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Nafion®/SiO2/m-BOT composite membranes for improved direct methanol fuel cell performance

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Abstract: Bentonite (BOT) has excellent hygroscopicity and large specific surface, so it is chosen as dopant of Nafion® membrane in this paper. By using the sol-gel method, bentonite has been modified by dodecylamine and fixed to the Nafion 212 membrane to prepare Nafion/SiO2/m-BOT composite membrane. The results of SEM and FT-IR shows that m-BOT is successfully synthesized and bound well with Nafion 212 membrane. The limiting current density of cathode methanol oxidation indicates that the methanol permeability of composite membrane is 20.40 % lower than that of Nafion 212 membrane. Although the conductivity of composite membrane (6.67×10^{-2} S·cm^{-1}) declines slightly compared with that of Nafion 212 (9.91×10^{-2} S·cm^{-1}), the performance of the cell using composite membrane (135.17 mW·cm^{-2}) is better than Nafion 212 membrane (118.7 mW·cm^{-2}) at 55 °C. Besides, as anode methanol concentration increases, higher performance is obtained, which indicates that the composite membrane is more suitable for cells running with high concentration of methanol.

Key words: Proton exchange membrane; Methanol permeability coefficient; Proton conductivity; Direct methanol fuel cell

1. Introduction

Direct methanol fuel cell (DMFC), an active research area of proton exchange membrane fuel cell, is expected to have the best business outlook for small mobile cell, due to its characteristics of high energy density, light weight, low working temperature and small size and convenient fuel storage etc.. However, two main problems prevent DMFC from commercial production, which are the low catalytic activity of anode catalyst for methanol oxidation reaction and the high methanol permeability of proton exchange membrane that can cause the cathode catalyst poisoning and "mixed-potential". Therefore, current DMFC research aims to moderate methanol permeability in proton exchange membrane.

In order to overcome high methanol permeability, two methods have been developed. One method is to adopt new proton exchange membranes using new materials to such as sulfonated polyether ether ketone (SPEEK) [1], polyethersulfone (PES), polyvinyl alcohol (PVA) as well as other materials to replace traditional Nafion® proton exchange membrane. Zhang [2] decreased methanol permeability significantly by using sulfonated PEEK membranes instead of Nafion membranes to. In his research, the power density using sulfonated PEEK membrane reached 18.7 mW·cm^{-2} when the current density was 75 mA·cm^{-2}. Lin [3] selected poly(ethylene glycol) as organic segment and silica as inorganic part to make high selectivity organic-inorganic hybrid-laminated Nafion 115 membranes. Methanol permeability in hybrid-laminated membranes was about an order of magnitude lower than that of Nafion 115, but the proton conductivity decreased only slightly at low hybrid content (13.6 wt.%). Yang [4] prepared PVA/SiO$_2$ nanocomposite membranes to realize the highest power density of the DMFC, with 19.57 mW·cm^{-2} ambient conditions. Although these membranes have close hydrophobic network structure which can lower methanol permeability, the lack of proton transfer carrier and channel leads to poor proton conductivity. Thus the performances of cells using new materials are much lower than cells using Nafion membrane. Another method adopted widely is to modify the original Nafion by doping one or multiple materials. This method can

decrease the methanol permeability with relatively lesser reduction of proton conductivity [5, 6]; therefore, the cell performances with membranes are higher than that with traditional Nafion membranes. Rhee, et al., used montmorillonite (MMT) as Nafion membrane's doped metarial. The methanol permeability of the composite membrane decreased dramatically as the content of HSO_3-MMT in the composite membrane increased, resulting in fewer decrease of the proton conductivity comparing to that of pristine Nafion 115.

In order to further improve the cell performances, Bentonite which has big specific surface area (750 $m^2 \cdot g^{-1}$) and favorable hygroscopicity (adsorbs 8 ~ 15 times of water compared to its quality) was firstly used as the dopant of Nafion membrane in this paper. Bentonite was doped with dodecylamine by Sol-gel method and treated with tetraethyl orthosilicate afterwards. In this composite membrane, SiO_2 was used to absorb water and inhibit methanol crossover, m-BOT to control proton channel's aperture, and dodecylamine to form skeleton and make composite membrane steadier. The physical and chemical properties of as-prepared composite membrane were later analyzed and the cell's performance with composite membrane was also evaluated.

