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A Novel Composite PEM with Long-range Ionic Nanochannels Induced by Carbon Nanotube/Graphene Oxide Nanoribbon Composites

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Abstract: In the current study, carbon nanotube/graphene oxide nanoribbon (CNT/GONR) composites were obtained via a chemical “unzipping” method. Then novel CNT/GONR Nafion composite proton exchange membranes (PEMs) were prepared via a blending method. The CNT/GONR nanocomposites induce the adjustment of \((-\text{SO}_3^-)_n\) ionic clusters in Nafion matrix to construct long-range ionic nanochannels and keep the activity of ionic clusters at the same time. This dramatically promotes the proton transport of the CNT/GONR Nafion composite PEMs at low humidity and high temperature. The proton conductivity of the composite PEM with 0.5 wt% CNT/GONR is as high as 0.18 S·cm\(^{-1}\) at 120 °C and 40 %RH, nine times of recast Nafion (0.02 S·cm\(^{-1}\)) at the same conditions. The 1D/2D nanostructure of CNT/GONR nanocomposite also contributes to restrain the methanol permeability of CNT/GONR Nafion. The composite
PEM shows a one-order-of-magnitude decrease (2.84E-09 cm$^2$·s$^{-1}$) in methanol permeability at 40 °C. Therefore, incorporation of this 1D/2D nanocomposite into Nafion PEM is a feasible pathway to conquer the trade-off effect between proton conductivity and methanol resistance.

Introduction

Fuel cell (FC) technology is regarded as one of the most prospective clean energy technologies$^1$. Direct methanol fuel cells (DMFCs) have aroused extensive interest on account of its outstanding properties like high power density per unit mass, convenient storage, plentiful fuel sources and so on$^2$. However, there are two thorny problems the present DMFCs have to solve, including the slow oxidation kinetics as well as CO poison of the catalyst at low operation temperature$^3,4$. This will lead to the depolarization of the cell, decrease in open circuit voltage and the reduction in fuel utilization efficiency. These problems could be partly solved when the operation temperature of DMFC are increased by using the PEMs capable of enduring higher operation temperature (≥ 100 °C). Besides, DMFC at higher operation temperature has simpler device structure due to omitting cooling and humidification units, which presents numerous advantages over conventional DMFC fuel cells$^1$.

DuPont commercial perfluorosulfonic acid polymer Nafion is one of the most widely applied PEM materials because of its several superior advantages including good chemical durability, thermostability, mechanical strength and proton conductivity$^5$. Nafion consists of a linear polytetrafluoroethylene backbone with short, perfluoroether side chains terminated by sulfonic
groups. There is a nanophase-separation phenomenon in Nafion matrix, resulting in the structure of interpenetrating hydrophilic and hydrophobic sections in the matrix. The hydrophilic sections, often hydrated, exploit \((-\text{SO}_3)^n\) ionic clusters to construct ionic channels for proton transportation, while the hydrophobic sections endow the Nafion membrane with essential chemical and mechanical stabilities. However, Nafion membrane is not appropriate for high-temperature operation since in high-temperature and low relative humidity (RH) environment, Nafion PEMs undergo fast water loss due to its poor water uptake capability under such conditions. This results in an obvious decline in proton conductivity of the PEMs. Besides, high methanol permeability is another big drawback for Nafion since methanol molecules and protons share the same conductivity channels, which is harmful to the fuel efficiency and cell performance. This problem would even be more severe at high operation temperature, largely impeding the industrialization of DMFC. In another word, there is a trade-off effect that the methanol resistance is probably weakened when proton conductivity is attempted to be improved. Hence, it is of great practical significance to modify Nafion with simple methods to increase its proton conductivity and restrain its methanol crossover simultaneously for high temperature operation.

There are several pathways to improve the performance of Nafion-based PEMs at high temperature including incorporating nanofillers, blending polymers, surface modification and etc. Among them, incorporating hydrophilic inorganic nanofillers has proven to be a simple
and effective way\textsuperscript{12-14}. On one side, nanoparticles such as SiO\textsubscript{2}\textsuperscript{15-17} and TiO\textsubscript{2}\textsuperscript{18, 19} with a large amount of hydrophilic functional groups would highly elevate the water uptake of composite PEMs, which might benefit the proton conductivity at high temperature. However, suitable hydrophilicity of inorganic nanofiller is especially important for high-performance PEMs because excessive hydrophilicity of nanoparticles could scramble water from ionic clusters of Nafion, leading to an unwilling decline in proton conductivity\textsuperscript{20}. Furthermore, nanofillers with specific geometric structures, which induce ionic clusters aggregation to reach a thermodynamically stable state, would prospectively influence the hydrophilic domains of Nafion and construct long-range ion-exchange nanochannels at the interface among nanofillers and Nafion matrix\textsuperscript{21}. Ionic clusters inside the nanochannels are induced to the form well-connected hydrogen-bonded networks or water structures so that high ion mobility could be achieved even at low-humidity conditions\textsuperscript{22, 23}. On the other side, nanofillers would prospectively make the transportation channels in Nafion matrix more zig-zag to suppress the methanol cross-over phenomenon in the composite PEM and improve the fuel efficiency as well as the cell performance\textsuperscript{24}.

