Methanol permeability and proton conductivity of Nafion membranes modified electrochemically with polyaniline

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ABSTRACT

Nafion membrane was modified with polyaniline by electrochemical methods, including constant current, constant potential and potential cycling. The methanol permeability and the proton conductivity of the Nafion membranes with and without modification were determined by the electrochemical oxidation of the permeated methanol and electrochemical impedance spectroscopy, respectively. It is found from FTIR results that the polyaniline formed by electrochemical method is in emeraldine state. With the modification of polyaniline, the methanol permeability of the Nafion membrane is reduced by one decade but there is only a slight decrease in proton conductivity. The power density output of direct methanol fuel cell using polyaniline-modified Nafion membrane is 40% larger than that using pure Nafion membrane. The modification with polyaniline is better than that with polypyrrole. The methanol permeability of the polyaniline-modified Nafion is about half of that of the polypyrrole-modified Nafion but the proton conductivity of the former is higher than the later.

1. Introduction

Direct methanol fuel cell is regarded as one of the most promising energy technologies in the 21st century [1]. Nevertheless, in order to compete with proton-exchange membrane fuel cell with hydrogen as fuel, direct methanol fuel cell has to overcome some drawbacks, including lower anode electrocatalytic activity and high methanol crossover through membrane [2]. Methanol crossover results in the decrease in fuel cell voltage and efficiency due to the oxidation of methanol at the cathode. Up to now, the Nafion membrane has been shown the best membrane as electrolyte for direct methanol fuel cell in chemical stability and proton conductivity. However, the use of Nafion membrane is associated with a high rate methanol permeation [3].

Much effect has been made to reduce methanol crossover in the membranes. Many researchers focused their work on the development of new membranes, including modification of Nafion membrane with organic and/or inorganic compounds and development of non-Nafion membranes [4–14]. However, the improvement in lowering methanol penetrability of the new membranes always leads to the decrease in the proton conductivity of the membranes.

Recently, conductive polymers, polyaniline and polypyrrole, were introduced into Nafion to suppress the methanol permeability [15–17], The membrane obtained by the electropolymerization of aniline at Nafion-coated Pt electrode has lower ionic conductivity and lower methanol permeability compared with Nafion membrane [15]. Sungpet developed an impure Nafion membrane with polypyrrole [16]. The membrane was immersed in pyrrole solution for 18.5 h, then hydrogen peroxide was added to the solution. The polymerization reaction proceeded for 48 h at room temperature. The presence of polypyrrole in Nafion membrane resulted in the decrease of the percentage of sorption capacity of methanol from 38 to $19 \, \mathrm{g \, g^{-1}}$ and the decrease of the methanol flux to the one third of that of Nafion. Smit et al. developed a modified Nafion membrane with in situ polymerized polypyrrole [17]. They showed that the polypyrrole could also reduce the methanol permeability. This surface modification of Nafion membrane with conductive polymer seems much simpler than the reconstruction of Nafion membrane to reduce the methanol permeability.

Polyaniline is a good conductive polymer. It was shown that polyaniline could improve not only the activity of catalyst toward methanol oxidation but also the stability of the catalyst [18,19]. In this paper, a Nafion membrane was modified with polyaniline electrochemically and the effect of preparation conditions on the methanol permeability and ionic conductivity of the membranes were considered. The results show that a decade decreases in methanol permeability of Nafion membrane can be

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reached by the polyaniline modification at the cost of a small decrease in ionic conductivity.

2. Experimental

2.1. Pretreatment of Nafion membrane

Nafion117 membrane (Dupont) was cut into 2.5 cm × 3 cm and treated by boiling in 3% hydrogen peroxide for 45 min, rinsed in distilled water, treated by boiling in 1 M sulfuric acid for 45 min, and finally rinsed with and immersed in deionized water for use.