2. Experimental

2.1 Preparation of composite membrane

Nafion 212 membrane was purchased from the DuPont Company as the basic membrane of the composite membrane. Bentonite (analytical reagent, SCRB) has a 2:1 type crystal structure composed of two silica tetrahedron with a layer of alumina octahedral bentonite between them. Because of the existence of various cationics such as Cu^{2+}, Mg^{2+}, Na^+, K^+ etc. in lamellar structure of montmorillonite and the weak combination between these cationics and montmorillonite, cationic can be easily exchanged by hydrogen ion [7]. Dodecylamine (analytical reagent, SCRB) was inserted into the bentonite laminated structure via intercalated reaction [8], which changed the character of bentonite and brought about modified bentonite (dodecylamine-exchanged bentonite, m-BOT). Because tetraethyl orthosilicate (TEOS) is easy to hydrolyze, sol-gel reaction was realized to fix modified bentonite after

Nafion 212 membrane was soaked into water.

The m-BOT was prepared as follows: 5 g bentonite was added to 100 mL NaOH/methanol solution (NaOH was 20 wt. % in NaOH solution, and the volume ratio of methanol and NaOH solution was 2:1), which was stirred 2 h under 90 $^{\circ}$C, and then Na$^+$-based bentonite (Na$^+$-BOT) was obtained. The as-synthesized Na$^+$-BOT was flushed several times with deionized water to make sure no extra OH$^-$ existence, which was confirmed through Fe(OH)$_3$ precipitation reaction by using 1 mol·L^{-1} FeCl$_3$ solution. H$^+$-BOT (H$^+$ base bentonite) was prepared later by adding 5 g Na$^+$-BOT into 50 mL 1 mol·L^{-1} H$_2$SO$_4$ solution, and then it was stirred for 3 h under 90 $^{\circ}$C. In order to obtain m-BOT, 2.25 g dodecylamine was first added to 25 mL 1 mol·L^{-1} HCl solution which was continuously stirred until it was completely dissolved under 90 $^{\circ}$C, and then mixed with the other portion of solution that was prepared by disperse 5 g H$^+$-BOT in 100 ml of deionized water. The above mixed solution was later kept at 80 $^{\circ}$C for 3 h to allow the reaction to proceed by using microwave hydrothermal method. The as-obtained participation was filtered and flushed several times until no AgCl precipitation observed by using 0.1 mol·L^{-1} AgNO$_3$ solution as indicator. Finally, the white powder (m-BOT) was obtained by being dried under 80 $^{\circ}$C for 24 h.

In oreder to remove the impurity in membrane, the Nafion 212 membrane was boiled in turn for 1 h under 80 $^{\circ}$C in 5 vol. % H$_2$O$_2$ solution, deionized water, 0.5 mol·L^{-1} H$_2$SO$_4$ solution and deionized water. Different quantities of m-BOT powder was added into the mixture of tetraethyl orthosilicate (TEOS, analytical reagent, SCRB) and methanol (mass ratio 3:2), and ultrasonic dispersion was used until solid's dispersion was uniform. Nafion 212 membrane was soaked in the methanol/water solution (volume ratio 3:2) for 1 h at ambient temperature. Then the Nafion membrane was impregnated in m-BOT/TEOS/methanol solution, stirred for 6 h, and rinsed using 50 vol. % methanol/water solution to wash away the weak combining components on membrane's surface. The as-fabricated membrane was dried for 12 h under 80 $^{\circ}$C in drying vacuum oven to obtain Nafion/SiO$_2$/m-BOT composite membrane.

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2.2 SEM analysis

The Nafion/SiO$_2$/m-BOT composite membrane samples for SEM analysis were prepared by cutting the membranes into small pieces with a scissor, pasting them on the titanium plate with conductive adhesive, and sputtering the surface with carbon. The SEM images were taken using a FE-SEM device (Zeiss Supr ATM 55 microscope, German) with acceleration voltage at 5 kV.

2.3 Fourier transform infrared spectroscopy (FT-IR)

The samples of composite membranes were tested by Nicolet NEXUS-470 type Fourier Infrared Spectrometer, the scanning range of which was 4000-400 cm^{-1} with resolution at 4 cm^{-1} and KBr as tackifier. The samples were dried in the vacuum oven at 80 ^{o}C for 24 h to remove absorbed water, and then sputtered with carbon before the test.

2.4 Thermal analyses

Thermal gravimetric analysis (TGA) of membranes was performed on STA409 thermal analyzer (Netzsch, German) in nitrogen atmosphere from 25 ^{o}C to 600 ^{o}C with the heating rate of 10 ^{o}C·min^{-1}. To remove the internal water, the samples were dried in vacuum oven at 100 ^{o}C for 12 h before testing.

