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Poly(ethylene glycol) modified activated carbon for high performance proton exchange membrane fuel cells

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ABSTRACT

A high water retention membrane is developed by co-assembling poly(ethylene glycol) (PEG) grafted activated carbon (AC-PEG) with Nafion. The AC-PEG is prepared via a sol–gel process. The use of PEG as a transporting medium in AC-PEG shows a largely improved water retention ability, a higher proton conductivity and a reduced swelling ratio, making it well suited for proton exchange membrane fuel cells (PEMFCs). Further, the composite membranes show improved mechanical properties at high temperature, thus ensuring the structural stability of membranes during the fuel cell operation. Compositional optimized AC-PEG/Nafion composite membrane (15 wt% compared to Nafion) demonstrates a better performance than the commercially available counterpart, Nafion 212, in fuel cell measurements. To identify the key factor of the improved performance, current interrupt technique is used to quantitatively verify the changes of resistance under different relative humidity environment.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is considered to be one of the most promising alternative energy conversion devices for electric vehicles and residential power generation, due to its high energy density and environmental friendly properties [1,2]. The proton exchange membrane is centered

between anode and cathode, and acts as proton ion conductor and fuel separator at the same time. Polyperfluorosulfonic acid ionomer developed by Dupont, with the trademark of Nafion, is the most extensively used proton exchange membrane for PEMFCs because of its excellent chemical stability, low fuel permeability, and high proton conductivity. Nafion consists of hydrophilic pathways for proton transporting and

semicrystalline hydrophobic backbones act as a mechanical constraint to avoid the excessive swelling in water and ensure mechanical stability at high temperature. However, Nafion has some problems of maintaining high proton conductivity under low relative humidity due to dehydration of the membrane, thus deteriorating the fuel cell efficiency [3—5]. Nafion membranes require external water management to humidify the fuel and oxygen in order to maintain the proton conductivity. The reduction of PEM thickness addresses the aforementioned dehydration problems through back-diffusing water from the cathode [6]. However, the H_2 and O_2 crossover become severe and accelerate the degradation of PEMFCs as the thickness reduces. Therefore, the water retention ability of PEMs is considered as an important requirement for PEMFCs.

Many published strategies have suggested that the introduction of hydrophilic materials into the Nafion membrane evidently enhances the intrinsic low-water retention drawback. Alternatively, incorporation of metal oxide, carbon, clays, etc. into Nafion has proved to efficiently extend the window of working temperature and to collectively act as the reinforcement in the hybrid membranes [7—12]. In addition to hybrid inorganic fillers, carbon nano-materials, such as carbon nanotube, fullerene, graphene and carbon nanofibers, have emerged as promising additives to simultaneously enhance the mechanical stability and proton conductivity of the PEMs [13—15]. However, introduction of relatively conductive carbon materials into PEMs adversely causes shortage of the fuel cell with lower performance [16]. Nafion membranes infiltrated with carbon by hydrothermal reaction processes high proton conductivity and water retention, while accompanied by a detrimental increase in dimensions that deteriorate the performance of the fuel cell [17]. As a result, there remains a pressing need on identifying a cost-effective and high water retention material for PEMFC application.

Activated carbon (AC) with highly porous morphology on the surface has been considered as a promising water storage material for PEMFC. In our previous study, AC/Nafion composite membranes show outstanding water uptake, enhanced storage modulus, and improved proton conductivity at low humidity level [18]. However, the rugged terrain-like surface roughness on the PEM greatly limits the possibility of introduction functional adducts through synergistic co-assembly, deteriously increasing the contact resistance. In this article, we modified the AC with poly (ethylene glycol) (PEG) via a sol—gel process. The suitability of these composite membranes for PEMFC application was explored through systematic study of the PEM, including water uptake, swelling ratio and proton conductivity. The AC-PEG based membranes are found to exhibit smoother surfaces as well as desired properties for PEMFC application, including high water uptake with desired proton conductivity, and excellent single cell performances.

2. Experimental

2.1. Material

Activated carbon from Osaka Gas was ground with fused Zirconia powder before use. Nafion® NR212 membrane (50 μm)

and Nafion DE2020 (18 wt% in low aliphatic alcohols and water) were obtained from Ion power inc., Delaware, United States. Platinum supported on activated carbon (Pt/C) was used with further purification as received from Tanaka, Japan. 2-[Methoxy(polyethyleneoxy)-propyl] trimethoxy silane (90%) from Gelest was used to modify the AC surface.

2.2. Preparation of poly(ethylene glycol) modified activated carbon

The acidification of AC was conducted by soaking AC powders into a mixture of HNO_3/H_2SO_4 (1/5, v/v) under ultrasonicator for 1 h. Then the solution was diluted with deionized water (DI water) and the product was collected after centrifugation. The acidified AC was iteratively washed with DI water until the pH value reached 7. The product was dried in vacuum oven before further implementation into active device stacks.

To modify the AC, 1 g acidified AC was dispersed in 80 mL DI water with a pH value adjusted to 4.5. Subsequently, 1.1 g 90% of 2-[Methoxy (polyethyleneoxy)-propyl] trimethoxy silane was dissolved in 20 mL DI water and added dropwisely into the acidified AC dispersion while maintaining the reaction temperature at 80 °C and stirring for another 12 h. The resulting mixture was then collected with 0.2 μm filter. To remove the unreacted silane in the AC surface, the products were washed with absolute alcohol several times. In the final step, the poly(ethylene glycol) modified AC (hereafter referred as AC-PEG) particles were dried in a vacuum oven at the 125 °C for 12 h. Functional groups of AC-PEG particles were experimentally characterized by XPS (X-ray photoelectron spectroscopy, Thermo VGESCAlab 250).