2.2. Surface modification of Nafion117 membrane with polyaniline

The cleaned membranes were dried to a constant weight at 100 °C and then immersed in 0.5 M H_2SO_4 solution with 0.1 M aniline monomer for 30 s. The membranes were removed from this solution and placed as electrolyte in an electrochemical cell with two stainless steel sheets (2 cm × 2 cm) as the electrodes, then were modified with polyaniline under different conditions. The preparation conditions and the weight of polyaniline per square of the Nafion membrane are listed in Table 1. Samples modified with polyaniline under constant currents were obtained by electrolyzing with a current of 0.4 mA cm^{-2} for 5, 10 and 20 min, denoted as PA01, PA02 and PA03, respectively. Samples modified with polyaniline under constant potential were obtained at 1.6 V for 5, 10 and 20 min, denoted as PA04, PA05 and PA06, respectively. Samples modified with potential cycling were obtained by cycling at 50 mV s^{-1} for one, two and five cycles between 1.2 and 2.4 V, denoted as PA07, PA08 and PA09, respectively. For a comparison, samples modified with polypyrrole were obtained with a constant current of 0.4 mA cm^{-2} for 5, 10 and 20 min, denoted as PY01, PY02 and PY03, respectively.

The modified samples were immersed in 1 M H_2SO_4 solution to remove residual aniline, cleaned with deionized water, dried at 130 °C for 5 min, and kept in a desiccator for performance determination.

2.3. Methanol permeability determination

Methanol permeability of membranes was determined in a two-compartment cell by cyclic voltammetry, as shown in Fig. 1. The cell was setup with two compartments of 4 cm × 4 cm × 4 cm, each has an open of 2 cm × 2 cm in the center of the counter side. The sample membrane was fixed in between the two compartments. The left compartment was filled with 0.5 M H_2SO_4 solution and the right compartment was filled with 0.5 M H_2SO_4 + 1 M CH_3OH solution. A three-electrode cell was established by placing the working electrode (hole 1) and the reference electrode (hole 2) in the left compartment and placing the auxiliary electrode (hole 5) in the
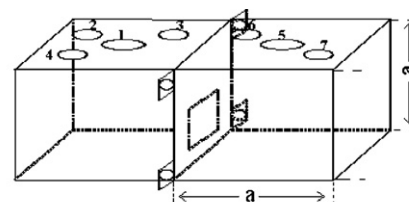
1. the working electrode 2. the reference electrode
4 and 7. the exit for the N2 3 and 6. the entrance for N2
5. the auxiliary electrode a = 4 cm

Fig. 1. Cell for the determination of methanol permeability through membranes, with 0.5 M H_2SO_4 and 1 M CH_3OH + 0.5 M H_2SO_4 in left and right compartment, respectively.

right compartment. A platinum disc electrode with an area of 0.1963 cm^2 was used as the working electrode, the Hg/Hg_2SO_4 electrode as the reference electrode and a platinum foil as the auxiliary electrode. During the experiment, the solutions in two compartments were bubbled with nitrogen through the entrance of holes 3 and 6 and the exits of holes 4 and 7. The potentials in this paper are with respect to Hg/Hg_2SO_4 electrode. Cyclic voltammetry was performed every half an hour with a scan rate of 50 mV s^{-1} from −0.6 to 0.5 V.

2.4. Proton conductivity determination

The proton conductivity of membranes was determined by electrochemical impedance spectroscopy. Membranes were immersed to be saturated with water in distilled water for 24 h before the measurement. The membrane was cut into 0.7 cm × 0.7 cm and sandwiched with two gold plates that have the same surface area with that of the membrane to setup a cell for the measurement of electrochemical impedance spectroscopy. In the measurement of ac impedance spectroscopy, the cell was sealed in a plastic bag with deionized water in it to maintain the humidity. The frequency of the AC singer was from 10 mHz to 1 MHz and its potential magnitude was 5 mV. The obtained impedance spectra are linear relation between real part and imaginary part of the impedance. The resistance of the measured membrane was obtained by the intercept of the linear line with the real axis.

A PGSTAT-30 (Autolab) was used for electrochemical measurement. The thickness of membranes was measured with an instrument (No. 7301, Mututoyo). The Fourier transform infrared spectra of membranes were obtained with a PerkinElmer1730 (PE). All the experiments were carried out under room temperature.

2.5. Fuel cell performance determination

A single fuel cell was setup to compare the performances of the cells using pure Nafion and polyaniline-modified Nafion mem-