2.5 Proton conductivity

The proton conductivity of the membranes was measured by three-electrode system using Electrochemical Impedance Spectroscopy (EIS) method. The samples of membrane (3 cm × 2.5 cm) were sandwiched between two Teflon parts which were attached with two stainless steel foils and connected with two copper wires. The EIS was measured using VMP-2 electrochemical workstation (Bio-logic, France) with the amplitude of 200 mV in the frequency range from 10 Hz to 100 kHz. The system temperature was regulated by heating jacket while humidity was controlled by water bath. The experiments were conducted in a closed container and the saturated state of humidity was ensured. The conductivity (σ, S·cm^{-1}) of membranes was calculated using the following equation:

$$\sigma = \frac{l}{R \times A}$$

where σ, l, R and A denote the proton conductivity, the distance between the electrodes to measure the potential, the impedance and the effective cross-sectional area of membrane which equals to the product of effective length and thickness of membranes, respectively.

2.6 Methanol permeability measurements

Methanol permeability of membranes was tested with a self-designed device. The membrane was prepared as described in section 2.1 and first soaked for 1 hour in a mixed solution including 1 mol·L^{-1} methanol and 0.5 mol·L^{-1} H$_2$SO$_4$ to absorb enough water. Then the membrane was assembled between diffusion container and test container which both have a hole to ensure methanol can diffuse though membrane from one container to another. Two different solutions had been added to the containers: one was composed of 1 mol·L^{-1} methanol and 0.5 mol·L^{-1} H$_2$SO$_4$, and the other was 0.5 mol·L^{-1} H$_2$SO$_4$. After some time for methanol permeating, methanol oxidation current was gotten by chronoamperometry, and then the methanol concentration was calculated with the linear fitting equation between concentration and methanol oxidation current previously. The methanol permeability P was calculated with the following equation：

$$P = \frac{S \times V \times l}{A \times C}$$

Where S is the slope of the linear fit curve of time and penetrative methanol concentration in the test container, V is the volume of solution in the test container , C is the initial methanol concentration of methanol solution in the diffusion container, l represents for the Nafion 212 membrane's thickness, and A is effective area of membrane.

2.7. Water content

The water absorption of membrane is the ratio of absorbed water's quality to the dry membrane's quality. The membrane was first soaked in deionized water at

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different temperatures for about 8 h, and filter paper was used to absorb surface water to weigh the quality (W_1). Then, the membrane was put in vacuum drying chamber at 80 °C for 24 h and was weighed again (W_2). The moisture contained in the membrane can be calculated according to the following equation:

$$W_c = \frac{W_1 - W_2}{W_2} \times 100\%$$

Where, W_C is water absorption of membrane, W_1 is the swelling membrane's quality, and W_2 is the dry membrane's quality.

According to thermal spray methods [9], the diffusion layer was prepared as follows: XC-72 conductive carbon black (Cabot Corporation), Polytetrafluoroethylene (PTFE) solution (6 %, Shanghai), isopropanol (99.7 %, SCRB) and deionized water were firstly compounded as slurry, then were sprayed onto the carbon paper TGP-H-090 (Toray) surface after hydrophobic treatment. The anode and cathode catalyst are PtRu black (Johnson Matthey) and Pt black (Johnson Matthey), and their loadings were both 4 mg/cm^2. The catalyst, Nafion solution (5 %, Aldrich company) and isopropanol were scattered using ultrasound, and then sprayed onto a PTFE film surface by Sono-tek MEA ultrasonic spray system to form the catalyst layer. After being dried in vacuum at 80 °C (-0.1 MPa) 1 h, the prepared film with anode and cathode catalyst layer was placed on both sides of the Nafion 212 membrane (DuPont Company) after pretreating and was pressed under 0.6 ~ 0.7 MPa at 135 °C for 150 s. The MEA's active area is 5 cm^2. Finally, DMFC's multi-level activation was performed [10]. After preconditioning, initial DMFC performance curves were obtained by feeding 1.5 M methanol (2.5 ml·min^{-1}) and humidified air (520 ml·min^{-1}) to the anode and cathode. The cathode limiting current density of methanol oxidation was also tested and the scanning range was 0 ~ 1.0 V (versus NHE) with a scanning rate of 2 mV·s^{-1}, which could reflect the influence of the modification for methanol permeability [11, 12].

