



Highly conductive, methanol resistant fuel cell membranes fabricated by layer-by-layer self-assembly of inorganic heteropolyacid

Chengji Zhao^{a,*}, Haidan Lin^a, Zhiming Cui^b, Xianfeng Li^c, Hui Na^{a,*}, Wei Xing^b

^a Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Qianjin Street 2699#, Changchun 130012, Jilin, PR China

^b Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

^c Proton Exchange Membrane Fuel Cell Key Materials and Technology Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

ARTICLE INFO

Article history:

Received 31 March 2009

Received in revised form 13 May 2009

Accepted 13 May 2009

Available online 22 May 2009

Keywords:

Sulfonated poly(arylene ether ketone)

Proton-exchange membrane

Layer-by-layer

Chitosan

Phosphotungstate

ABSTRACT

Layer-by-layer (LBL) self-assembly is a simple and elegant method of constructing organic–inorganic composite thin films from environmentally benign aqueous solutions. In this paper, we utilize this method to develop proton-exchange membranes for fuel cells. The multilayer film is constructed onto the surface of sulfonated poly(arylene ether ketone) (SPAEK–COOH) membrane by LBL self-assembly of polycation chitosan (CTS) and negatively charged inorganic particle phosphotungstic acid (PTA). The highly conductive inorganic nanoparticles ensure SPAEK–COOH–(CTS/PTA)_n membranes to maintain high proton conductivity values up to 0.086 S cm⁻¹ at 25 °C and 0.24 S cm⁻¹ at 80 °C, which are superior than previous LBL assembled electrolyte systems. These multilayer systems also exhibit extremely low water swelling ratio and methanol permeability. The selectivity of SPAEK–COOH–(CTS/PTA)₈ is 2 orders of more than Nafion[®] 117, which is attractive in direct methanol fuel cells (DMFCs).

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are considered as promising candidates for transportation, distributed power, and portable power applications, as they can be operated at low temperatures and without any fuel processing equipment [1,2]. Superior proton conductivity, thermal and chemical durability, and oxidative stability have made perfluorosulfonic polymers (Nafion[®]) as commonly used electrolytes in DMFCs [3]. However, methanol readily migrates through Nafion[®] membrane between the electrodes and causes reduction of DMFCs voltage and poisoning at cathode. Furthermore, high cost, difficulty in synthesizing and processing have impeded their commercial development [4–6]. Considerable efforts to explore new PEM materials have been carried out. Sulfonated aromatic polymers, including poly(aryl ether ketones) (SPAEEKs), fell into this category [7–9]. The membranes require a high sulfonation level to achieve sufficient proton conductivity. Unfortunately, increasing loading of acidic groups leads to undesirable high swelling and excessive methanol crossover [7,10,11]. For example, McGrath and co-workers reported that once the degree of disulfonation reached 60 mol%, the membranes swelled dramatically to form a hydrogel that would not be useful as a PEM [7,11]. Several attempts have been carried out

to modify the SPAEEKs membranes, e.g. addition of basic polymers, incorporating inorganic fillers or particles, coating barrier films on the surface, and so on. The modification of SPAEEKs membranes could suppress the methanol crossover and, in general, improve the performance of DMFCs to some extent [12–14]. However, in most of these cases, the proton conductivity also decreased significantly due to the addition of non-conductive materials.

The layer-by-layer (LBL) self-assembly is a powerful and simple method to deposit a thin multilayer film on a substrate by sequential electrostatic adsorption between the negatively and positively charged polyelectrolytes [15,16]. This technique can also be used to blend functional polymers with inorganic particles at the nanometer scale by utilizing electrostatic forces or secondary interactions such as hydrogen bonding. Recently, LBL technology has been used successfully in the area of both proton-exchange membranes and direct methanol fuel cell electrodes and electrolytes [17–21]. Jiang et al. found that the LBL self-assembly of oppositely charged polyelectrolytes poly(diallyldimethylammonium chloride) and polystyrene sulfonic acid) on a Nafion[®] membrane showed significant effect on reduction in methanol crossover without much reduction in conductivity [22]. Kang and co-workers also demonstrated that the multilayer films on the Nafion[®] membranes reduced methanol permeability by half, while maintaining a high conductivity [23]. In most of the cases, the multilayered polyelectrolytes complex (PEC) membranes were prepared on the substrate of Nafion[®], which are very expensive. As LBL method was not limited for polymers, any shaped nanostructures with charges can be

* Corresponding author. Tel.: +86 431 85168870; fax: +86 431 85168870.

E-mail addresses: zhaochengji@jlu.edu.cn (C. Zhao), huina@jlu.edu.cn (H. Na).

