



Design of a stable and methanol resistant membrane with cross-linked multilayered polyelectrolyte complexes for direct methanol fuel cells

Jing Wang, Chengji Zhao, Haidan Lin, Gang Zhang, Yang Zhang, Jing Ni, Wenjia Ma, Hui Na *

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:

Received 16 December 2010
Received in revised form 14 February 2011
Accepted 16 February 2011
Available online 22 February 2011

Keywords:

Layer-by-layer
Cross-linking
Proton exchange membrane
Sulfonated poly (ether ether ketone)

ABSTRACT

Sulfonated poly (arylene ether ketone) bearing carboxyl groups (SPAEEK-C) membranes have been prepared as proton exchange membranes for applications in direct methanol fuel cells (DMFCs). Multilayered polyelectrolyte complexes (PECs) which applied as methanol barrier agents are prepared by alternate deposition of the oppositely charged amino-containing poly (ether ether ketone) (Am-PEEK) and the highly sulfonated SPAEEK-C via a layer-by-layer method. The cross-linked PEC (c-PEC) is derived from a simple heat-induced cross-linking reaction between Am-PEEK and SPAEEK-C. Fourier transform infrared spectroscopy confirms that Am-PEEK and SPAEEK-C are assembled successfully in the multilayers. The morphology of the membranes is studied by scanning electron microscopy, which shows the presence of the thin layers coated on the SPAEEK-C membrane. After PEC and c-PEC modification, the methanol permeability decreases obviously when compared to that of the pristine membrane. Notably, improved proton conductivities are obtained for the PEC modified membranes in comparison with the pristine membrane. Moreover, the selectivity of these modified membranes is one order of magnitude higher than that of Nafion 117. The thermal stability, oxidative stability, water uptake and swelling of PEC and c-PEC modified membranes are also investigated.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

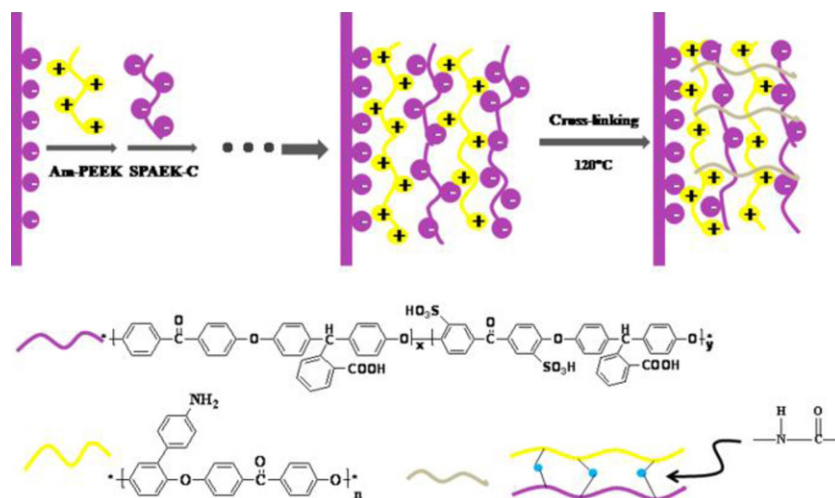
The proton exchange membrane fuel cells (PEMFCs), especially direct methanol fuel cells (DMFCs) are promising candidate power sources because of the simple fuel setup, low emissions and low operating temperatures [1–4]. The proton exchange membrane (PEM) acts as the key component in a DMFC. Currently, perfluorinated sulfonic acid polymers such as Nafion are the commonly used PEM materials in DMFCs, owing to their excellent chemical and electrochemical stabilities in an oxidizing environment as well as high proton conductivity when fully hydrated. However, Nafion has low conductivity at low humidity or high temperature, high cost and high methanol permeability, which have limited its commercialization. Especially, the methanol crossover of Nafion membrane reduces the open-circuit potential by as much as 0.15–0.2 V and increases the over-potential of the cathode due to the poisoning of the cathode catalyst [5]. Thus, many strategies have been developed to overcome the problem of methanol crossover, such as in situ polymerization of Nafion with poly (1-methylpyrrole) [6], and the development of composite membranes such as Nafion-silica