2.3. Preparation of AC-PEG/Nafion composite membranes

Nafion ionomers were transferred to N, N-dimethylacetamide (DMAc, Aldrich) by distilling a mixing solution containing 500 mL Nafion DE2020 solution and 500 mL DMAc under reduced pressure (70 °C) to remove water and low boiling point solvent. To assemble the AC-PEG/Nafion composite membranes, 5, 10 and 15 weight percentage of a modified AC (compared to Nafion) were added to the Nafion/DMAc solution, respectively. Ultrasonication was used to ensure stable dispersion and the mixture was further stirred for another 12 h. The composite membranes were prepared by blade-coating with controlled thickness. The wet film was dried at 50 °C to remove low boiling point solvent and DMAc, and cured at the 140 °C for 2 h. To activate the proton substitution reaction, the AC-PEG/Nafion composite membrane were soaked in 1 M $H_2SO_{4(aq)}$ at the 80 °C for 1 h. The membrane was immersed into the water bath (80 °C) for another 1 h to fully remove the residual acid.

2.4. Structural characterizations

The morphologies of modified AC and composite membrane were observed with a scanning electron microscope (SEM, JEOL JSM-6500F) and a transmission electron microscope (TEM, JEOL JEM-2100F). For the directly characterization for the distribution of the ionic cluster, the membrane was immersed in 1 N lead acetate (Pb(Ac)₂) solution overnight to stain the

ionic clusters. The membranes were rinsed with DI water and dried under vacuum at 80 °C for 12 h. TEM samples were prepared by sectioned the membranes with an ultramicrotome and picked up with copper grids.

2.5. Evaluation of the proton conductivity

The proton conductivity was obtained using electrochemical impedance spectroscopy (Solartron 1260 Impedance/Gain-Phase Analyzer, Solartron Analytical, United Kingdom). The impedance was measured from the range of 7 M Hz to 0.1 Hz with a perturbation voltage amplitude 0.01 V.

$$\sigma = L/AR \tag{1}$$

where σ, L, A, and R refer to the proton conductivity, sample thickness, cross-sectional area and the resistance of the membranes, respectively [18].

2.6. Determination of water uptake and volume swelling ratio and ion exchange capacity (IEC)

The water uptake (WU) was obtained by immersing membranes in DI water at the 30 °C for 24 h to ensure the membranes fully saturated. Later, membranes were dried in vacuum oven at 70 °C and weighed. The WU was calculated by following equation.

$$WU(\%) = \left(W_{wet} - W_{dry}\right)/W_{dry} \times 100 \tag{2}$$

where WU (%), W_{wet} and W_{dry} are the water uptake, the weight of the wet membrane, and the weight of the dry membrane, respectively.

The dimensions of the membranes were measured with a micrometer (Mitutoyo). Each membrane was cut into 5 × 5 cm^2 and recorded the average thickness. Typically, the thickness of the membranes was measured more than four times. The volume swelling ratio was conducted at the 30 °C for 24 h and calculated according to the volume changes.

Ion exchange capacity (IEC) titration was measured with the following procedure. Typically, 0.1 g Nafion or AC-PEG/Nafion composite membrane was soaked in 50 mL 1 M NaCl$_{(aq)}$ for 12 h. The membrane was taken out and titrated the NaCl$_{(aq)}$ with 0.01 M NaOH$_{(aq)}$ until the pH value reached 7 (pH meter, Suntex SP-2200). The IEC value was calculated based on the equation

$$IEC = VC/W \tag{3}$$

where V is the volume used for titration, C is the concentration of the NaOH$_{(aq)}$ and W is the sample weight.

2.7. Water desorption

Water desorption measurements were conducted using a thermal gravimetric analysis (TA, Q5000) to determine weight changes over time at 50 °C. The water diffusion coefficient was calculated with the following equation.

$$M_t/M_\infty = 4\left(D_t/\pi L^2\right)^{1/2} \tag{4}$$

where: D, M_t/M_∞, and L are the water diffusion coefficient, the water desorption, and the membrane thickness, respectively [19].

2.8. Dynamic mechanical analysis (DMA) of the membrane

Each sample was cut into 1.5 × 2 cm^2 and the thickness was measured with a micrometer (Mitutoyo) before DMA measurement. The mechanical properties were measured by dynamic mechanical analysis (DMA, TAQ800) using the film/fiber tension clamp within the temperature range from 35 °C to 150 °C (Scanning rate 3 °C/min).

2.9. Preparation of membrane electrode assemble (MEA) and single cell

The catalyst ink was prepared by mixing Pt/C, Nafion, IPA and DI water. The ink was blade-coating onto gas diffusion layers (GDLs, Sigracet 10BC, SGL Technologies GmbH., Germany) with controlled thickness. The active area of the MEA was around 25 cm^2 while the Pt loading of the anode and cathode were 0.4 and 0.5 mg cm^{-2}, respectively. Then, the anodic and cathodic catalysts were adhered on the pristine Nafion 212 and AC-PEG/Nafion composite membranes by hot pressed (140 °C) with 20 kg/cm^2. The MEA and two pieces of the gaskets were sealed by two graphite plates engraved with a double serpentine. Finally, the unit cell was properly sealed between two conductive plates under controlled pressure. Detail characterization of I–V polarization had been described in our previous study [20]. The fuel cell system was operated at the 90 °C under different relative humidity environment. I–V plots were obtained by potentiostatically decreasing the cell voltage stepwise at intervals of 0.025 V. The measurement of the I–V curve started from 1.0 V and each successive step was maintained for 60 s. The measurements were performed until the cell voltage reached 0.4 V. The resistances of the fuel cells were determined using current interrupt technique built into the cell testing system (850e, Scribner Associates Inc. North Carolina, United States) at the voltage of 0.6.

