Short communication

Polyelectrolyte complexes of chitosan and phosphotungstic acid as proton-conducting membranes for direct methanol fuel cells

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Abstract

Polyelectrolyte complexes (PECs) of chitosan and phosphotungstic acid have been prepared and evaluated as novel proton-conducting membranes for direct methanol fuel cells. Phosphotungstic acid can be fixed within PECs membranes through strong electrostatic interactions, which avoids the decrease of conductivity caused by the dissolving of phosphotungstic acid as previously reported. Scanning electron microscopy (SEM) shows that the PECs membranes are homogeneous and dense. Fourier transform infrared spectroscopy (FTIR) demonstrates that hydrogen bonding is formed between chitosan and phosphotungstic acid. Thermogravimetric analysis (TGA) shows that the PECs membranes have good thermal stability up to 210 °C. The PECs membranes exhibit good swelling properties and low methanol permeability (P, 3.3×10^{-7} cm^2 s^{-1}). Proton conductivity (σ) of the PECs membranes increases at elevated temperature, reaching the value of 0.024 S cm^{-1} at 80 °C.
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Keywords: Polyelectrolyte complexes; Proton conducting; Chitosan; Phosphotungstic acid

1. Introduction

Direct methanol fuel cells (DMFCs) with polymer electrolyte membranes are promising candidates for portable devices or transportation applications in view of their high energy density, easy manipulation, and high efficiency [1–3]. As one of the crucial components of DMFCs, polymer electrolyte membranes function as both electrolyte and separation of the cathode and anode. Perfluorosulfonic acid membranes, such as Nafion® membranes, are the primary membranes applied in DMFCs presently. However, commercial Nafion® membranes do not meet the requirement for low methanol permeability especially at low temperatures (<100 °C) [4]. The methanol permeation results in a reduced open-circuit potential (OCP) and a poisoning of the electrocatalysts at the cathode.

To date, effort has been made to develop new alternatives and extensive researche has been done on the modifications to Nafion® to reduce methanol cross-over. The approaches are diverse, ranging from doping with inorganic materials such as sulfonated montmorillonite [2], silica [5], silica/phosphotungstic acid [6], etc., depositing a Pd thin film on the surface of Nafion® [7] to in situ polymerization with poly(1-methylpyrrole) [8]. Polymer materials based on the arylene main chain such as poly (ether ether ketone)s [9] and polybenzimidazoles [10], have been prepared and functionalized as proton-conducting membranes. Composite membranes, which consist of polymer materials and inorganic materials, for example, phosphoric acid-doped polybenzimidazole [11] and polysulfone/heteropolyacid [12], have also been studied because of the controllable chemical and physical properties produced by combining different properties of the components. Pore-filling membranes, which are composed of a porous substrate and a filling polymer electrolyte, have shown good performance and have been widely studied as proton-conducting membranes [13,14].

Generally, oppositely charged polyions (polycations or polyanions) interact electrostatically to form polyelectrolyte complexes (PECs). Such PECs have recently attracted considerable attention due to their application in a broad field [15]. However, little literature about PECs as proton-conducting membranes has been found except in ref [16]. Chitosan (Fig. 1A) is a natural and low-cost biopolymer which has many excellent properties such as biocompatibility, nontoxicity, chemical and thermal stability, thus it has been widely studied as a

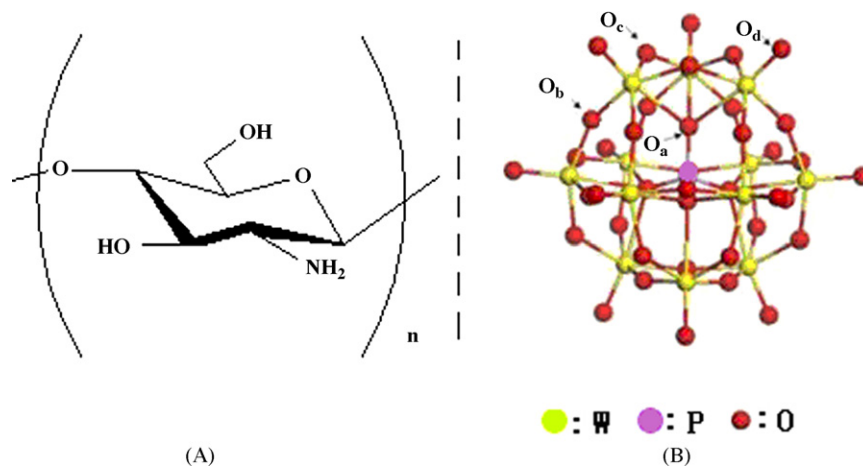Fig. 1. Molecular structures of chitosan (A) and $[PW_{12}O_{40}]^{3-}$ (B).

