Short communication

Chemical modification of Nafion membrane with 3,4-ethylenedioxythiophene for direct methanol fuel cell application

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Abstract

Nafion 117 membranes were modified by *in situ* chemical polymerization of 3,4-ethylenedioxythiophene using H_2O_2 as oxidant for direct methanol fuel cell application. Methanol permeability and proton conductivity of the poly(3,4-ethylenedioxythiophene)-modified Nafion membranes as a function of temperature were investigated. An Arrhenius-type dependency of methanol permeability and proton conductivity on temperature exists for all the modified membranes. Compared with Nafion 117 membrane at 60 °C, the methanol permeability of these modified membranes is reduced from 30% to 72%, while the proton conductivity is decreased from 4% to 58%, respectively. Because of low methanol permeability and adequate proton conductivity, the DMFC performances of these modified membranes were better than that of Nafion 117 membrane. A maximum power density of 48.4 mW cm^{-2} was obtained for the modified membrane, while under same condition Nafion 117 membrane got 37 mW cm^{-2}.

1. Introduction

The direct methanol fuel cell (DMFC) has attracted considerable attention due to its simple system design, low operating temperature, convenient fuel storage and supply. The proton exchange membrane is one of the most critical components in the DMFC. In general, membranes with high proton conductivity and low methanol permeability are desirable for efficient DMFC operation. Currently, Nafion (DuPont, USA), a perfluorosulfonic acid ionomer, is the major membrane material used in proton exchange membrane fuel cells. It has good chemical and thermal stability, high proton conductivity. However, Nafion membrane is a poor barrier to methanol crossover, which limits its wide application in DMFC. The methanol crossover to the cathode not only reduces fuel efficiency, but also increases the over-potential

of the cathode, thus resulting in lower cell performance [1].

To decrease the methanol crossover in conventional perfluorosulfonic acid membrane, a number of methods of modifying Nafion® membranes were reported in the literature. Ma et al. [2] and Choi et al. [3] deposited palladium and palladium alloys on Nafion membranes to reduce the methanol crossover. Liu et al. [4] modified Nafion membrane by acid-catalyzed *in situ* copolymerization of furfuryl alcohol and Nafion. The nano-composite membrane largely exhibited a reduced methanol permeability. Shao et al. [5] prepared Nafion–polyvinyl alcohol composite membranes with a good selectivity of water over methanol and an enhanced cell performance compared with Nafion membranes. Banaszak et al. [6] demonstrated a lower methanol permeation by doping Nafion with 1-ethylimidazolium. Recently, several research groups [7–15] have prepared modified Nafion membranes with electronically conducting polymers including polypyrrole and poly(3,4-ethylenedioxythiophene) (PEDOT). A lower methanol permeation and proton conductivity were reported for polypyrrole-modified Nafion

membranes with enhanced performance in a single fuel cell [14,15].

In general, Nafion membranes were modified by chemical polymerization of electronically conducting polymer monomer with either cationic (Fe^{3+}) [8,13–15] or anionic ($S_2O_8{}^{2-}$) [7,9,10] as oxidant. In both cases, a thin electronically conducting polymer film on the surface of Nafion membrane was observed, which could effectively reduce the methanol permeability. However, this thin film also causes its poor bonding to fuel cell electrode, which lead to a lower catalyst utilization and increased interfacial resistance, thus finally resulting in the lower cell performance [14]. In our previous report on PEDOT-modified Nafion membranes, we found the proton conductivity measured using $FeCl_3$ as oxidant was lower than using H_2O_2 as oxidant [16]. In that report, however, we did not measure the proton and methanol transport properties of these modified Nafion membranes using H_2O_2 at high temperature, also we did not test their performances in DMFC. In this paper, we will study the proton and methanol transport properties of these modified membranes as a function of temperature. The electrochemical performance of these modified membranes also will be investigated in a single DMFC.