Carbon nanomaterials have unique properties and offer multiple opts in structure, which has aroused widely research interest on modifying Nafion-based PEMs\textsuperscript{25-27}. Among carbon nanomaterials, 1D carbon nanotube (CNT) and 2D graphene oxide (GO) have been extensively researched. CNT with 1D structure has a distinct structure, high aspect ratio and ideal
flexibility. It is favorable to interconnect the ionic clusters and therefore promotes the proton transport at high temperature. Asgari et al. blended histidine modified carbon nanotube with Nafion to prepare a composite PEMs. The proton conductivity of the composite PEM with 0.5 wt% filler content reached 0.15 S cm\(^{-1}\) at 120 °C. Kanan et al. prepared sulfonic acid functionalized SWCNT/Nafion composite PEM and achieved much improved proton conductivity. Such works demonstrate that functional groups decorated onto CNT are especially significant for high-performance PEMs. GO with 2D structure is believed to be another good potential nanofiller for PEMs benefitting from large surface area, abundant functional groups and good chemical stability. GO has been proved to be an ideal candidate for long-range ionic channels due to its unique ductility on micro- and nanoscale. Additionally, GO exhibits good potential of restraining fuel crossover benefitting from their preferable in-plane orientation and impermeability to penetrant molecules. Choi et al. used GO nanosheets to modify the microstructures of both hydrophilic and hydrophobic domains of Nafion. The GO/Nafion composite membranes presented decreased methanol crossover as well as preserved proton conductivity. Our group adopted sulfonated graphene oxide–silica composite to restrain methanol crossover in Nafion. The methanol permeability of the composite PEM was decreased by one order of magnitude compared to recast Nafion at 50 °C. Based on these unique properties, appropriately combining the advantages of 1D (CNT) and 2D (GO) nanomaterials to modify Nafion membrane creates the possibility to conquer the trade-off effect between proton conductivity and methanol resistance to enhance the overall performance of the composite PEMs.
especially at high operation temperature. To the best of our knowledge, PEMs modified with 1D/2D nanocomposite are limitedly reported. Chen et al.\textsuperscript{37} incorporated 1D sulfonated halloysite nanotube and 2D sulfonated GO into sulfonated poly (ether ether ketone) matrix but the composite membrane with double-kinds fillers presented lower proton conduction than the single-filler membranes. That was ascribed to the more zig-zag interfacial pathways at excessive content of disordered nanofillers. Hence, simply incorporating CNT and GO into Nafion matrix would have to confront several problems including weak interaction, difficulty in matching size and controlling hydrophilicity to enhance the performance of the composite PEMs.

Herein, carbon nanotube/graphene oxide nanoribbon (CNT/GONR) nanocomposite was achieved via partially in situ unzipping multi-wall CNTs to obtain a desirable 1D/2D nanocomposite. Through this method, GONR and unzipped CNT were linked with strong π-π interaction and matched in size, which provided the possibility to combine advantages of 1D and 2D carbon nanomaterials to a great extent. Besides, the hydrophilicity of CNT/GONR could also be controlled properly, which ensures the activity of (−SO₃⁻)ₙ ionic clusters. Then the CNT/GONR nanocomposite was blended into Nafion matrix. By exploiting the hydrophilic and hydrophobic interaction with ionic clusters, CNT/GONR nanocomposite induced (−SO₃⁻)ₙ ionic clusters in Nafion matrix to build long-range oriented ion-exchange nanochannel structure, resulting in a remarkable increase in proton conductivity especially at harsh conditions. Furthermore, the CNT/GONR nanocomposite with well size-matched 1D/2D nanostructure also
presents an excellent barrier effect to suppress methanol permeability by making the methanol transport channels more zigzag. This 1D/2D nanocomposite material prepared by in-situ chemical unzipping method proves to be a feasible pathway to conquer the trade-off effect of Nafion-based composite PEMs between proton conductivity as well as methanol resistance.

