Alkaline Polymer Electrolyte Membranes from Quaternized Poly(phthalazinone ether ketone) for Direct Methanol Fuel Cell

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ABSTRACT: Quaternized poly(phthalazinone ether ketone)s (QPPEK)s were synthesized by the chloromethylation and quaternization of poly(phthalazinone ether ketone) (PPEK) with chloromethyl methyl ether in 98% concentrated sulfuric acid and following trimethylamine. The presence of —CH_2Cl groups in chloromethylated PPEK was confirmed by ^{1}H-NMR. An alkaline QPPEK membrane was prepared and its thermal and mechanical properties were tested. The alkaline QPPEK membrane had a methanol permeability 6.57×10^{-7} cm^2/s and the highest anion conductivity 1.14×10^{-2} S/cm. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1756–1762, 2008

Key words: quaternization; poly(phthalazinone); alkaline polymer electrolyte membrane; DMFC

INTRODUCTION

Direct methanol fuel cells (DMFCs) are receiving increasing attention due to their highly advantageous features such as a low-operating temperature, sustained operation at high-current density, low weight, compactness, potential for low cost and volume, long stack life, fast start-ups, and suitability for discontinuous operation.[1,2] Polymer electrolyte membrane (PEM) is a key component of in DMFCs. Much effort has devoted to develop the proton-exchange membranes,[3–16] but little interest has been shown in the alkaline PEMs.[17] Comparing the DMFC using anion conducting PEM with the DMFC using proton conducting PEM, the former has several advantages,[17–20] (i) the kinetics of the cathode reaction (oxygen reduction) is more favorable in alkaline media than in acidic ones, enabling the use of cheaper non-noble metals, e.g., Ni and Ag; (ii) the conducting ions now move from the cathode (where they are generated) to the anode and the water is produced at the anode, so the water management regime is altered and potentially simplified; (iii) at high *in situ* pH, the oxidative radical mechanism for polymer degradation is suppressed and the durability of PEMs will be improved; (iv) for the proton conducting PEMs, the proton conductivities increase with methanol permeabilities since they transport to the same direction through same hydrophilic ionic channels in the membranes, while the anion conducting PEMs, the conduction pathway of the OH^- ions proceeds from the cathode to the anode, opposing to the direction of, and hence reducing the level of, methanol crossover.

Several alkaline PEMs based on quaternized polymers have been developed, such as, quaternized polyethersulfone cardo anion exchange membranes, radiation-grafted PVDF and FEP, quaternized poly(phthalazinon ether sulfone ketone) membranes and pyri- dinium-type PEMs,[21–24] but no methanol permeability and DMFC performance about them have been reported.

Poly(phthalazinone)s such as poly(phthalazinone ether ketone) (PPEK), poly(phthalazinone ether sulfone) (PPES), and the copolymer poly(phthalazinone ether sulfone ketone) (PPESK) have excellent chemical and oxidative resistance, mechanical properties, and thermal stability. As a class of thermoplastics, poly(phthalazinone)s have a very high glass-transition temperature (T_g) of 250–370°C, excellent high-temperature stability, and many other good properties.[25] In this study, the quaternized PPEKs (QPPEKs) are modified by chloromethylation/quaternization, QPPEK membranes membrane are investigated.

EXPERIMENTAL

Materials

PPEK was purchased from Dalian Polymer New Material Co., Ltd., China. It was dried at 105°C for

4 h before used. *N*-methyl-2-pyrrolidone (NMP) (Shanghai Chemicals Co., China) was distilled under reduced pressure and stored with 4 Å molecular sieves until used. Chloromethyl methyl ether (Shanghai Bangcheng Chemical Co.,Ltd, China), Trimethylamine (Shanghai Chemicals Co., China) were all analytical reagents and were used as received.

Quaternization of Ppek

In a typical experiment, 5 g PPEK powder was dissolved in 50 mL of concentrated sulfuric acid of 98% under 20°C. Ten milliliter of chloromethyl methyl ether dissolved in 40 mL of 98% concentrated sulfuric acid was added in dropwise at the same temperature, and then the reaction mixture was vigorously stirred for 5 h. The reaction mixture was poured onto crushed ice, and the resulting precipitate was recovered by filtration. By washing with deionized water until pH 6–7, drying at 80°C for 15 h, chloromethylated PPEK (CMPPEK) was obtained. Then the CMPPEK was immersed into 30 wt % trimethylamine solution for 48 h to induct quaternary groups into the CMPPEK and the quaternized PPEK (QPPEK) were synthesized. At last, the QPPEK was put into $1M$ KOH solution for 24 h to obtain alkaline QPPEK (QPPEK-OH). The reaction was schemed in Figure 1.