2. Experimental

2.1. Membrane preparation

Nafion 117 membranes were cleaned by immersion in boiling 3 wt% H_2O_2 followed by boiling 1 M H_2SO_4 for 1 h each. The membranes were then rinsed in boiling de-ionized water for 1 h and the procedure was repeated at least twice to remove sulfuric acid completely. After this purification procedure the membranes were stored in de-ionized water at room temperature before use.

PEDOT-modified Nafion membranes were prepared by the diffusion *in situ* polymerization method [7–10]. Nafion membrane was placed between a two-compartment glass cell. One side of membrane contained 3,4-ethylenedioxythiophene (EDOT) monomer dissolved in 0.1 M NaPSS (sodium polystyrenesulfonate) solution and the other side 5 wt% H_2O_2 aqueous solution as oxidant. In our experiments, the molar ratio of EDOT to NaPSS was 5:1. The compartment containing the EDOT monomer was magnetically agitated during polymerization. After polymerization, the resulting modified membranes were treated in boiling 1 M H_2SO_4 followed by boiling de-ionized water for 1 h each. The modified membranes were black. All samples were stored in de-ionized water before test.

2.2. Water uptake

Equilibrium absorption of de-ionized water in membrane was determined at room temperature. The wet weight (G_w) of membrane was measured immediately after removing excess water from the membrane surface. The membrane dry weight (G_d) was obtained after drying the wet membrane in a vacuum oven for 24 h at 80 °C. The water uptake of the membrane at room

temperature was calculated as follows:

$$\text{Water uptake (\%)} = \frac{G_w - G_d}{G_d} \times 100$$

2.3. Morphology of membranes

The morphology of membranes was investigated using a scanning electron microscope (PHILIPS XL-30). Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of Au prior to SEM examination.

2.4. Methanol permeability

Methanol permeability of the samples was measured using a diaphragm cell [17]. The glass cell consisted of two identical compartments ($V = 16$ ml), separated by the test membranes and containing 1 M methanol on one side and de-ionized water on the other side. Both compartments were magnetically stirred during the permeation experiments. The concentration of permeated methanol was measured by Gas Chromatograph (FULI 9790). The methanol permeability was calculated from the slope of the linear plot of methanol concentration versus permeation time. The measured temperature was controlled from room temperature to 70 °C.

2.5. Proton conductivity

Proton conductivity of the samples was derived from dc measurements using a potentiostatic four-electrode technique as described in the literatures [7,18]. The experimental cell was composed of two identical compartments. Each compartment was filled with 1 M H_2SO_4 solution and contained a platinum electrode and an Ag–AgCl reference electrode. All electrodes were connected to an EG&G Princeton Applied Research Model 273 Potentiostat/Galvanostat. The measured temperature was controlled from room temperature to 80 °C. Proton conductivity of the membranes was determined by the potential difference between the reference electrodes, the first without membrane, and the second with the membrane between two compartments.

2.6. Cell performance

Our experiments used unsupported Pt–Ru/C (20 wt% Pt and 10 wt% Ru, Johnson Matthey) as anode catalyst, and Pt/C (20 wt% Pt, Johnson Matthey) as cathode catalyst, respectively. The platinum loading for all electrodes used was 1.0 mg cm^{-2}. The reaction layer, for both anode and cathode, was prepared by direct mixing in an ultrasonic bath a suspension of Nafion ionomer in water with the catalyst powders, the obtained paste was spread on carbon cloth backings. The membrane-electrode assemblies (MEAs) were manufactured by pressing the electrode onto the membrane at 120 °C and 15.4 MPa for 2 min.

The cell performance was evaluated at a fuel cell test station (Arbin FCTS-PEM-DM) using a single DMFC with active area 5 cm^2 at 60 °C. 2 M methanol solution was pumped through the anode at a flow rate of 20 ml min^{-1} with atmosphere pressure

while humidified oxygen was fed to the cathode at 75 ml min^{-1} at a pressure of 0.1 MPa.