promising source of membrane materials [17,18]. As a kind of polycation, chitosan is extremely attractive to prepare PECs by electrostatic interaction with polyanions [19]. The acids and salts of heteropolyanions constitute a large category of compounds which have high potential for practical applications [20]. However, no report has been found about the PECs formed between chitosan and heteropolyanions so far. $[PW_{12}O_{40}]^{3-}$ is a kind of heteropolyanion and its molecular structure is shown in Fig. 1B. Phosphotungstic acid, $H_3PW_{12}O_{40}$, possesses a unique discrete ionic structure and exhibits extremely high proton conductivity [21]. As a good inorganic proton conductor, phosphotungstic acid has played an important role in developing proton-conducting membranes [22–32]. However, phosphotungstic acid is likely to be dissolved in the electrochemically produced water and leak out during the cell operation, thus performance would decay [24,25]. It has been found that the mixing of chitosan solution and phosphotungstic acid solution leads to electrostatic interactions to form PECs. Therefore, phosphotungstic acid can be fixed within the membranes through electrostatic interaction and the PECs of chitosan and phosphotungstic acid in the form of thin films can be considered as novel proton-conducting membranes.

In the present work, we firstly report the PECs formed between chitosan and phosphotungstic acid. The PECs as proton-conducting membranes for DMFCs were evaluated in terms of SEM, FTIR, TGA, swelling behavior, proton conductivity, and methanol permeability.

2. Experimental

2.1. Materials

Chitosan powder (Haidebei Ltd., China) has the degree of deacetylation of 95% and the molecular weight of $50000\,g\,mol^{-1}$. Phosphotungstic acid (Keggin-type) was supported by Aldrich and used as received. Sodium hydroxide and acetic acid were purchased from Beihua Fine Chemical, Beijing, China. The deionized water was prepared with Millipore ($>18.23\,M\Omega$).

2.2. Formation of insoluble PECs of chitosan and phosphotungstic acid

1% (w/v) chitosan solution was prepared by dissolving chitosan powder in 2% (v/v) acetic acid solution. After chitosan powder had been fully dissolved, this chitosan solution was filtered and deformed by leaving it quiescent at ambient temperature for 2 h. Then, 0.5 ml chitosan solution was put into a test-tube and then 0.5 ml 0.02 M phosphotungstic acid (Keggin-type) solution was added.

2.3. Membrane preparation and the stability of phosphotungstic acid in membrane

The chitosan solution above was poured onto a glass plate and left to dry via evaporation for 24 h and then heated at $60\,^{\circ}C$ for 6 h. The dried membranes were neutralized in 1 M NaOH and then washed thoroughly [33]. The membranes above were immersed in 0.05 M phosphotungstic acid solution for 24 h, and then were washed with deionized water and stored in deionized water prior to the different measurements.

The stability of phosphotungstic acid in the membranes was tested as follows: the prepared membranes (in the following referred to as PECs membranes) were washed thoroughly in water with stirring at $60\,^{\circ}C$ for 12 h, then the resulted membranes from the process were termed washed membranes. The percent weight of tungsten in PECs membranes and washed membranes were determined with inductively coupled plasma-mass spectrometry (ICP-MS), POEMS MODEL (TJA Corporation).

2.4. Scanning electron microscopy

The morphology of the PECs was characterized by a LEO 1525 FE-SEM scanning electron microscope.

