Preparation and characterization of nanocomposite membranes made of poly(2,6-dimethyl-1,4-phenylene oxide) and montmorillonite for direct methanol fuel cells

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ABSTRACT

Partially sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (sulfonated PPO) with various degrees of sulfonation were prepared. The solutions were mixed with organically modified montmorillonite (MMT) to prepare membranes by solvent casting. By increasing the sulfonation degree up to 40% for membranes without MMT, ion exchange capacity, water uptake and proton conductivity reached 2.59 mequiv. g^{-1}, 21% and 0.0182 S cm^{-1}, respectively. The Fourier transfer infrared (FTIR) analysis of sulfonated membranes revealed absorption bands at 1060 and 1100–1300 cm^{-1} for sulfur–oxygen S=O bonds. X-ray diffraction analysis showed the exfoliated structure of clay in polymeric matrices. A sulfonated PPO/MMT membrane with 27% sulfonation and 2.0 wt% MMT loading showed a membrane selectivity of approximately 63,500 compared to 40,500 for Nafion® 117, and also a higher power density (125 mW cm^{-2}) than Nafion® 117 (108 mW cm^{-2}) for single cell DMFC in a 5 M methanol feed.

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1. Introduction

Fuel cells are an attractive alternative to many energy conversion or storage devices. One particularly lucrative market is power sources for portable, stationary and automotive systems applications [1]. Unlike conventional power generation technologies, fuel cells work without combustion and its environmental side effects. Fuel cells act like continuously fueled batteries, producing direct current (DC) by using an electrochemical process. Among the various types of fuel cells, direct methanol fuel cells (DMFCs) are suitable for portable device or transportation applications due to their lower weight, high energy density at low operating temperatures, simple design, low emissions and the ease of handling their liquid fuel [2].

The proton exchange membrane (PEM) material is a key component of the DMFC for transferring protons from the anode to the cathode. They provide a barrier to methanol crossover (which leads to poisoning of the catalyst and reduction of the electrical performance and fuel efficiency) between the anode and cathode [3].

PEM properties can be optimized by high proton conduction (the number of acidic groups and the thickness of the membrane), good mechanical strength, chemical/thermal stability and low electro-osmotic drag coefficient and gas permeability [4].

Nafion®, the fluorinated membrane from DuPont, and similar membranes commercialized by Dow and Asahi have been intensively used in fuel cells as PEMs. These membranes combine mechanical strength and chemical/thermal stability with high proton conductivity, methanol permeability and a large-scale cost of production [5,6].

In recent years, there has been an intensive research effort towards the development of alternative membranes with potentially lower costs and better processability [6]. Many polymers, such as sulfonated poly(ether sulfones) [7,8], sulfonated poly(arylene ether sulfone) [9], and various other polymeric systems [9–23] have been described in the literature. However, the methanol permeability, in many cases, is still relatively high. Reduction of methanol permeability was investigated by modifying the membrane surface and the size of the proton transport channels, developing new types of polyelectrolytes and introducing tortuous pathways [24,25]. Tortuous pathways can be introduced by dispersing inorganic fillers, such as silica [26,27] heteropolyacid [28], zeolite [29], zirconium phosphate [30] and montmorillonite (MMT) [31,32] within the

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polymer. MMT is a type of layered silicate composed of silica tetrahedral and alumina octahedral sheets. The general formula of MMT is $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$, in which M and x are monovalent cations and the degree of isomorphous substitution (between 0.5 and 1.3), respectively. To render layered silicates miscible with polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one. Organically modified MMT is made by ion exchange reactions with cationic surfactants, such as alkylammonium or alkylphosphonium cations [33,34].

Non-fluorinated membranes based on the poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been presented as materials with excellent chemical/thermal stability, mechanical strength and good processability [35]. Their poor proton conductivity is improved by the sulfonation process. Sulfonation is a powerful and versatile process that can be used to simultaneously render these polymers proton conductive as well as hydrophilic in nature [36]. Like other sulfonated aromatic main-chain polymers, these sulfonated PPOs require certain acidic groups to achieve high proton conductivity. However, overly high loading of acidic groups induces excessive water swelling and methanol diffusion. Sulfonated PPO membranes have been used for gas separation and reverse osmosis due to its good permeation properties, as well as thermal and chemical stability [37–39].

