



# Chitosan/heteropolyacid composite membranes for direct methanol fuel cell

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## ABSTRACT

As inorganic proton conductors, phosphomolybdic acid (PMA), phosphotungstic acid (PWA) and silicotungstic acid (SiWA) are extremely attractive for proton-conducting composite membranes. An interesting phenomenon has been found in our previous experiments that the mixing of chitosan (CS) solution and different heteropolyacids (HPAs) leads to strong electrostatic interaction to form insoluble complexes. These complexes in the form of membrane (CS/PMA, CS/PWA and CS/SiWA composite membranes) have been prepared and evaluated as novel proton-conducting membranes for direct methanol fuel cells. Therefore, HPAs can be immobilized within the membranes through electrostatic interaction, which overcomes the leakage problem from membranes. CS/PMA, CS/PWA and CS/SiWA composite membranes were characterized for morphology, intermolecular interactions, and thermal stability by SEM, FTIR, and TGA, respectively. Among the three membranes, CS/PMA membrane was identified as ideal for DMFC as it exhibited low methanol permeability ( $2.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ) and comparatively high proton conductivity ( $0.015 \text{ S cm}^{-1}$  at  $25^\circ \text{C}$ ).

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## 1. Introduction

Direct methanol fuel cells (DMFCs) are promising candidates for portable devices or transportation applications in view of their high energy density, easy manipulation, and high efficiency [1–3]. Polymer electrolyte membranes, a crucial component in the DMFCs separating the cathode and anode, function as proton conductor as well as methanol separator between the cathode and anode. Nowadays, perfluorosulfonic acid membranes, such as Nafion<sup>®</sup> membranes, are the primary membranes used in the DMFCs. Although commercial Nafion<sup>®</sup> membranes have high proton conductivity, they do not meet the requirement for low methanol permeability especially at low temperatures ( $<100^\circ \text{C}$ ) [4]. Methanol permeation results in reducing the open-circuit potential (OCP) and poisoning the electrocatalysts at the cathode.

Various attempts have been made to overcome the drawbacks of Nafion<sup>®</sup> membranes for DMFC applications. The approaches described are diverse, ranging from doping with inorganic materials such as sulfonated montmorillonite [2], silica [5], silica/phosphotungstic acid [6], zeolite [7] and zirconium phosphate [8] etc., in situ polymerization with poly(1-methylpyrrole) [9] or polyfurfuryl alcohol [10] to modify the surface of Nafion<sup>®</sup> [11–14]. Most of the modified Nafion<sup>®</sup> membranes indeed reduce methanol permeation, but their proton conductivity is often markedly lower

than that of the original ones. On the other hand, enormous efforts have been made to develop new alternatives. Pore-filling membranes, which are composed of a porous substrate and a filling polymer electrolyte, have shown good performance [15,16]. Polymer materials based on the arylene main chain such as poly(ether ether ketone)s [17] and polybenzimidazole [18] 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 [19] and polysulfone/heteropolyacid [20], have also been studied.

Solid heteropolyacids (HPAs) possess a unique discrete ionic structure including heteropoly anions and countercations ( $\text{H}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ , etc.), and consequently exhibit extremely high proton mobility [21]. Such high ionic conductivity properties make HPAs very attractive for fuel cells. Phosphomolybdic acid (PMA) as a solid-protonic electrolyte in the fuel cells was first investigated by Nakemura et al. [22]. In addition, many proton-conducting composite membranes doped with HPAs have been reported [23–33]. However, HPAs are likely to be dissolved in water and leak out during the cell operation, ultimately resulting in degradation in performance [23,30]. This problem could be resolved by introducing the electrostatic interactions between chitosan and HPAs. It has been found that the mixing of chitosan solution and HPAs solution leads to the formation of insoluble complexes. Therefore, HPAs can be immobilized in the membranes through electrostatic interaction. Generally, oppositely charged polyions (polycations or polyanions) interact electrostatically to form polyelectrolyte complexes. Such complexes as proton-conducting membranes have

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been reported in the literatures [34–36]. Chitosan is a natural and low-cost biopolymer with unique properties such as biocompatibility, nontoxicity, chemical and thermal stability, and has been widely studied as a promising source of membrane materials [37,38]. As a kind of polycation, chitosan is extremely attractive to prepare polyelectrolyte complexes through electrostatic interactions with polyanions [39]. The acids and salts of heteropolyanions constitute a large category of compounds, thus a variety of polyelectrolyte complexes would be formed between heteropolyanions and chitosan.