3. Results and discussion

3.1. Characterization of the PEG modified activated carbon

As shown in Fig. 1(a), three peaks originated in 284.6, 286.1 and 288.6 (eV), can be assigned to C–C, C–O and C=O, respectively. After a sol–gel process, a predominant C 1s peak of C–O appeared at 286.0 eV, indicating the presence of ether groups. The great enhancement of C–O intensity can be explained by the active surface modified with 2-[methoxy (poly-ethyleneoxy)-propyl] trimethoxy silane. Moreover, the pronounced Si 2p peak evidently confirmed that the AC was successfully modified with PEG. The AC-PEG dispersed homogeneously in Nafion/DMAc solution without any visibly distinquishable agglomeration. The TEM images and the energy dispersive X-ray (EDX) mapping results of the AC-PEG in line with the XPS study (Supporting information (SI) Fig. S1). The EDX mapping results confirmed the successful modification of the PEGs.
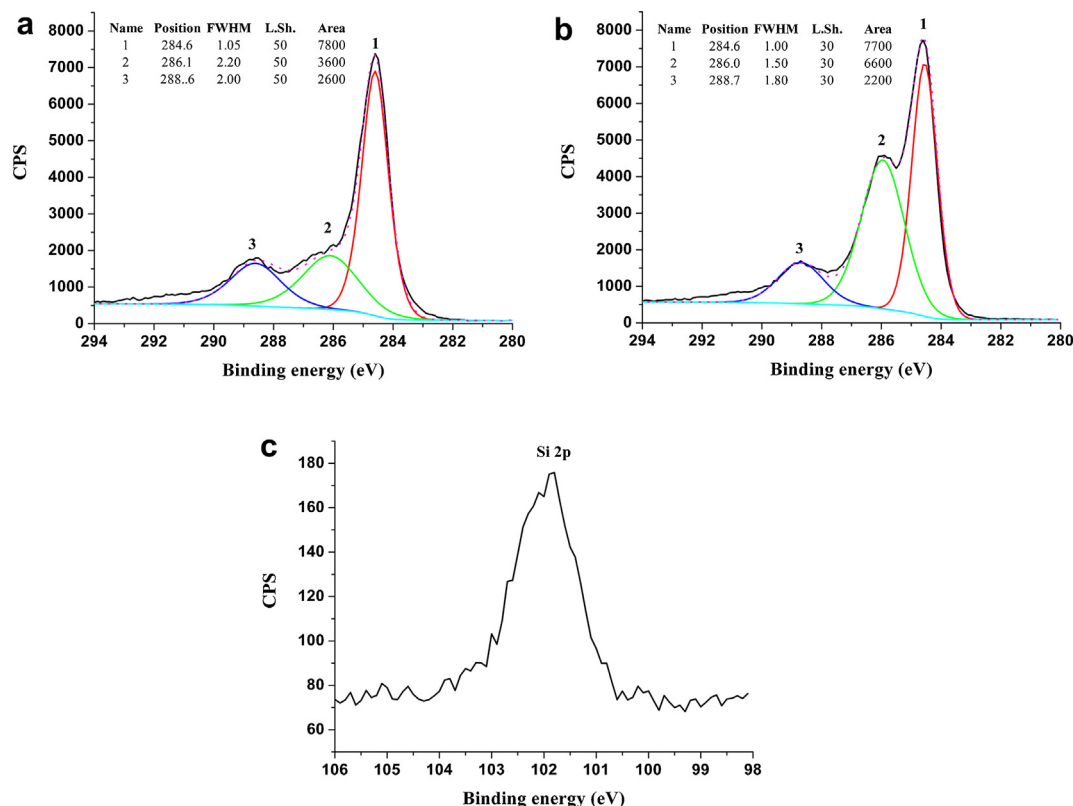
Name	Position	FWHM	L.Sh.	Area
1	284.6	1.05	50	7800
2	286.1	2.20	50	3600
3	288..6	2.00	50	2600

Name	Position	FWHM	L.Sh.	Area
1	284.6	1.00	30	7700
2	286.0	1.50	30	6600
3	288.7	1.80	30	2200

Fig. 1 — XPS of the AC (a) and after silanization (b). A predominant peak of Si2p can be observed in (c).

3.2. Characterization of the composite membrane

The optical image and the corresponding scanning electronic microscopy (SEM) of the AC-PEG/Nafion composite membrane is shown in Fig. 2. The SEM image, as shown in Fig. 2(a) provides a close-up view to reveal a slightly rough morphology with some sub-micron AC-PEG embedded in the Nafion membrane. However, the matte black composite membrane shows smooth morphology in optical image as shown in Fig. 2(a) inset. Compared to the AC (Fig. 2(b)), the AC-PEG/Nafion composite membrane showed a smoother surface contributed to the higher density of AC-PEG. The density was increased from 0.22 to 0.35 g cm^{-3} after the modification of PEG. Additionally, the surface of AC-PEG was reduced from original 1688.3 m^2 g^{-1}—251.1 m^2 g^{-1} due to some of the micropores were filled with PEG as shown in SI Fig. S2. The unique structure of AC-PEG, composed PEG as water transporting valve and micropores as a water reservoir, showed lower surface roughness with a potential water storage property. The surface roughness of the proton exchange membranes determines the coating technique, e.g. spraying coating and hot press coating with catalyst layers. Membranes with larges roughness show higher contact resistances during the membrane assembly electrodes due to the inhomogeneous contact area. The TEM images showed in Fig. 2(c) and (d) further explain the spatial distribution of the sulfonic clusters. Populated Pb ions, represented the sulfonic groups, were clustered around the surface of the AC which suggested the hydrophilic channels can effectively transport water molecules inside and outside the AC. PEG offered an extra area for ionic clusters and AC to exchange water molecules and transport protons.