In this study, to reduce methanol crossover of membrane while maintaining essential proton conductivity, we have investigated the preparation of polymer-layered silicate composite membranes composed of sulfonated PPO and multi-layered alumina-silicate (MMT).

2. Experimental

2.1. Materials

PPO ($M_w = 244,000\,\mathrm{g\,mol^{-1}}$, polydispersity index = 1.64) was supplied by Sigma–Aldrich. N,N-Dimethylacetamide (DMAc), chloroform, methanol and chlorosulfonic acid were obtained from Merck. All analytical-grade reagents from commercial sources were used without further purification. Organically treated MMT clays (trade name: Closite® 15A) were purchased from Southern Clay Products Inc., Gonzales, TX, USA. Deionized water (purified with Milipore) was used in this work. The catalysts, Platinum (Pt) black for the cathode and Pt/Ru black for the anode, were purchased from Johnson–Matthey, England. Nafion® 117 membranes, 178 μm thickness, from DuPont Co. were used to compare the data. A Nafion® 5 wt% solution from DuPont Co. was used for membrane electrode assembly (MEA).

2.2. Sulfonation process

PPO was sulfonated by chlorosulfonic acid in several steps [40,39]. In the first step, PPO was dissolved in chloroform (under vigorous stirring) at room temperature for half an hour. In the next step, PPO and colorosulfonic acid were added dropwise to the previous solution under vigorous stirring at room temperature for 20 min. The polymer was filtered and washed several times with deionized water until the pH became neutral. The sample was dried under a vacuum at 100 °C for 12 h.

2.3. Membrane preparation

Sulfonated PPO at different degrees of sulfonation was dissolved in DMAc and stirred for 24 h. MMT at various concentrations (1, 1.5, 2.0, 3.0, 5.0 and 10.0 wt%) was suspended in DMAc at room temperature, stirred for 2 h, ultra-sonicated for another hour and mixed with the polymer solution. The resultant mixture was ultra-sonicated for another 30 min, stirred at 80 °C for 8 h and concentrated in a rotary evaporator. The viscose solution was casted on a clean glass plate, dried at room temperature for one night, and at 70 °C for 8 h before the final drying at 120 °C overnight. Membranes were also prepared from non-sulfonated polymers by a similar procedure.

2.4. Membrane modification

All membranes were boiled in hydrogen peroxide (3%, v/v, for 30 min), washed several times with deionized water and boiled for 1 h in deionized water. Membranes were then boiled in sulfuric acid (0.5 M) for another hour and washed several times with deionized water.

2.5. Preparation of membrane electrode assembly (MEA)

The electrodes were prepared by catalyst decaling and painting techniques [41,42]. Pt and Pt/Ru black were used as catalysts for the anode and cathode, respectively. They were mixed with a 7 wt% Nafion® solution in isopropanol and several drops of glycerol (suspension/painting agent).

The suspension was brushed directly ($4\,\mathrm{mg\,cm^{-2}}$) onto dry membranes, and hot-pressed to increase the contact area between the catalyst layer and membranes. The obtained membranes were boiled in a dilute solution of sulfuric acid, and washed several times with distilled water.

2.6. Characterization

2.6.1. Fourier transfer infrared
The infrared spectra of the membranes were placed on KBr pellets and scanned between wave numbers of 400–4000 $\mathrm{cm^{-1}}$ in a Nicolet AVATAR370 infrared spectrophotometer.

2.6.2. Sulfonation degree and ion exchange capacity determination
The degree of sulfonation (DS) is the average number of sulfonic groups per sulfonated PPO, and the ion exchange capacity (IEC) indicates the number of milli-equivalents of ions in 1 g of the dry polymer. Degree of sulfonation and ion exchange capacity were determined by classical titration for each sulfonated polymer [43].