Table 1
Conditions for the modification of Nafion 117 with polyaniline

| Samples	Methods	Conditions	Content of polyaniline on Nafion (mg cm^{-2})
PA01	Constant current	0.4 mA cm^{-2} for 5 min	1.10
PA02	Constant current	0.4 mA cm^{-2} for 10 min	1.90
PA03	Constant current	0.4 mA cm^{-2} for 20 min	4.25
PA04	Constant potential	1.6 V for 5 min	1.40
PA05	Constant potential	1.6 V for 10 min	3.00
PA06	Constant potential	1.6 V for 20 min	4.90
PA07	Potential cycling	Between 1.2 and 2.4 V for one cycle	0.43
PA08	Potential cycling	Between 1.2 and 2.4 V for two cycles	0.5
PA09	Potential cycling	Between 1.2 and 2.4 V for five cycles	0.53
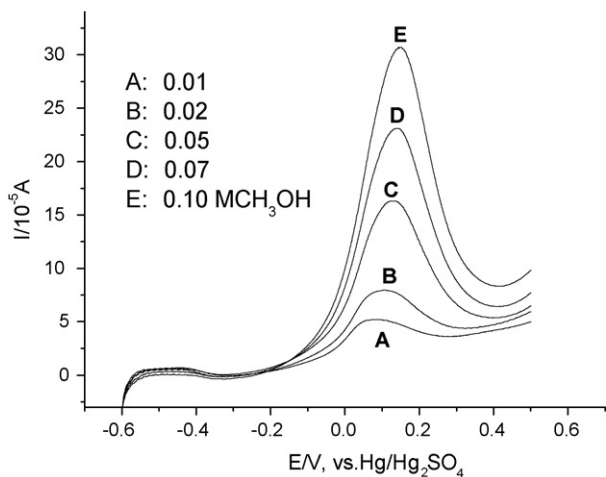
Fig. 2. Current responses of platinum electrode in 0.5 M H$_2$SO$_4$ solutions with different concentrations of methanol, scan rate: 50 mV s^{-1}.

branes. Membrane electrode assembles were prepared as reference [20]. Pt–Ru (1:1 in atom, Johnson Mattheys Company) was used as anodic catalyst with a load of 5 mg cm^{-2} and Pt (Johnson Mattheys Company) was used as cathodic catalyst with a load of 4 mg cm^{-2}. The effective area of the membrane electrode assembles was 4 cm^2. Anodic electrolyte was 2 M CH$_3$OH aqueous solution at a flow rate of 1 ml min^{-1} and pure oxygen was used as cathodic reactant with a flow rate of 5 ml s^{-1}. The relations of voltage and power with current were obtained using constant resistance discharge at 35 °C.

3. Results and discussion

3.1. Permeability of methanol and conductivity of proton through Nafion117

To obtain the relation of methanol concentration with electrochemical response, cyclic voltammograms were recorded for the Pt electrode in 0.5 M H$_2$SO$_4$ solutions with methanol concentrations from 0.01 to 0.1 M. Fig. 2 shows the current responses at fifth cycle from −0.5 to 0.6 V for each methanol concentration. It can be seen that the oxidation of methanol takes place at about −0.2 V, and the oxidation current reaches the maximum at about 0.1 V and forms a peak as the potential is scanned. The peak current increases with the increase of the methanol concentration and this relation is linear, as shown in Fig. 3. The linear relationship of peak current (I_p
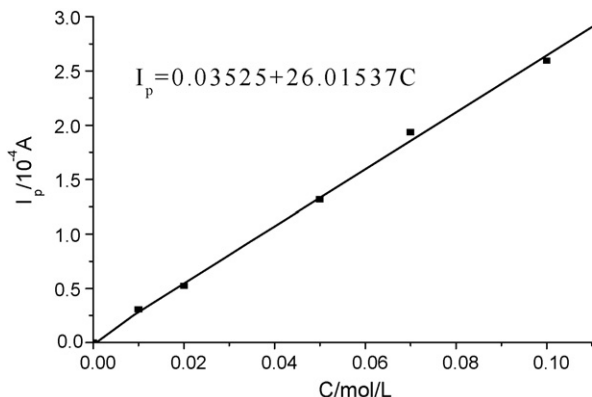
(A)) with methanol concentration (C (M)) obtained by fitting is

$$I_p = 0.0325 \times 10^{-4} + 26.01537 \times 10^{-4}C \tag{1}$$

Therefore, based on the peak current for platinum in the methanol-containing solution, it is easy to determine the methanol concentration in the solution.