2.5. Fourier transform infrared spectroscopy

The IR spectra (4000–$500\,cm^{-1}$, resolution $4\,cm^{-1}$) were recorded in absorbance mode with a Bruker Vertex 70 RTIR spectrometer.

2.6. Thermal analysis

The thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer thermal analysis system. Measurements were made heating from 40 to 650 °C, at a heating rate of 10 °C min^{-1} under N$_2$ atmosphere.

2.7. Swelling behavior

The swelling of membranes was evaluated by water uptake and dimensional change. The water uptake of the membranes was determined in the following way: membrane samples were equilibrated in deionized water at ambient temperature for 24 h, and the swollen membranes (W_w) were weighed as quickly as possible after surface-attached water on the membranes was removed with filter paper. Weight of dry membrane (W_d) was determined after being completely dried in 60 °C for 12 h. The water uptake was calculated using the following equation:

$$WU\,(\%) = \frac{W_w - W_d}{W_d} \times 100 \tag{1}$$

The dimensional change of the PECs was also investigated in the procedure above. The changes of thickness and width were calculated by the following equations:

$$\Delta L = \frac{L - L_d}{L_d}, \qquad \Delta T = \frac{T - T_d}{T_d} \tag{2}$$

where L and T are the length and thickness of the membranes, respectively, and the subscript "d" denotes the dry membranes.

2.8. Measurements of proton conductivity

Proton conductivity of the PECs and Nafion®112 membranes was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage. Impedance spectra were recorded using a Princeton Applied Research Model 273A Potentiostat (Model 5210 Frequency Response Detector, EG&G PARC, Princeton, NJ). The membranes were fixed in a measuring cell made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops [34]. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. The proton conductivity (σ) of the membranes was calculated using the following equation:

$$\sigma = \frac{L}{RA} \tag{3}$$

where L, R, and A denote the distance between the two inner gold wires, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

2.9. Measurements of methanol permeability

Methanol permeability of these membranes was determined utilizing a glass diffusion cell. This glass cell consisted of two chambers each approximately 100 ml; one chamber of the cell was filled with 2 M methanol solution, and the other with deionized water. The membrane (effective area 4.5 cm^2) was clamped between the two compartments which were kept under stirring during an experiment. The methanol concentration in the receptor chamber was measured versus time using a gas chromatography (Shimazu GC-14B) equipped with a thermal conductivity detector. The methanol permeability was calculated by the following equation:

$$C_B(t) = \frac{AP}{V_B L} C_A(t - t_0) \tag{4}$$

where $C_B(t)$ is the concentration of methanol measured in the receptor compartment as a function of time, V_B the volume of receptor compartment, and L and A are the thickness and effective area of membrane, respectively. P is the methanol permeability and can be determined from the slope of the plot of methanol concentration in the receptor compartment versus time.

3. Results and discussion

3.1. Formation and stability of insoluble PECs membranes

Insoluble PECs were formed in a test-tube when phosphotungstic acid solution was added. The percent weight of tungsten in the PECs membranes and washed membranes were 15.2 and 14.5%, respectively, therefore the percent weight of phosphotungstic acid (excluding crystalline water) in PECs membranes and washed membranes could be calculated. The results show that the percent weight of phosphotungstic acid in washed membranes (19.2%) is lower than that in PECs membranes (20.1%), which might be attributed to physically absorbed phosphotungstic acid. Based on the above phenomenon, phosphotungstic acid could be fixed by electrostatic interaction, which avoids the decrease of proton conductivity as a result of dissolving and leak of phosphotungstic acid.

3.2. Scanning electron microscopy

Part A and B of Fig. 2 show the surface and cross-sectional images of PECs. From the both images, it can be observed that the PECs membranes are homogeneous, dense, and with no obvious phase separation, which suggests that phosphotungstic acid does not recrystallize into large particles, but interact electrostatically with chitosan.