2.6.3. Water uptake determination
The dried membranes were soaked in deionized water at room temperature for a day, and then quickly weighed in different time intervals by carefully removing the excess water with filter paper, and immersed back in the water. This process was repeated several times until there was no further weight gain. The water uptake was calculated by

$$\text{water uptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100$$

where W_{wet} and W_{dry} are the weight of the wet and dried membranes, respectively.

2.6.4. X-ray diffraction
Dispersion of clay particles in the membranes was detected by XRD (SIEMENS XRD-D5000 diffractometer, Cu Kα). The scanning diffraction angle, 2θ, was between 2° and 10°.

2.6.5. Proton conductivity
The proton conductivity of hydrated membranes was measured at room temperature by the AC impedance method. Impedance measurements were made using a Solartron Interface 1260 gain

phase analyzer, over the frequency range of 1–10 kHz. The conductivity was calculated from the following equation:

$$\sigma = \frac{L}{RA}$$

where, L is the membrane thickness, A is the surface area of the electrodes and R is the resistance [44].

2.6.6. Methanol permeability

The methanol diffusion coefficient was measured by using homemade two compartment glass diffusion cells. Methanol solution was placed on one side of the diffusion cell (cell A) and pure water was placed on the other side (cell B). The solution in each compartment was continuously stirred to ensure uniformity. The concentration of the methanol in cell B was measured by gas chromatography. The methanol diffusion coefficient was determined as follows:

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C(t - t_0)$$

where $C_{B(t)}$ is the concentration of methanol in cell B (mol L^{-1}), DK is the methanol diffusion coefficient (cm^2 s^{-1}), C is the concentration of methanol in cell A (mol L^{-1}), V_B is the volume of diffusion reservoir (cm^3), A is the membrane area (cm^2) and L is thickness of the membrane (cm).

2.6.7. Performance tests for a single cell

The DMFC was made from four 316 stainless steel (end plates and flow fields plates), two carbon papers (gas diffusion layers, GDL, TGP-H-120 Toray) and a membrane electrode assembly. Silicon rubber was used to seal internal sections. The performance of the single cell was evaluated at two methanol concentrations (1 and 5 M) and oxygen flow rates in the anode and cathode sides at 90 °C. Methanol was fed to the anode side at 20 psi back pressure for 1 h. Oxygen was introduced at the cathode side with gradual increase to 20 psi, and the cell was allowed to run for half an hour before collecting polarization curves. All single cell tests were conducted three times, and the presented results are the average data.

3. Results and discussion

FTIR spectras of the non-sulfonated and the sulfonated PPO samples with 27% degree of substitution are shown in Fig. 1. The reaction between benzene rings in PPO and sulfuric acid molecules occurs through electrophilic aromatic substitution. The sulfonation process produces benzenesulfonic acid and water. The broad band in the sulfonated PPO samples at around 3500 cm^{-1} is
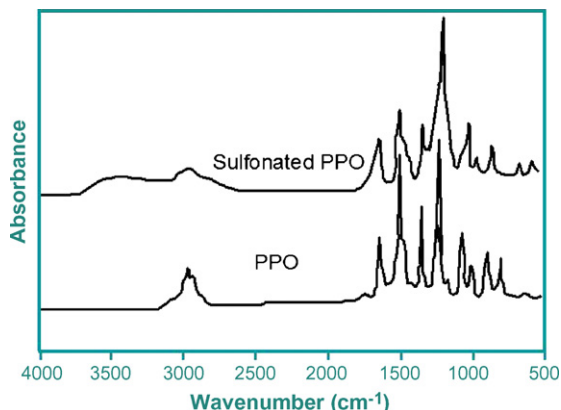

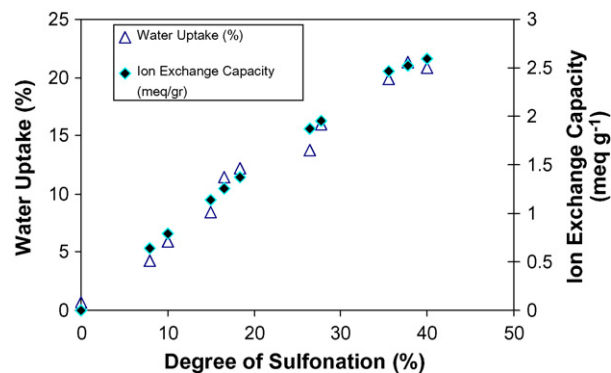**Fig. 1.** FTIR spectra of PPO and sulfonated PPO.