2. Experimental details

2.1 Materials

Multi-wall carbon nanotube (MWCNT, outer diameter > 50 nm, length 10 – 20 µm, purity > 95 wt%) was purchased from Timesnano (China). Nafion solution (perfluorinated resin solution, 5 wt%) was purchased from DuPont. H$_2$SO$_4$, H$_3$PO$_4$, KMnO$_4$, H$_2$O$_2$ and N, N-dimethyl formamide (DMF) were acquired from Sinopharm Chemical Reagent Co.(China). GO was prepared through modified Hummer’s method$^{38}$. All the chemical agents were directly used without further processing.

2.2 Synthesis of CNT/ GONR nanocomposite

The synthesis of CNT/GONR nanocomposite was carried out referring to the reported method$^{39}$. Typically, 0.1 g MWCNTs were dispersed in 35 mL concentrated H$_2$SO$_4$ by stirring for 1.5 h. Then the dispersion was gradually heated up to 70 °C while 5 mL H$_3$PO$_4$ was added into the dispersion under stirring for 20 min. The reaction dispersion was acquired by adding 0.1 g of powdered KMnO$_4$ with an addition rate of 0.1 g h$^{-1}$. The reaction was conducted under 70 °C for 2 h. The obtained dispersion was allowed to cool to room temperature and slowly dropped
into 300 mL 3 wt% H₂O₂ solution at 0 °C. After that, the dispersion was centrifuged and washed with deionized water for 3 times. Finally, the dispersion was dialyzed for a week and freeze-dried. The acquired nanocomposite was named as CNT/GONR-1. CNT/GONR-2 and CNT/GONR-3 were synthesized through the same process except that the reaction time was 4 h and 8 h, respectively.

2.3 Preparation of CNT/ GONR Nafion composite PEM

In a typical procedure⁵, 10 mg CNT/GONR-1 was first dispersed in 5 ml H₂O. The mixture was ultrasonicated for 30 min to get a homogenous dispersion. Then, a certain amount of CNT/GONR-1 dispersion was added into 4 mL 5 wt% as-received Nafion solution. After that, the mixture was ultrasonicated and exchanged with DMF by rotary evaporation to obtain a homogeneous CNT/GONR-1 Nafion DMF dispersion. Second, the obtained dispersion was cast onto a glass mold in a vacuum oven. The temperature was moderately increased from 80 °C to 120 °C and kept at 120 °C for 24 h to eliminate the solvent completely. Third, the membrane was transferred into a 3 wt% H₂O₂/H₂O solution, stirring for 2h at 70 °C. Then the membrane was soaked in a 1 M H₂SO₄ solution, stirring for 1 h at 80 °C. Finally, the CNT/GONR-1 Nafion composite PEM was washed with deionized water several times to eliminate excess H₂SO₄. The obtained composite membrane was named as x-CNT/GONR-1 Nafion, where x means the weight percentage of nanofiller in Nafion matrix. The recast Nafion membrane and other composite membranes (CNT/GONR-2, CNT/GONR-3, CNT and GO composite PEM) were prepared and named similarly.
2.4 Characterization of CNT and CNT/GONR nanocomposites

Transmission electron microscopy (TEM, JEOL, JEM-2100F) and field-emission scanning electron microscopy (FE-SEM, Zeiss, Ultra 55) were performed to observe the morphology of CNT and CNT/GONR nanocomposites. Raman spectra were measured to characterize the structure changes during the unzipping process of CNTs on a Renishaw inVia Reflex micro-Raman spectrometer with 638 nm laser excitation. The Fourier transform infrared spectroscopy (FTIR) spectra were conducted on a Thermofisher NEXUS 470 spectrometer with a resolution of 4 cm$^{-1}$ and 64 scans. The thermogravimetric analyses (TGA) were obtained on TGA 1 Thermo Gravimetric Analyzer under N2 atmosphere with a 20 °C min$^{-1}$ heating rate. The X-ray diffraction (XRD) analysis (PANalytical X’pert diffractometer) was undertaken to determine the unzipping degree of MWCNTs under Cu Kα radiation.