3. Results and discussion

Fig.1 is the surface morphology of Nafion 212 membrane and Nafion/

SiO$_2$/m-BOT membrane. In Fig.1 (a), Nafion 212 membrane presents a dense structure, and small separate areas exist in a limited area. However, in Fig.1 (b) and (d), the stacking structure whose size is 50 nm and the thickness is 5 μm was observed on the surface of membrane, which may be SiO$_2$ as hydrolysate of m-BOT in TEOS [13]. The possible mechanism of hydrolysis is as follows: when Nafion 212 membrane was dipped in m-BOT/TEOS/methanol solution, m-BOT was cross-linked with Si-O key to make them adhere to the membrane's surface and gradually concentrate as stacking structure.

The IR spectrum of bentonite before and after preprocessing is shown Fig.2. In the IR spectra of bentonite before preprocessing, the region from 3650 to 3400 cm^{-1} reflects internal water's -OH group. The stretching vibration of C=O is at 1637 cm^{-1} [14]; the stretching vibration of Si-O is at 1053 cm^{-1}; the symmetric stretching vibration of Si-O-Si is at 796 cm^{-1}; and the stretching vibration of Al-O and the bending vibration of Si-O key are at 650~400 cm^{-1} [15]. However, in IR spectra of bentonite after preprocessing, the stretching vibration absorption peak of C-H appears between 2926 cm^{-1} and 2855 cm^{-1}; the stretching vibration bands of -CH$_3$ locates between 2960 cm^{-1} and 2876 cm^{-1}; the stretching vibration of N-H appears at the 3278 cm^{-1} and the stretching vibration of -NH$_2$ locates at 3500 cm^{-1} ~ 3100 cm^{-1} [16]. The stretching vibration peak at 1385~1340 cm^{-1} stands for sulphonic groups [17] and it only appears in m-BOT, which means that there was an interaction between sulfuric acid and BOT when Na$^+$-BOT was converted to H+-BOT. The existence of the three above stretching vibrations proves the presences of dodecylamine and sulphonic groups in m-BOT composite membrane, which confirms m-BOT has been successfully synthesized.

Fig.3 is the Thermal Gravimetric Analysis (TGA) curve of Nafion 212 membrane and compsite membrane. The TGA graph of Nafion membrane can be divided into four regions: the first region is from room temperature to 280 ^{o}C, and the mass loss in this stage is about 6 wt. %, which may be caused by the evaporation of bound water [18]; the second region is from 280 ^{o}C to 370 ^{o}C [19], and the mass loss of

this stage is about 18 wt. %, when SO_2 and CO_2 are generated at this region; the third region is from 370 °C to 430 °C, the mass loss is about 25 wt. % [19], and this stage is the degradation process of sulfonic acid group, where some side chain $-SO_3H$ of Nafion is lost; the fourth transition region is above 430 °C, and the main chain C-F skeleton is decomposed in this stage [19]. The first region of composite membrane is the same as that of Nafion membrane before modified, and the mass loss is about 5 wt. % due to the evaporation of water below 280 °C [18]. Because of the thermal decomposition of the sulfonic acid group and amino group, the mass loss is about 15 wt. % from 280 °C to 390 °C in second region [19]. The third region from 390 °C to 450 °C is the thermal decomposition process of sulfonic acid group, amino group and the main chains of Nafion membrane, where some gaseous species such as SF_4, CO and CF generate gradually, and the mass loss is about 35 wt. % [19]. The fourth region above 450 °C is the thermal decomposition of the main chain of C-F and dodecylamine C-C chain. Finally, SiO_2 and silicon compounds remain as residuum [20]. The TGA figure reveals that there is a little offset for the thermal decomposition temperature platform of composite membrane compared with that of the Nafion membrane at high temperature. The mass loss of Nafion/SiO_2/m-BOT composite membrane is more serious than that of Nafion membrane from 400 °C to 500 °C, mainly because of the thermal decomposition of dodecylamine at the lamellar structure. And yet, below 400 °C, the mass loss of composite membrane is less than that of Nafion membrane.

As Fig.4 shows, while the content of m-BOT increases from 0 wt. % to 8.59 wt. %, composite membrane conductivity drops from 0.0991 S/cm to 0.0488 S/cm at 35 °C, which implies that the conduction of proton is blocked because of m-BOT [21]. Higher temperatures can promote the conduction of proton and the swell of membrane; however, m-BOT group has strong absorbent, which may decrease proton content in the membrane's channel, so the membrane's conductivity increases with temperature rising and reduces with the increase of m-BOT content in the membrane.