Fig. 4 shows the current responses of platinum electrode in the left compartment of Fig. 1 at different times when Nafion 117 is used. This compartment is methanol free at the beginning and methanol can be detected with increasing time due to the permeating of methanol through membrane from the right compartment. It can be seen from Fig. 4 that the peak current of methanol oxidation increases with increasing time, indicating that the permeated methanol concentration increases. The permeated methanol concentration can be obtained by the relation of methanol concentration with peak current of methanol oxidation in Eq. (1). The relation of the permeated methanol concentration with time is shown in Fig. 5. The permeated methanol concentration (C (M)) is related linearly to time (T (s)):

$$C = 5.9 \times 10^{-3} + 9.3611 \times 10^{-6}T \tag{2}$$

The permeability of methanol through the membrane can be expressed with diffusion coefficient (D (cm^2 s^{-1})), which follows approximately the equation [21]:

$$\frac{D\,\Delta C}{\Delta X} = \frac{kV}{A} \tag{3}$$

where ΔC is the difference of methanol concentration between two compartments at the beginning (M), ΔX the thickness of the mem-
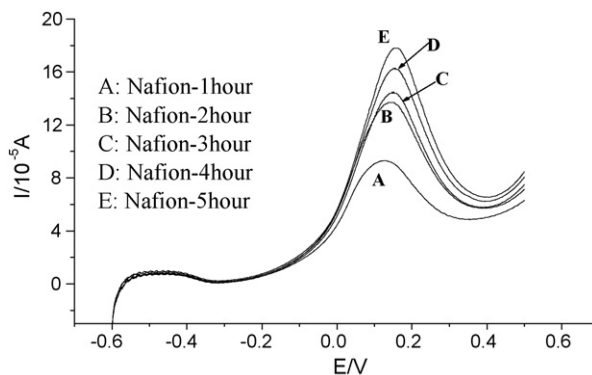

Fig. 4. Current responses of platinum electrode in the left compartment of Fig. 1 at different times when Nafion 117 is used, scan rate: 50 mV s^{-1}.

Fig. 3. The relation of peak current of methanol oxidation on platinum electrode with methanol concentration in 0.5 M H$_2$SO$_4$ solution.
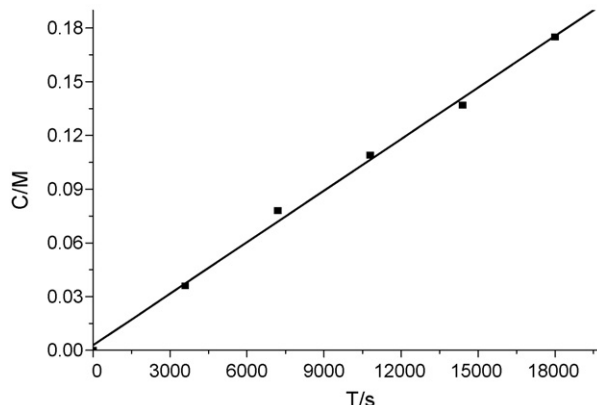

Fig. 5. The variation of methanol concentration in the left compartment of Fig. 1 with time when Nafion 117 is used.
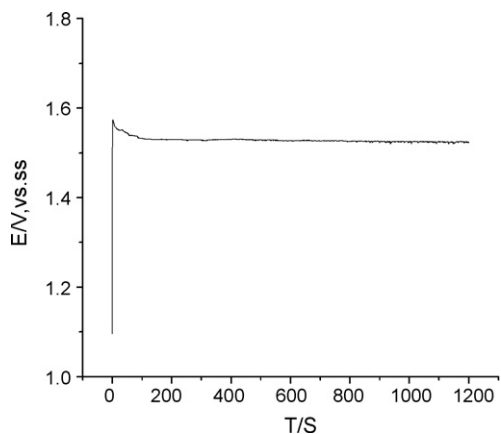
Fig. 6. Potential response for the formation of polyaniline on Nafion 117 saturated with 0.5 M H_2SO_4 + 0.1 M aniline at 0.4 mA cm^{-2}.

brane (cm), k the slope of the linear line of Fig. 5 (M s^{-1}), V the volume of solution of the compartment (cm^3), and A is the membrane area (cm^2). With the results of Fig. 5 and the calculation of Eq. (3), the permeability of methanol through Nafion 117 in 0.5 M H_2SO_4 solution can be obtained, it is 1.092×10^{-6} cm^2 s^{-1}.

The conductivity (K) of proton in Nafion can be obtained by

$$K = \frac{\Delta X}{AR} \tag{4}$$

where ΔX is the thickness of the Nafion membrane, R the resistance obtained from electrochemical impedance spectrum and A is the area of the Nafion. The obtained conductivity of Nafion 117 is 2.301×10^{-2} S cm^{-1}. The membrane is wet, thus its conductivity is larger than the dry Nafion 117, which is usually in the order of 10^{-3} S cm^{-1} [14].