2.5 Characterization of PEMs

Field-emission scanning electron microscope (FE-SEM, Zeiss, Ultra 55) was used to characterize the surface and cross-sectional morphology of PEMs at 2 kV, where all the membranes were sprayed with gold. The atomic force microscope (AFM) images of PEMs were carried out on Bruker Multimode 8 in peak force QNM imaging mode. The FTIR spectra were characterized on Thermofisher NEXUS 470 with a resolution of 4 cm$^{-1}$ and 64 scans using an ATR attachment. Thermogravimetric analyses were conducted on TGA 1 Thermo Gravimetric Analyzer under N2 atmosphere with a 20 °C min$^{-1}$ heating rate. The XRD analyses were undertaken on PANalytical X’pert diffractometer with Cu Kα radiation to analyze the
crystallinity of the PEMs. The experimental methods and data analyses were according to the previous report\textsuperscript{40}. The water uptake (WU) at room temperature was measured by following steps. First, membranes were dried at 80 °C for 12 h and weighed to get \( W_{\text{dry}} \). Then, dried membranes were immersed into deionized water at 30 °C for 12 h. After that, the membranes were taken out and quickly weighed after carefully removing the excess water on the surface of membranes with filter paper to get \( W_{\text{wet}} \). WU was calculated with reference to formula (1):\[ WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \] (1)

High-temperature WU was calculated with formula (1) as well. Membranes were placed in BPHJ-120AF temperature and humidity test chamber (Shanghai Bluepard Instruments Co., Ltd) at 100 °C and 40 %RH for 4h. Weight data was collected on TGA 1 Thermo Gravimetric Analyzer under N\(_2\) atmosphere. First, the temperature was kept at 50 °C and got \( W_{\text{wet}} \). Then, the temperature was increased from 50 °C to 100 °C with a 20 °C min\(^{-1}\) heating rate and kept at 100 °C for 5 min. At last, the temperature was increased to 200 °C with a 20 °C min\(^{-1}\) heating rate and kept at 200 °C for 30 min when weight becomes constant to get \( W_{\text{wet}} \).

All proton conductivity tests of PEMs were conducted on electrochemical workstation (CHI660D) via a fourelectrode method under AC Impedance spectroscopy from 0.1 MHz to 1 Hz. BPHJ-120AF temperature and humidity test chamber (Shanghai Bluepard Instruments Co., Ltd) was used to control the humidity and temperature. All the membranes were kept under
certain environment for 1.5 h in order to reach the steady state. The proton conductivity $\sigma$ was calculated from the following formula\textsuperscript{24}:

$$\sigma = \frac{L}{R W d}$$  \hspace{1cm} (2)

where $L$ is the length of the PEM between two reference electrodes and $R$, $W$, $d$ are the impedance, width and thickness of the PEM, respectively.

The methanol permeability ($P$) was measured in an ATR cell (Thermofisher NEXUS 470) as was previously reported\textsuperscript{41}. The methanol permeability test was conducted under 40 °C with 80 v/v% methanol/H$_2$O solution. Briefly, the diffusion coefficients ($D$) of methanol molecules in the PEMs are calculated from the Fickian diffusion equation by simulating time-corresponding peak area (attributed to $\text{-CH}_3$ stretching vibration) curves. Then the $P$ values of the PEMs could be obtained via the formula (3):

$$P = \frac{4d^2D}{\pi^2}$$  \hspace{1cm} (3)

where $d$ is the thickness of the PEMs.

Formula (4) was used to calculate the membrane selectivity ($S$) of the PEMs to characterize the overall performance of the PEMs at 40 °C:

$$S = \frac{\sigma}{P}$$  \hspace{1cm} (4)
where $\sigma$ and $P$ are the proton conductivity and the methanol permeability of the PEMs at 40 $^\circ$C, respectively.

3. Results and discussion

3.1 Characterization of CNT and CNT/ GONR nanocomposite

The morphologies of CNT and CNT/GONRs were studied by TEM. As presented in Fig. 1(a-d), more and more GONRs are closely attached upon CNTs from CNT/GONR-1 to CNT/GONR-3. In Fig. 1(d) of CNT/GONR-3 image, CNTs are almost unzipped to form GO nanoribbons due to higher oxidation condition during the unzipping reaction. So it could be inferred that the unzipping degree increases with oxidation condition via a chemical unzipping method. In Raman spectra (Fig.2 (a)), the ratio between the intensities of the D and G bands ($I_D/I_G$) gradually increases with the unzipping degree from CNT/GONR-1 to CNT/GONR-3 which indicates a decrease in average $sp^2$ domain sizes due to a growing GONR weight percentage$^{42}$. Fig. 2 (b) shows the typical XRD patterns for CNT/GONR nanocomposites. The characteristic CNT peak is at 26.4$^\circ$ while the characteristic GONR peak is around 11$^\circ$ $^{39}$. The ratio between CNT peak intensity and GONR peak intensity decreases from CNT/GONR-1 to CNT/GONR-3, which also demonstrates the increcent GONR content in the nanocomposites. Besides, TGA results (Fig.2 (c)) show a decrease in thermostability with the increasing unzipping degree. According to the DTG curves (Fig. S1), the degradation temperature of CNT/GONR-1, CNT/GONR-2, and CNT/GONR-3 are 216 $^\circ$C, 189 $^\circ$C and 187 $^\circ$C, respectively. The weight loss of CNT, CNT/GONR-1, CNT/GONR-2 and CNT/GONR-3 are 0.5 %, 37.2 %, 39.3 % and 43.4 %,
respectively. The decreasing degradation temperature and enlarged weight loss could be ascribed to increasing oxygen-containing functional groups of CNT/GONR composites. The emergence of characteristic peaks of C=O (1726 cm\(^{-1}\)), -O-H (1400 cm\(^{-1}\)) and C=C (1618 cm\(^{-1}\)) in FTIR spectra of CNT/GONR (Fig. 2 (d)) provide the spectroscopy evidence\(^{39}\). Conclusively, CNT/GONR nanocomposites with various unzipping degrees were successfully synthesized via a time-controlling chemical unzipping method, in which oxygen-containing functional groups were decorated onto the surface of CNT/GONR nanocomposites.