[7,8], Nafion-zirconium phosphate [9], Nafion-cesium ions [10], and Nafion/poly (furfuryl alcohol) nanocomposite membranes [11]. Another effective approach to suppress the methanol crossover is to coat a thin methanol barrier layer, such as polyvinyl alcohol and poly (ether ether ketone), onto the surface of Nafion [12,13]. The methanol permeability was significantly reduced by these strategies. However, the proton conductivity was also decreased. Therefore, researchers have been stimulated to investigate promising alternatives.

Layer-by-layer (LBL) self-assembly technology is a versatile thin-film fabrication technique which is based on electrostatic interactions or secondary interactions [14,15]. The technique has progressed significantly since the pioneering work by Decher et al. [16,17]. Jiang et al. [18] and Lin et al. [19] have reported the preparation and the properties of multilayered polyelectrolyte complex (PEC) membranes, which were deposited on Nafion membrane by a LBL method. They observed that the methanol permeability of these multilayered membranes decreased with an increase in the number of deposited layer. LBL processing also provides nanometer-scale blending of polymers and other organic/inorganic materials that are otherwise impossible to construct. For example, Zhao et al. reported a novel approach to construct a stable multilayer membrane onto the surface of sulfonated poly (arylene ether ketone) membrane by the LBL self-assembly of polycation (chitosan) and negatively charged inorganic particle (phosphotungstic acid) [20]. In general, all the results demonstrated that the multilayered PEC

* Corresponding author at: Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Qianjin street 2699#, Changchun, Jilin 130012, China.
Tel.: +86 431 85168870; fax: +86 431 85168870.

E-mail address: huina@jlu.edu.cn (H. Na).



Scheme 1. Schematic representation of the fabrication of (Am-PEEK/SPAEK-C)_n multilayer films.

films are promising towards lowering the methanol permeability while maintaining a decent conductivity for applications in DMFCs.

Polymers containing basic groups, such as amine, imine, imidazole, sulfur, and oxygen, have demonstrated low methanol permeability in DMFCs [13]. For example, a rigid aromatic amino-containing poly(ether ether ketone) (Am-PEEK) has been synthesized and blended into sulfonated poly(aryl ether ketone) bearing carboxylic acid groups (SPAEC-C) membrane as a cross-linker in our previous work [21]. In this research, Am-PEEK was used as a polyelectrolyte for the first time in PEC preparation. An anticipated result would be a loss in proton conductivity; however, by incorporating a highly sulfonated, water soluble SPAEK-C into the LBL process, we can produce multilayered membranes with low methanol permeability and high proton conductivity (Scheme 1). Lowly sulfonated SPAEK-C with medium ionic content was selected as the support material in the preparation of multilayered PECs to ensure good adhesion between the top layer and the support. In addition, cross-linking is deemed to be an excellent method to obtain highly stable and impermeable membranes. Harris et al. have reported that the permeability and the stability of the multilayered PEC membranes can be improved simply by heating them to form amide bonds [22]. Herein, we prepared a cross-linked PEC modified membrane by a thermal-cross-linked method. The cross-linked PEC (c-PEC) modified membrane may be a promising candidate for PEMs used in DMFCs.

2. Experimental

2.1. Materials

SPAEC-Cs with sulfonation degree (DS) 0.8 and 1.4, respectively, were synthesized according to a similar procedure in our previous report [23]. Am-PEEK were synthesized according to a similar procedure reported previously [24]. Other chemicals and solvents were used as received. Milli-Q water (Millipore, 18.2 MΩcm at 25 °C) was used in the experiments.

2.2. Layer-by-layer assembly and cross-linking treatment

The SPAEK-C membrane (DS=0.8) as substrate was immersed into 1.0 M HCl solutions for 24 h, then the membrane was rinsed in Milli-Q water three times to remove the traces of HCl. The membrane was stored in Milli-Q water before use.