In this study, we use three commercially available HPAs (Keggin-type): phosphomolybdic acid, phosphotungstic acid (PWA) and silicotungstic acid (SiWA) to prepare three kinds of CS/HPAs composite membranes (CS/PMA, CS/PWA and CS/SiWA). These composite membranes were evaluated as novel proton-conducting materials for DMFC in terms of SEM, FTIR, TGA, mechanical properties, ion exchange capacity, water uptake, 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  $50000 \text{ g mol}^{-1}$ . Phosphomolybdic acid (PMA,  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ ), phosphotungstic acid (PWA,  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) and silicotungstic acid (SiWA,  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ ) were purchased from Beijing Chemical Reagent Factory and used as received. Nafion<sup>®</sup> membranes were obtained from DuPont. Sodium hydroxide and acetic acid were purchased from the Bei Hua Fine Chemical, Beijing, China. The deionized water was prepared with Millipore ( $>18.23 \text{ M}\Omega$ ).

### 2.2. Formation of insoluble complexes of chitosan and HPAs

1% (w/v) chitosan solution was prepared by dissolving chitosan powder in 2% (v/v) acetic acid solution. After the chitosan powder was fully dissolved, the solution was filtered and deformed by leaving it quiescent at ambient temperature for 2 h. 2 ml of 0.02 M PMA, PWA and SiWA solutions were put into three different test-tubes and then 2 ml chitosan solution was added into each of them.

### 2.3. Preparation of composite membranes

Chitosan/heteropolyacids composite membranes (CS/HPAs) were prepared in an infiltration and self-assembly method. As an example, chitosan/phosphomolybdic acid (CS/PMA) was used here to describe the sample preparation procedure. The 1% (w/v) chitosan solution was poured onto a glass plate and left to dry via evaporation for 24 h and then heated at  $60^\circ\text{C}$  for 6 h. After the dried membranes were neutralized in 1 M NaOH and then washed thoroughly [40], they were immersed in 0.05 M phosphomolybdic acid solution for 24 h and then were washed with deionized water and stored in deionized water prior to the different measurements.

### 2.4. The stability of HPAs in membranes

The stability of HPAs in composite membranes was tested as follows: the CH/HPAs membrane was washed thoroughly in water with stirring at  $80^\circ\text{C}$  for 24 h, and then the resulted membranes from this process were termed as W-CH/HPAs membrane. The percent weight of molybdenum (or tungsten) in the CH/HPAs membrane and the W-CH/HPAs membrane were determined with

inductively coupled plasma–mass spectrometry (ICP–MS), POEMS MODEL (TJA Corporation).

### 2.5. Characterizations of composite membranes

Scanning electron microscope (SEM) was carried out on a Philips XL30 ESEM at 30 kV.

IR spectra ( $4000\text{--}500 \text{ cm}^{-1}$ , resolution  $4 \text{ cm}^{-1}$ ) were recorded with a Bruker Vertex 70 FTIR spectrometer.

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

Tensile measurement was performed with a mechanical tester Instron-1211 instrument at a speed of  $10 \text{ mm min}^{-1}$ .

The swelling of membranes was evaluated by the water uptake 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 membrane samples was removed with filter paper. Weight of dry membranes ( $W_d$ ) was determined after completely drying in  $60^\circ\text{C}$  for 12 h. The water uptake was calculated by using the following equation:

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

Ion exchange capacity (IEC) was determined through titration. The membranes in the  $\text{H}^+$  form were immersed in a 1-M NaCl solution for 24 h to liberate the  $\text{H}^+$  ions (the  $\text{H}^+$  ions in the membrane were replaced by  $\text{Na}^+$  ions). The  $\text{H}^+$  ions in solution were then titrated with 0.01 M NaOH.