![Fig. 1 TEM images (a1-d1) and FE-SEM images (a2-d2) of CNT, CNT/GONR-1, CNT/GONR-2 and CNT/GONR-3.](image-url)
Fig. 2 Raman spectra (a), XRD patterns (b), TGA curves (c) and FRIR spectra (d) of CNT, CNT/GONR-1, CNT/GONR-2 and CNT/GONR-3.

3.2 Characterization of PEMs

The surface FE-SEM images shown in Fig. 3 reveal the good dispersity of CNT/GONR nanocomposites in Nafion matrix when CNT is moderately unzipped. 0.5 wt% CNT/GONR-3 Nafion composite membrane (Fig. 3(e1)) shows a slight aggregation behavior due to the deepest unzipping degree and the biggest GONR content. According to the previous report, the GONRs would decrease the π-π interactions among CNT/GONRs and excessive GONRs would lead to the aggregation of CNT/GONRs in Nafion matrix. In Fig. 3 (a1 and f1), both CNT and GO show undesirable dispersibility more or less in Nafion matrix. The results mean CNT/GONR nanocomposites with suitable unzipping degree would be favorable to its dispersibility in Nafion.
matrix on account of highly matching in size and strong \( \pi-\pi \) interaction among CNT/GONR. Additionally, the cross-sectional FE-SEM images shown in Fig.3 (a2-f2) display the diblock morphologies of the PEMs due to the distinct bicontinuous microstructures of Nafion. The diblock morphologies of CNT/GONR Nafion composite PEMs become more obvious with increasing unzipping degree. It reveals that the CNT/GONRs has an individual effect on the nanophase separation as well as the crystallization behavior of Nafion Matrix.

![Fig. 3 Surface (a1-f1) and cross-sectional (a2-f2) FE-SEM images of recast Nafion, 0.5-CNT Nafion, 0.5-CNT/GONR-1 Nafion, 0.5-CNT/GONR-2 Nafion, 0.5-CNT/GONR-3 Nafion and 0.5-GO Nafion PEMs.](image)