Preparation of membranes

The QPPEK membrane was fabricated by solution casting. At first, the CMPPEK was dissolved in NMP to make a 10% w/v solution, stirred, and filtrated. Then the solution was cast onto a flat glass with a glass knife. The film was dried under ambient conditions for 3 days and then under vacuum at 80°C for 24 h and 120°C for 24 h. The resultant membrane was immersed into 30 wt % trimethylamine solution for 48 h to induct quaternary groups into the membrane (QPPEK), thereafter, the membrane was put into $1M$ KOH solution for 24 h, and the QPPEK-OH membrane was obtained. At last, the QPPEK membrane was washed several times with distilled water, and naturally dried under ambient environment to avoid great shrinkage with water losing.

MEASUREMENTS

To study the molecular structure of the polymers and CMPPEK degree of chloromethylation, ^{1}H-NMR spectra of PPEK and CMPPEK were recorded using a BRUKER Avance DMX500 NMR spectrometer.

A TA Instruments thermogravimetric analyzer (TGA) instrument Perkin–Elmer TGA-7 was used to measure the degradation temperatures (T_d). Polymer samples for TGA analysis were heated to 850°C from room temperature at 10°C/min under nitrogen atmosphere.

X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max-rA X-ray diffractometer using Cu $K\alpha$ radiation (λ = 0.15406 nm) at 40 kV and 80 mA. Diffraction patterns of Powders and membranes of PPEK, CMPPEK, and QPPEK were obtained.

Tensile strength was measured by using Shimadzu AG-1 Mechanical Testing Machine.

The surfaces of hybrid membranes and their cross sections cut in liquid nitrogen (77 K) with two small nippers were characterized with a field-emission scanning electron microscope (FE-SEM, Sirion) using an in-lens detector at 5 kV incident beam voltage.

The ionic conductivity was measured by alternating-current (ac) impedance spectroscopy over a frequency range of $1–10^7$ Hz with oscillating voltage 50–500 mV under 100% relative humidity, using a system based on a Solartron 1260 gain phase analyzer. A sample with size of 30 mm ×30 mm was placed in an open, temperature controlled cell where it was clamped between two blocking stainless steel electrodes. Specimens were soaked in deionized water prior to the test. The conductivity (σ) of the samples in the transverse direction was calculated from the impedance data, using the relationship $\sigma = d/RS$, where d and S are the thickness and face area of the sample, respectively, and R was derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Re (Z) axis.

Methanol permeability measurement was carried out using a diaphragm diffusion cell described in Ref. 10 The membrane to be tested was swollen in $1M$ methanol solution at room temperature for 24 h, and then was sandwiched by O-ring shaped Teflon on purpose of sealing and fastened between the two compartments tightly, separating the two chambers of the cell. One chamber was filled with 15.8 wt % methanol solution and the other filled with only deionized water. As methanol penetrating across the membrane, the methanol concentration at the water side increased with time and was detected using a Varian Vista 6000 gas chromatograph. Permeability of methanol was obtained by analyzing the methanol flux with time, and methanol permeability was calculated by[10]

$$C_B(t) = \frac{A}{V_B}\frac{D \cdot K}{L}C_A(t - t_0) \qquad (1)$$

$$\text{Slope} = \left(\frac{dC_B(t)}{dt}\right) = \frac{A}{V_B}\frac{D \cdot K}{L} \cdot C_A \qquad (2)$$

$$P = D \cdot K = \text{slope} \times \left(\frac{V_B \cdot L}{A \cdot C_A}\right) \qquad (3)$$