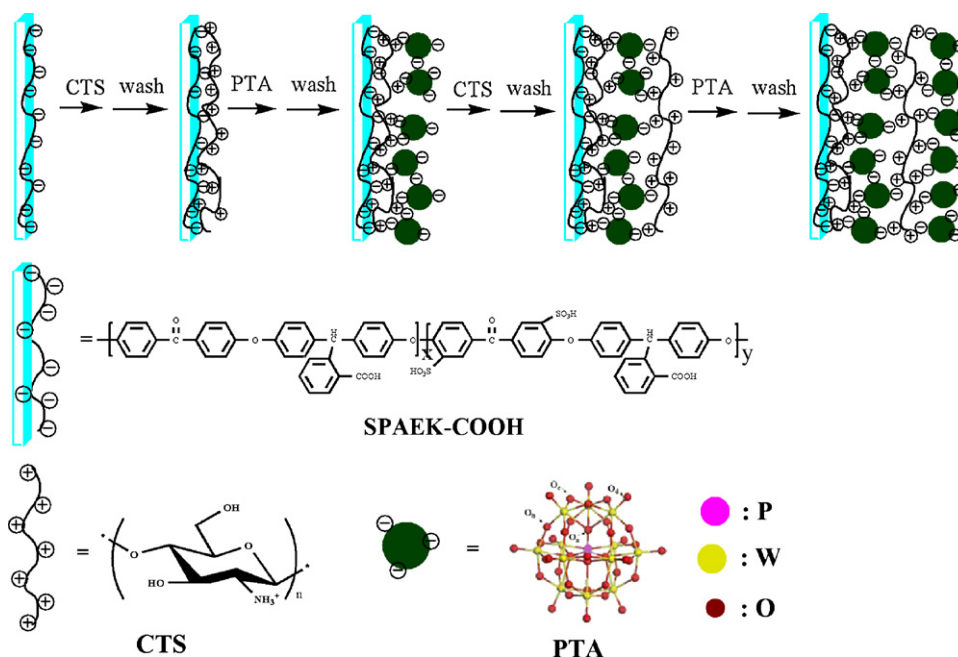


Fig. 1. Schematic representation of the fabrication of (CTS/PTA)_n multilayer films.

used as well, highly conductive inorganic nanoparticles becomes another possibility to further increase the conductivity and keep their extremely high methanol resistance.

Here, we report a novel approach to construct a stable multilayer film onto the surface of SPAEK membrane by LBL self-assembly polycation chitosan (CTS) and negatively charged inorganic particle phosphotungstic acid (PTA) (Fig. 1). It can suppress the methanol diffusion while maintaining a high proton conductance. Negatively charged SPAEK containing alternative sulfonic and carboxylic pendant groups (SPAEK-COOH) were selected as support materials for the preparation of multilayered film to ensure good adhesion between the top and support layer, thanks to high electrostatic interactions. CTS is extremely attractive to prepare polyelectrolyte complexes (PECs) because of the presence of both amino and hydroxyl groups [24]. Phosphotungstic acid, H₃PW₁₂O₄₀, is one of the Keggin-type heteropolyacids and exhibits extremely high proton conductivity (between 0.02 and 0.1 S cm⁻¹ at 25 °C). By LBL method, PTA can be firmly fixed in the thin multilayer PECs through electrostatic interaction. Then, the multilayer PECs coated on the SPAEK-COOH membranes were evaluated in terms of SEM, TGA, swelling behavior, proton conductivity, and methanol permeability.

2. Experimental

2.1. Materials

Chitosan (MW 500,000 and 90% degree of deacetylation) was purchased from Sanland-chem International Inc. (Xiamen, China). Phosphotungstic acid was obtained from Shanghai Mayao Chemical Technology Co., Ltd., China. Sulfonated poly(arylene ether ketone) bearing carboxylic groups was synthesized according to our previous report with ion exchange capacity (obtained from the titration) (1.84 mmol g⁻¹) [25]. Other chemicals and solvents were used as received. Milli-Q water (Millipore, 18.2 MΩ at 25 °C) was used in the experiments.

2.2. Layer-by-layer assembly

The SPAEK-COOH membranes (the thickness is about 50 μm) were immersed into 1.0 M HCl solutions for 24 h, then the mem-

brane was rinsed in Milli-Q water three times to remove traces of HCl. The membranes were stored in Milli-Q water before use. 2% (w/v) chitosan solution was prepared by dissolving chitosan powder in 2% (v/v) acetic acid solution. After chitosan powder was completely dissolved, solution was filtered and deformed by leaving it quiescent at ambient temperature for 2 h. The PTA powder was dissolved in Milli-Q water to form PTA (1 mmol L⁻¹) solutions (pH 2.5).

The LBL deposition of CTS-PTA multilayer's was carried out by alternate dipping of the pretreated SPAEK-COOH membrane in CTS (2 g L⁻¹) and PTA (1 mmol L⁻¹) solutions at room temperature for 10 min. After each dipping step, the membrane was rinsed with Milli-Q water to remove weakly bonded polyelectrolyte molecules and dried in a stream of N₂ gas for 5 min. The process was repeated to increase the number of CTS/PTA bilayers [15]. The resulted polyelectrolyte multilayer modified membrane was finally cleaned with Milli-Q water and stored before usage. Depositing CTS/PTA multilayers on glass plates and silicon wafers were performed by a similar method.

2.3. Characterization

UV-vis spectra were recorded with a SHIMADZU-UV2501 PC spectrometer after each layer of deposition on a glass plate. The morphology and thickness of CTS/PTA multilayered film on the SPAEK-COOH substrate were determined by using JSM-6700F scanning electron microscope (SEM).

The water uptake (WU) of the membrane was determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously [26]. The water swelling ratio was defined as follows:

$$\text{swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (1)$$

where L_{wet} and L_{dry} are the length of wet and dry membranes, respectively.

The swelling degree in methanol solution of the membrane was determined by the reference report [27]. The dried membrane was immersed into 2 M methanol solution for 1 day. The swelling degree

was calculated by the change in weight between dry and wet samples. The conductivity of the LBL self-assembled SPAEK-COOH 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 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. The impedance measurements were performed in water with 100% relative humidity at desired temperature. The proton conductivity was calculated by the following equation (2):

$$\sigma = \frac{L}{RA} \quad (2)$$

where σ is proton conductivity in $S\text{ cm}^{-1}$, L is the distance between electrodes, R is the membrane resistance and A is the cross-sectional area of membrane.