The XRD patterns of Nafion-based composite PEMs were therefore performed to further investigate the crystallization behavior of Nafion Matrix and the results are presented in Fig. 4 (a). The peak occurring at 10 ~ 20° could be split to two peaks. One broad peak is at 16.1°, corresponding to hydrophilic and amorphous domains and the other sharp peak is at 17.7°
corresponding to crystalline domains. According to the analyses of XRD patterns (Fig. 4 (a) and Fig. S2), the crystallinity degree of Nafion matrix is decreased after adding CNT/GONR nanocomposite, which indicates its interaction with Nafion matrix. To further probe the inner change in polymer chain after incorporated CNT/GONR nanocomposites, TGA analyses were conducted and the results are shown in Fig. 4 (b) and (c). The desulfonation temperatures (340 ~380 °C) of the CNT/GONR Nafion composite PEMs are decreased compared with recast Nafion. This phenomenon may be attributed to two factors. One is the stronger electrostatic repulsion among –SO₃⁻ groups. Since the dimensions and shapes of the ionic clusters of Nafion-based PEMs are decided by the equilibrium between the internal osmotic pressure of the ionic clusters and the counteracting elasticity of the polymer matrix, CNT/GONR nanocomposites have limited impact on the ionic cluster size due to the lack of sulfonic groups on their surfaces. Hence, the decreased desulfonation temperature is probably caused by the adjustment of (–SO₃⁻)ₙ ionic clusters’ state of aggregation induced by CNT/GONR. The other is the formation of H-bonding interaction between CNT/GONR and –SO₃⁻ groups. The lowest desulfonation temperature of CNT/GONR-2 Nafion demonstrates the relatively strongest interaction between CNT/GONR-2 and Nafion matrix. This could be attributed to more oxygen-containing functional groups and more suitable geometric structure of CNT/GONR-2 nanocomposite. However, CNT/GONR-3 Nafion composite PEM displays a close desulfonation temperature to recast Nafion, which might be ascribed to the decreased π-π interactions among CNT/GONR-3 as mentioned above. The obvious aggregation phenomenon of CNT/GONR-3 in
the membrane matrix is the direct evidence presented in the FE-SEM image (Fig. 3). As a result, CNT/GONR-3 presents a weak induction ability to \((-\text{SO}_3)^n\) ionic clusters. The side-chain degradation temperatures (440 ~ 480 °C) are also decreased when CNT/GONR was incorporated into Nafion matrix, indicating the side chains are also motivated by \((-\text{SO}_3)^n\) ionic clusters’ adjustment and become more flexible\(^\text{41}\). However, the backbone degradation temperatures of CNT/GONR Nafion composite PEMs stay close to the recast Nafion, which reveals that CNT/GONR Nafion composite PEMs still maintain good thermal stability after undergoing the adjustment of ionic clusters. Combining the XRD with TGA analyses results, it could be inferred that the interactions among CNT/GONRs and \((-\text{SO}_3)^n\) ionic clusters (hydrophilic domains) trigger the move of perfluoroether side chain, which mobilizes the adjustment of polytetrafluoroethylene backbone (the crystalline part) during the membrane-forming process. Hence, CNT/GONR nanocomposites could exert an influence on the nanophase separation as well as the crystallization behavior of Nafion matrix by inducing \(-\text{SO}_3^-\) groups on the end of Nafion’s side chain through the hydrophilic-hydrophobic interactions. Consequently, the performance of composite PEMs is significantly influenced by CNT/GONR.
**Fig. 4** XRD patterns (a), TGA curves (b) and DTG curves (c) of recast Nafion, 0.5-CNT/GONR-1 Nafion, 0.5-CNT/GONR-2 Nafion and 0.5-CNT/GONR-3 Nafion.

The temperature-dependent proton conductivity of Nafion composite PEMs at 40 %RH are presented in Fig. 5 (a). The proton conductivity of CNT/GONR composite PEMs is close or little higher than that of recast Nafion at a lower temperature (40 ~ 80 °C). The similar water uptakes of composite PEMs might be mainly responsible for it (Fig. 5 (b)). As well known, the proton conduction of PEM at low temperature/high humidity largely depends on Vehicle mechanism, in which protons diffuse in the form of hydration. However, at high temperature (>100 °C), the composite PEMs modified with CNT/GONR nanocomposites show outstanding advantages in proton conductivity over recast Nafion membrane. 0.5-CNT/GONR-2 Nafion composite PEM presents the highest proton conductivity (0.18 S·cm⁻¹) at 120 °C and 40 %RH, nine times of recast Nafion (0.02 S·cm⁻¹) at the same conditions. We speculate that there might be four possible reasons for the improved proton conductivity performance. First is the good dispersibility of CNT/GONR-2 in Nafion matrix at 0.5 wt% content, which ensures desirable interaction between the nanocomposite and Nafion. Second is the good activity of (–SO₃⁻)ₙ ionic clusters in the composite PEM. The similar water uptake of CNT/GONR-2 Nafion composite PEM and recast Nafion (Fig.5(b)) at room temperature reveals that the activity of ionic clusters is not affected after adding CNT/GONR-2 nanocomposite and attract water molecules desirably. Third is the enhanced water retention capability at high temperature due to the incorporated CNT/GONR-2 nanocomposites. As demonstrated in Fig.5 (b), the WU of 0.5-CNT/GONR-2
Nafion composite PEM at 100 °C and 40 %RH is higher than that of recast Nafion, which indicates the improved water retention capability of CNT/GONR-2 composite PEM at high temperature and low humidity. Last but the most important one is the adjustment of ionic clusters in hydrophilic domains of Nafion matrix and the formation of long-range ionic nanochannels induced by CNT/GONR-2 such a 1D/2D nanocomposite. The morphology of hydrophilic domains in Nafion matrix (dark area for the hydrophilic domain) was observed with AFM\textsuperscript{47, 48}. The ionic clusters of recast Nafion are relatively disconnected, while the ionic clusters of CNT/GONR-2 Nafion composite PEMs are more connected. As shown in Fig. 6(d), the long-range proton conduction nanochannels (marked with red short dash line) consisted of \((–\text{SO}_3)^n\) ionic clusters could be observed around CNT/GONR-2 nanocomposites (large nanotube/nanoribbon-like bright area) in 0.5-CNT/GONR-2 Nafion composite PEM. Although CNT/GONR-2 itself could not provide ideal sites for proton conductivity due to few sulfonic groups on the surface, protons could achieve high mobility in the long-range ionic nanochannels induced by the nanocomposite\textsuperscript{29}. In summary, the CNT/GONR-2 nanocomposite has a moderate interaction with \((–\text{SO}_3)^n\) ionic clusters through hydrophilic and hydrophobic interaction to reach a thermodynamically stable state during the membrane-forming process. This moderate interaction induces the rearrangement of \((–\text{SO}_3)^n\) ionic clusters as well as side chains, making the hydrophilic parts of Nafion \((–\text{SO}_3^–\) groups) aggregate around CNT/GONR-2 nanocomposite to lower the energy of the system, which motivates the adjustment of nanophase separation and crystallization behavior of Nafion as well as the construction of long-range ionic nanochannels\textsuperscript{49}. 
Benefitting from CNT/GONR-2’s induction ability, the ionic clusters in the composite PEMs are much more connected and keep desirable activity. Similarly, CNT/GONR-1 Nafion and CNT/GONR-3 Nafion composite PEMs also present improved proton conductivity at high temperature (>100 °C). However, the proton conductivity of both composite PEMs is lower than that of CNT/GONR-2 Nafion composite PEM due to the following disadvantages such as lower water uptake at high temperature, less long-range ionic nanochannels, less connected ionic clusters and aggregation problem.