The methanol permeabilities of the composite membrane with different m-BOT

content are measured using the method introduced in section 2.6, and the results are shown in Fig.5. The methanol permeability of Nafion 212 membrane is 1.337×10^{-7} $cm^2 \cdot s^{-1}$, and yet, the methanol permeability of the composite membrane reaches $2.515 \times 10^{-8} cm^2 \cdot s^{-1}$, which is significantly lower than that of Nafion membrane, droping by 81.19 %. As the content of m-BOT increases, the methanol permeability of the composite membrane decreases at first, then rises. The main reason is that the m-BOT's embedded structure in membrane, which is combined with Si-O group simultaneously, makes the distance of methanol permeation increase and leads to the block of the $CH_3OH_2^+$ transfer channel [22, 23]. The methanol permeability presents an increased trend with the m-BOT content over 4.58 wt. %. Because excessive m-BOT begins to form agglomerates in the composite membrane, the hydrophobic polymer backbones will occur around the hydrophilic ion-cluster for methanol permeation, which increases the whole permeability [24].

Hygroscopic property and humectant property are two important indicators of membrane's performance. Low level of water in the membrane easily leads to the membrane's contraction, which reduces the diffusion coefficient of water and increases the steric hindrance of water's diffusion [25]. The water absorptions of Nafion/SiO$_2$/m-BOT membrane with different m-BOT contents at different temperatures were shown in Fig.6. It can be seen that membrane's water absorption is increases as the result of the rise of the m-BOT content: Nafion 212 membrane's is 11.41 wt. %, but the water absorption of the composite membrane with 8.59 wt. % m-BOT reaches 46.27 wt. %, which is 4.06 times as high as that of Nafion 212 membrane. Two factors make composite membrane have excellent hygroscopic property and humectant property: one factor is that modified bentonite's stacking structure can accommodate a large amount of water, and the -NH$_2$ group added by dodecylamine is also hydrophilic; another factor is that nano-SiO$_2$ shows high water absorption since its three-dimensional network structure has large specific surface area [26]. The excellent absorbent ability may improve the membrane's proton conductivity after composition and decrease the methanol crossover.

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  Fig.7 shows the limiting current density of cathode's methanol oxidation of Nafion 212 membrane and that of the composite membrane, and the magnitude of the current density characterizes different membrane's methanol diffusion extent [27]. It is showed that the cell under different temperatures and the different concentration methanol has different limiting current density. The limiting current density of the composite membrane is 144.9 mA·cm^{-2} (30 ^{o}C) and 285.3 mA·cm^{-2} (55 ^{o}C), and it reduces by 30.74 % and 20.40 % compared with that of Nafion 212 membrane, which is 209.2 mA·cm^{-2} (30 ^{o}C) and 358.4 mA·cm^{-2} (55 ^{o}C). The limiting current density of composite membrane increases from 285.3 mA·cm^{-2} to 513.8 mA·cm^{-2} with the increase of the methanol concentration (from 1.5 mol·L^{-1} to 6 mol·L^{-1}). The increased trend of limiting current density of composite membrane is significantly less than that of Nafion 212 membrane (from 358.4 mA·cm^{-2} to 833.8 mA·cm^{-2}), which demonstrates that the methanol permeability of composite membrane is significantly less than that of Nafion 212 membrane, especially in high concentration of methanol.

  Fig. 8 shows the polarization and power density curves of cells under different conditions. Compared with Nafion 212 membrane at different temperature, the MEA using composite membrane does not show obviously better performance at 30°C under 1.5 mol·L^{-1} in Fig. 8. The peak power densities of Nafion 212 membrane and composite membrane at 30°C are 32.75 mW·cm^{-2} and 22.37 mW·cm^{-2}. However, if operation temperature is 55 ^{o}C, the MEA using the composite membrane, whose peak power density reaches 135.17 mW·cm^{-2}, is higher than that of Nafion 212 membrane, which is 118.7 mW·cm^{-2}. Meanwhile, the open circuit potentials of the MEA using the composite membrane are 0.524 V at 30 ^{o}C and 0.595 V at 55 ^{o}C, which are higher than the MEA using Nafion 212 membrane whose open circuit potentials are 0.511 V at 30 ^{o}C and 0.587 V at 55 ^{o}C. It means that the methanol permeability of composite membrane performance is lower than that of Nafion 212 membrane [26]. The mixed potential formed by methanol crossover in the cathode reduces, which raises the cell's open circuit voltage. As a result, cell's performance is improved.