Methanol diffusion coefficient was measured using a home-made glass diffusion cell, which consisted of two compartments and divided by a membrane sample. 100 ml methanol–water solution (10 M) was placed on one side of the diffusion cell (cell A) and 100 ml water was placed on the other side (cell B). Both compartments were continuously stirred using submersible magnetic stirrers. The concentration of the methanol in cell B was measured by using SHIMADZU GC-8A chromatograph. Peak areas were converted to the methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by Eq. (3):

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (3)$$

where A , L and V_B are the effective area, membrane thickness and receptor reservoir volume, respectively. C_A and C_B are the methanol concentration in the donor and receptor reservoirs, respectively. DK and t_0 are the methanol diffusion coefficient and the time lag, respectively.

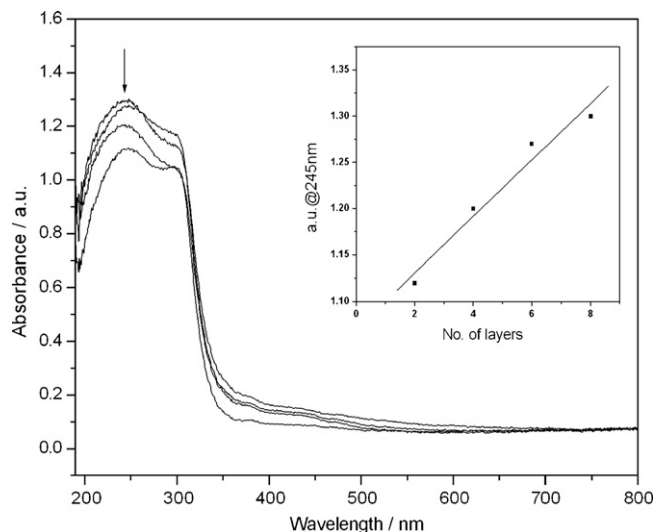


Fig. 2. UV-vis absorption spectra of the multilayer films deposited on glass plates. The inset shows plots of the absorbance values at 245 nm vs. the number of layers.

3. Results and discussion

3.1. UV-vis spectra

The CTS/PTA multilayer buildup process was monitored by the UV-vis spectra after deposition of each layer on a glass plate. Fig. 2 shows the UV-vis spectra of $(\text{CTS/PTA})_n$ ($n = 2, 4, 6, 8$) multilayered PEC. These films exhibit the characteristic bands at 245 nm, which can be ascribed to the oxygen-to-tungsten charge transfer (CT) transitions of PTA. Since CTS has no absorption in the UV-vis spectral range, the linear increase of absorbance peak at about 245 nm with increasing the number of CTS/PTA bilayers confirms the successful incorporation of PTA into multilayer films. The slope of the line, or the absorbance of one bilayer, is about 0.032. This linear feature sug-

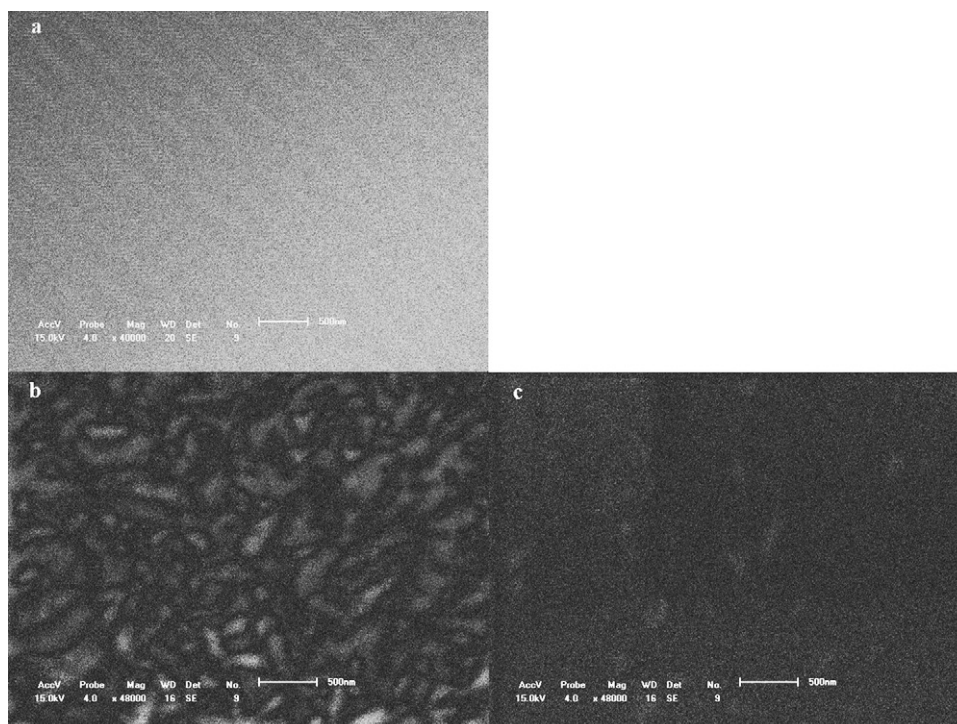


Fig. 3. Surface of CTS/PTA multilayered films deposited on silicon substrates as observed by SEM. (a) CTS; (b) $(\text{CTS/PTA})_1$; (c) $(\text{CTS/PTA})_2$.