The proton conductivity of the CS/HPAs membranes was measured by a four-electrode AC impedance method from 0.1 Hz to 100 KHz, 10 mV ac perturbation and 0.0V 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

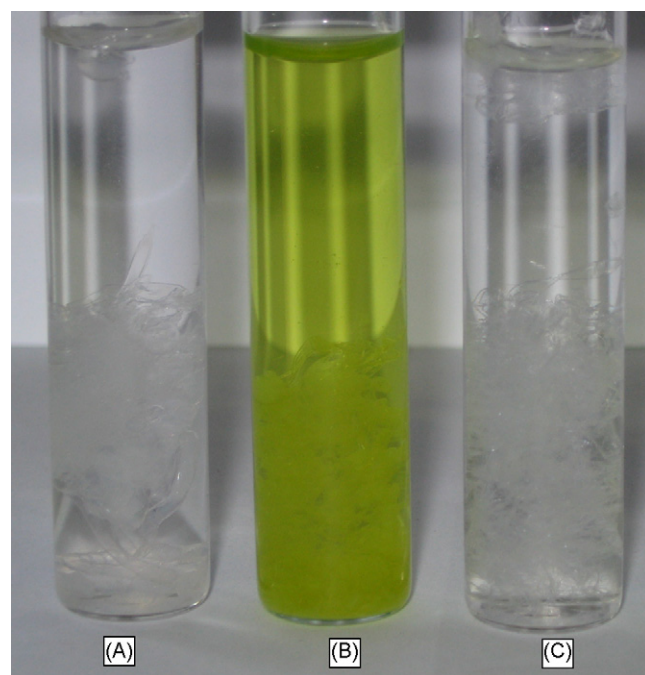
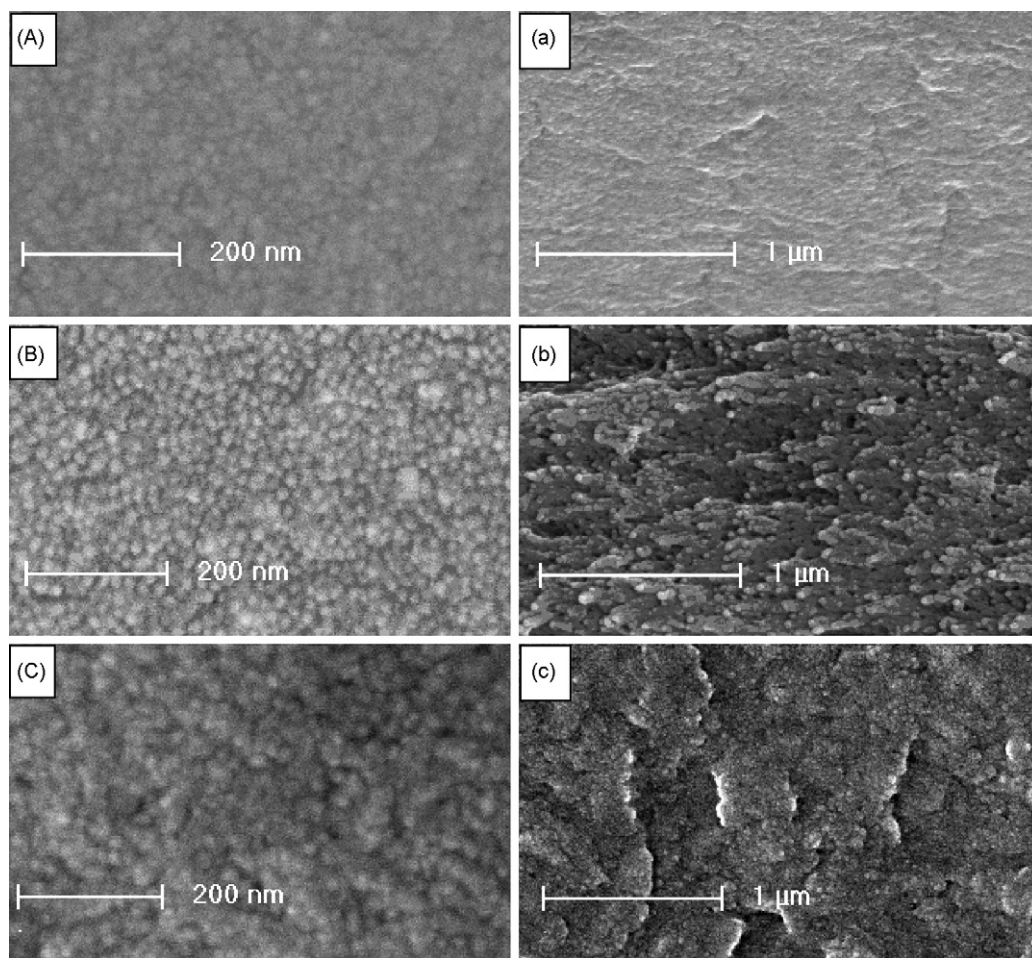


Fig. 1. Electrostatic interaction between chitosan and HPAs: (A) chitosan and PMA, (B) chitosan and PWA and (C) chitosan and SiWA.