3.3. Fourier transform infrared spectroscopy

Figs. 3 and 4 present the IR spectrum of phosphotungstic acid, chitosan and PECs membranes. The IR spectra of phosphotungstic acid (Keggin-type) in Fig. 3 show four characteristic bands at 1080 (P–O$_a$), 983 (W=O$_d$), 891 (W–O$_b$–W) and 803 cm^{-1} (W–O$_c$–W) [31]. All of these characteristic bands of phosphotungstic acid (Keggin-type) are also presented in the spectra of PECs membranes, which indicates the preservation of the Keggin ion geometry in the PECs membranes. The bands at 951 and 785 cm^{-1} of the PECs membranes, which
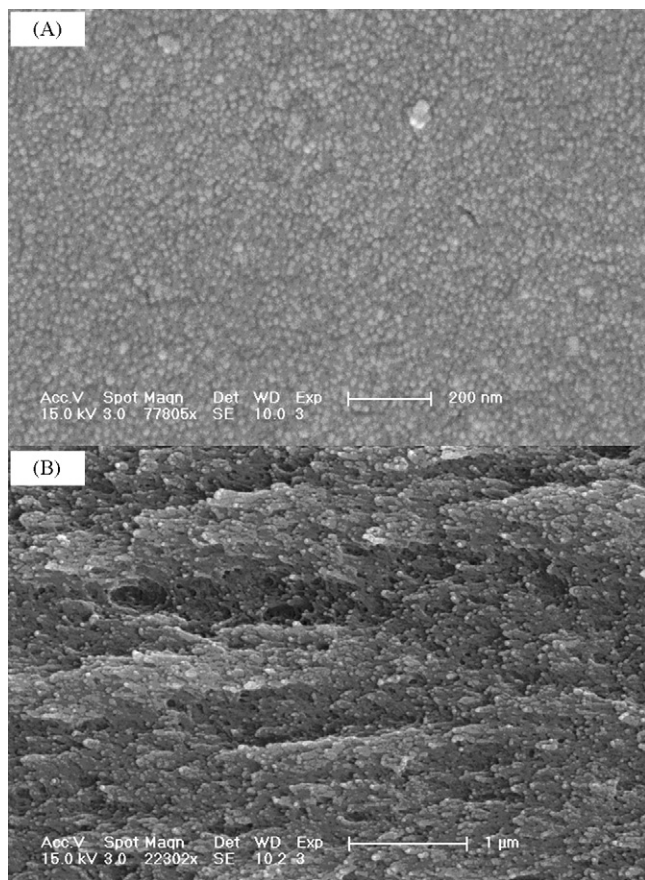
Fig. 2. SEM micrographs of the PECs membranes: (A) surface and (B) cross-section.

are attributed to $W=O_d$ band and $W-O_c-W$ band, decrease significantly in comparison with pure phosphotungstic acid. Such behavior indicates that the Keggin unit of phosphotungstic acid interacts (hydrogen bonding) with hydroxyl groups or amino groups of chitosan [29,30]. The peaks of the PEC membranes near 1077 and 890 cm^{-1} are ascribed mainly to P–O$_a$ band and
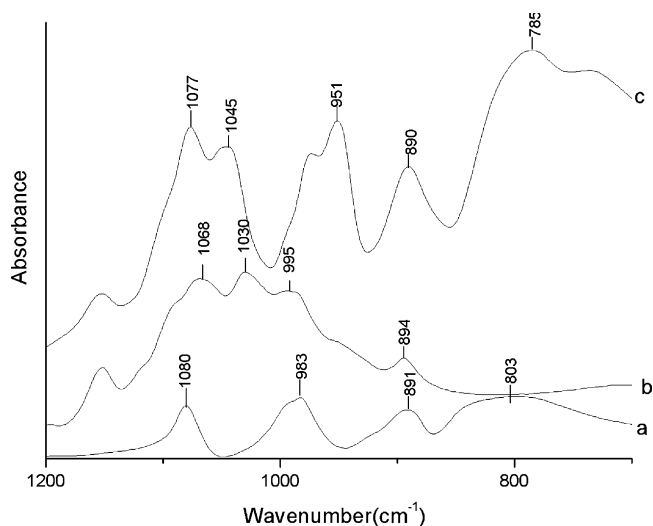