3.3. Water uptake, water desorption and proton conductivity of the membrane

As shown in Table 1, the WU of the pristine Nafion membrane was 28.2% and it slightly increased with AC-PEG content to 44.5, 51.9 and 64.5% for the 5, 10 and 15 wt% loading, respectively. The introduction of hydrophilic materials effectively improves the hydration of Nafion membranes. Several related studies show significant enhancement on WU by introducing inorganic fillers, such as laponite, sulfonated mesoporous silica and Zirconia, into Nafion matrix [21—24]. Moreover, the volume swelling ratios of the AC-PEG/Nafion membranes tended to decrease with the increasing carbon content. The volume swelling ratio of pristine Nafion was 40.9% and obviously declined to 23.0% for 15 wt% composite membrane. Dimensional stability is an important requirement for a proton exchange membrane since excessive swelling is detrimental to the assembly of the membrane and results in poor performance as well as long-term durability of the fuel cell. The unique swelling characteristics of AC-PEG/Nafion membranes are built up of a non-expandable nature of the AC particles, grafted PEG and the ionic clusters. These promising signs of AC-PEG/Nafion membranes demonstrated here underscore the importance of introducing the AC-PEG into the Nafion matrix for controlling WU and minimizing membrane swelling during the relative humidity changes.
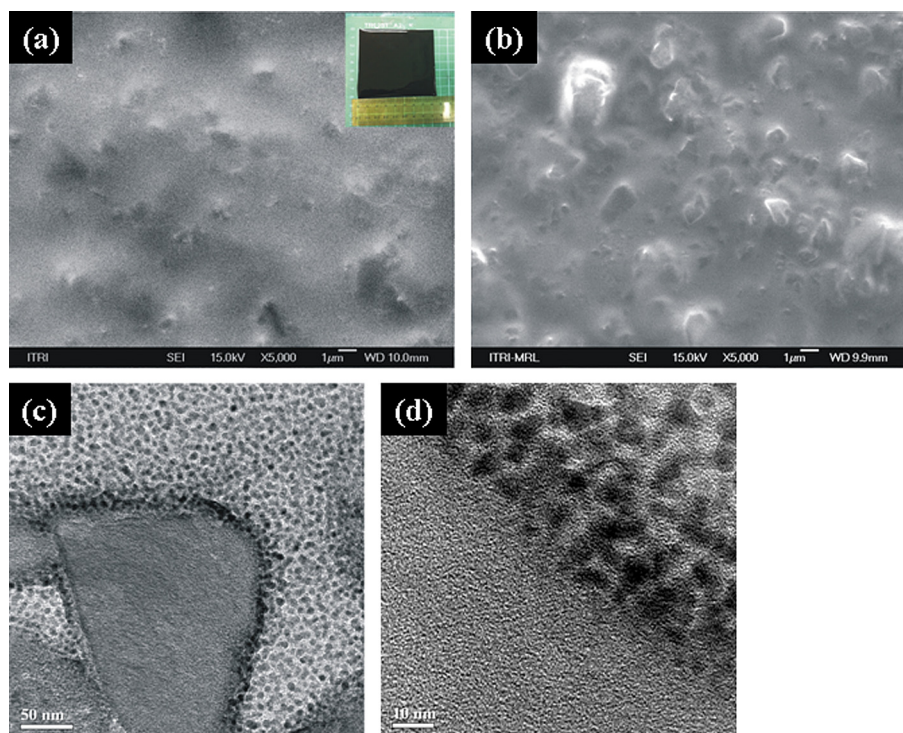
Fig. 2 – SEM image of 15 wt% AC-PEG/Nafion (a) (inlet is the optical microscopy) and 15 wt% untreatment AC/Nafion composite membrane and (c), (d) TEM images of 15 wt% AC-PEG/Nafion.

