(2\gamma)]} \times \sum_{n=0}^{\infty} \frac{\exp(g)\exp(-2\gamma)}{(2n+1)(4\gamma^2 + f^2)}
\]

(1)

Where \( g = \frac{D(2n+1)^2\pi^2 t}{4L^2} \) and \( f = \frac{(2n+1)\pi}{2L} \); \( A_t \) is the absorbance area at diffusion time \( t \); \( A_e \) is the equilibrium area; \( D \) is the diffusion coefficient; \( L \) is the thickness of PEMs; \( n \) and \( \pi \) are constants.

The parameter \( \gamma \) is defined as...
\[ \gamma = \frac{2n_2\pi}{\lambda} \sqrt{\sin^2 \theta - \left( \frac{n_1}{n_2} \right)^2} , \]

where \( \lambda \) is the wavelength of infrared beam in the ATR element; \( \theta \) (\( \theta = 45 \, ^\circ \mathrm{C} \)) is the angle of the incidence of the infrared radiation; \( n_1 \) and \( n_2 \) are the refractive indexes of Na\( \mathrm{f} \)on and the ATR crystal.\(^{35}\)

3 Results and discussion

3.1 Characterization of S-GO–SiO\(_2\) particles

APTS is a well investigated agent to bind SiO\(_2\) onto the GO surface.\(^{48}\) As the FTIR spectra of GO and GO–SiO\(_2\) shown in Fig. 1(A), the peaks at 2929 \( \mathrm{cm}^{-1} \) and 2862 \( \mathrm{cm}^{-1} \) is attributed to the asymmetric and symmetric stretching vibrations of –CH\(_2\)– of the SiO\(_2\) precursor (APTS), respectively.\(^{48,49}\) The significant absorbance around 1120 \( \mathrm{cm}^{-1} \) is ascribed to both –Si–O–C–(mostly) and GO’s –C–O–C– linkages, and the peak at 1039 \( \mathrm{cm}^{-1} \) corresponds to –Si–O–Si– linkages.\(^{49}\) With respect to the FTIR spectrum of S-GO–SiO\(_2\), the obvious peak at 1202 \( \mathrm{cm}^{-1} \) assigned to the asymmetric stretching vibration of –SO\(_3\) group confirms the successful attachment of the sulfonic acid groups onto the GO–SiO\(_2\) surface.\(^{51}\) It is noteworthy that the alkyl chain of MPTMS also contributes to the absorption peaks around 2929 \( \mathrm{cm}^{-1} \) in the FTIR spectrum of S-GO–SiO\(_2\).

The decoration of SiO\(_2\) onto the GO surface lowers its thermal stability,\(^{52}\) as the obvious decrease in the decomposition temperature of the labile oxygen-containing functional groups demonstrated in the TGA analyses [Fig. 1(B)].\(^{52}\) According to the TGA results, the percentage of SiO\(_2\) and sulfonic acid group of S-SiO\(_2\)–GO could be calculated as about 12.5% (g g\(^{-1}\)) and 2.7% (g g\(^{-1}\)), respectively. Fig. 1(C) presents the XRD patterns of GO, GO–SiO\(_2\) and S-GO–SiO\(_2\), respectively. An obvious peak appears at approximately 10.9° in the XRD pattern of GOs, which is typical for the layered structure of GO.\(^{33}\) Its disappearance in the XRD patterns of GO–SiO\(_2\) and S-GO–SiO\(_2\) indicates the loss of long-range order in the GO-based sheets because of the decoration of SiO\(_2\) onto the GO surface. A new broad peak around 23° could be attributed to the characteristic XRD pattern of SiO\(_2\).\(^{52}\) The conclusion is also validated by the Raman measurement shown in Fig. 1(D). The apparent up-shift of the G band in the Raman spectra of GO–SiO\(_2\) and S-GO–SiO\(_2\) could be rationalized by the increase in the C (sp\(^3\)) content and/or the destruction of the original π network of GO.\(^{34}\) Interestingly, the broad and symmetrical shape of their G’ bands exactly illustrates that GO–SiO\(_2\) and S-GO–SiO\(_2\) are few-layer GO-based materials,\(^{34}\) which is in accordance with the observations by the AFM images in Fig. 2(A)–(C) and the FE-SEM and EDX in Fig. 2(D) and (E).