Fig. 3. The IR spectra in the region 700–1200 cm^{-1} of phosphotungstic acid (curve a), chitosan (curve b) and PECs membranes (curve c).
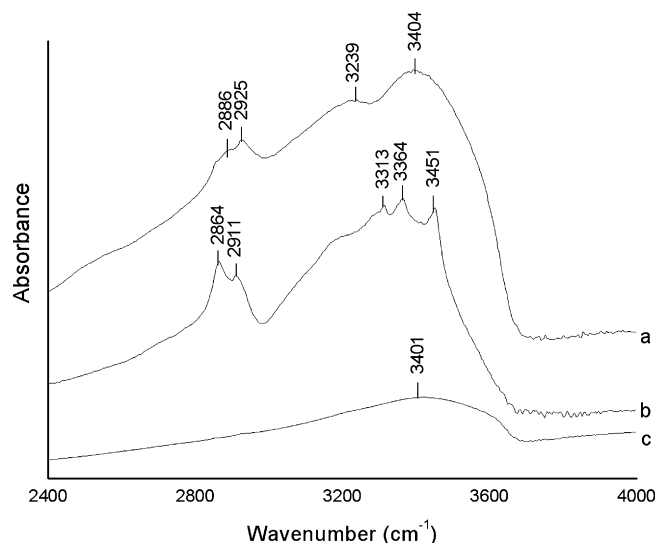

Fig. 4. The IR spectra in the region 2400–4000 cm^{-1} of phosphotungstic acid (curve a), chitosan (curve b) and PECs membranes (curve c).

W–O$_b$–W band, even partially to chitosan. The IR spectra of chitosan in Figs. 3 and 4 show a strong band at 3451 cm^{-1} for OH stretch, two strong bands at 3364 and 3313 cm^{-1} for NH stretch, and two weak CH stretch bands at 2910 and 2864 cm^{-1}. The bands at 1152, 1068 and 1030 cm^{-1} can be assigned to the saccharide structure [35]. In comparison with the IR spectra of chitosan, the IR spectra of PECs in Fig. 4 show a broad band at 3404 cm^{-1} for OH stretch, and single band at 3239 cm^{-1} for NH stretch.

3.4. Thermal analysis

The thermal stability of the PECs membranes was studied by thermogravimetric analysis, as shown in Fig. 5. There are three major weight loss stages around 40–150, 210–280, and 280–650 °C in the tested temperature range. The 5% weight loss takes place in the first stage and the lost components mainly are small molecules such as physically absorbed water and acetic acid [24]. The thermal degradation of PECs membranes takes
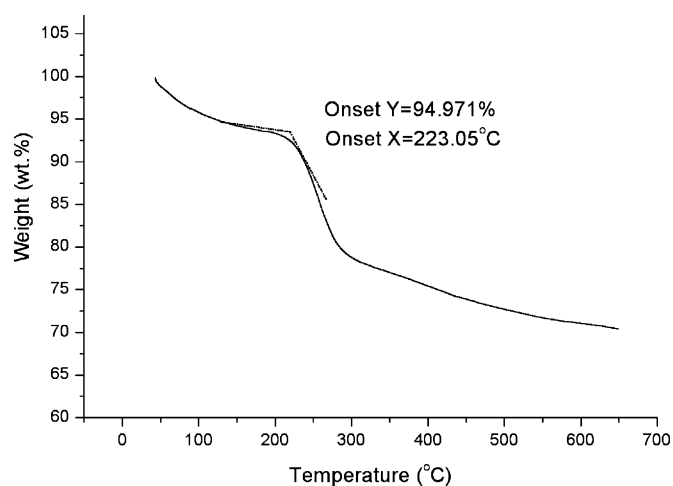

Fig. 5. TGA diagrams of the PECs membranes.