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The temperature in Fig. 9 is 55 $^\circ$C, and the methanol concentrations in anode are 1.5 mol·L^{-1}, 3 mol·L^{-1}, 4 mol·L^{-1} and 6 mol·L^{-1} respectively. The peak power densities of Nafion 212 membrane electrode increase firstly and then it decrease with the increase of methanol concentration. The peak power densities of Nafion 212 membrane are 118.70 mW·cm^{-2}, 127.86 mW·cm^{-2}, 123.12 mW·cm^{-2}, and 116.39 mW·cm^{-2} from 1.5 mol·L^{-1} to 6 mol·L^{-1}, and the peak power densities of composite membrane are 135.17 mW·cm^{-2}, 143.26 mW·cm^{-2}, 142.59 mW·cm^{-2} and 136.45 mW·cm^{-2}. The open circuit voltages of the Nafion 212 membrane and the composite membrane decrease with anode methanol concentration increasing. While the methanol concentrations increase from 1.5 mol·L^{-1} to 6 mol·L^{-1}, the open circuit voltages of Nafion 212 membrane are 0.587 V, 0.570 V, 0.550 V and 0.522 V and that of the composite membrane are 0.595 V, 0.584 V, 0.568 V and 0.538 V. Peak power density, open circuit voltage and cathode methanol limiting current density reveal that high methanol concentration at anode will result in the mixed potential and the cathode catalyst poisoning, so the cell's peak power density of Nafion 212 membrane decreases at 6 mol·L^{-1}. And yet, when methanol concentration rises up, the peak power density of composite membrane does not decease so seriously as that of Nafion 212 membrane as the result of excellent methanol resistance.

4. Conclusion

Nafion/SiO$_2$/m-BOT composite membrane was prepared with sol-gel method to improve the property of Nafion 212 membrane. Although the proton conductivity of the composite membrane slightly decreased compared with that of Nafion 212 membrane, the methanol permeability coefficient dramatically deceased which contributed to a much better cell's performance at high temperatures and high methanol concentration.

As an indicator of methanol resistance of the proton exchange membrane, the cathode methanol oxidation's limiting current density of MEA using the composite membrane was less than MEA's using Nafion 212 membrane, which contributed to higher peak power density than the cell using Nafion 212 membrane at 55 $^\circ$C.

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Besides, at high methanol concentration, the peak power density of cell using Nafion 212 membrane decreased seriously. And yet, at the same high methanol concentration, the cell's performance using composite membrane did not decline remarkably and its peak power density at high methanol concentration (4.5 mol·L^{-1}) was close to that at low methanol concentration (3 mol·L^{-1}). Moreover, the composite membrane presented excellent methanol resistance which could reduce the cathode catalyst poisoning. The outstanding performance of Nafion/SiO$_2$/m-BOT composite membrane made it one of the best choice of the low methanol permeability proton exchange membrane for DMFC.

Acknowledgements

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Figure captions

Fig.1 The SEM images of the Nafion 212 membrane (a) (b) and Nafion/SiO$_2$/m-BOT composite membrane (b) (d).

Fig.2 IR spectrum of bentonite before and after preprocessing.

Fig.3 The Thermal Gravimetric Analysis (TGA) curves of Nafion 212 membrane and Nafion/SiO$_2$/m-BOT compsite membrane.

Fig.4 The proton conductivities of composite membranes fabricated with different amounts of m-BOT.

Fig.5 The methanol permeabilities of membranes with different m-BOT contents at 25 $^{\circ}$C.

Fig.6 The water absorptions of Nafion/SiO$_2$/m-BOT membrane with different m-BOT contents at different temperatures.

Fig.7 The limiting current densities of cathode's methanol oxidation about Nafion 212 membrane and Nafion/SiO$_2$/m-BOT composite membrane.