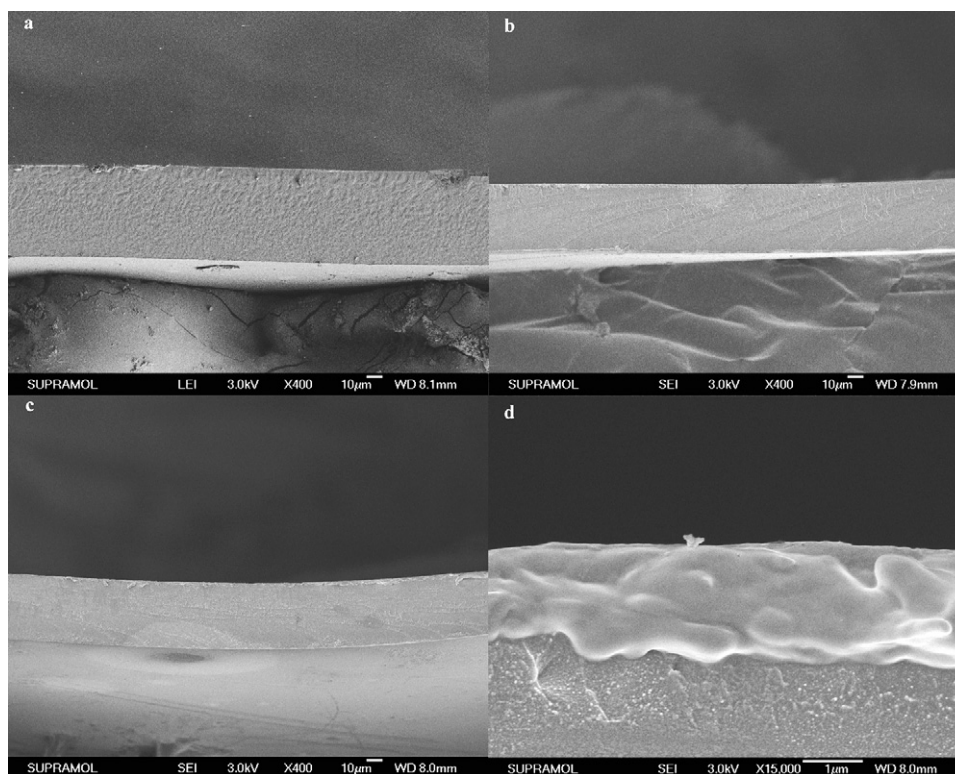


Fig. 4. SEM cross-sectional image of SPAEK-COOH membrane coated with different bilayers of CTS/PTA. (a) SPAEK-COOH support; (b) 6 bilayers of CTS/PTA; (c) and (d) 8 bilayers of CTS/PTA at different magnifications.

gests that each adsorption cycle contributes an equal amount of PTA into the thin films, which provide strong evidence for the regular growth of the multilayer and for high reproduction of layer-by-layer assembly.

3.2. SEM

Multilayered CTS/PTA films were first deposited on negatively charged silicon wafers to study the surface morphology, following the protocol [28]. As seen in Fig. 3, CTS precursor layer exhibits a quite uniform and homogeneous surface while CTS/PTA bilayer film shows a phase-separated structure. The PTA uniformly disperses in the PEC films. It does not recrystallize into large particles and agglomerate, but interact with CTS electrostatically. After several deposition cycles, a homogeneous morphology with no obvious separation is achieved again. This homogeneity of PEC membrane confirms that the ionic interaction between them leads PTA particles to be entrapped or surrounded by CTS chains.

The SEM measurements were also used to provide visual evidence that the SPAEK-COOH supporting membrane is uniformly coated in the LBL assembly process. The cross-sectional SEM images of SPAEK-COOH coated with CTS/PTA multilayered films are shown in Fig. 4. In contrast to the pristine SPAEK-COOH supporting membrane (Fig. 4a), a very thin dense layer coated on the surface is clearly visible in the images of CTS/PTA multilayer modified membranes (Fig. 4b and c). There is a sharp transition between the amorphous SPAEK-COOH and the lighter shaded band of LBL film. The thickness of LBL films deposited onto the SPAEK-COOH support can increase to 2 μm upon changing the number of CTS/PTA bilayers, as confirmed at a higher magnification (Fig. 4d). Compared with conventional multilayered films, the CTS/PTA multilayers coated on SPAEK-COOH is surprisingly thicker when prepared under similar conditions. This might be caused by the higher charge density of the polyelectrolyte complex used and

the supporting SPAEK-COOH membrane bearing more charge sites [28].

3.3. Thermal analysis

The thermal properties of SPAEK-COOH substrate and CTS/PTA PECs coated membranes were studied by thermogravimetric analysis under N₂ atmosphere at a heat rate of 10 °C min⁻¹. All membranes exhibited two distinct degradation steps (Fig. 5(a)). Fig. 5(b) shows the first derivative of their TG traces. SPAEK-COOH exhibited two main peaks in the first-derivative plot. During the first step, a broad peak centered at 281 °C was produced. This weight loss is believed to be associated with the loss of sulfonic acid groups. The second weight loss step started at about 400 °C can be divided into two regions. The shoulder at around 527 °C is related to the side-chain decomposition, while the intense peak centered at 621 °C corresponds to the decomposition of the polymer main chain. In the case of CTS/PTA PECs coated membrane, the peak maximum in the first stage is similar to that found with SPAEK-COOH substrate. However, the 5% and 10% weight loss temperatures of coated membrane are higher than the SPAEK-COOH substrate, indicating that electrostatic forces and hydrogen bonding between the oppositely charged polyelectrolytes improve thermal stability of a polymer below 400 °C [29]. In the second stage, the peak centered at 556 °C for the coated membrane is lower than that of the substrate, which is caused by the lower decomposition temperatures of PECs and CTS. The TGA studies revealed that the PECs coated membranes are still thermally stable within the temperature range for fuel cell applications.