Fig. 2. Water uptake and ion exchange capacity of membranes as a function of sulfonation degree.

assigned to O–H vibration from water molecules. Absorption bands at 1060 and 1100–1300 cm^{-1} (broad peak) in sulfonated PPO indicate sulfur–oxygen S=O bonds.

Fig. 2 shows the equilibrium sorption percentage of water and ion exchange capacity for PPO as a function of sulfonation degree. As seen, by increasing the sulfonation degree up to 40%, water uptake was increased to more than 20%. Water resides in the hydrophilic domains and facilitates transport of protons; however, too much water absorption results in the loss of mechanical stability [45]. Sulfonation of PPO samples opens up the hard to reach area of crystalline parts and thus accommodates more H$_2$O molecules. Water sorption depends on the extent of sulfonation, and higher degree of substitution stimulates more water uptake. For a degree of sulfonation of more than 40%, the sulfonated PPO membrane becomes soluble in water during the washing process. The ion exchange capacity provides an indication of the acid groups present in a polymer matrix. Fig. 2 indicates that the ion exchange capacity was increased to more than 2.5 mequiv. g^{-1} at a 40% sulfonation degree. The high ionic conductivity at elevated sulfonation level suggests that the water in the ionic domains of the membrane's pores is interconnected to form a network structure. The lower proton conductivity observed in membranes with lower degree of sulfonation may relate to the diffusion limitation caused by segregation in the ionic domains. When the degree of sulfonation increased to a sufficient level, the ionic domains became more interconnected and simultaneously overcame the diffusion limitations and allowed the ionic conductivity to reach a maximum value. Fig. 3 shows the effect of degree of sulfonation on the proton conductivity and methanol permeability of sulfonated PPO membranes. For identification of the optimum degree of sulfonation, membrane selectivity parameters are calculated and illustrated in Fig. 4. This parameter illustrates the ratio of proton conductivity to methanol permeability of the sul-
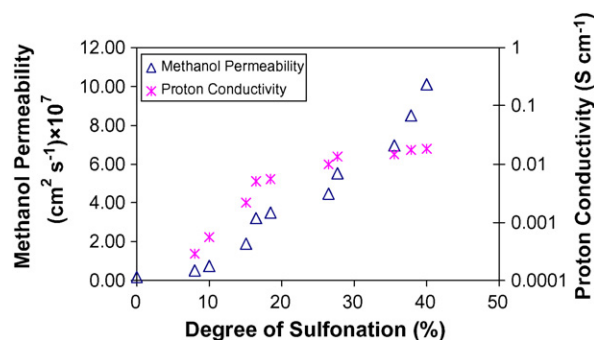

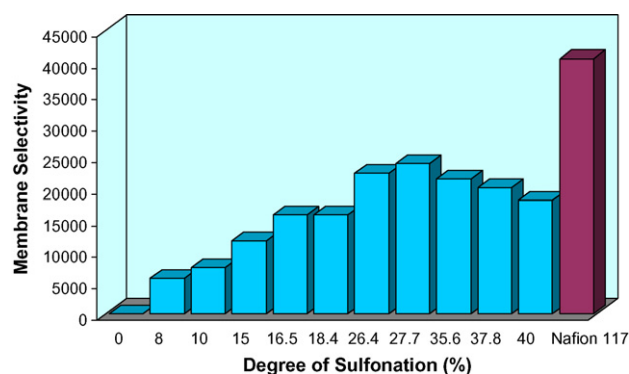**Fig. 3.** Water uptake and proton conductivity of membranes as a function of sulfonation degree.