Fig.8 The polarization and power density curves of Nafion 212 membrane and Nafion /SiO$_2$/m-BOT composite membrane with 1.5 mol·L^{-1} methanol.
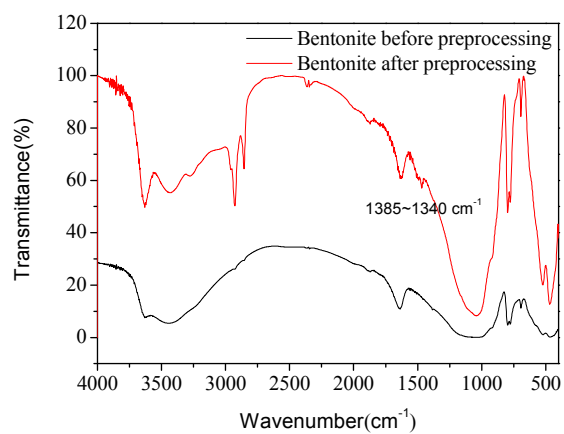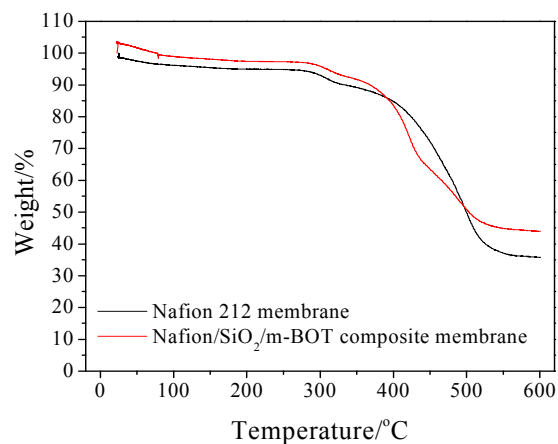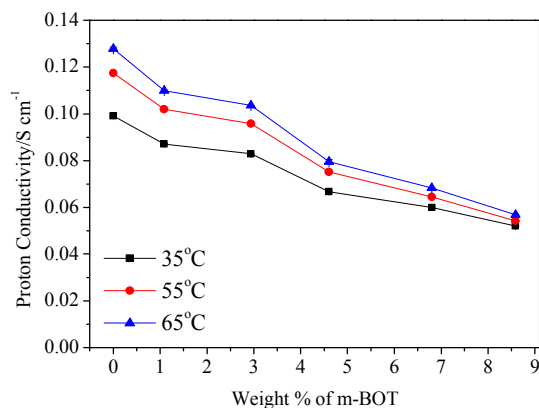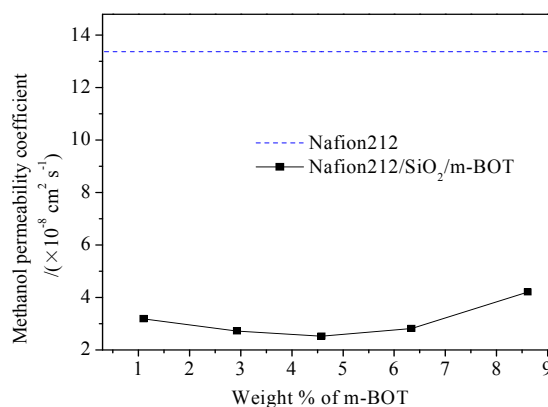
Fig.9 The peak power densities and OCVs of Nafion 212 membrane and

Nafion/SiO$_2$/m-BOT compsite membrane at 55 ^{o}C with different methanol concentrations.
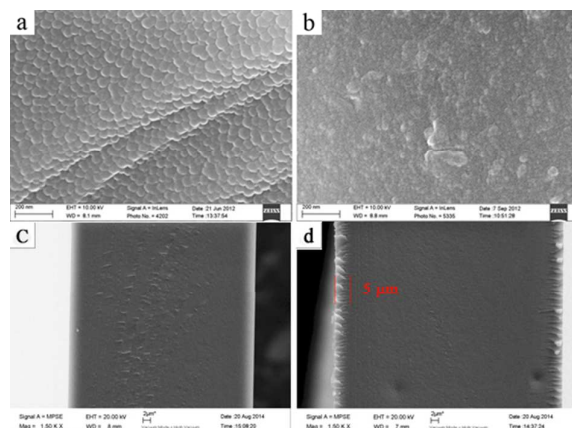
Fig.1 The SEM images of the Nafion 212 membrane (a) (c) and

Nafion/SiO$_2$/m-BOT composite membrane (b) (d).