The Am-PEEK was dissolved in *N*-methyl-2-pyrrolidinone (NMP) and Milli-Q H₂O well-mixed solutions (2% v/v) to form the

Am-PEEK (1 mmolL⁻¹) active polycation solutions (pH 2.5). The water soluble SPAEK-C (DS = 1.4) was dissolved in Milli-Q water to form the SPAEK-C (1 mmolL⁻¹) solutions (pH 2.5).

To construct Am-PEEK/SPAEC-C multilayer films, the pretreated SPAEK-C substrates were immersed in Am-PEEK solution at room temperature for 10 min, followed by three 2 min rinses in Milli-Q water, and then in SPAEK-C solution for 10 min followed by three 2 min rinses in Milli-Q water. After each dipping step in polyelectrolyte solution, the membrane was rinsed with 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 Am-PEEK/SPAEC-C bilayers [16]. The resulting polyelectrolyte multilayer modified membrane was finally cleaned with Milli-Q water and stored before use. The thickness of the polyelectrolyte multilayer modified membranes is about 65 ± 5 μm. For the reference systems prepared on glass plates (for FT-IR measurement) and silicon wafers (for SEM measurement), a similar method as mentioned above was used for deposition. The silicon wafers were cleaned with piranha solution (a 1:3 mixture of 30% H₂O₂ and concentrated H₂SO₄), rinsed in water, sonicated for 15 min and again thoroughly rinsed with water.

The cross-linking treatment of 15-bilayer Am-PEEK/SPAEC-C modified membrane was prepared by heating it for 4 h in a vacuum oven at 120 °C and the thickness of the membrane is about 65 ± 5 μm.

2.3. Characterization

2.3.1. Structural characterization

Fourier transform infrared spectroscopy (FT-IR) spectra of multilayers were recorded with a Bruker Vector 22 FT-IR instrument.

Scanning electron microscopy (SEM) was done on a SHIMADZU SSX-550 scanning electron microscope. The LBL self-assembled SPAEK-C membranes were fractured in liquid nitrogen and the fractured sections and surfaces were sputter-coated with Au prior to SEM imaging.

2.3.2. Water uptake and swelling ratio

The membranes were dried at 80 °C under vacuum for 12 h, until a constant weight was obtained. They were immersed into deionized water at a desired temperature for 24 h to make these membranes saturated. Then the membranes were taken out, wiped with a tissue paper, and quickly weighted on a microbalance. Water uptake (WU) and swelling ratio (SR) were calculated by the changes in weight and thickness between the dry and the fully hydrated

samples as follows:

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

where W_d and W_s are the weight of dry and corresponding water-swollen membranes, respectively.

The swelling ratio was calculated by the following equation:

$$SR (\%) = \frac{T_s - T_d}{T_d} \times 100\% \quad (2)$$

where T_s and T_d are the thickness of the wet and dry membranes, respectively.

2.3.3. Proton conductivity and methanol permeability

The proton conductivity (σ) of each membrane was measured by a four-probe AC impedance method from 0.1 Hz to 100 kHz using a Parstat 2273 potentiostat/galvanostat/FRA. The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurement. Repeated measurements were taken at that given temperature with 10 min interval until no more change in impedance value was observed. The proton conductivity of the membrane was calculated from the observed sample resistance from the relationship:

$$\sigma = \frac{L}{RS} \quad (3)$$

where σ is the proton conductivity (in $S\text{ cm}^{-1}$), L is the distance between the electrodes used to measure the potential ($L = 1\text{ cm}$). R is the impedance of the membrane (in ohm), which was measured at the frequency that produced the minimum imaginary response and S is the membrane section area (in cm^2).