Fig. 4. Membrane selectivity of sulfonated PPO as a function of sulfonation degree.

Fig. 6. Effect of particles loading weights on the proton conductivity and methanol permeability of sulfonated PPO membranes (27% degree of sulfonation).

fonated PPO membranes at various degrees of sulfonation. Based on these results, sulfonated PPO at 27% sulfonation with approximately 0.009 S cm^{-1} proton conductivity and 5.50 × 10^{-7} cm^2 s^{-1} methanol permeability was selected as the optimum degree of sulfonation because of good membrane selectivity, processability and dimensional stability in aqueous environments.

XRD was used to identify the microstructure of sulfonated PPO/MMT composite membranes. Fig. 5 illustrates the XRD patterns of the MMT, sulfonated PPO and sulfonated PPO/MMT composites. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (intercalated or exfoliated) may be identified. The intercalation of the polymer chains usually increases the interlayer spacing of MMT. In an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers [46,47].

As seen, MMT shows one crystalline peak at around 3 degrees. However, when MMT mixes with sulfonated PPO the crystalline peak almost disappears. In other words, MMT particles obtained from crystalline parts of the original material diffused inside the sulfonated PPO polymer chains and produced exfoliated composite membranes.

Fig. 6 shows the effect of MMT particle's loading on the proton conductivity and methanol permeability of membranes. As seen, the proton conductivity and methanol permeability of the membranes were around 0.0009 S cm^{-1} and 4.5 × 10^{-8} cm^2 s^{-1} for 10%

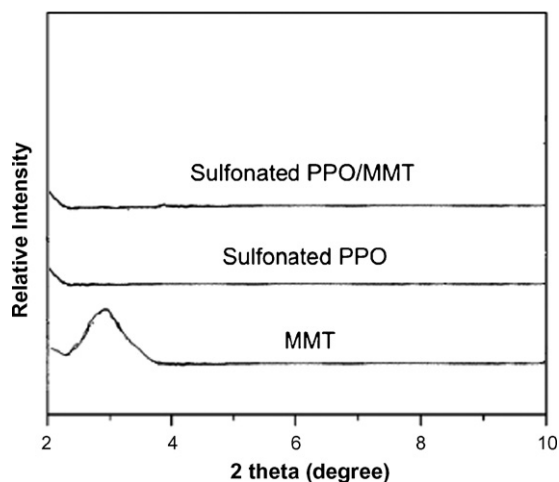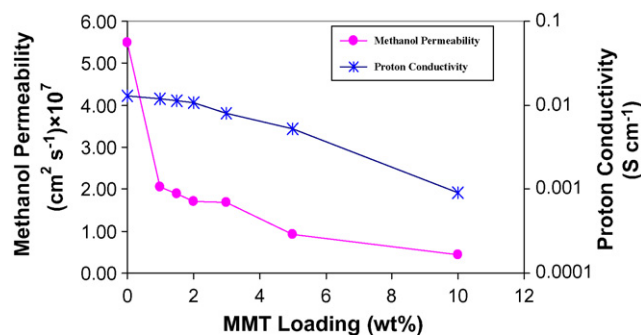MMT and about 0.0108 S cm^{-1} and 1.7 × 10^{-7} cm^2 s^{-1} for 2% MMT, respectively. The presence of impermeable MMT sheets introduces a tortuous pathway for a diffusing penetrant. The reduction of permeability arises from the longer diffusive path in the presence of filler. The hydrophobic nature of organically treated MMT particles leads to a decrease in the proton conductivity. Thus, methanol crossover is decreased.