3.2. Modification of Nafion with polyaniline

Fig. 6 shows the potential responses for the polyaniline modification on Nafion with a constant current density of 0.4 mA cm^{-2}. It can be seen that the potential hardly changes with time, indicating that the reaction for the formation of polyaniline proceeds incessantly and no other reaction takes place.

Fig. 7 shows the FTIR spectra of Nafion and the Nafion modified with polyaniline. The peaks at 1200, 1147, 1056, 981, and 969 cm^{-1} are ascribed to Nafion [22], as shown by the curve A of Fig. 7. Besides these peaks, the modified Nafion shows its FTIR peaks at 3236,
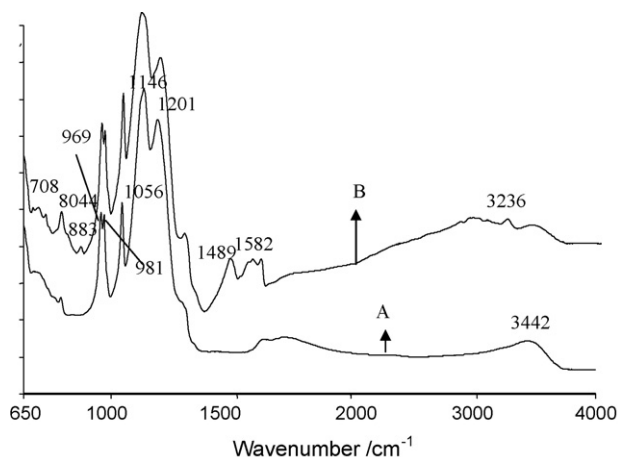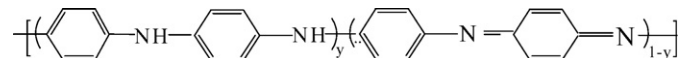
1582, 1489, 1304, 708, 804, and 883 cm^{-1}, as shown by the curve B of Fig. 7. Polyaniline have three kinds of structures and can be expressed by

The polyaniline is in a completely reductive state corresponding to leucoemeraldine (LM) when $y = 1$, in a completely oxidative state corresponding to pernigranline (PG) when $y = 0$, and in middle oxidation state corresponding to emeraldine (EM) when $y = 0.5$. Only EM is conductive electronically. The peaks at 1582 cm^{-1} is ascribed to the stretching vibration of N=B=N, 1489 cm^{-1} to C=C, 1304 cm^{-1} to C–N, and peaks at 708, 804 and 883 cm^{-1} to the C–H [23]. Thus, the polyaniline on Nafion belongs to EM and is conductive.

3.3. Effect of modification on methanol permeability and proton conductivity

To get the Nafion membrane modified with different amounts of polyaniline, samples, PA01, PA02 and PA03, were prepared by electrolyzing with a constant current of 0.4 mA cm^{-2} for 5, 10 and 20 min. The samples contain polyaniline, in electric quantity per square centimeter, 0.12, 0.24 and 0.48 C cm^{-2}, respectively. Their methanol permeability and proton conductivity were determined by the methods developed in Section 3.1. Table 2 shows the obtained results. The permeability of methanol in pure Nafion 117 membrane was far higher, with a value of 1.09×10^{-6} cm^2 s^{-1}, than that of polyaniline-modified Nafion 117 (1.78×10^{-7} to 2.41×10^{-7} cm^2 s^{-1}). This indicates that the methanol permeability of Nafion can be reduced significantly by the polyaniline modification. This reduction is better than or as good as the reductions by other methods reported in the literatures. For example, the permeability of methanol in Pd-impregnated membrane is 4.3×10^{-7} cm^2 s^{-1} [14]. On the other hand, proton conductivity of the membranes has less changed due to the polyaniline modification. This suggests that polyaniline-modified membrane allows selective permeability to the water molecules or hydrogen ions.