3. Results and discussion

The morphology of PEDOT-modified Nafion membranes depends on the type of oxidant used in the polymerization process of EDOT monomer. When the cationic oxidant was used, a thin PEDOT layer was formed onto the membrane surface [8]. The same results were obtained in the polypyrrole-modified Nafion membranes using cationic or anionic oxidant [9,10]. In our experiments, however, the PEDOT layer was not observed on the membrane surface using H_2O_2 as oxidant, even if the polymerization was carried out for 20 h. Fig. 1 shows SEM micrographs of the membrane surface for Nafion 117 membrane and PEDOT-modified Nafion membranes with various polymerization times. It can be observed that PEDOT-modified membranes are homogeneous and smooth, whose morphologies are similar to that of pure Nafion. There were not any PEDOT particles observed on the membrane surface. It is supposed that the PEDOT particles were present within the pores of the Nafion matrix. When H_2O_2 aqueous solution was used as the oxidant for EDOT polymerization, there were no available counter ions in the neutral oxidant solution compared with using cationic oxidant. The EDOT and H_2O_2 only meet inside the Nafion membrane when they diffuse into the membrane from its opposite sides. Then, the sulfonated groups of Nafion membrane can be interacted with EDOT, and can act as counter ions for the polymerization of EDOT. Therefore, PEDOT particles can be present into the pores of Nafion membrane.

When the Nafion membrane was modified with PEDOT for 10 h in our experiments, its proton conductivity was below 0.01 S cm^{-1}, which is not suitable for DMFC application. Considering the requirement of proton conductivity for DMFC, the modified membranes with various polymerization times were investigated in our experiments. These modified membranes are named PN-02 for 2 h, PN-03 for 3 h and PN-06 for 6 h of the polymerization time, respectively.

Water uptakes of all the modified membranes were shown in Fig. 2. It can be found that the water uptakes of these modified membranes decreased with increasing the polymerization time. The decrease in water uptake indicated that the sulfonated groups of Nafion polymer was combined with PEDOT, and the hydration of ion cluster was decreased due to the hydrophobic property of PEDOT backbone.
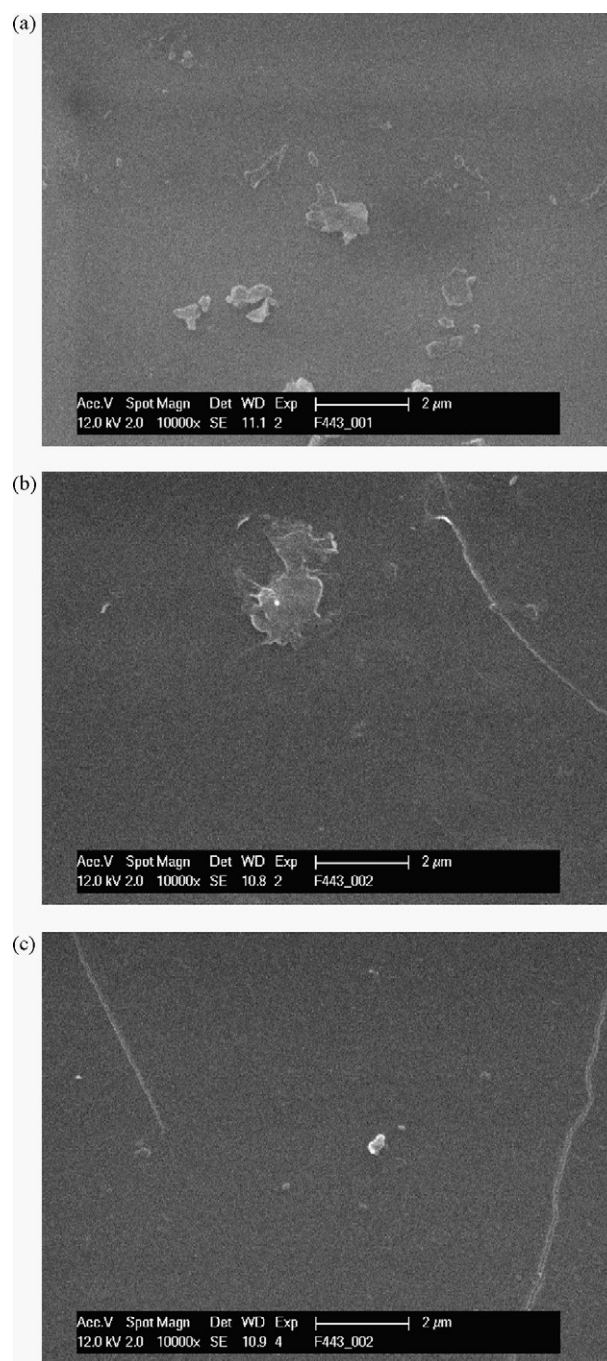
Fig. 1. SEM micrographs of the membrane surface for Nafion 117 membrane (a), PEDOT-modified Nafion membranes of polymerization 2 h (b) and 6 h (c).