Fig. 5 (a) Temperature-dependent (40 %RH) proton conductivity of recast Nafion, 0.5- CNT Nafion, 0.5-CNT/GONR-1 Nafion, 0.5-CNT/GONR-2 Nafion, 0.5-CNT/GONR-3 Nafion and 0.5-GO Nafion PEMs. (b) Water uptake at 30 °C and 100 °C of recast Nafion, 0.5-CNT Nafion, 0.5-CNT/GONR-1 Nafion, 0.5-CNT/GONR-2 Nafion and 0.5-CNT/GONR-3 Nafion.
In order to further verify this 1D/2D nanofiller’s promotion ability on proton conductivity of the composite PEMs, the influences of CNT/GONR-2 content on the performance of composite PEMs are investigated as well. In Fig. 7, all CNT/GONR-2 Nafion composite PEMs with different filler content show elevated proton conductivity at high operation temperatures and 0.5-CNT/GONR-2 presents highest proton conductivity. As presented in Fig. S3 (a3-c3), more connected ionic clusters and long-range ionic nanochannels would be formed at a higher content of CNT/GONR-2. Because there would be more interfaces between nanofillers and Nafion matrix at a higher content of CNT/GONR-2 and more long-range ionic nanochannels constructs along the interfaces. What’s more, the interaction among $-\text{SO}_3^-$ groups and the H-bonding interaction between CNT/GONR and $-\text{SO}_3^-$ groups become stronger with moderately increasing
CNT/GO-2 content (Fig. S4), which leads to more impact on nanophase-separation and crystallization behavior of Nafion matrix. However, this superiority is destroyed when too much CNT/GONR-2 was incorporated on account of inevitable aggregation of inorganic nanofillers (Fig. S3). As a result, the 1-CNT/GONR-2 Nafion membrane presents a drop in proton conductivity. The proposed CNT/GONR inducing mechanism is schematically illustrated in Fig. 8.