3.4. Water uptake and swelling ratio

It has been widely reported in the literature that the water swelling behavior plays an important role in membrane conductiv-

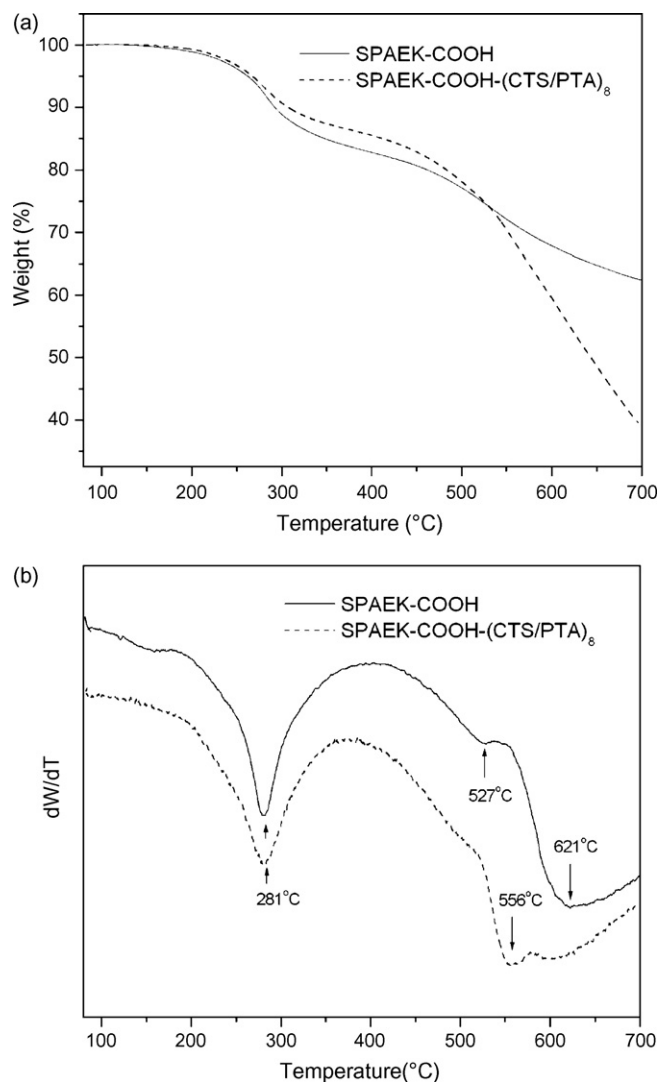


Fig. 5. TGA (a) and derivative (b) curves of SPAEK-COOH membrane and PECs coated membrane.

ity, dimensional stability and mechanical strength [11]. Generally, the water within the membrane provides a carrier for the proton and maintains high proton conductivity. However, excessive water uptake results in membrane fragility and dimensional change, which leads to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly (MEA). The results of water uptake and swelling ratios for CTS/PTA multilayer's modi-

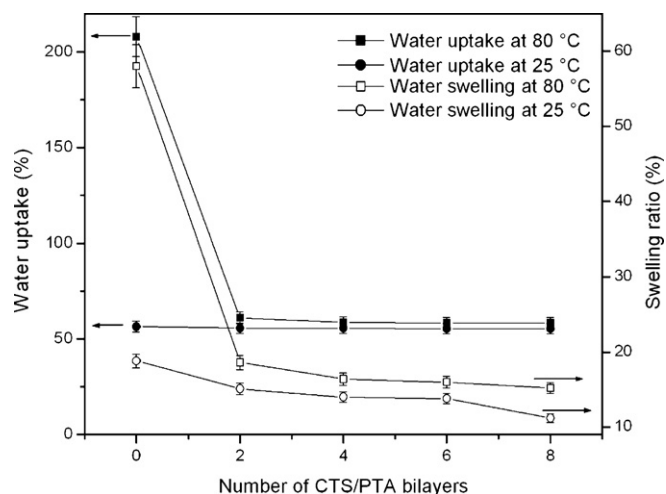


Fig. 6. Water uptake and swelling ratio of SPAEK-COOH-(CTS/PTA)_n membranes with different numbers of bilayers.

fied SPAEK-COOH and pristine SPAEK-COOH membrane at 25 and 80 °C are illustrated in Fig. 6. It is noticed that CTS/PTA multilayer assembled on the surface of SPAEK-COOH membrane effectively reduces the excessive water swelling and dimensional change at high temperature of 80 °C. For example, the water uptake of pristine SPAEK-COOH membrane is approximately 208% at 80 °C, whereas, the CTS/PTA multilayer modified membranes shows the water uptake of 61.1%, 58.7%, 58.5% and 58.4%, respectively. Although these values are still higher than that of Nafion[®] 117 (38%), excessive water uptake is restricted. Maintaining an appropriate water uptake level is indispensable to ensure superior proton conductivity and to simultaneously reduce undesirable side effects. Similarly, the swelling ratio of SPAEK-COOH-(CTS/PTA)_n is approximately four fold lower than that of pristine SPAEK-COOH membrane and is smaller than that of Nafion[®] 117 (about 20%). The swelling degrees in methanol solution (2 M) of the membranes were also measured and are listed in Table 1. In this experiment, the membrane is primarily hydrated by water and the methanol plays a small role in hydration of the polymer structure. Similar to the swelling degree in the pure water, the assembled membranes have slightly lower swelling degrees than that of pristine SPAEK-COOH membrane at ambient temperature. When the CTS/PTA multilayered PEC with much low swelling property is coated, the hydrophilic -SO₃⁻ and -COOH- clusters on the surface of SPAEK-COOH substrate is failed to be available to form hydrogen bond with water molecules. Thus, the CTS/PTA PEC multilayers can suppress membrane swelling in water effectively, which is also related to the methanol permeation.