where C_B and C_A were the methanol concentration of permeated and feed side through the membrane, respectively. A, L, and V_B were the effective area of
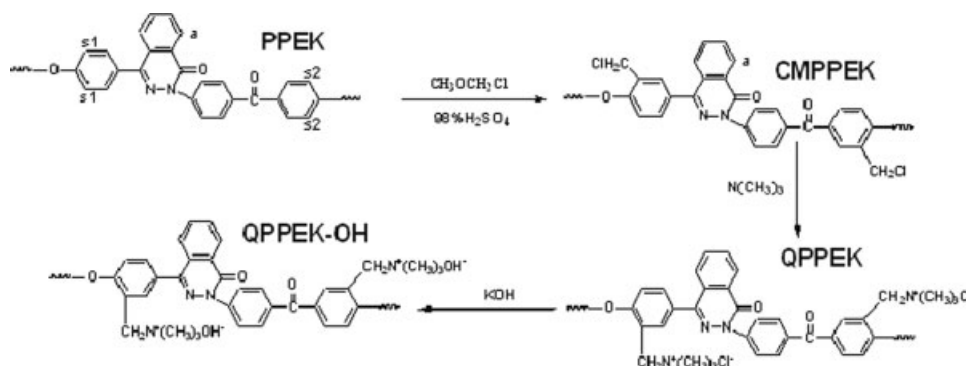
Figure 1 Preparation of alkaline quaternized PPEK.

membrane, the thickness and the volume of permeated compartment. D, K, and t_0 were the methanol diffusivity, the solubility and the time lag, respectively.

Membrane electrode assemblies (MEA) with a geometric area of 6.0 cm^2 were prepared using PtRu/Vulcan XC-72 (E-Tek Inc.) and Pt/Vulcan XC-72 (E-Tek Inc.) as the cathode and anode catalysts, respectively, each at a loading of 3.0 mg/cm^2. MEA inks were prepared as follows: 40 mg catalyst and 200 mg 10 wt % PTFE solution (as catalyst layer binding material, no Nafion binder was used) were mixed thoroughly with 200 mg isopropyl alcohol. Inks were painted onto single sided supporting carbon paper, followed by solvent drying at 80°C. The MEAs were obtained by hot-pressing the anode and cathode on both sides of the pretreated membranes under 120°C and 8 atm for 1.5 min.

DMFC tests were carried out in a 6.0 cm^2 single cell connected to a electrochemistry working station(CHI) after equilibrium at 70°C for 2 h. Two molar methanol solution at the anode was fed with a rate of 1.8 mL/min, while the air at the cathode was supplied by natural convection (viz. air breathing).

RESULTS AND DISCUSSION

NMR, XRD spectra, and morphology studies

The chloromethylation of PPEK was an electrophilic reaction, the reaction occurred only at the *ortho*-ether s1 and s2 sites (See Fig. 1), because except for ether linkages, all other groups attached to the aromatic rings contained more electron-withdrawing functionality, which decreased the electrophilic reactivity of the polymers. From Figure 2, it could be seen that the aromatic region of PPEK polymer in CDCl$_3$ is divided into three sections: H-a at low field (8.46–8.62 ppm) (See Fig. 1),[16] the *ortho*-ether linkage 4H (H-s1,H-s2) at high field (7.05–7.30 ppm) and the remaining 11H aromatic hydrogen signals (7.60–8.10 ppm). The apparent differences between the PPEK and CMPPEK spectra were a group of new upfield

signals (4.60–4.86 ppm) which was thought of arising from the H in —CH$_2$Cl group.[26] And the presence of —CH$_2$Cl group made the remanent *ortho*-ether linkage H signals to appear at a higher field (6.09–7.30 ppm). In addition, PPEK was not dissolved well in CDCl$_3$, so H-a signals of PPEK were no entirely identical with that of CMPPEK, yet the H-a sum did not change in PPEK and CMPPEK. The integration value of the low field H-a absorptions as an internal standard was set to 1.00, then the degree of chloromethylation could be calculated through the integration value upfield (4.60–4.86ppm) absorptions. The CMPPEK degree of chloromethylation was 1.30. In the next two steps, the CMPPEK might be converted into QPPEK-OH due to the facile reactivity.