3.2 Characterization of S-GO–SiO\(_2\)/Na\(_x\)f on composite membranes

Most of S-GO–SiO\(_2\) particles disperse well and are tightly embedded inside the membrane matrix when the content of S-GO–SiO\(_2\) is 0.1–0.5 wt%, as demonstrated by the surface SEM
image in Fig. 3(A) and (B) and the cross-sectional TEM images in Fig. 3(E) and (F) [including Fig. S2(A) and (B)]. It is further confirmed by the relatively high-contrast surface AFM image of 0.5 wt% S-GO–SiO$_2$/Nafion composite membrane [Fig. 3(D)]. It is worth noting that some aggregation of S-GO–SiO$_2$ was present in the 0.8 wt% S-GO–SiO$_2$/Nafion composite membrane as shown in Fig. 3(C) and S3† (its digital photos). This phenomenon indicates that further increasing the incorporated quantity of S-GO–SiO$_2$ is not proper and would damage its dispersibility inside the membrane matrix.

Usually, the distinct IR peaks of the side chains of Nafion polymer could be observed by the stretching vibrations of $\text{\text{C\text{\text{O}}\text{C}}}$ linkages around 970 and 982 cm$^{-1}$ (16, 38 and 51) [Fig. 4(A)]. Its hydrophilic ionic clusters (\text{\text{SO$_3$H}}) and hydrophobic backbones (\text{\text{CF$_2$}}) present their symmetric stretching vibrations at 1055 cm$^{-1}$ and 1151 cm$^{-1}$, respectively [Fig. 4(A)].$^{16,38,51}$ And their asymmetric stretching vibrations correspond to the superimposed absorption peak occurring around 1213 cm$^{-1}$ [Fig. 4(A)].$^{16,38,51}$ Compared with those of the recast Nafion membrane, these IR peaks of the S-GO–SiO$_2$/Nafion composite membranes present a broadening and/or shifting phenomenon [Fig. 4(A)], indicating the existence of strong interactions between S-GO–SiO$_2$ and the Nafion matrix derived from the good dispersion of S-GO–SiO$_2$.$^{14,16,38,51}$ It is worth noting that the $\text{\text{Si--O--C}}$ linkages whose IR absorption is at 1120 cm$^{-1}$ also contribute to the broadening phenomenon of the peak around 1151 cm$^{-1}$.$^{49}$ In particular, an increase in $\text{\text{SO$_3$H}}$ groups with increasing S-GO–SiO$_2$ inside the membrane

![Fig. 2](image1.png) (A) 2D AFM height image, (B) AFM phase image, (C) 3D AFM height image and (D) FE-SEM image of GO–SiO$_2$; (E) FE-SEM image and EDX analysis of S-GO–SiO$_2$.

![Fig. 3](image2.png) (A)–(C) Surface SEM images of the 0.1–0.8 wt% S-GO–SiO$_2$/Nafion composite membranes and the magnified observations of the parts indicated by the white box could be obtained from the corresponding insets; (D) surface AFM height image and (E) and (F) cross-sectional TEM images of the 0.5 wt% S-GO–SiO$_2$/Nafion composite membrane.
matrix strengthens the peak at 1055 cm\(^{-1}\). Besides, the broad absorption around 3400 cm\(^{-1}\) in Fig. 4(A) is assigned to the hydroxyl groups of SiO\(_2\) or GO as well as the carboxyl groups of GO. The TGA analyses [Fig. 4(B)] of the composite PEMs demonstrate that the incorporation of S-GO–SiO\(_2\) into Nafion matrix would not damage its thermal stability.\(^{38}\) The very small shift in desulfonation and backbone decomposition temperature is due to the interactions between the Nafion matrix and S-GO–SiO\(_2\) particles. Besides, S-SiO\(_2–\)GO suppressing the diffusion of decomposition products may also contribute to this phenomenon to some extent.

Normally, diblock morphology is usually observed in the cross-sectional SEM image of a Nafion membrane due to its unique character of bicontinuous microstructure [Fig. 5(A\(_1\)]\(^{16,17,38}\) Whereas with S-GO–SiO\(_2\) being incorporated into the Nafion matrix, such a unique morphology was less evident at 0.1 wt% [Fig. 5(B\(_1\)]\(_{–}\)B\(_{3}\)] and more evident at 0.5 wt% [Fig. 5(C\(_1\)]\(_{–}\)C\(_{3}\)] and at last almost uniform at 0.8 wt% [Fig. 5(D\(_1\)]\(_{–}\)D\(_{3}\)]. The change in a bicontinuous microstructure of Nafion is actually caused by two opposite effects: the compatibility effect of GO\(^{14,16,17}\) and the \(\text{–SO}_3\text{H}\) groups derived from S-GO–SiO\(_2\).\(^{14,17}\) The former one causes Nafion microstructures to uniformly align,\(^{14,16}\) while the latter makes Nafion microstructures nonuniform. The microstructure of the composite PEM is dependent on which effect plays a dominant role in Nafion microstructures under certain S-GO–SiO\(_2\) content. For example, with respect to the 0.5 wt% S-GO–SiO\(_2–\)Nafion membrane, the excellent dispersion of S-GO–SiO\(_2\) (illustrated by the morphology characterizations in Fig. 3) probably significantly facilitates the interactions between the \(\text{–SO}_3\text{H}\) groups derived from S-GO–SiO\(_2\) and the ionic cluster domains, causing its microstructures to align in a non-uniform manner. Meanwhile, the compatibility effect of GO plays a major role in the microstructures of the 0.8 wt% S-GO–SiO\(_2–\)Nafion membrane, probably because the increase in the effective concentration of \(\text{–SO}_3\text{H}\) groups is now smaller than that of GO-based sheets due to the aggregation of S-GO–SiO\(_2\) (Fig. S3†).