Proton conductivity and methanol permeability are the two transport properties that determine DMFC performance. The presence of MMT has a beneficial influence on methanol permeability and the opposite effect on proton conductivity. For identification of optimum composition, the parameter of membrane selectivity of the sulfonated PPO and their MMT composite membranes at various MMT loadings is calculated and shown in Fig. 7. The higher selectivity value leads to a better membrane performance. The maximum selectivity of about 63,500 appears at 2.0 wt% of MMT loading. This selectivity parameter for the Nafion® 117 is about 40,500. We can conclude from the selectivity and proton conductivity values that the MMT composite sulfonated PPO membrane with 27% sulfonation and 2.0 wt% of MMT loading is approximately 1.6 times greater than that of Nafion® 117. Comparisons of proton conductivity, methanol permeability and membrane selectivity for various DMFC membranes are shown in Table 1. This table indicates the highest value of selectivity for sulfonated PPO (27% sulfonation) plus 2% MMT in comparison to the other ones.

The single cell DMFC performance or the plots of cell potential (polarization curves) and power density versus current density for the manufactured DMFC using two different methanol concentra-
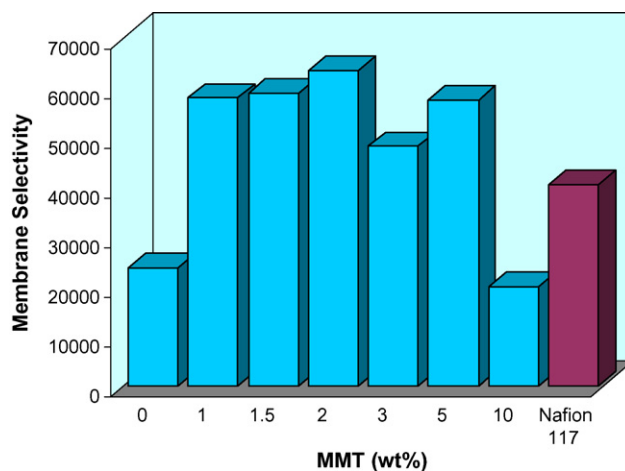

Fig. 5. The XRD pattern of MMT, sulfonated PPO and sulfonated PPO/MMT MMT composite.

Fig. 7. Membrane selectivity at different MMT loading weight for samples with 27% degree of sulfonation.

Table 1
Comparison of parameters for various DMFC membranes

Proton exchange membrane	Proton conductivity[a,b] $(S\,cm^{-1})$	Methanol permeability[b] $(cm^2\,s^{-1})\,(\times10^6)$	Membrane selectivity	Reference
Sulfonated PPO (27% of sulfonation)	0.0131	0.55	23,400	Current research
Sulfonated PPO (27% of sulfonation) + 2% MMT	0.0108	0.17	63,500	Current research
Nafion® 117	0.081	2.00	40,500	Current research
Nafion® + 5% SiO$_2$	0.270[c]	4.17	48,000	[25,48]
Nafion® + 5% MMT	0.092	1.63	56,500	[49]
Sulfonated polystyrene and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) blend	0.034	2.35	14,500	[40]
Crosslinked poly(vinyl alcohol)/poly(acrylic acid)/silica hybrid	0.012	0.21	57,200	[50]
Crosslinked poly(vinyl alcohol) using sulfosuccinic acid	0.015	0.33	45,500	[22]
Tetra-fluoroethylene with poly(styrene sulfonic acid) (Pall Gelman Sciences)				[25,51,52]
Pall R1010 (36 μm)	0.08	6	13,350	
Pall R4010 (63 μm)	0.072	4.2	17,500	

[a] Along the plane of the membrane.
[b] Measured at room temperature.
[c] Conductivity measured at 20 °C.