The microstructures of the PPEK, CMPPEK, and QPPEK membranes were studied with XRD. All of the membranes showed very similar XRD patterns (Fig. 3) and exhibited ''structure less'' amorphous morphology. As a whole, the XRD pattern of the three membranes was diffuse which indicated the absence of the crystalline phase. It indicated that the chloromethylation and the next quaternization
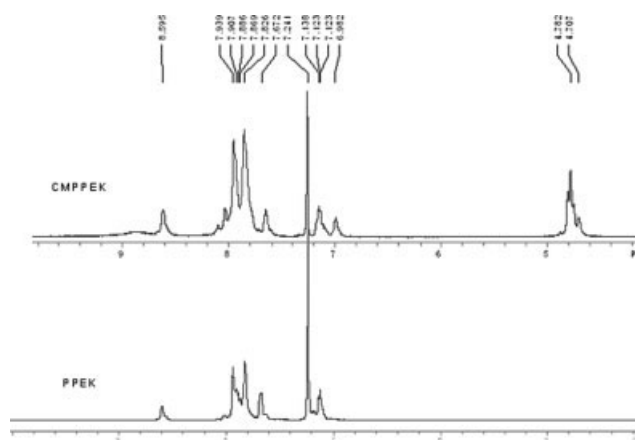

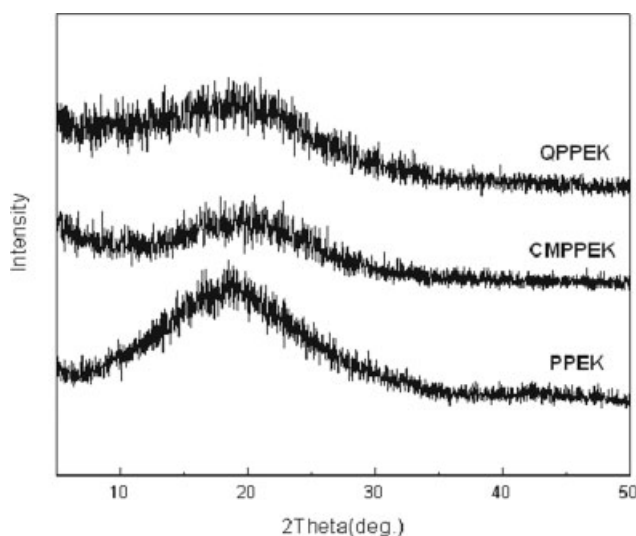**Figure 2** ^{1}H-NMR spectra of PPEK and CMPPEK in CDCl$_3$.

Figure 3 XRD spectra of PPEK, CMPPEK and QPPEK membranes.

did not induce reorganization of those polymer structures.

From Figure 4, It could be found that the membranes of CMPPEK and QPPEK membranes were dense and clean. The FE-SEM images, even up to magnifications of 20,000×, did not show any evidence of the presence of a micro-porous structure, but on the surface of QPPEK membrane [Fig. 4(c)]

there were some defects which did not penetrate to the other side of the membrane. They were shallow pits on QPPEK membrane surface and the cross-sectional morphologies were compact. The transport of OH^- ions was vertical to the surface of the membrane, so the shallow pits would not affect the membrane property or lifetime.