**Fig. 2.** SEM pictures of the CS/HPAs membranes: (A) surface of CS/PMA; (B) surface of CS/PWA; (C) surface of CS/SiWA; (a) cross-section of CS/PMA; (b) cross-section of CS/PWA and (c) cross-section of CS/SiWA.

feed current to the sample and two inner gold wires to measure the voltage drops [41].

The methanol permeability of these membranes was determined and calculated by the method described in the literature [36]. The methanol concentration in the receptor chamber was measured versus time by using a gas chromatograph (Shimazu GC-14B) equipped with a thermal conductivity detector.

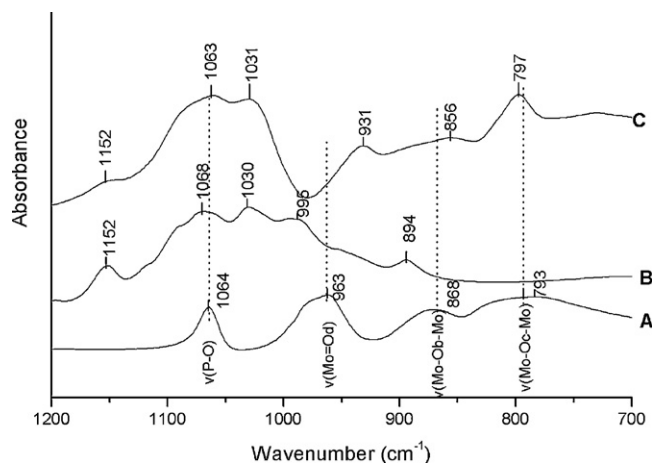
### 3. Results and discussion

#### 3.1. Formation of insoluble CS/HPAs of chitosan and HPAs

Chitosan is a weak base and its solubility is pH-dependent. When the pH value exceeds its  $pK_a$  (about 6.3), chitosan becomes insoluble [42,43]. When the chitosan solution was added into the HPAs solution, insoluble complexes were formed in those tubes, as shown in Fig. 1. The same phenomenon occurred even when the pH value of the chitosan solution was changed. These results suggest that: firstly, there is a strong electrostatic interaction between HPAs and chitosan, which makes HPAs immobilized in the complexes, a mechanism to prevent the HPAs from water leakage from membranes. Secondly, the traditional method (mixing of the chitosan solution with inorganic fillers or polyelectrolyte solution in different proportions followed by casting) cannot be applied in the preparation of CS/HPAs composite membranes. Instead, the procedure of infiltration and self-assembly should be used, as detailed in the previous section.

#### 3.2. The stability of HPAs in membranes

The percent weight of the HPAs (excluding crystalline water) in the CS/HPAs membranes and W-CS/HPAs can be calculated by the percent weight of molybdenum (or tungsten). The percent weights of the HPAs in the three W-CS/HPAs membranes were 24.5% (PMA), 19.0% (PWA) and 21.4% (SiWA), respectively; while



**Fig. 3.** IR spectra in the region 700–1200  $\text{cm}^{-1}$  of PMA (curve A), chitosan (curve B) and CS/PMA (curve C).

the percent weight of the HPAs in the three CS/HPAs membranes were calculated to be 26.5% (PMA), 20.1% (PWA) and 22.9% (SiWA), respectively. Clearly the percent weight of the HPAs in the W-CS/HPAs membranes is slightly lower than that in the CS/HPAs membranes, which might be attributed to dissolving and leaking of physically absorbed HPAs. Consequently, the HPAs are very stable in the CS/HPAs membranes and could be stabilized by the strong electrostatic interaction.

### 3.3. Scanning electron microscopy

Fig. 2 shows the surface and cross-sectional images of the three CS/HPAs composite membranes. It is clearly seen from this figure that the CS/HPAs composite membranes are homogeneous with no phase separation, implying that the HPAs do not recrystallize into large particles, but electrostatically interact with chitosan to form the CS/HPAs.