Water absorption and diffusion in PEMs has a significant effect on proton conductivity, especially at low relative humidity. As shown in Fig. 3, the velocity of water desorption was slightly reduced with an increase of AC-PEG. These results were consistent with the findings of the WU mentioned above.
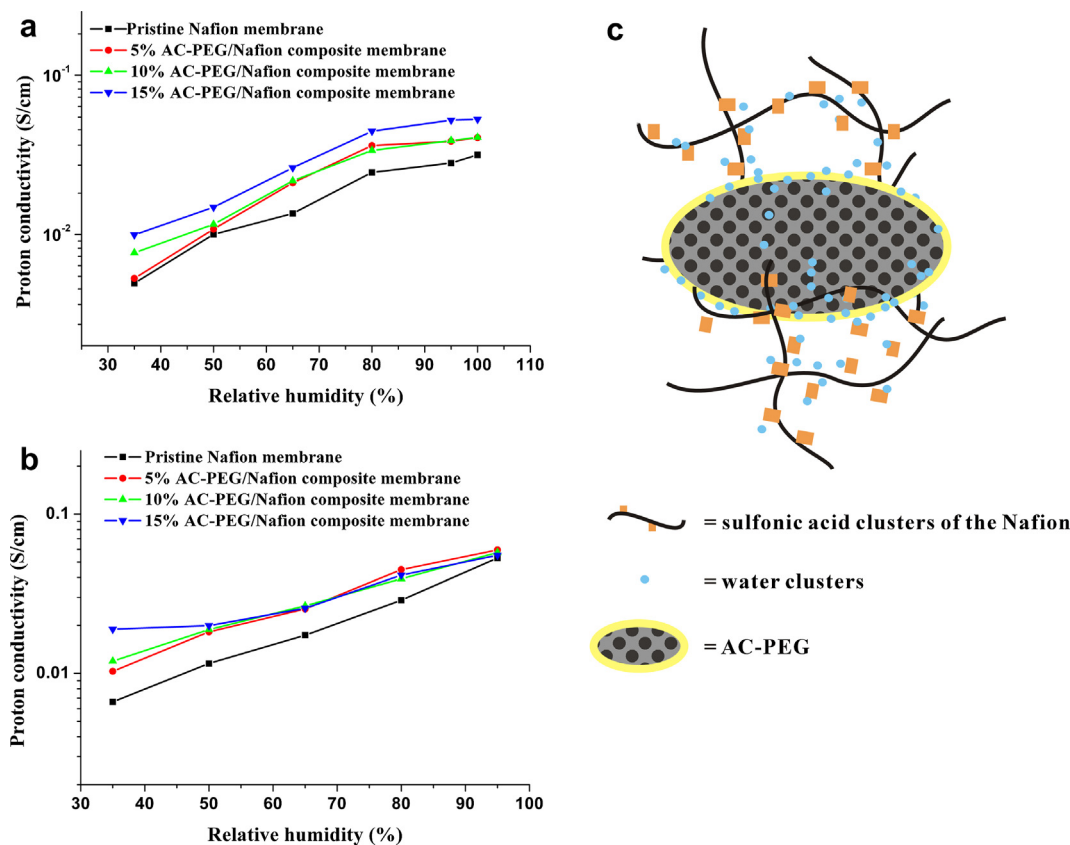
The proton conductivity of pristine Nafion membranes generally increases with higher relative humidity (RH) due to the hydrophilic domains (clusters of the sulfonic group) absorbing more water molecules in the high RH and facilitate the proton transfer easily. In Fig. 4(a), the incorporation of AC-PEG systematically enhanced proton conductivity throughout the entire RH range. In addition, the proton conductivity was obvious improved under low RH both at 30 and 80 °C. The conductivity of 15 wt% AC-PEG/Nafion composite membrane was 3 times higher than pristine Nafion at 35% RH (80 °C). Proton conductivity is greatly associated with the ion exchange capacity of the PEM. The IEC of the composite membrane partially decreases upon the addition of the filler, indicating that the proton conductivity enhancement was contributed to the better water retention ability of the AC-PEG. Moreover, the DSC result of AC-PEG (SI Fig. S3) showed that
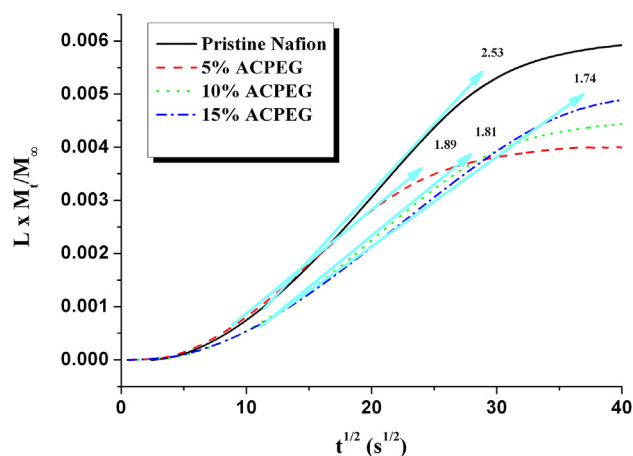
Fig. 3 – The water desorption of pristine Nafion membrane and different ratio of AC-PEG/Nafion composite membranes. The numbers correspond to the water diffusion coefficients ($\times 10^{-5}$ cm^{-2} s^{-1}).

Table 1 – The water uptake, swelling ratio and ion exchange value of the Nafion and the composite membranes.

	Recasted Nafion	5% AC-PEG	10% AC-PEG	15% AC-PEG
Water uptake (%)	28.2	44.5	51.9	64.5
Volume swelling ratio (%)	40.9	37.1	24.5	23.0
IEC (mmol g^{-1})	0.932	0.913	0.907	0.897

Fig. 4 – Proton conductivity of the pristine Nafion membrane and different loading percentage of AC-PEG/Nafion composite membranes as function of RH at (a) 30 °C and (b) 80 °C. The mechanism of water transfer of the AC-PEG is shown in (c).

the PEG was at its melted state as the temperature surpassed 60 °C. The PEG had better molecular movement at its melted state which facilitates water molecule and the proton transfer and thus enhances the proton conductivity. These observations indicated that the better proton conductivity of the composite membranes at low humidity environments could be traced back to their superior water uptake, a synergistic effect of high porosity structure and PEG. The illustration of the water transportation of the AC-PEG is shown in the Fig. 5(c). The water molecules could be transferred by PEG into AC because the oxygen on PEG backbone had a high affinity with water molecules through hydrogen bonding, providing effective transportation.