Thermal and mechanical properties

The thermal stability of the PPEK, CMPPEK, and QPPEK membranes was measured with a thermogravimetric analyzer. The thermograms were shown in Figure 5. From the Figure 5, it could be seen that the PPEK membrane showed two-step degradation pattern and the 5 wt % loss temperature of PPEK was nearly 500°C and there was only one sharp weight loss that was ascribed to the decomposition of polymer main chain. While the CMPPEK and QPPEK membranes exhibited three-step degradation pattern. For the QPPEK membrane, it had nearly 10% weight loss before 100°C, because it was dried at room temperature at last. Because of the existing of water in QPPEK membrane and instability of quaternary amination groups,[21] the QPPEK membrane gradually lost weight between 100 and 200°C, then the next degradation mainly assigning to the dissociation of quaternary amination groups occurred. The
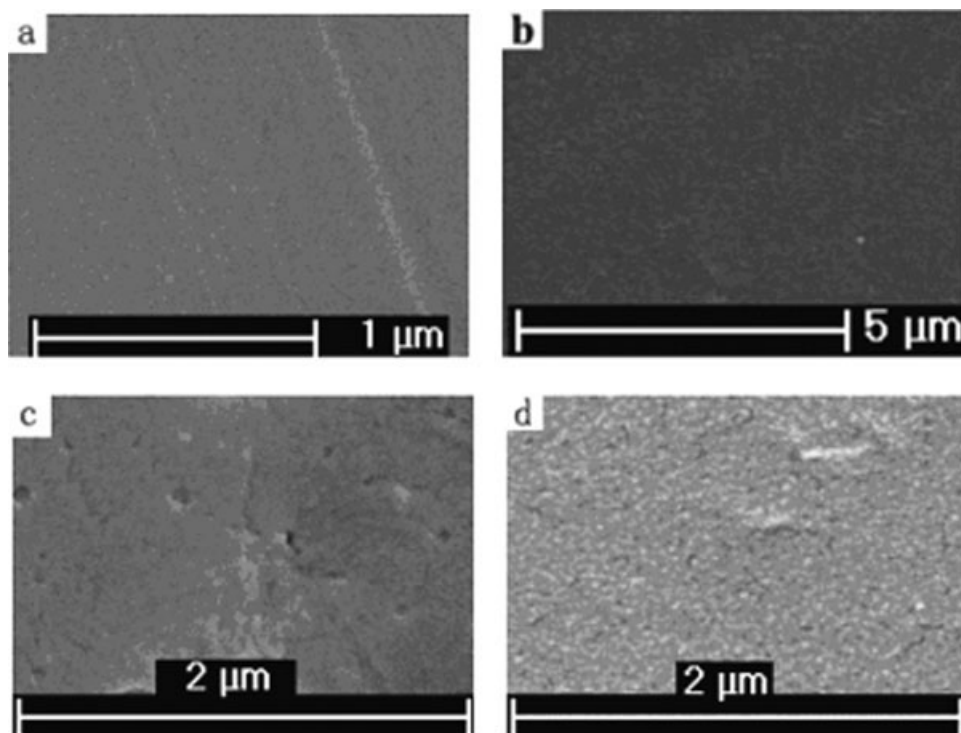

Figure 4 FE-SEM images of surface and cross-sectional morphology for CMPPEK and QPPEK membranes (a) surface of CMPPEK membrane; (b) cross section of CMPPEK membrane; (c) surface of QPPEK membrane; (d) cross section of QPPEK membrane.
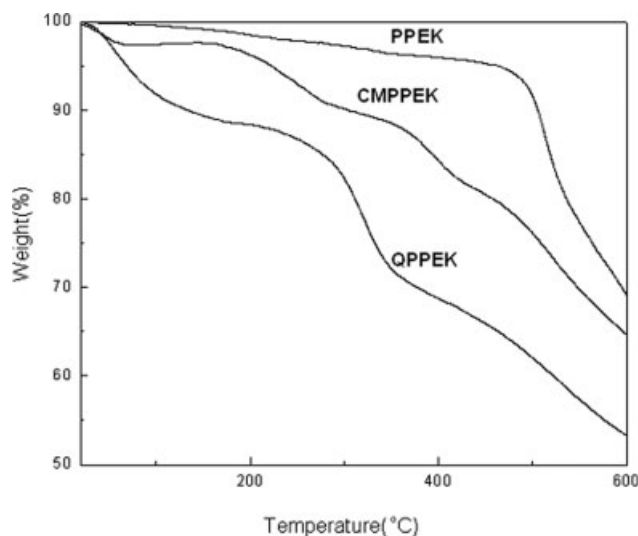
Figure 5 TG curves of PPEK, CMPPEK and QPPEK membranes.

last step above 400°C was associated with the decomposition of the PPEK matrix.