Table 1
Comparisons of proton conductivity and methanol diffusion coefficient of SPAEK-COOH-(CTS/PTA)_n membranes, the reported SPEEK/PHR blend membrane, and Nafion[®] membrane.

Number of CTS/PTA bilayers	Swelling degree in methanol solution (%)	Methanol diffusion coefficient ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$)		Proton conductivity (S cm^{-1})		
		25 °C	60 °C	25 °C ^a	80 °C	25 °C ^b
2	59.8	1.71	3.81	0.086	0.240	0.083
4	59.7	1.50	2.99	0.081	0.211	0.078
6	59.7	1.08	2.02	0.080	0.190	0.078
8	59.5	0.12	0.22	0.075	0.134	0.074
SPAEK-COOH	60.5	8.15	24.1	0.069	0.27	0.066
SPEEK/PHR ^c	-	8.5	-	0.056	0.115	-
Nafion [®] 117	-	23.8	-	0.077	0.13	-

^a Proton conductivity before water stability test.

^b Proton conductivity after water stability test.

^c Data adapted from Ref. [26].

3.5. Proton conductivity and methanol permeability

The proton conductivities of pristine SPAEK–COOH and CTS/PTA modified SPAEK–COOH membranes were measured and are shown in Table 1. For comparison, the proton conductivity of Nafion® 117 membrane in its fully hydrated state was also measured under the same condition. With an increase in the number of self-assembled CTS/PTA bilayers, the conductivity of the membrane decreases slightly. After the self-assembly eight CTS/PTA bilayers, the proton conductivity is 0.075 S cm^{-1} at 25°C , a decrease of 13% compared with that of a membrane deposited two CTS/PTA bilayers. However, the value is still superior to the pristine SPAEK–COOH (0.069 S cm^{-1}) and comparable to Nafion® 117 (0.077 S cm^{-1}). Compared to a SPAEK composite membrane with 10 wt.% phenoxy resin (PHR) as a promising candidate in DMFC, the CTS/PTA assembled membranes also show much higher conductivities [26]. This result indicates that the incorporation of highly conductive PTA ensures the multilayer modified membranes to maintain high proton conductivity values. The self-assembled PEC multilayers seem to have some negative effect on the conductivity of the membrane. However, this effect can be reduced into a minimum by using a proper combination of polycation and polyanion, as shown in the case of self-assembly of highly conductive inorganic nanoparticles.

Two factors affects the proton conductivity of modified membranes: (i) it is interesting to find SPAEK–COOH–(CTS/PTA)_n membranes shows slight higher proton conductivity when the temperature is relatively low. This phenomenon may be explained by the addition of high proton conductive ability of PTA. (ii) CTS/PTA multilayers restrict water swelling of SPAEK–COOH membrane at high temperature. The modified membranes exhibit extremely low water uptake and swelling values compared to the pristine SPAEK–COOH membrane. So the mobility of charge carrier species in SPAEK–COOH membrane could be restricted, resulting in a decrease in proton conductivity of the self-assembled composite membrane. These two factors determine the overall proton conductivity of the CTS/PTA multilayer modified membranes.

The conductivity data are also analyzed in terms of Arrhenius plot, as reported in Fig. 7. From the Arrhenius plots, the activation energy (E_a) can be calculated, which is an indication of the mechanism of proton transport. The E_a for the pristine SPAEK–COOH membrane is 21.9 kJ mol^{-1} . With the increase in the number of self-assembled CTS/PTA bilayers, the activation energies for the modified membranes decrease (Fig. 8). The values are 16.4, 15.3,

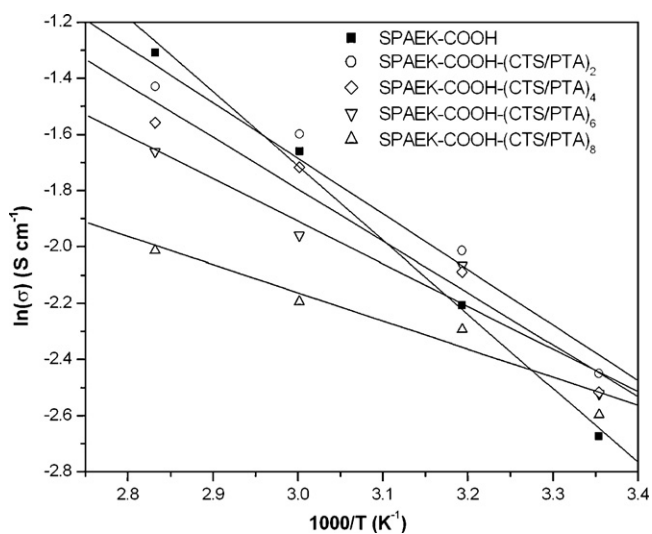


Fig. 7. Arrhenius plots for proton conductivity of the SPAEK–COOH–(CTS/PTA)_n membranes.