### 3.4. Fourier transform infrared spectroscopy

Fig. 3 presents the IR spectra of PMA, chitosan and CS/PMA membranes. The IR spectra of PMA (Keggin-type) in Fig. 3A shows four characteristic bands at 1064, 963, 868, 793  $\text{cm}^{-1}$ , and these bands are ascribed to the stretching vibrations  $\nu_{\text{as}}(\text{P-O})$ ,  $\nu_{\text{as}}(\text{M}_\text{O}=\text{O})$ ,  $\nu_{\text{as}}(\text{M}_\text{O}-\text{O}_\text{c}-\text{M}_\text{O})$  and  $\nu_{\text{as}}(\text{M}_\text{O}-\text{O}_\text{e}-\text{M}_\text{O})$ , respectively [44]. The bands at 931, 856 and 797  $\text{cm}^{-1}$  of the CS/PMA membranes are attributed to  $\nu_{\text{as}}(\text{M}_\text{O}=\text{O})$ ,  $\nu_{\text{as}}(\text{M}_\text{O}-\text{O}_\text{b}-\text{M}_\text{O})$  and  $\nu_{\text{as}}(\text{M}_\text{O}-\text{O}_\text{c}-\text{M}_\text{O})$ , respectively. The peak of the CS/HPAs membranes at 1063  $\text{cm}^{-1}$  is ascribed to  $\nu_{\text{as}}(\text{P-O})$  and the saccharide structure of chitosan. All of these characteristic bands are also presented in the spectra of the CS/PMA membranes, which indicates the preservation of the Keggin ion geometry in the CS/PMA membranes. In the IR spectra of CS, the bands at 1152, 1068 and 1030  $\text{cm}^{-1}$  can be assigned to the saccharide structure [45].

Fig. 4 presents the IR spectra of PWA, chitosan and CS/PWA membranes and Fig. 5 presents IR spectra of SiWA, chitosan and CS/SiWA membranes. Similarly, all characteristic bands of PWA and SiWA are also appeared in the spectra of the CS/PWA membranes and the CS/SiWA membranes respectively, which confirms the preservation of the Keggin ion geometry in the CS/HPAs membranes.

### 3.5. Thermal analysis

The thermal stability of the CS/PMA, CS/PWA and CS/SiWA membranes was studied by thermogravimetric analysis, as shown in

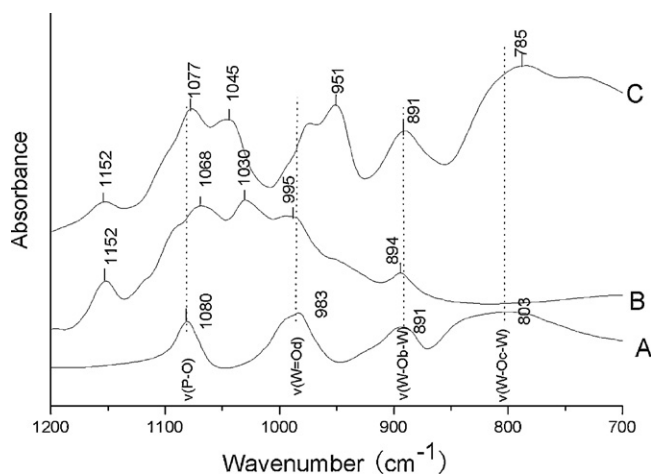


Fig. 4. IR spectra in the region 700–1200  $\text{cm}^{-1}$  of PWA (curve A), chitosan (curve B) and CS/PWA (curve C).

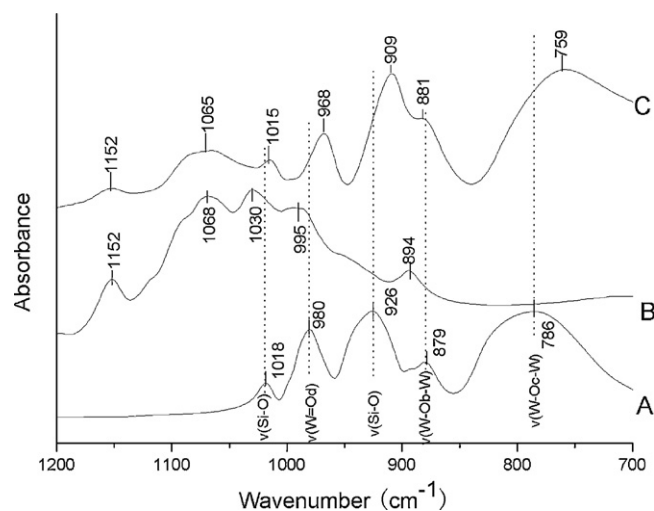


Fig. 5. IR spectra in the region 700–1200  $\text{cm}^{-1}$  of SiWA (curve A), chitosan (curve B) and CS/SiWA (curve C).