Table 1
Proton conductivity and methanol permeability at 60 °C of membranes

Samples	Thickness (μm)	PEDOT content (wt%)	Conductivity σ (S cm^{-1})	Permeability P (cm^2 s^{-1})	E_m[b] (kJ mol^{-1})	E_p[b] (kJ mol^{-1})	β[a]
Nafion 117	185	–	0.090	8.77×10^{-6}	16.02	13.70	4.01
PN-02	186	1.2	0.086	6.24×10^{-6}	19.32	13.73	4.14
PN-03	187	1.8	0.078	4.67×10^{-6}	20.12	12.56	4.22
PN-06	189	2.6	0.038	2.45×10^{-6}	22.31	12.33	4.19

[a] $\beta = \log(\sigma/P)$.
[b] E_m is the activation energy of methanol permeation and E_p is the activation energy of proton migration, respectively.
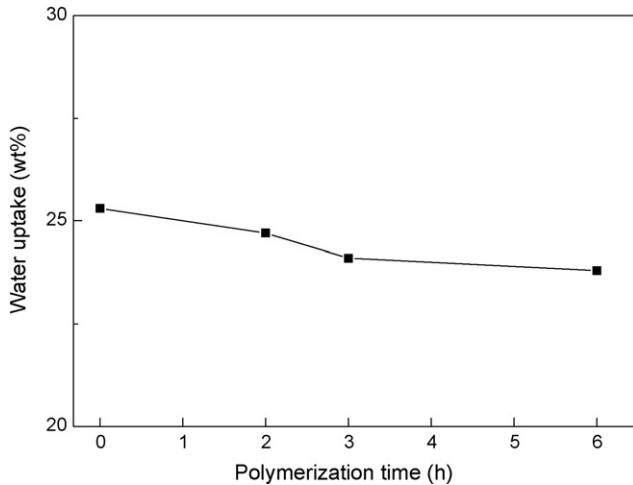
Fig. 2. Water uptake of PEDOT-modified Nafion membranes.

Fig. 4. Proton conductivity of PEDOT-modified Nafion membranes as a function of temperature. Nafion 117 membrane (□), and PEDOT-modified Nafion membranes for polymerization 2 h (○), 3 h (△) and 6 h (▽).

Fig. 3 shows the methanol permeability as a function of temperature for these modified membranes and Nafion 117 membrane. It can be found that an Arrhenius-type dependency of the methanol permeability on temperature exists for all the membranes. The apparent activation energies for methanol permeation E_m through theses membranes are also reported in Table 1 along with the methanol permeability at 60 °C. The activation energies of the modified membranes are higher than that of unmodified membrane. In addition, it can be easily observed that the methanol permeability of these modified membranes was smaller than that of Nafion 117 membrane over the temperature range 25–70 °C.

Fig. 4 is an Arrhenius plot of proton conductivity as a function of temperature at 100% RH (relative humidity) for the PEDOT-modified membranes and Nafion 117 membrane. It can be found that the relation between the proton conductivity and temperature basically accords with the Arrhenius equation. From the Arrhenius equation, the apparent activation energy of mem-

brane can be calculated. The apparent activation energies of proton migration E_p are reported in Table 1 along with the proton conductivity at 60 °C. The activation energy of Nafion 117 membrane is 13.7 kJ mol^{-1}, which is in reasonable agreement with the literature value of 13.4 kJ mol^{-1} [19]. The activation energies of the PEDOT-modified membranes are from 13.73 kJ mol^{-1} to 12.33 kJ mol^{-1}. Until now, we cannot explain why the activation energies of these modified Nafion membranes were lower than that of unmodified Nafion membrane when the former showed lower proton conductivity.