**Fig. 7** Temperature-dependent (40 %RH) proton conductivity of recast Nafion, 0.1-CNT/GONR-2 Nafion, 0.5-CNT/GONR-2 Nafion and 1-CNT/GONR-2 Nafion PEMs.
Methanol permeability is another important parameter for evaluating its application potential in DMFC. The results of methanol permeability tests are listed in Table 1. Since methanol and protons share the same conductivity channels, there is a trade-off effect that the methanol resistance ability is probably worsened when proton conductivity is attempted to be improved. However, the unique 1D/2D nanostructure of CNT/GONR nanocomposites results in methanol permeability of CNT/GONR Nafion composite PEMs even lower than the recast Nafion PEM at 40 °C. The CNT/GONR nanocomposites are capable of adjusting the nanophase separation and crystallization behavior of Nafion, which makes methanol permeation channels more zigzag. 0.5-CNT/GONR-3 Nafion composite PEM shows a one-order-of-magnitude decrease (2.84E-09 cm²·s⁻¹) in methanol permeability than the recast Nafion PEM (1.03E-08 cm²·s⁻¹). 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permeability of 0.5-CNT/GONR-2 Nafion composite PEM remains at 1.05E-08. Since the proton conductivity of the composite PEMs is close to the recast Nafion at 40 °C, the selectivity of the composite PEMs is mainly promoted by the decrease in methanol permeability. The selectivity of the CNT/GONR Nafion composite PEMs is promoted by 2~5 times at 40 °C. The methanol permeability and selectivity of CNT/GONR-2 Nafion composite PEMs with different nanofiller contents are shown in Table.S1. Finally, it could be concluded that it is successful to modify Nafion with CNT/GONR nanocomposites to achieve the outstanding transportation performance especially in harsh environment by inducing the rearrangement of (–SO₃)ₙ ionic clusters as well as side chains through the moderate interaction among CNT/GONR and Nafion, which motivates the adjustment of nanophase-separation and crystallization behavior of Nafion to form long-range ionic nanochannels. 0.5-CNT/GONR-2 Nafion composite PEM show outstanding performance of proton conductivity at 120 °C and methanol permeability compared with previously reported articles (Table. S2).
Table 1 Transport properties of recast Nafion and composite PEMs at 40 °C.

<table>
<thead>
<tr>
<th>PEMs (40 °C)</th>
<th>Methanol Permeability (cm²·s⁻¹)</th>
<th>Error</th>
<th>Selectivity (S·s·cm⁻³)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recast Nafion</td>
<td>1.03E-08</td>
<td>± 1.4E-09</td>
<td>1.05E+06</td>
<td>± 1.8E+05</td>
</tr>
<tr>
<td>0.5-CNT Nafion</td>
<td>7.63E-09</td>
<td>± 6.5E-10</td>
<td>1.96E+06</td>
<td>± 2.2E+05</td>
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<tr>
<td>0.5-CNT/GONR-1 Nafion</td>
<td>8.61E-09</td>
<td>± 1.0E-09</td>
<td>2.86E+06</td>
<td>± 4.9E+05</td>
</tr>
<tr>
<td>0.5-CNT/GONR-2 Nafion</td>
<td>1.05E-08</td>
<td>± 5.3E-10</td>
<td>2.40E+06</td>
<td>± 1.5E+05</td>
</tr>
<tr>
<td>0.5-CNT/GONR-3 Nafion</td>
<td>2.84E-09</td>
<td>± 5.7E-10</td>
<td>3.85E+06</td>
<td>± 9.9E+05</td>
</tr>
<tr>
<td>0.5-GO Nafion</td>
<td>9.11E-09</td>
<td>± 4.4E-10</td>
<td>2.62E+06</td>
<td>± 2.1E+05</td>
</tr>
</tbody>
</table>

4. Conclusions

Herein, highly selective CNT/GONR Nafion composite PEMs with excellent transportation properties have been achieved. Both of the proton conductivity and the methanol resistance of the composite PEMs are enhanced by simply incorporating CNT/GONR nanocomposites. The unique properties of CNT/GONR nanocomposites lead to a desirable interaction with Nafion matrix, which induces the adjustment of nanophase-separation and crystallization behavior of Nafion as well as the formation of long-range ionic nanochannels. At the meantime, the (–SO₃)ₙ ionic clusters still keep good activity. Therefore, CNT/GONR Nafion composite PEMs present outstanding performance in harsh environment. The proton conductivity of 0.5-CNT/GONR-2 Nafion composite PEM is 0.18 S·cm⁻¹ at 120 °C and 40 %RH, nine times of recast Nafion (0.02
S·cm⁻¹) at the same conditions. The CNT/GONR nanocomposites are also capable of making methanol transportation channels more zig-zag to restrain methanol permeability. 0.5-CNT/GO-3 Nafion composite PEM shows a one-order-of-magnitude decrease (2.84E-09 cm²·s⁻¹) in methanol permeability than the recast Nafion PEM (1.03E-08 cm²·s⁻¹) at 40 °C.

ASSOCIATED CONTENT

Supporting Information Available. Additional FESEM images, AFM images, XRD patterns, TGA curves, methanol permeability characterization and comparison of transport properties with reported work. This materials is available free of charge via the internet at http://pubs.acs.org.

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References:


(17) Chalkova, E.; Fedkin, M. V.; Wesolowski, D. J.; Lvov, S. N. Effect of TiO2 Surface Properties On


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