Fig. 6. The degradation processes of the three CS/HPAs composite membranes are similar. There are three major weight loss stages (40–120, 200–275 and 275–650  $^{\circ}\text{C}$  for CS/PMA, 40–120, 210–280 and 280–650  $^{\circ}\text{C}$  for CS/PWA and 40–120, 220–315 and 315–650  $^{\circ}\text{C}$  for CS/SiWA) in the tested temperature range. Around 6% weight loss takes place in the first stage and the lost components mainly are small molecules such as physically absorbed water and acetic acid. The thermal degradation of the CS/HPAs composite membranes

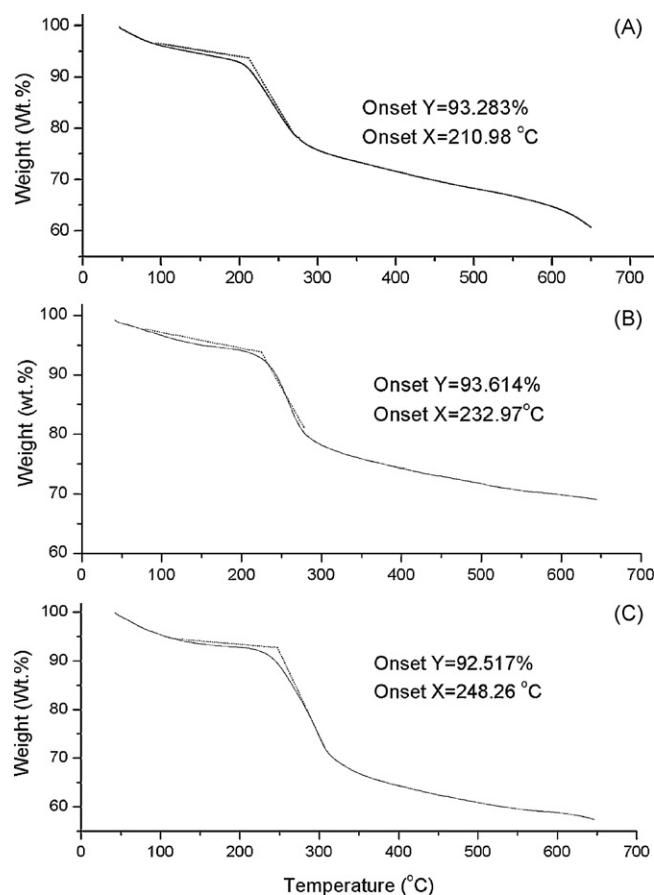


Fig. 6. TGA diagrams of CS/HPAs membranes: (A) CS/PMA, (B) CS/PWA and (C) CS/SiWA.

**Table 1**  
Break strength, elongation at break, water uptake (WU), IEC, proton conductivity ( $\sigma$ , 25 °C), methanol permeability ( $P$ ) and selectivity factor ( $\sigma/P$ ) of CH/HPAs, CS and Nafion® 117.

Membranes	Break strength (MPa)	Elongation at break (%)	WU (%)	IEC (mmol g <sup>-1</sup> )	$\sigma$ (S cm <sup>-1</sup> )	$P$ (10 <sup>-7</sup> cm <sup>2</sup> s <sup>-1</sup> )	$\sigma/P$ (10 <sup>4</sup> S s cm <sup>-3</sup> )
CS/PMA	38.7	4.3	18.6	0.46	0.015	2.7	5.6
CS/PWA	36.5	4.7	17.0	0.38	0.0122	3.3	3.7
CS/SiWA	32.3	5.2	17.4	0.41	0.01	3.8	2.6
CS	20.1	7.4	11.6	0.22	0.0035	–	–
Nafion® 117	–	–	15.2	0.90	0.084	24	3.5

takes place at a maximum rate in the second stage. The weight loss (17% for CS/PMA, 14% for CS/PWA and 21% for CS/SiWA) can be attributed to the release of structural water from PMA [31] and the scission of the ether linkage in chitosan backbone [46]. In the third stage, above 290 °C, the weight loss is assigned to structure collapse of the HPAs [31] and the thermal decomposition of glucosamine residue [33,46]. So it can be concluded that the CS/HPAs composite membranes are stable at desired operating temperatures (<100 °C) for DMFCs.

### 3.6. Mechanical properties

The break strength and elongation at break of CS/HPAs and CS membranes are given in Table 1. From the results, it can be observed that CS/HPAs membranes exhibit much larger break strength than CS membranes, but smaller elongation at break than CS membranes. These results may be attributed to the strong electrostatic interaction between HPAs and chitosan, which results in an increase in the rigidity and a reduction in elongation at break.