Table 1
Thickness, water uptake (WU), dimensional change (ΔL, ΔT) and methanol permeability (P) of the PECs and Nafion®112

Membranes	Thickness (μm)	WU (%)	ΔL (%)	ΔT (%)	P (10^{-7} cm^2 s^{-1})
PECs	42	17.0 ± 0.8	17.6 ± 0.3	17.6 ± 0.3	3.3 ± 0.7
Nafion112	50	15.0 ± 0.6	20.0 ± 0.2	20.8 ± 0.2	18 ± 4

place at a maximum rate in the temperature range from 210 to 280 °C. The 14% weight loss can be attributed to the release of structural water from phosphotungstic acid [29]. In the third stage, above 280 °C, the weight loss is assigned to structure collapse of phosphotungstic acid [29,32] and thermal decomposition of polymeric netwok. So it can be concluded that the PECs membranes are stable at desired operating temperatures (<100 °C) for DMFCs.

3.5. Swelling behavior

The swelling property has a profound effect on proton transport and dimensional stability of proton-conducting membranes. Proton transport requires a significant amount of water to coordinate with protons. However, excessively high levels of water uptake can result in the dimensional change of membranes, which leads to the loss of mechanical properties. Table 1 shows the results of water uptake and dimensional change for the PECs and Nafion®112 membranes. The water uptake of the PECs is 17%, slightly higher than that of Nafion®112 (15%). The dimensional change (ΔL, ΔT) of PECs membranes is smaller than that of Nafion®112 (about 20%). Furtherly, the dimensional change of PECs membranes both in length and in thickness are all the same (17.6%), indicating an isotropic property of the PECs membranes. The experimental results above indicate that the PECs membranes display better swelling property than Nafion®112.

3.6. Proton conductivity

Fig. 6 shows the variations in proton conductivity with temperature for the PECs membranes. The conductivity of the PECs
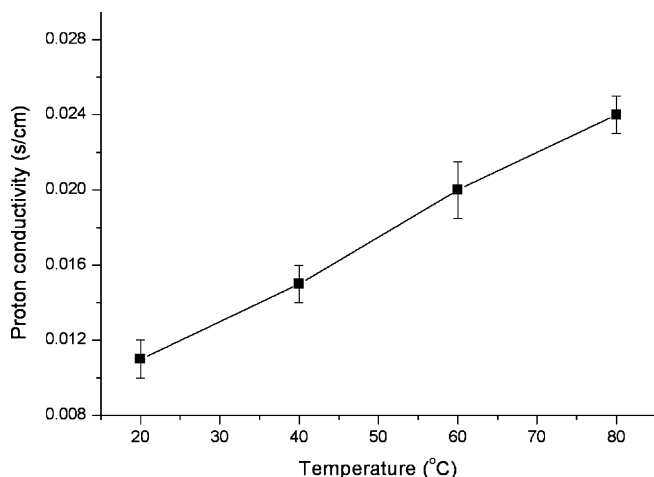
membranes is measured at four different temperatures. The PECs membranes exhibit a marked increase in proton conductivity with increasing temperature and reach the highest proton conductivity of 0.024 S cm^{-1} at 80 °C in the tested temperature range. The conductivity of PECs is in the order of 10^{-2} S cm^{-1}, which is inferior to that of Nafion®112 membranes (in the order of 10^{-1} S cm^{-1}).

The change of proton conductivity with temperature follows the Arrhenius relationship as depicted in Fig. 7. From the Arrhenius plots, the activation energy can be calculated, which is 15.2 kJ mol^{-1}. In solid phosphotungstic acid with crystalline water, the proton migration can be ascribed to the vehicle mechanism [36]. For the Grotthuss mechanism, activation energy for proton conduction is around 14–40 kJ mol^{-1} [16] and the value obtained for the PECs membranes falls into the range. We suspect that both the vehicle mechanism and the Grotthuss mechanism are responsible for the proton conduction of PECs membranes.

3.7. Methanol permeability

The methanol permeability of the PECs and Nafion®112 membranes are measured at ambient temperature, respectively, and the results are shown in Table 1. The methanol permeability of the PECs is 3.3×10^{-7} cm^2 s^{-1}; while the permeability of Nafion®112 is 1.8×10^{-6} cm^2 s^{-1}. The permeability of PECs is approximately 1/6 of that of Nafion®112. This indicates that methanol cross-over may significantly be reduced if the PECs are used in DMFCs.