3.4.   Mechanical properties of the composite membrane

Nafion membranes exhibited different mechanical properties and proton conductivity, depending on the recasting solvent and annealing temperature [24,25]. In this study, all the composite membranes were recast from Nafion/DMAc dispersion (see the Experimental section) with identical drying and annealing processes. The incorporation of AC-PEG particles to the Nafion membranes significantly reinforce the mechanical properties as shown in Fig. 5(a). The storage modulus of the composite membranes enhanced as the loading increased. The obvious improvement in storage

modulus was contributed to the physical cross-linking network between the hydrophilic side chain of Nafion and functionalized AC. The storage modulus of 15 wt% AC-PEG/ Nafion was higher than pristine Nafion by a factor of 2.78 and 4.91 at 40 and 90 °C, respectively. The mechanical enhancements greatly extended the window of fuel cell operation temperature. Nafion composites with high mechanical strength have been extensively studied such as hybrid systems based on TiO_2, SiO_2, clays and carbon materials [26–28]. In practical applications, the thinner and stiffer PEMs are known to reduce internal resistance without the possibility of generating pinhole and crack. Moreover, during the MEA fabrication, the high mechanical strength membrane allows a wide range of assembling pressure without wrinkle formation, excluding the thickness differences and poor adhesion.

The temperature-dependent tanδ curves of the composite membranes, obtained from DMA (Fig. 5(b)), reflected the limited interface between Nafion molecules and the AC-PEG particles. The α relaxation is related to the mobility of the hydrophilic site of the polymer chains. Nano-filler/Nafion composite membranes typically display an obvious temperature increase of the α relaxation due to large organic–inorganic interface [29,30]. Unlike previous studies, only the minor displacement in this study indicated the limited interface between Nafion and AC-PEG because of submicron size of the AC-PEG particles.
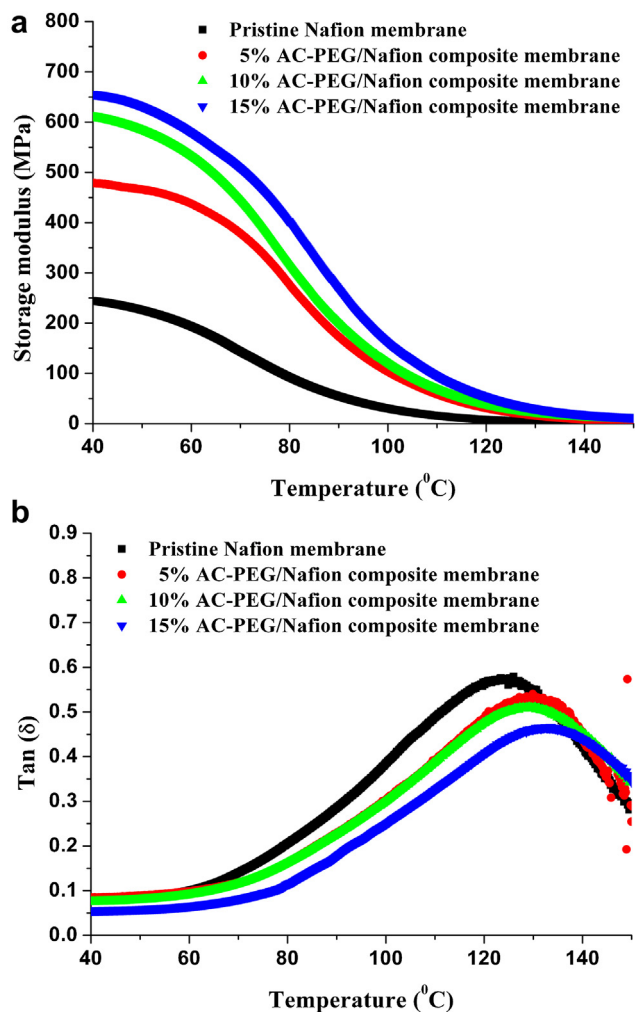
Fig. 5 – DMA traces of pristine Nafion and AC-PEG/Nafion composite membranes; (a) Storage modulus and (b) tanδ. Color denote; pristine Nafion (black), 5 wt% AC-PEG (red), 10 wt% AC-PEG (green) and 15 wt% AC-PEG (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.5. Performance of the PEMFC under different humidity conditions

The performance of fuel cell under different humidity condition is associated with the properties of the PEMs. The output characteristics of the PEMFCs were measured at 90 °C with controlled relative humidity. The polarization curves for a PEMFC composed of Nafion 212 and 15 w% AC-PEG/Nafion composite membranes are shown in Fig. 6. The performance of Nafion 212 dropped drastically with decreasing RH. At a cell voltage of 0.60 V, fuel cells exhibited current densities of 857 mA cm^{-2}, 650 mA cm^{-2}, and 187 mA cm^{-2} at 100, 50 and 20% RH, respectively. Additionally, the maximum power density dramatically decreased from 582 to 119 mW cm^{-2} as the RH was reduced from 100% to 20%. The 15 wt% AC-PEG/Nafion composite membrane revealed similar output
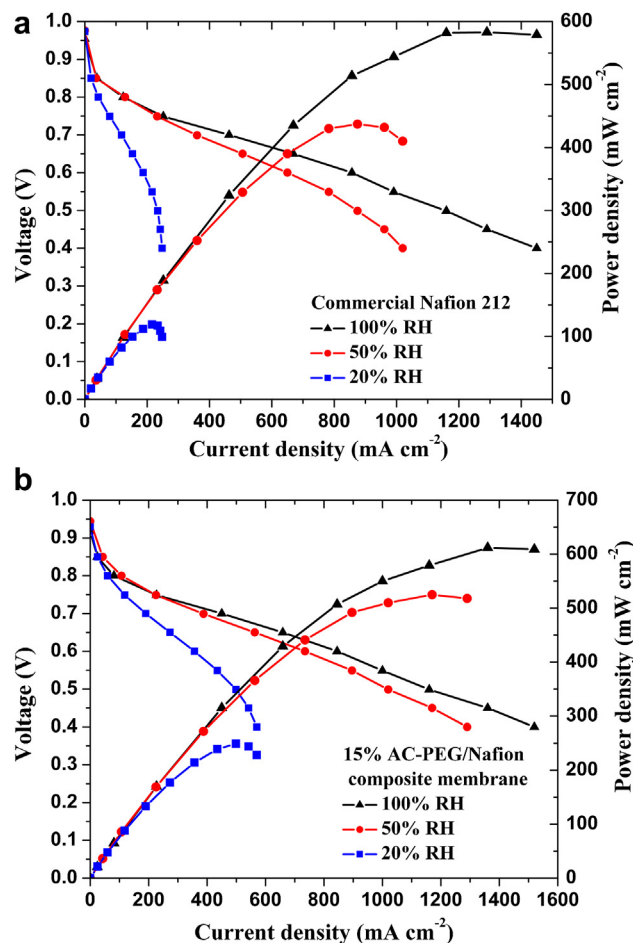