High proton conductivity (σ) and low methanol permeability (P) are two of the essential characteristics, which a PEM must posses in order to be validly proposed for use in DMFC. We combined the two into a selection criterion β (=log(σ/P)) as the characteristic parameter of a membrane, so that the different membranes can be more easily compared. The practical significance of this selection criterion is explained in quantitative terms as in the literature [20]. In this paper, it is supposed that the higher the value of selection criterion β is, the better the membrane performance is. The β values at 60 °C of the PEDOT-modified Nafion membranes are shown in Table 1. It can be seen that all the modified membranes have higher selection criterion values than that of pure Nafion 117 membrane.

The polarization curves of MEAs equipped with Nafion 117 and the PEDOT-modified Nafion membranes are shown in Fig. 5. The open circuit voltages of these modified membranes (0.65–0.67 V) are higher than that of Nafion 117 membrane (0.61 V). The reason is that these modified membranes have lower methanol permeability compared with Nafion 117. Because of adequate conductivity and low methanol permeability, the DMFC performances of these modified membranes were better than that of Nafion 117 membrane. The maximum power density for PN-02- and PN-03-modified membranes obtained was 38 mW cm^{-2} at 0.2 V and 48.4 mW cm^{-2} at 0.22 V, respectively. Under the same conditions, a maximum power density for pure Nafion 117 membrane obtained was
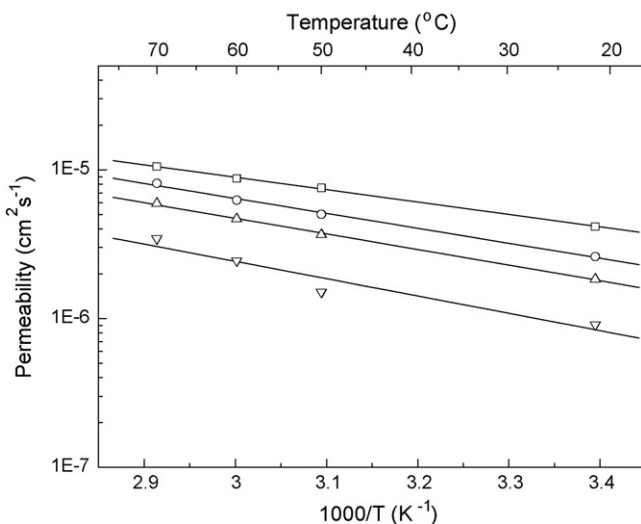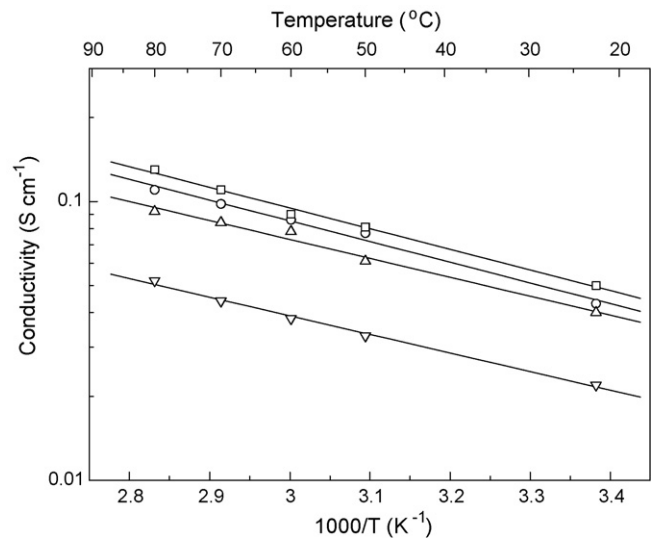