As is well known, the “proton hopping” (Grotthuss) mechanism and the migration of hydrated protons \([\text{H}^+(\text{H}_2\text{O})_n]\) mainly govern the proton conduction in Nafion matrix. The WU of the recast Nafion membrane is 20.5 wt\%.\(^{16}\) Herein, the obviously promoted water retention capability of the S-GO–SiO\(_2–\)Nafion composite membranes, as the WU measurement shown in Fig. 6(A), could provide abundant \(\text{H}_2\text{O}\) available for both the hopping mechanism and solvating protons for migration and hence significantly enhance their proton conductivity [Fig. 6(B) and (C)].\(^{16,17,24–26,38}\) Besides, the incorporation of a sulfonic acid group provides a more facile hopping of protons according to the Grotthuss mechanism, which in turn helps to increase the proton conductivity.\(^{3}\) This performance enhancement is much more evident in the lower-humidity circumstances [Fig. 6(C)],\(^{16}\) as indicated by the calculated activation energies presented in Fig. 6(C).\(^{16}\)

Fig. 6(D) shows the swelling ratio of the recast Nafion and the 0.1–0.8 wt% S-GO–SiO\(_2–\)Nafion composite membranes. Compared with the recast Nafion, no obvious increase in swelling ratio in both \(\text{H}_2\text{O}\) and methanol has been observed in the S-GO–SiO\(_2–\)Nafion composite membranes. Actually, it seems that the existence of two-dimensional S-GO–SiO\(_2\) particles have a positive effect on the structure maintenance of a PEM by suppressing the movement of polymer chains.
Fig. 6(E) and (F) present the AFM phase image of the recast Na\textsubscript{ion} and the 0.5 wt\% S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membrane, respectively. The relatively lighter parts correspond to the softer hydrophilic ionic cluster domains, whereas the darker ones are assigned to the neutral hydrophobic backbone in the membrane.\textsuperscript{16,38,55–57} As we know, the AFM phase imaging could probe the fraction of hydrophilic surface domains that are electrochemically active and largely contribute to the proton conductivity of a PEM. Generally, both the size and the connectivity of the surface ionic cluster domains are important for the membrane conductivity. A much more connective network of the ionic clusters would greatly facilitate the proton transport in the PEMs (Fig. 7).\textsuperscript{16,38,55,56,58} Compared with the AFM phase image of the recast Na\textsubscript{ion} membrane,\textsuperscript{16,38} the 0.5 wt\% S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membrane has relatively larger surface ionic clusters of varying sizes and better connectivity, which positively improve its significant conductivity [Fig. 6(B) and (C)].\textsuperscript{16} Accordingly, an increase in proton conductivity by several times could be observed in the 0.5–0.8 wt\% S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membranes. In Fig. 6(B), the proton conductivity of the 0.1 wt\% S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membrane is little smaller than that of the recast Na\textsubscript{ion} membrane under relatively low-humidity conditions,\textsuperscript{16} which could be attributed to the “non-proton-conductor” nature of SiO\textsubscript{2}.\textsuperscript{33,34}

Meanwhile, as mentioned above, the dispersibility of S-GO–SiO\textsubscript{2} in the 0.8 wt\% S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membrane becomes poorer, leading to no significant increase in its proton conductivity compared with that of the 0.5 wt\% one.

Fig. 6  (A) WUs, (B) proton conductivity (80 °C), (C) Arrhenius plots (40% RH), (D) swelling ratio of the recast Na\textsubscript{ion}\textsuperscript{16,55} and the 0.1–0.8 wt\% S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membranes. (E) and (F) AFM phase images of the recast Na\textsubscript{ion} membrane\textsuperscript{16,55} and the 0.5 wt\% S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membrane.