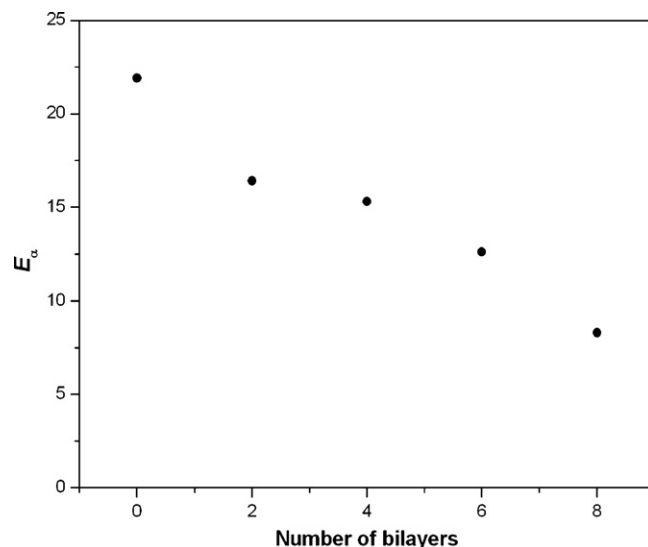


Fig. 8. Activation energy for proton conduction for SPAEK–COOH–(CTS/PTA)_n membranes with different numbers of bilayers.

12.6 and 8.3 kJ mol^{-1} , respectively. In the pristine SPAEK–COOH membrane, the proton migration is primarily by the Grothuss or “jump” mechanism, which can be idealized as the proton which forms as H_3O^+ ion jumps to the neighboring lone pair of electrons of a water molecule. In this mechanism, the activation energies for proton conduction should be between 14 and 40 kJ mol^{-1} [24]. The smaller activation energy indicates the easier proton transfer. The smaller activation energies of modified membranes might be due to the addition of HPAs (Keggin-type) with proton mobility and the existence of continuous hydrophilic channels in the multilayered CTS/PTA films [30,31], which promoted the conduction of protons in the modified membranes.

In addition, the water stability of modified membranes was evaluated by comparing the proton conductivity values before and after immersing in water for 2 weeks. It is thought that little change in proton conductivity corresponds to good water stability. As shown in Table 1, the multilayer modified membranes exhibit good water stability with negligible change in proton conductivity. This result indicates that the water swollen PTA can be immobilized in the multilayer PEC membranes through electrostatic interaction and be much less prone to leaching out.

Proton conductivity and methanol permeability are two crucial transport properties that determine the fuel cell performance. In general, methanol prefers to permeate through membranes with high sulfonated degree, thus eliminating any advantage with respect to Nafion® when used in solid state. However, by introducing CTS and PTA self-assembled with SPAEK–COOH, it is effective to decrease methanol permeability while maintaining high proton conductivity. For example, the methanol permeability of SPAEK–COOH–(CTS/PTA)₈ is over 1 order of magnitude less than pristine SPAEK–COOH, SPEEK/PHR composite membrane and over 2 order of magnitude less than Nafion® 117. It is known that the highly sulfonated aromatic polymers usually contain two domain regions: ion-rich hydrophilic domains and hydrophobic domains. The methanol diffuses primarily through the hydrophilic water-rich domains. When the surface of SPAEK–COOH is coated by the PEC multilayers, the electrostatic interactions or the ionically crosslinking effects between the polyacid/polybase pairs block the water-rich domains, which are mainly associated with $-\text{SO}_3^-$ and $-\text{COOH}$ clusters on the substrate surface [22]. Thus, the PEC multilayer is effective as a methanol barrier. Furthermore, it can be seen from Table 1 that the methanol diffusion coefficient increases with

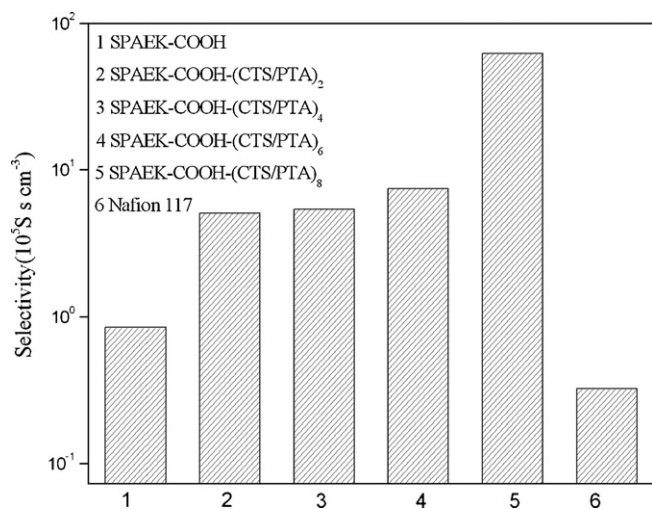


Fig. 9. The selectivity of SPAEK-COOH-(CTS/PTA)_n membranes with different numbers of bilayers.

an increase in the temperature. Similar to the proton conduction, the methanol diffusion is also thermally stimulated.

The selectivity, which is defined as the ratio of proton conductivity to methanol permeability, is often used to evaluate the potential performance of DMFC membranes [32]. Fig. 9 shows the selectivity of SPAEK-COOH-(CTS/PTA)_n and Nafion[®] 117 at 25 °C. CTS/PTA multilayer modified SPAEK-COOH membranes show a gradually increasing tendency with an increase in the number of deposited bilayers. The selectivity of SPAEK-COOH-(CTS/PTA)₈ is 2 orders of more than Nafion[®] 117, which is attractive for applications in DMFC.