Fig. 3. Methanol permeability of PEDOT-modified Nafion membranes as a function of temperature. Nafion 117 membrane (□), and PEDOT-modified Nafion membranes for polymerization 2 h (○), 3 h (△) and 6 h (▽).
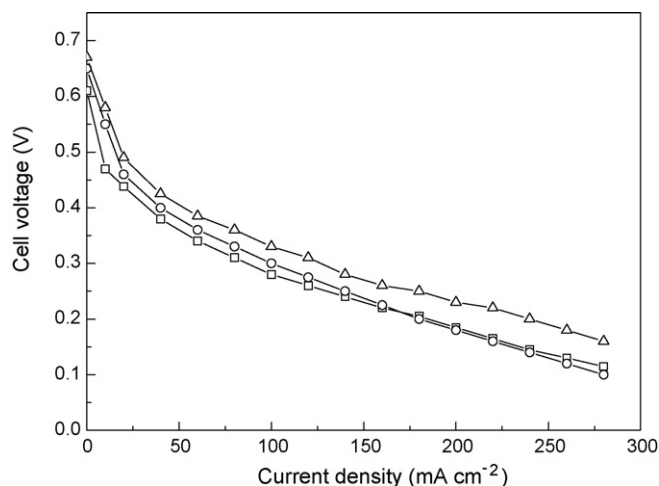
Fig. 5. Polarization curves for various MEAs equipped with Nafion 117 membrane (□), and PEDOT-modified Nafion membranes for polymerization 2 h (○) and 3 h (△). Operating conditions: 2 M methanol solution, pure O_2 and 60 °C.

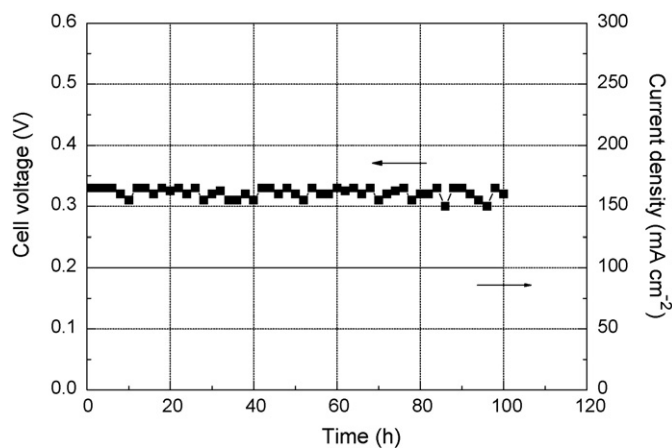Fig. 6. The durability of MEA equipped with PEDOT-modified Nafion membrane for polymerization 3 h. Operating conditions: 2 M methanol solution, pure O_2 and 60 °C.

37 mW cm^{-2} at 0.2 V. To confirm the durability of the modified Nafion membranes operating in fuel cell, the MEA made from PN-03 membrane was continuously tested in a single DMFC. From Fig. 6, it can be found that the cell performance was maintained for 100 h of operation.

4. Conclusions

Commercial Nafion 117 membranes have been modified by *in situ* chemical polymerization of 3,4-ethylenedioxythiophene using H_2O_2 as oxidant for direct methanol fuel cell application. An Arrhenius-type dependency of methanol permeability and proton conductivity on temperature exists for all these modified membranes. The activation energies of methanol permeation for the modified membranes are higher than that of unmodified membrane, and the activation energies of proton migration for the modified membranes are similar to that of bared membrane. Because these modified membranes have higher the selection criterion values at 60 °C, their DMFC performances were better than that of Nafion 117 membrane. The maximum power density for PN-02- and PN-03-modified membranes obtained was 38 mW cm^{-2} at 0.2 V and 48.4 mW cm^{-2} at 0.220 V, respectively. Under same conditions, a maximum power density for pure Nafion 117 membrane obtained was 37 mW cm^{-2} at 0.2 V. In addition, the cell performance of the MEA equipped with the PN-03-modified membrane can be maintained for 100 h of operation.

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