tions (1 and 5 M) at 70 °C is shown in Fig. 8. The current densities for the sulfonated PPO/MMT membrane (at 27% sulfonation and 2.0 wt% MMT loading) and Nafion® 117, were 280 and 351 mA cm^{-2} (at a potential of 0.2 V and 1 M methanol concentration) and 601 and 420 mA cm^{-2} (at a 0.2 V potential and 5 M methanol concentration), respectively. The power densities for the sulfonated PPO/MMT membrane (at 27% sulfonation and 2.0 wt% MMT loading) and Nafion® 117 were 90 and 77 mW cm^{-2} (at potential of 0.2 V and 1 M methanol concentration) and 108 and 125 mW cm^{-2} (at 0.2 V potential and 5 M methanol concentration), respectively.
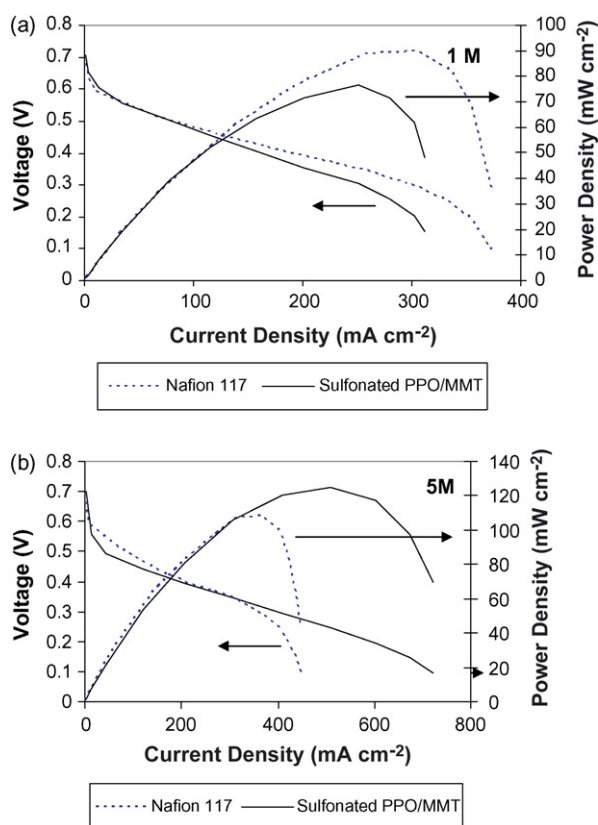

Fig. 8. Polarization curves of DMFC single cells consisted of sulfonated PPO/MMT membrane and Nafion® 117. The single cell test was performed using: (a) 1 M methanol solution and (b) 5 M methanol solution for the anode and oxygen for the cathode at 70 °C.

The open circuit voltages (OCV) of a DMFC for sulfonated PPO/MMT and Nafion® 117 were 0.71 and 0.69 (for 1 M methanol), and 0.7 and 0.66 (for 5 M methanol), respectively. OCV is closely related to the methanol crossover. This shows that the higher the OCV, the lower the methanol crossover, for the sulfonated PPO/MMT membrane with a 5 M methanol feed compared to a nearly identical OCV at 1 M methanol concentration. The electro-osmotic contribution becomes more important when the electric current increases, and it depends on the methanol concentration of the feed solution. The higher OCV clearly indicates that MMT impregnated into sulfonated PPO membrane truly decreases the rate of methanol crossover. The higher power density, at high methanol concentration, indicates a better performance of sulfonated PPO/MMT than commercial Nafion® 117. Therefore, according to the results for a single cell, the performance of the DMFC was improved.

4. Conclusion

In this study, we first prepared sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (sulfonated PPO) with different degrees of sulfonation. Afterwards, the optimum degree of sulfonation was determined according to transport properties and processability of the membranes. Then, particles of organically treated MMT were introduced into sulfonated PPO solutions. The MMT composite membranes were formed by solution casting. The composite membranes showed good proton conductivity (up to 1.08×10^{-2} S cm^{-1}), low methanol permeability (down to 1.7×10^{-7} cm^2 s^{-1}) and good processability. The membrane selectivity of the sulfonated PPO/MMT composite was comparable to the Nafion® 117 membrane when the MMT loading was less than 10 wt%. MMT composite membranes with 2 wt% of MMT showed a high selectivity and power density at a concentrated 5 M methanol feed. The composite membranes are easy to prepare and much less expensive than the commercial per-fluorinated membranes such as Nafion®. Due to their high proton conductivity, low methanol permeability and high power density, sulfonated PPO/MMT composite membranes have good potential to be used as membranes of DMFCs.

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