It can be seen from Table 2 that there is a decrease of one decade in the methanol permeability for the Nafion modified with polyaniline. The proton conductivity of the Nafion also decreases due to the modification but its decrease is minor compared with the large increase in methanol permeability. The methanol permeability and the proton conductivity of the Nafion membranes are affected by the amount of polyaniline. Among three samples, the sample PA02 shows its lowest methanol permeability. The modification of Nafion with polyaniline blocks the channel for methanol permeability and the modification with increasing the amount of polyaniline results in the decrease of the permeability to a greater extent. As the polyaniline on Nafion increases further, the methanol permeability increases further again. This might be caused by the poorer cohesion of polyaniline onto the Nafion due to the increase of deposited polyaniline. In fact, polyaniline separated from the Nafion can been observed when the time for the modification under constant current lasts too long. It seems that the proton conductivity

Fig. 7. FTIR spectra of Nafion (A) and Nafion modified with polyaniline (B).

Table 2
Comparison of methanol permeability (D) and proton conductivity (K) of polyaniline-modified Nafion under constant current

Samples	D (cm^2 s^{-1})	K (S cm^{-1})	K/D (s S cm^{-3})
Nafion	1.09×10^{-6}	2.30×10^{-2}	2.11×10^4
PA01	1.78×10^{-7}	1.74×10^{-2}	9.74×10^4
PA02	1.06×10^{-7}	1.79×10^{-2}	1.69×10^5
PA03	2.41×10^{-7}	1.62×10^{-2}	6.73×10^4

Table 3

Comparison of methanol permeability (D) and proton conductivity (K) of polyaniline-modified Nafion under constant potential

Sample	D ($cm^2 \, s^{-1}$)	K ($S \, cm^{-1}$)	K/D ($s \, S \, cm^{-3}$)
Nafion	1.09×10^{-6}	2.30×10^{-2}	2.11×10^{4}
PA04	1.69×10^{-7}	1.70×10^{-2}	1.01×10^{5}
PA05	1.60×10^{-7}	1.37×10^{-2}	8.57×10^{4}
PA06	7.20×10^{-8}	1.26×10^{-2}	1.75×10^{5}

hardly depends on the amount of polyaniline for the modification under constant current.

Samples, PA04, PA05 and PA06, were prepared under constant potential for different times. The methanol permeability and proton conductivity of these samples are shown in Table 3. It can be seen from Table 3 that the modification of Nafion under constant potential is similar to that under constant current: about a decrease of one decade in methanol permeability. Different from the modification under constant current, the proton conductivity of the Nafion modified under constant potential depends to a greater extent on the amount of polyaniline, decreasing with increasing amount of polyaniline. This might be ascribed to the more uniform modification of polyaniline under constant potential than under constant current.

Samples, PA07, PA08 and PA09, were prepared with potential cycling at a scan rate of $50 \, mV \, s^{-1}$ for one, two and five cycles. The methanol permeability and proton conductivity of these samples are shown in Table 4. It can be seen from Table 4 that the modification of Nafion with potential cycling is similar to those under constant current and constant potential, resulting in about a decrease of one decade in methanol permeability. It is noted that the methanol permeability and the proton conductivity of the membranes is hardly affected by cyclic number.

Apparently, the reduction of methanol permeability due to the modification is always accompanied by the decrease in proton conductivity. It is expected that larger reduction of methanol permeability is reached at the cost of small decrease in proton conductivity for a modification. Thus, the ratio of proton conductivity to methanol permeability (K/D) can be used to compare different modifications. The calculated results are shown in the Tables. It can be seen that samples PA02 and PA06 have the best modification results, but the amount of polyaniline in the sample PA02 is about one third of that in the sample PA06.

To compare the polyaniline modification with the polypyrrole modification, samples, PY01, PY02 and PY03, were prepared under a constant current of $0.4 \, mA \, cm^{-2}$ for 5, 10 and 20 min. It can be seen from Table 5 that the modification of Nafion with polypyrrole has similar effect to that with polyaniline: the methanol permeability is reduced and the proton conductivity decreases. However, the methanol permeability of Nafion modified with polyaniline is reduced to a greater extent but its proton conductivity decreases to a slighter extent than the Nafion modified with polypyrrole under the same condition. For example, with the modification under a constant current of $0.4 \, mA \, cm^{-2}$ for 10 min, the methanol permeability of Nafion changes from 1.09×10^{-6} to $1.06 \times 10^{-7} \, cm^2 \, s^{-1}$ for the polyaniline modification but to $5.83 \times 10^{-7} \, cm^2 \, s^{-1}$ for the

Table 4

Comparison of the methanol permeability (D) and proton conductivity (K) of polyaniline-modified Nafion under cycling potential