### 3.7. Water uptake and IEC

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 the membranes, which leads to the loss of their mechanical properties. Table 1 shows the results of water uptake for CS/HPAs and Nafion® 117 membranes. The water uptakes of CS/PMA, CS/PWA and CS/SiWA are 18.6%, 17.0% and 17.4% respectively, markedly higher than that of CS (11.6%) and Nafion® 117 (15.2%), which is due to the distinct hydrophilicity of the HPAs (Keggin-type) and CS.

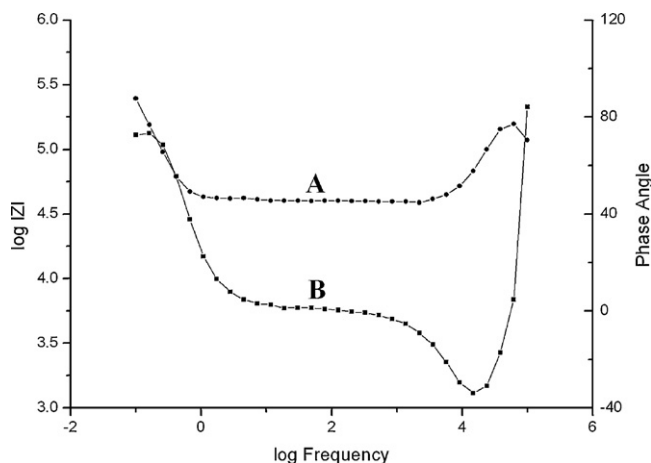
Ion exchange capacity is an indirect and reliable approximation of the proton conductivity. The IEC values of all the membranes

are listed in Table 1. The IEC values of CS/HPAs range from 0.38 mmol g<sup>-1</sup> for CS/PWA to 0.46 mmol g<sup>-1</sup> for CS/PMA, which are lower than that of the Nafion® 117 (0.9 mmol g<sup>-1</sup>), but much higher than that of the CS membranes (0.22 mmol g<sup>-1</sup>). This result is consistent with that of proton conductivity.

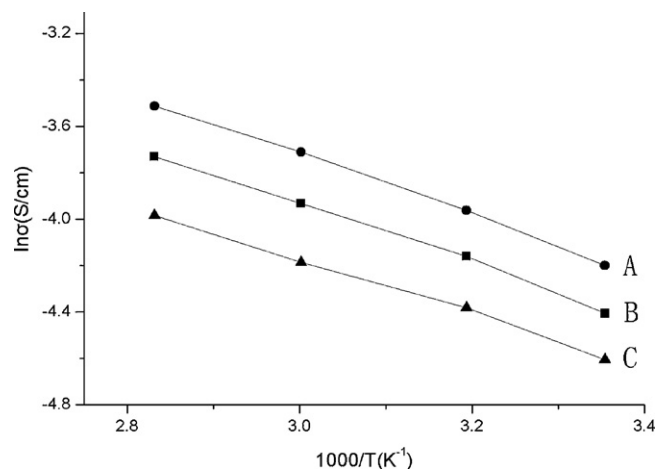
### 3.8. Proton conductivity

Proton conductivity ( $\sigma$ ) is one of the most important properties for proton-conducting membranes used in fuel cell. Fig. 7 shows typical impedance spectrum of CS/PMA membrane obtained using four-electrode longitudinal geometry. The  $\sigma$  values of the CS/HPAs, CS and Nafion® 117 membranes at 25 °C were listed in Table 1. Among the three membranes, the CS/PMA membranes exhibited higher proton conductivity than the CS/PWA and CS/SiWA, which is mainly because the proton conductivity of PMA is higher than those of PWA and SiWA. Note that currently no standard methods are adopted to determine proton conductivity, and the  $\sigma$  value of same membrane reported in the literatures were not always consistent due to the different test methods and various conditions applied. For example, the  $\sigma$  value of chitosan reported by Ramírez-Salgado et al. [47] and Wan et al. [48] was in the order of 10<sup>-4</sup> S cm<sup>-1</sup>, much lower than that (in the order of 10<sup>-2</sup> S cm<sup>-1</sup>) obtained by Jiang et al. [34] and Smitha et al. [35]. In this study, the  $\sigma$  values of the Nafion® 117 and CS membranes are 8.4 × 10<sup>-2</sup> and 3.5 × 10<sup>-3</sup> S cm<sup>-1</sup>. The  $\sigma$  value of CS/HPAs is lower than that of the Nafion® 117, but much higher than that of the CS membranes.