The methanol diffusion coefficient was measured according to a detailed procedure reported previously [25]. The cell consisted of two reservoirs, each with a capacity of approximately 100 mL, separated by a vertical membrane. Prior to testing, the membranes were immersed in deionized water for at least 12 h. Initially, reservoir V_A contained 10 M methanol–water solution, and reservoir V_B contained pure deionized water. The magnetic stirrers were used continuously during the measurement. Methanol concentrations in the water cell were determined by using a SHIMADZU GC-8A chromatograph. Methanol diffusion coefficient was calculated in formula:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (4)$$

where A (in cm^2), L (in cm) and V_B (in ml) are the effective area, the thickness of the membranes and the volume of permeated reservoirs, respectively. C_A and C_B (in mol m^{-3}) are the methanol concentration in feed and in permeate, respectively. D , K and t_0 are the methanol diffusivity, the partition coefficient and the time lag, respectively. The methanol permeability (P in $\text{cm}^2\text{ s}^{-1}$) is defined as the product of diffusivity and partition coefficient, i.e., $P = DK$, and the concentration change of C_B with time is obtained from a linear slope (α), using Eq. (5)

$$P = DK = \alpha \frac{V_B}{A} \frac{L}{C_A} \quad (5)$$

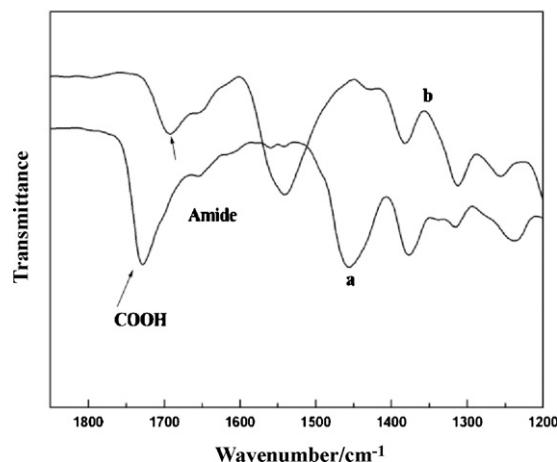


Fig. 1. FT-IR spectra of 15-bilayer Am-PEEK/SPAEC-C (a), and cross-linked 15-bilayer Am-PEEK/SPAEC-C films coated on glass plates (b).

2.3.4. Thermogravimetric analyses and derivative thermogravimetry

Thermo-gravimetric analysis (TGA) and derivative thermo gravimetry (DTG) was recorded on a Pyris-1 (Perkin Elmer) series thermal analysis system at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 atmosphere. Before the test, all the membranes were preheated to 120°C and kept at this temperature for 20 min to remove any residual moisture and solvent.

2.3.5. Oxidative stability

The oxidative stability of the membranes was tested by immersing them into Fenton's reagent (3% H_2O_2 solution containing 2 ppm FeSO_4) at 80°C . The oxidative stability was evaluated by recording the time that the membrane began to break into pieces.

3. Results and discussion

3.1. Structure characterization

The PEC membranes were first prepared on a glass plate to study the interaction between Am-PEEK and SPAEK-C. FT-IR spectra were used to confirm the LBL deposition of Am-PEEK/SPAEC-C on the support and the heat-induced cross-linking of the multilayered membrane. Fig. 1 shows the typical spectra of fifteen-bilayer Am-PEEK/SPAEC-C films before (a) and after heating (b). Before heating, the most notable bands are ascribed to the $-\text{COOH}$ carbonyl (1731 cm^{-1}) [26,27]. After the slide was heated at 120°C for 4 h, the carboxylated peaks almost disappear, and the amide bands appear at 1690 cm^{-1} as seen in spectrum (b). The result verifies that the cross-linking between the amino groups of Am-PEEK and the carboxyl groups of SPAEK-C occurs by the formation of amide bonds.