4. Conclusions

Novel multilayered PEC proton-exchange membranes based on SPAEK-COOH were successfully prepared from CTS and PTA by the LBL method. SEM results showed the presence and stability of thin CTS/PTA layers coated on SPAEK-COOH membranes. It shows significant effect on reduction in methanol diffusion, water uptake and swelling. The methanol diffusion values are about 1 order of magnitude less than SPAEK-COOH and 2 orders of magnitude less than Nafion[®] 117. Most importantly, the modified SPAEK-COOH membranes by LBL self-assembly shows a slightly higher or much smaller negative effect on proton conductivity, a significant advantage compared to other modification approaches and previous LBL assembled electrolyte systems [22]. The selectivity of SPAEK-COOH-(CTS/PTA)_n membranes are over 2 orders of magnitude higher than Nafion[®] 117, which is attractive in DMFC. Thus, LBL

self-assembly of inorganic heteropolyacid is a convenient and effective method for preparing excellent polyelectrolyte membranes for DMFC applications.

Acknowledgement

The authors would like to thank the China High-Tech Development 863 program (Grant No. 2007AA03Z218) for financial support of this work.

References

- [1] P. Costamagna, S. Srinivasan, *J. Power. Sources* 102 (2001) 253.
- [2] V. Mehta, J.S. Cooper, *J. Power. Sources* 114 (2003) 32.
- [3] K.D. Kreuer, *Solid State Ionics* 97 (1997) 1.
- [4] P. Costamagna, S. Srinivasan, *J. Power Sources* 102 (2001) 242.
- [5] C. Stone, A.E. Morrison, *Solid State Ionics* 152–153 (2002) 1.
- [6] J.R. Varcoe, R.C.T. Slade, *Fuel Cells* 5 (2005) 187.
- [7] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, *J. Membr. Sci.* 197 (2002) 231.
- [8] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, S. Kaliaguine, *Polymer* 46 (2005) 3257.
- [9] C.J. Zhao, H.D. Lin, K. Shao, X.F. Li, H.Z. Ni, Z. Wang, H. Na, *J. Power Sources* 162 (2006) 1003.
- [10] F. Lufrano, G. Squadrito, A. Patti, E. Passalacqua, *J. Appl. Polym. Sci.* 77 (2000) 1250.
- [11] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Chem. Rev.* 104 (2004) 4587.
- [12] C.J. Zhao, Z. Wang, D.W. Bi, H.D. Lin, K. Shao, T.Z. Fu, S.L. Zhong, H. Na, *Polymer* 48 (2007) 3090.
- [13] S.L. Zhong, X.J. Cui, T.Z. Fu, H. Na, *J. Power Sources* 180 (2008) 23.
- [14] Z.G. Shao, X. Wang, I.-M. Hsing, *J. Membr. Sci.* 210 (2002) 147.
- [15] G. Decher, *Science* 277 (1997) 1232.
- [16] G. Decher, M. Eckle, J. Schmitt, B. Struth, *Curr. Opin. Colloid Interface Sci.* 3 (1998) 32.
- [17] M. Pan, H.L. Tang, S.P. Jiang, Z.C. Liu, *J. Electrochem. Soc.* 152 (2005) A1081.
- [18] C.N. Kostelansky, J.J. Pietron, M.S. Chen, W.J. Dressick, K.E. Swider-Lyons, D.E. Ramaker, R.M. Stroud, C.A. Klug, B.S. Zelakiewicz, T.L. Schull, *J. Phys. Chem. B* 110 (2006) 21487.
- [19] T.R. Farhat, P.T. Hammond, *Adv. Funct. Mater.* 15 (2005) 945.
- [20] T.R. Farhat, P.T. Hammond, *Chem. Mater.* 18 (2006) 41.
- [21] T. Farhat, P.T. Hammond, *Adv. Funct. Mater.* 16 (2006) 433.
- [22] S.P. Jiang, Z. Liu, Q. Tian, *Adv. Mater.* 18 (2006) 1068.
- [23] D.W. Kim, H.-S. Choi, C. Lee, A. Blumstein, Y. Kang, *Electrochim. Acta* 50 (2004) 659.
- [24] B. Smitha, S. Sridhar, A.A. Khan, *Macromolecules* 37 (2004) 2233.
- [25] H.D. Lin, C.J. Zhao, Z.M. Cui, W.J. Ma, T.Z. Fu, H. Na, W. Xing, *J. Power. Sources* (2009) doi:10.1016/j.jpowsour.2009.04.036.
- [26] H.L. Cai, K. Shao, S.L. Zhong, C.J. Zhao, G. Zhang, X.F. Li, H. Na, *J. Membr. Sci.* 297 (2007) 162–173.
- [27] M.H. Yildirim, D. Stamatialis, M. Wessling, *J. Membr. Sci.* 321 (2008) 364–372.
- [28] X.F. Li, S.D. Feyter, D.J. Chen, S. Aldea, P. Vandezande, F.D. Prez, I.F.J. Vankelecom, *Chem. Mater.* 20 (2008) 3876.
- [29] Y. Wan, K.A.M. Creber, B. Peppley, V.T. Bui, *J. Appl. Polym. Sci.* 94 (2004) 2309.
- [30] K.D. Kreuer, M. Hampele, K. Dolde, A. Rabenau, *Solid State Ionics* 28–30 (1988) 589.
- [31] K.D. Kreuer, A. Rabenau, W. Weppner, *Angew Chem. Int. Ed. Engl.* 21 (1982) 208.
- [32] B.S. Pivovar, Y.X. Wang, E.L. Cussler, *J. Membr. Sci.* 154 (1999) 155.