Samples	D ($cm^2 \, s^{-1}$)	K ($S \, cm^{-1}$)	K/D ($s \, S \, cm^{-3}$)
Nafion	1.09×10^{-6}	2.30×10^{-2}	2.11×10^{4}
PA07	2.29×10^{-7}	1.27×10^{-2}	5.53×10^{4}
PA08	2.26×10^{-7}	1.25×10^{-2}	5.53×10^{4}
PA09	1.71×10^{-7}	1.18×10^{-2}	6.87×10^{4}

Table 5

Comparison of the methanol permeability (D) and proton conductivity (K) of polypyrrole-modified Nafion under constant current

Samples	Sample modification condition	D ($cm^2 \, s^{-1}$)	K ($S \, cm^{-1}$)	K/D ($s \, S \, cm^{-3}$)
Nafion		1.09×10^{-6}	2.30×10^{-2}	2.11×10^{4}
PY01	$0.4 \, mA \, cm^{-2}$ for 5 min	3.89×10^{-7}	0.86×10^{-2}	2.20×10^{4}
PY02	$0.4 \, mA \, cm^{-2}$ for 10 min	5.83×10^{-7}	1.65×10^{-2}	2.28×10^{4}
PY03	$0.4 \, mA \, cm^{-2}$ for 20 min	7.49×10^{-7}	1.67×10^{-2}	2.21×10^{4}
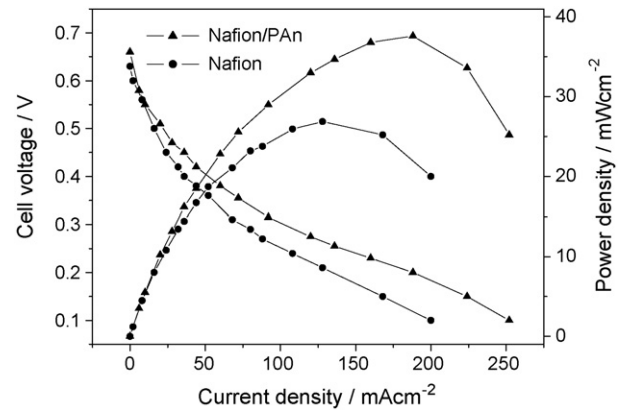
Fig. 8. Performances of direct methanol fuel cells using the pure Nafion and the polyaniline-modified Nafion (Nafion/PAn) at 35 °C. Anodic electrolyte was 2 M CH_3OH aqueous solution at a flow rate of $1 \, ml \, min^{-1}$ and pure oxygen was used as cathodic reactant with a flow rate of $5 \, ml \, s^{-1}$.

polypyrrole modification, and the proton conductivity of Nafion changes from 2.30×10^{-2} to $1.79 \times 10^{-2} \, S \, cm^{-1}$ for polyaniline modification but to $1.65 \times 10^{-2} \, S \, cm^{-1}$ for the polypyrrole modification. This indicates that the modification of Nafion with polyaniline is better than that with polypyrrole.

3.4. Performance improvement of direct methanol fuel cell using the polyaniline-modified Nafion

Fig. 8 presents the relations of voltage and power density with current density of the direct methanol fuel cells using pure Nafion 117 membrane and polyaniline-modified Nafion 117 membrane prepared under a constant current of $0.4 \, mA \, cm^{-2}$ for 10 min (sample PA02). It can be seen from Fig. 8 that the fuel cell using the polyaniline-modified membrane has higher voltage and power density output than the fuel cell using the pure membrane at the same current density. The performance of the fuel cell is improved significantly due to the polyaniline modification of the Nafion membrane. At 35 °C, the maximum power density output of the fuel cell is $38 \, mW \, cm^{-2}$ for the polyaniline-modified membrane, but only $27 \, mW \, cm^{-2}$ for the pure Nafion membrane. Apparently, this improvement is ascribed to the large reduction of methanol permeability of the Nafion membrane due to the polyaniline modification.

4. Conclusion

The electrochemical modification of Nafion membrane with polyaniline results in the reduction of one decade in methanol permeability of the membrane at the cost of a slight decrease of its proton conductivity. This contribution improves significantly the performances of direct methanol fuel cell. The modification with constant current shows larger reduction in methanol permeability and less decrease in proton conductivity than that with constant potential or with potential cycling. The Nafion membrane modified

with polyaniline shows its better methanol-resistant permeability and proton conductivity than that with polypyrrole.

Acknowledgements

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