The polymer electrolyte membranes applied in DMFCs should possess simultaneously high proton conductivity and low methanol permeability. Membrane performances can be
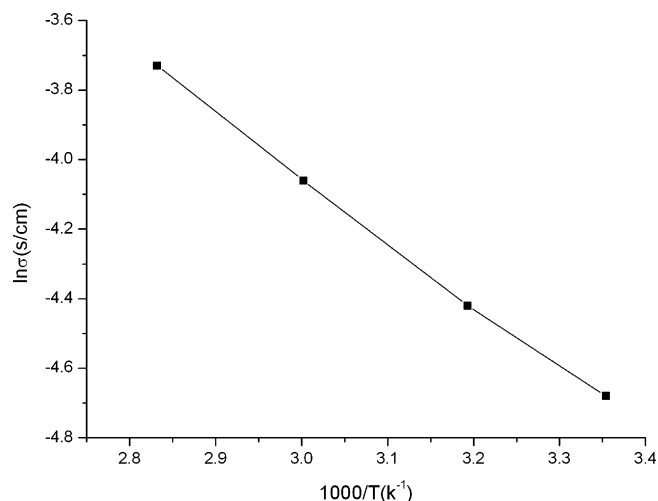

Fig. 6. Proton conductivity of the PECs membranes at different temperatures under fully hydrated conditions.

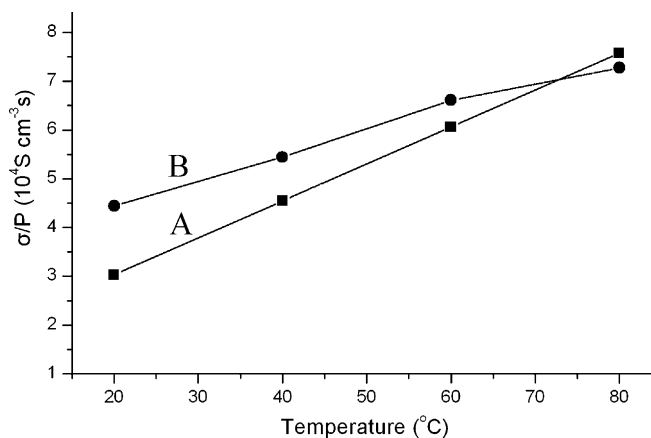Fig. 7. Arrhenius plots for proton conductivity of PECs membranes.

Fig. 8. Ratio of conductivity to methanol permeability (σ/P) for the PECs (A) and Nafion®112 (B) membranes at different temperature.

estimated from the ratio of proton conductivity (σ) to methanol permeability (P). That is to say, the higher the value of σ/P is, the better the performance of the membrane would be [31]. Fig. 8 shows the results of σ/P for the PECs and Nafion®112 at different temperature. It can be noticed that: (1) both the ratio of σ/P for the PECs and that for Nafion®112 increase with elevated temperature, yet the ratio of σ/P for the PECs changes comparatively faster than that for Nafion®112; (2) the ratio of σ/P for the PECs and that for Nafion®112 are close to each other in the tested temperature range; in other words, the PECs are equivalent to Nafion® 112 in terms of their performance.

4. Conclusions

Polyelectrolyte complexes (PECs) of chitosan and phosphotungstic acid have been prepared and evaluated as novel proton-conducting membranes for direct methanol fuel cells. The homogeneous PECs membranes show good thermal stability up to 210 °C and exhibit a relatively high proton conductivity (σ, 0.024 S cm^{-1} at 80 °C) and a low methanol permeability (P, 3.3×10^{-7} cm^2 s^{-1}). In addition, phosphotungstic acid can be fixed within the membrane through strong electrostatic interactions. Therefore, the PECs are promising proton-conducting materials and have great potential for application in DMFCs.

Acknowledgements

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