Fig. 7  Schematic illustration of the enhanced transport properties of the S-GO–SiO\textsubscript{2}/Na\textsubscript{ion} composite membranes.
Furthermore, the barrier effect of two-dimensional S-GO–SiO₂ bestows an increased tortuosity of the transport channels upon the S-GO–SiO₂/Nafion composite membranes. However, the 0.1 wt% one possesses increased methanol permeability (Table 1). Due to the strong interactions between the –SO₂H groups derived from S-GO–SiO₂ and the ionic cluster domains, the 0.1 wt% S-GO–SiO₂/Nafion membrane has a more facile ionic channel, compared with recast Nafion, to facilitate proton hopping under low-humidity conditions [Fig. 6(C)]. As is well known, proton and methanol almost transport through the same path (ionic channels) of PEM. Therefore, with such a low content of S-GO–SiO₂ being incorporated into Nafion matrix, the positive influence of its barrier effect on suppressing the methanol crossover is probably offset by the positive effect of a more facile ionic channel on enhancing the methanol permeability. With the increasing S-GO–SiO₂ content, the barrier effect gradually gains the dominant role on the methanol permeability, leading to the dramatic decrease in the methanol permeability of the 0.5/0.8 wt% S-GO–SiO₂/Nafion composite membranes, as demonstrated in Table 1 and schematically illustrated in Fig. 7. Generally, harsh operation conditions, such as increased temperature and/or higher methanol concentration, would lead to a high methanol permeability of a PEM. Under the “50 °C, 80 v/v% methanol–H₂O” condition, the 0.5/0.8 wt% S-GO–SiO₂/Nafion composite PEMs show an increase in the selectivity by nearly two orders of magnitude compared with that of the recast Nafion membrane. This result further proves that our approach is a very effective way to prepare low methanol-crossover PEMs in conjunction with excellent proton conductivity.

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### Nomenclature

- **A<sub>dry</sub>** The area of a dry PEM
- **A<sub>v</sub>** The absorbance area at diffusion time t
- **A<sub>wet</sub>** The area of a wet PEM saturated by H₂O or methanol
- **A<sub>eq</sub>** The equilibrium area
- **D** The diffusion coefficient
- **f** \( = \frac{(2n + 1)\pi}{2L} \)
- **g** \( = \frac{D(2n + 1)^2\pi^2t}{4L^2} \)
- **L** The thickness of a PEM
- **n** A constant
- **n₁** The refractive indexes of Nafion
- **n₂** The refractive indexes of the ATR crystal
- **t** The diffusion time
- **W<sub>dry</sub>** The weight of a dry PEM
- **W<sub>wet</sub>** The weight of a wet PEM saturated by H₂O

### Greek letters

- **γ** \( = \frac{2n\pi\sqrt{\sin^2 \theta - (n₁/n₂)^2}}{\lambda} \)
- **λ** The wavelength of infrared beam in the ATR element
- **π** The usual mathematical constant
- **θ** The angle of the incidence of the infrared radiation, \( θ = 45° \)

### 4 Conclusions

S-GO–SiO₂/Nafion composite membranes with enhanced transport properties are successfully prepared by a solution casting method in this study. Thanks to the increased water retention capability and the incorporation of –SO₂H groups, the composite membranes possess significantly increased proton conductivity even under low-humidity and/or elevated-temperature conditions. Meanwhile, the barrier effect of two-dimensional S-GO–SiO₂ contributes to the greatly reduced methanol permeability of these composite membranes due to the increased tortuosity of the transport channels in the membrane matrix. Therefore, an increase in selectivity by nearly two orders of magnitude could be easily observed in the 0.5/0.8 wt% S-GO–SiO₂/Nafion composite membranes, rendering this type of PEMs a very promising candidate for the application in DMFC operating under various harsh conditions.

### Table 1  Transport properties of the recast Nafion membrane<sup>48</sup> and 0.1–0.8 wt% S-GO–SiO₂/Nafion composite membranes

<table>
<thead>
<tr>
<th>PEMs</th>
<th>Membrane thickness (µm)</th>
<th>Permeability ( (P, \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}) )</th>
<th>Proton conductivity ( (σ, \text{ S cm}^{-1}) )</th>
<th>Selectivity ( (ϕ = σ/P, \times 10^6 \text{ S cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recast Nafion</td>
<td>75</td>
<td>30.58 ± 1.80</td>
<td>0.00513 ± 0.00012</td>
<td>0.0407 ± 0.0021</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td>70</td>
<td>77.33 ± 6.48</td>
<td>0.0104 ± 0.00012</td>
<td>0.055 ± 0.0056</td>
</tr>
<tr>
<td>0.5 wt%</td>
<td>55</td>
<td>10.95 ± 1.12</td>
<td>0.0340 ± 0.00006</td>
<td>1.574 ± 0.3830</td>
</tr>
<tr>
<td>0.8 wt%</td>
<td>50</td>
<td>5.74 ± 1.19</td>
<td>0.0481 ± 0.00083</td>
<td>2.945 ± 0.5228</td>
</tr>
</tbody>
</table>
Notes and references