It was desirable for a PEM to have good mechanical integrity to withstand fabrication of the membrane electrode assembly. The stress–strain characteristics of the PPEK, CMPPEK and QPPEK membranes were illustrated in Figure 6. From Figure 1, it could be deduced that the polymer main chains of PPEK were rigid and the elongation of PPEK membrane might be small. And this was confirmed by the result in Figure 6 too. The PPEK membrane had less than 5% strain at break and nearly 100 MPa maximum break stress. While the CMPPEK and QPPEK membranes only showed more than 60 MPa maximum break stress, which could be attributed to
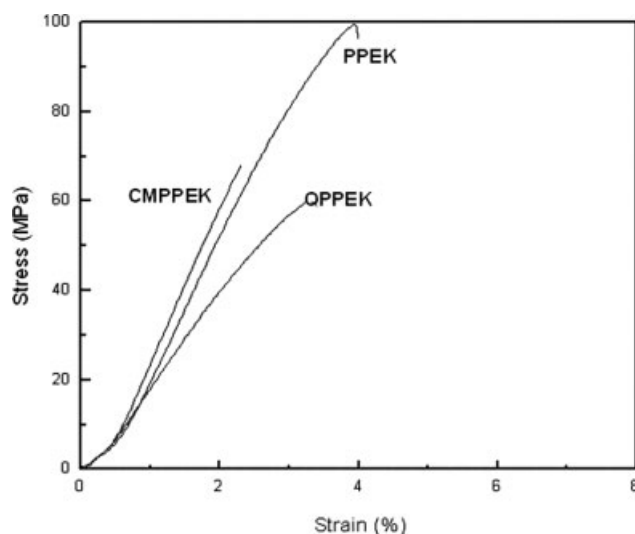

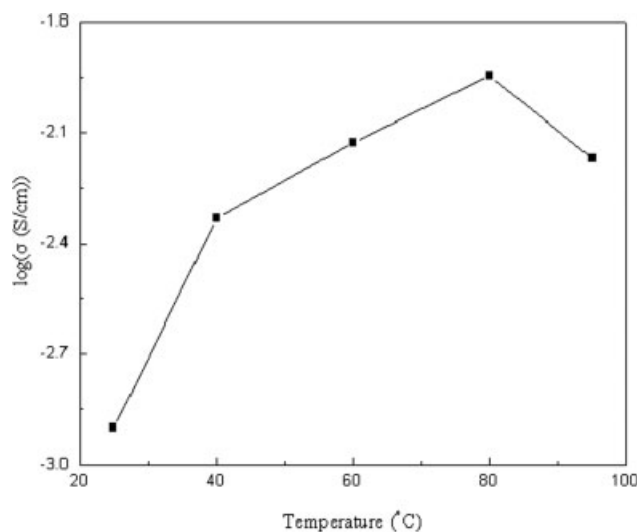**Figure 6** The stress-strain curves of PPEK, CMPPEK and QPPEK membranes.

Figure 7 Hydroxide ion conductivity of QPPEK-OH membrane.

the partial degradation of PPEK in chloromethylation. Comparing with the operation temperature and the maximum break stress (10.21 MPa)[27] of Nafion117 membrane, the QPPEK membrane had enough thermal stability and satisfactory tensile strength for use as a DMFC.

Hydroxide ion conductivity and methanol permeability

The hydroxide ion conductivity of QPPEK-OH membranes was measured against increasing temperature and was given in Figure 7. The conductivity of the QPPEK-OH membrane showed the highest hydroxide ion conductivity of 1.14×10^{-2} S/cm at 80°C (see Fig. 7), which was similar to that reported in Ref. 21, then the conductivity decreased slightly. Presumably, there were two factors. Firstly, the QPPEK-OH membrane absorbed a lot of water due to its abundant quaternary amination groups on repeat unit. Consequently, when the temperature was above 80°C, the QPPEK-OH membrane began to lose partially water. Secondly, the partial decomposition of QPPEK-OH membrane occurred via the nucleophillic displacement reaction.[21] Both of them induced the hydroxide ion conductivity decrease.

The methanol permeability was defined as the product of diffusivity and solubility, DK and the concentration change of CB with time was obtained by a linear slope as shown in Figure 8. The methanol permeability of QPPEK-OH membrane was 7.21×10^{-7} cm^2/s which was three times lower than 2.24×10^{-6} cm^2/s of Nafion 117 which was the similar value as measured in Ref. 10. The result indicated that QPPEK-OH membrane had an effective barrier to methanol crossover.
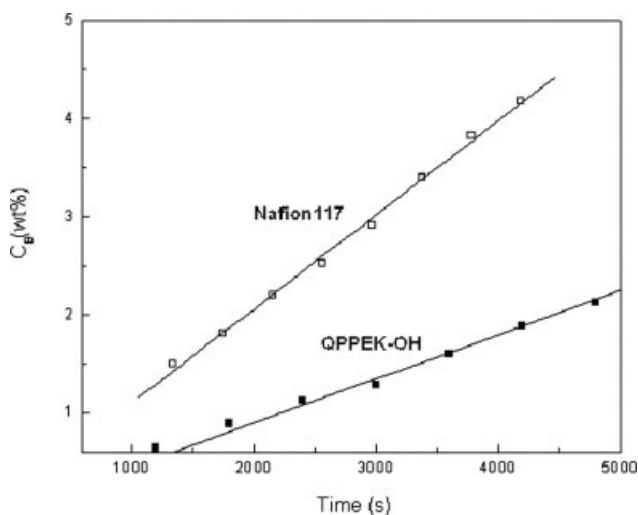
Figure 8 Concentration change of methanol with time of QPPEK-OH membrane.