Fig. 6 – Polarization curves of PEMFC with (a) commercial Nafion 212, (b) 15 wt% AC-PEG/Nafion under different relative humidity test conditions at 90 °C in H$_2$/Air system.

characteristics with Nafion 212 at high RH condition (100% RH). However, at 50% RH, the composite membrane had the current density 735 mA cm^{-2} (0.60 V) and maximum power density 525 mW cm^{-2} that was obviously better than Nafion 212. Moreover, at the critical condition (20% RH), the composite membrane had nearly twice current density and maximum power density compared to Nafion 212. The great improvement of the output characteristics of the AC-PEG composite membranes, especially at low RH, was a result of the introduction of high water retention material.

The resistance of the fuel cell under different RHs was determined using current interrupt technique. The resistances for PEMFC of the Nafion 212 and 15 wt% AC-PEG/Nafion composite membrane under different RHs are shown in Fig. 7. Both membranes showed the identical discharging current density and resistance above 90% RH. However, as the RH decreased, the cell resistances gradually increased because of the dehydration of the Nafion and AC-PEG/Nafion composite membrane. Nafion 212 showed a poor current density and high resistance (59 mΩ cm^{-2}) at 10% RH. In contrast, the AC-PEG/Nafion composite membrane exhibited only 22.2 mΩ cm^{-2} which was much lower than Nafion 212 membrane. In this light, the AC-PEG/Nafion composite
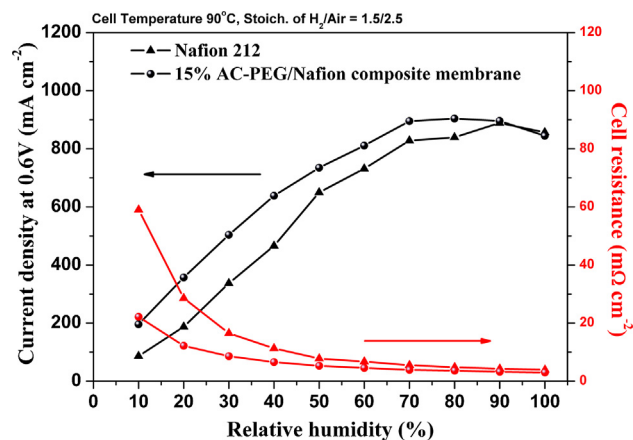
Fig. 7 — Resistance of the PEMFC measured under different relative humidity.

membrane could absorb water molecules from the cathode and acted as a water reservoir and thus maintain higher proton conductivity.

4. Conclusions

A high water retention AC-PEG/Nafion composite membrane was developed and characterized. XPS fitting results showed that the AC particles were indeed modified with PEG. The composite membranes exhibited high water uptake, lower water desorption rate and improved proton conductivity. Additionally, the incorporation of the AC-PEG with Nafion greatly enhanced the mechanical properties, affording to varied assembly process and showed great potential for practical application. The performance of PEMFC composed of 15 wt% AC-PEG/Nafion composite membrane showed superior current density and peak power density over the commercial Nafion 212. The resistance results during the fuel cell operation conclusively explained that the enhanced performance of the composite membrane was contributed to the high water retention ability of the composite membrane. The PEG modified activated carbon could be adopted for the mass production of proton exchange membranes for effective energy conversion fuel cell.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2013.06.054.