Fig. 8 shows the proton conductivity as a function of temperature. The  $\sigma$  values of the CS/HPAs composite membranes increase with increasing temperature and the change of  $\sigma$  values with temperature follows the Arrhenius relationship. From the Arrhenius plots, the activation energy ( $E_a$ ) can be calculated. The  $E_a$  of the CS/PMA, CS/PWA and CS/SiWA membranes is 11.2, 12.3 and 10.4 kJ mol<sup>-1</sup>, lower than that for only “jump” mechanism which was reported to be 14–40 kJ mol<sup>-1</sup> [49]. It has been gener-



**Fig. 7.** Typical impedance spectrum of CS/PMA membrane obtained using four-electrode longitudinal geometry: (A) log  $|Z|$  and log frequency, and (B) phase angle and log frequency.



**Fig. 8.** Arrhenius plots for proton conductivity of CS/HPAs membranes: (A) CS/PMA, (B) CS/PWA and (C) CS/SiWA.

ally accepted that Grotthuss mechanism and vehicle mechanism are commonly adopted in discussing the proton transfer. In the CS/HPAs membranes, HPAs are preserved in the form of the Keggin ion geometry, and in solid HPAs (Keggin-type) with crystalline water, the proton migration can be ascribed to the vehicle mechanism [50]; meanwhile, membranes could hold much water due to the distinct hydrophilicity of CS. Therefore, HPAs and CS construct continuous hydrophilic channels, which enables protons to transport by vehicle mechanism in the form of hydronium ions. Due to electrostatic interaction between CS and HPAs, CS/HPAs membranes contain numerous hydroxy group,  $-\text{NH}_3^+$  and heteropolyanions, the proton transferred along the ionic bonds and hydrogen bonds by “jumping” from one function group to another. Therefore we suggest that both the vehicle mechanism and the Grotthuss mechanism are responsible for the proton conductivity of the CS/HPAs membranes.

### 3.9. Methanol permeability

The methanol permeability of the CS/HPAs and Nafion<sup>®</sup>117 membranes were measured at ambient temperature, respectively, and the results are shown in Table 1. The methanol permeability of the CS/PMA, CS/PWA and CS/SiWA is  $2.7 \times 10^{-7}$ ,  $3.3 \times 10^{-7}$  and  $3.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , much lower than that of the Nafion<sup>®</sup>117 ( $2.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ). Compared to the Nafion<sup>®</sup>117, the CS/HPAs show strong resistance to methanol permeability. This indicates that methanol cross-over could be significantly reduced if the CS/HPAs were used in DMFCs.

The polymer electrolyte membranes applied in DMFCs should possess simultaneously high proton conductivity and low methanol permeability. Although the ratio of proton conductivity ( $\sigma$ ) to methanol permeability ( $P$ ) alone is not sufficient to evaluate the membranes performance, it is often used to describe and compare the total performances of various membranes. A high  $\sigma/P$  value implies a better performance of the membrane. The  $\sigma/P$  values obtained for the three CS/HPAs and Nafion<sup>®</sup>117 membranes are shown in Table 1. It can be found that the  $\sigma/P$  values obtained for the CS/PMA and CS/PWA are higher than that for the Nafion<sup>®</sup>117, but not for the CS/SiWA.

## 4. Conclusions

The three CS/HPAs composite membranes (CS/PMA, CS/PWA and CS/SiWA) have been prepared by an infiltration and self-assembly method, and evaluated as novel proton-conducting membranes for DMFC. HPAs can be immobilized within the membranes through electrostatic interaction, which overcomes the leakage problem from membranes. The homogeneous CS/HPAs membranes show good thermal stability up to 200 °C and high water uptake. FTIR spectra indicate the preservation of the Keggin ion geometry in the CS/HPAs membranes. Among the three CS/HPAs membranes, the CS/PMA membrane exhibits the highest proton conductivity and the lowest methanol permeability. Accordingly, the  $\sigma/P$  value of  $5.6 \times 10^4 \text{ S s cm}^{-3}$  for the CS/PMA membrane was obtained, about two times higher than that for Nafion<sup>®</sup>117. Therefore, the CS/HPAs composite membranes (especially the CS/PMA membrane) are promising proton-conducting materials and have great potential for application in DMFCs.

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