Fuel cell performance

Figures 9 and 10 showed the DMFC performance of the DMFC with QPPEK-OH and Nafion117 membrane, respectively. As could be seen from Figures 9 and 10, the open circuit voltage (OCV) value of QPPEK-OH membrane was 0.35 V and a peak power density of only 7.76 $\mu W/cm^2$ was obtained for the QPPEK-OH membrane, which was much lower than 2.42 mW/cm^2 of Nafion117 membrane. This could be attributed to the relative low conductivity of QPPEK-OH membrane and the high contact resistance between the electrodes and QPPEK-OH membrane because no appropriate binder could be used in the MEA process. It indicated that binding material in the MEA played an important role and finding appropriate binder between alkaline PEM and the electrodes was urgent. Looking for the suitable
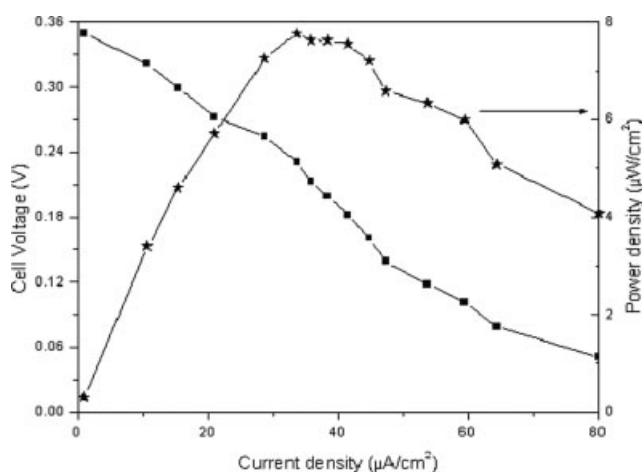

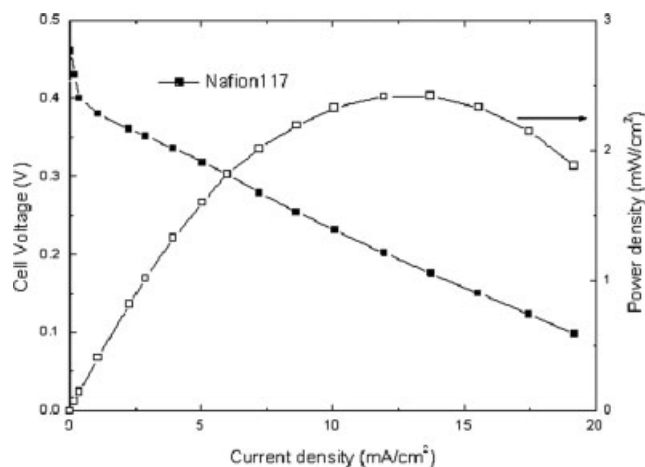**Figure 9** Electrochemical behavior of the DMFC with QPPEK-OH membrane.

Figure 10 Electrochemical behavior of the DMFC with Nafion117 membrane.

binder between the electrodes and alkaline PEM was underway.

CONCLUSIONS

The quaternized PPEKs (QPPEKs) were prepared by chloromethylation/quaternization, and ^{1}H-NMR spectrum, thermogravimetry analysis (TGA) were employed. The QPPEK-OH membrane had a methanol permeability 6.57×10^{-7} cm^2/s and the highest anion conductivity 1.14×10^{-2} S/cm. It might be suitable for low temperature alkaline PEM fuel cells if appropriate binders used for alkaline PEMs and the electrodes were found.

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