REFERENCES

[1] Mauritz KA, Moore RB. State of understanding of Nafion. Chem Rev 2004;104:4535–85.
[2] Kamarudin SK, Daud WRW, Ho SL, Hasran UA. Overview on the challenges and developments of micro-direct methanol fuel cells (DMFC). J Power Sources 2007;163:743–54.
[3] Ren S, Sun G, Li C, Song S, Xin Q, Yang X. Sulfated zirconia–Nafion composite membranes for higher temperature direct methanol fuel cells. J Power Sources 2006;157:724–6.
[4] Lanniello R, Schmidt VM, Stimming U, Stumper J, Wallan A. CO adsorption and oxidation on Pt and Pt/Ru alloys: dependence on substrate composition. Electrochim Acta 1994;39:1863–9.
[5] Shao ZG, Joghee P, Hsing IM. Unequivocal definition and determination of "dissolved gas" permeability and resistances of the liquid layers in contact lens applications. J Membr Sci 2004;229:43–51.
[6] Springer TE, Zawodzinski Jr TA, Gottesfeld S. In: White RE, Verbrugge MW, Stockel JF, editors. The electrochemical society proceeding series, Pennington, NJ 1991. p. 209. (PV 91-10).
[7] Jalani NH, Dunn K, Datta R. Synthesis and characterization of Nafion®-MO₂ (M = Zr, Si, Ti) nanocomposite membranes for higher temperature PEM fuel cells. Electrochim Acta 2005;51:553–60.
[8] Nakajima H, Nomura S, Sugimoto T, Nishikawa S, Honma I. High temperature proton conducting organic/inorganic nanohybrids for polymer electrolyte membrane: part II. J Electrochem Soc 2002;149:A953–9.
[9] Tang H, Wan Z, Pan M, Jiang SP. Self-assembled Nafion–silica nanoparticles for elevated-high temperature polymer electrolyte membrane fuel cells. Electrochem Commun 2007;9:2003–8.
[10] Savadogo O. Emerging membranes for electrochemical systems: part II. High temperature composite membranes for polymer electrolyte fuel cell (PEFC) applications. J Power Sources 2004;127:135–61.
[11] Bauer F, Willert-Porada M. Characterisation of zirconium and titanium phosphates and direct methanol fuel cell (DMFC) performance of functionally graded Nafion(R) composite membranes prepared out of them. J Power Sources 2005;145:101–7.
[12] Watanabe M, Uchida H, Seki Y, Emori M, Stonehart P. Self-humidifying polymer electrolyte membranes for fuel cells. J Electrochem Soc 1996;143:3847–52.
[13] Wu J, Yuan XZ, Martin JJ, Wang H, Zhang J, Shen J, et al. A review of PEM fuel cell durability: degradation mechanisms and mitigation strategies. J Power Sources 2008;184:104–19.
[14] Choi YG, Kim YK, Kang KY, Lee JS. A composite electrolyte membrane containing high-content sulfonated carbon spheres for proton exchange membrane fuel cells. Carbon 2011;49:1367–73.
[15] Kannan R, Kakade BA, Pillai VK. Polymer electrolyte fuel cells using Nafion-based composite membranes with functionalized carbon nanotubes. Angew Chem Int Ed 2008;47:2653–6.
[16] Liu YH, Yi B, Shao ZG, Xing D, Zhang H. Carbon nanotubes reinforced Nafion composite membrane for fuel cell applications. Electrochem Solid-State Lett 2006;9:A356–9.
[17] Chai Z, Wang C, Zhang H, Doherty CM, Ladewig BP, Hill AJ, et al. Nafion–carbon nanocomposite membranes prepared using hydrothermal carbonization for proton-exchange-membrane fuel cells. Adv Funct Mater 2010;20:4394–439.
[18] Chien HC, Tsai LD, Kelarakis A, Lai CM, Lin JN, Fang J, et al. Highly hydrated Nafion/activated carbon hybrids. Polymer 2012;53:4927–30.
[19] Huang YJ, Ye YS, Yen YC, Tsai LD, Hwang BJ, Chang FC. Synthesis and characterization of new sulfonated polytriazole proton exchange membrane by click reaction for direct methanol fuel cells (DMFCs). Int J Hydrogen Energy 2011;36:15333–43.
[20] Chien HC, Tsai LD, Lai CM, Lin JN, Fang J, Zhu CY, et al. Characteristics of high-water-uptake activated

carbon/Nafion hybrid membranes for proton exchange membrane fuel cells. J Power Sources 2013;226:87—93.

[21] Alberti G, Casciola M. Composite membranes for medium-temperature PEM fuel cells. Annu Rev Mater Res 2003;33:129—54.

[22] Pereira F, Valle K, Belleville P, Morin A, Lambert S, Sanchez C. Advanced mesostructured hybrid silica-Nafion membrane for high performance PEM fuel cell. Chem Mater 2008;20:1710—8.

[23] Ramani V, Kunz HR, Fenton JM. Stabilized heteropolyacid/Nafion® composite membranes for elevated temperature/low relative humidity PEFC operation. Electrochim Acta 2005;50:1181—7.

[24] Moore RB, Martin CR. Chemical and morphological properties of solution-cast perfluorosulfonate ionomers. Macromolecules 1988;21:1334—9.

[25] Gebel G, Aldebert P, Pineri M. Structure and related properties of solution-cast perfluorosulfonated ionomer films. Macromolecules 1987;20:1425—8.

[26] Cele N, Ray SS. Recent progress on Nafion-based nanocomposite membranes for fuel cell applications. Macromol Mater Eng 2009;294:719—38.

[27] Alonso RH, Estevez L, Lian H, Kelarakis A, Giannelis EP. Nafion—clay nanocomposite membranes: morphology and properties. Polymer 2009;50:2402—10.

[28] Thomassin JM, Koller J, Caldarella G, Germain A, Jerome R, Detrembleur C. Beneficial effect of carbon nanotubes on the performances of Nafion membranes in fuel cell applications. J Membr Sci 2007;303:252—7.

[29] Page KA, Cable KM, Moore RB. Molecular origins of the thermal transitions and dynamic mechanical relaxations in perfluorosulfonate ionomers. Macromolecules 2005;38:6472—84.

[30] Obsorn SJ, Hassan MK, Divoux GM, Rhoades DW, Mauritz KA, Moore RB. Glass transition temperature of perfluorosulfonic acid ionomers. Macromolecules 2007;40:3886—90.