Fig.2 IR spectrum of bentonite before and after preprocessing.
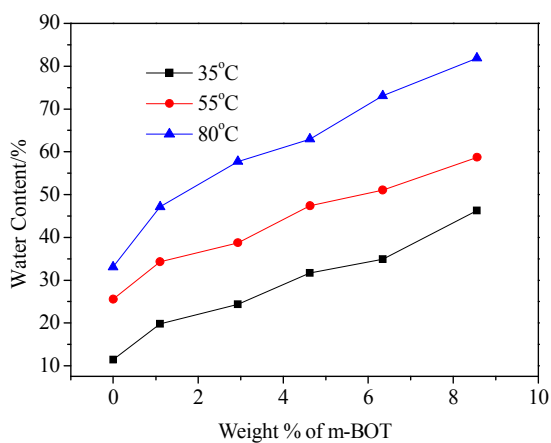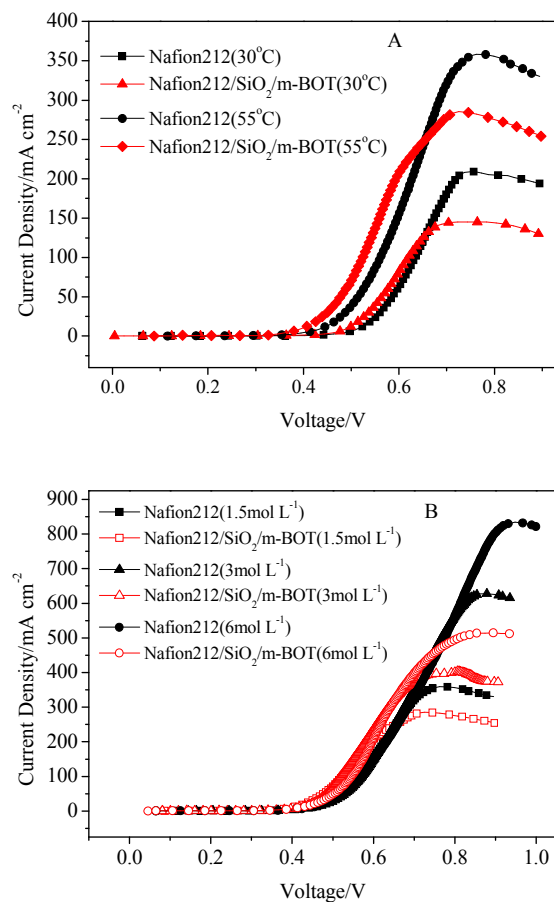

Fig.3 The Thermal Gravimetric Analysis (TGA) curves of Nafion 212 membrane and

Nafion/SiO$_2$/m-BOT compsite membrane.

Fig.4 The proton conductivities of composite membranes fabricated with different
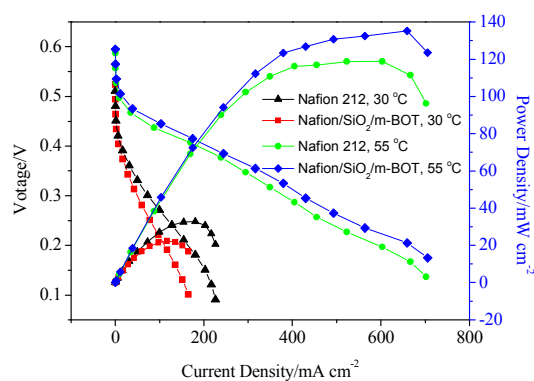
amounts of m-BOT.

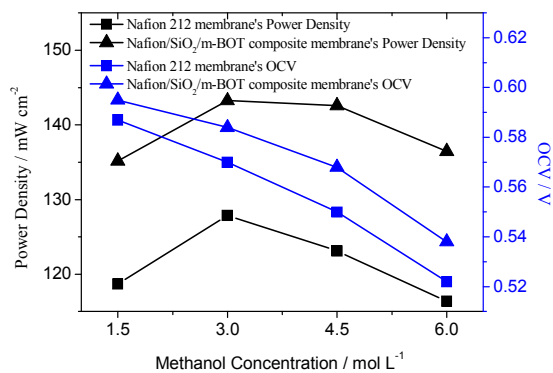**Fig.5** The methanol permeabilities of membranes with different m-BOT contents at 25

^oC

Fig.6 The water absorptions of Nafion/SiO_2/m-BOT membrane with different m-BOT

contents at different temperatures.

Fig.7 The limiting current densities of cathode's methanol oxidation about Nafion 212 membrane and Nafion/SiO$_2$/m-BOT composite membrane.

Fig.8 The polarization and power density curves of Nafion 212 membrane and Nafion /SiO$_2$/m-BOT composite membrane with 1.5 mol·L^{-1} methanol.

Fig.9 The peak power densities and OCVs of Nafion 212 membrane and Nafion/SiO$_2$/m-BOT compsite membrane at 55 ^{o}C with different methanol concentrations.