3.2. SEM

Fig. 2 (a)–(c) shows the surface images of Am-PEEK/SPAEC-C thin films assembled on a negatively charged silicon wafer. The PEC-coated silicon substrates show some light points, which represent the grains of the rigid aromatic Am-PEEKs. With an increase in the numbers of bilayer, more and more Am-PEEKs are assembled into the LBL films on the substrate. These images further confirm the sequential deposition of Am-PEEK and SPAEK-C in the multilayer films. After the cross-linking treatment, as shown in Fig. 2(d), the increased surface roughness and continuum are attributed to the interactions between Am-PEEK and SPAEK-C. Fig. 2(e) and (f) show the cross-sectional SEM images of the pristine and the PEC modi-

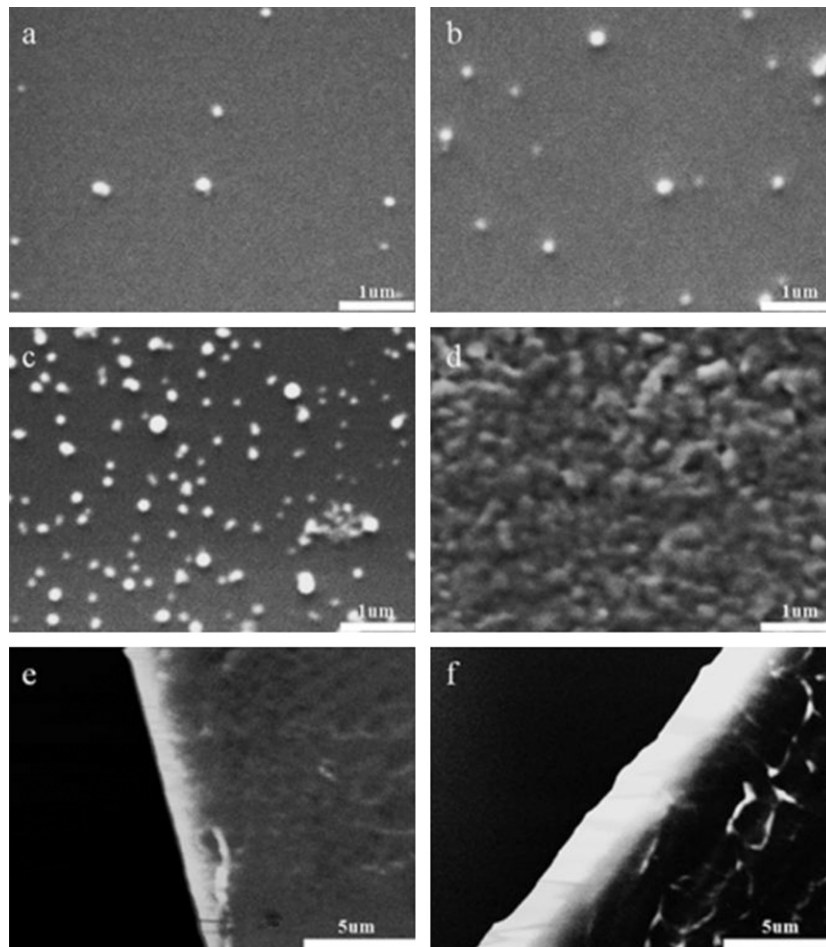


Fig. 2. SEM image (a) 2-bilayer Am-PEEK/SPA EK-C films, (b) 5-bilayer Am-PEEK/SPA EK-C films, (c) 15-bilayer Am-PEEK/SPA EK-C films, (d) cross-linked 15-bilayer Am-PEEK/SPA EK-C films, (e) cross-sectional image of pristine SPA EK-C, (f) cross-sectional image of 15-bilayer Am-PEEK/SPA EK-C.

fied membrane, respectively. The micrographs show clearly a sharp transition between the SPA EK-C substrate and the lighter shaded band of LBL film. The result confirms that the LBL film coats conformably, rather than penetrating into SPA EK-C membranes, also confirms the stability of the multilayers.

3.3. Thermal stability

The thermal stability of a PEM is a key property for the durability during the fuel cell operation at high temperature. Fig. 3 shows that all the membranes exhibit a typical two-step degradation pattern. The first weight loss corresponding to the decomposition of the sulfonic acid groups was observed in the range of 100–250 °C, while the second weight loss step starting at about 400 °C associated with the decomposition of polymer main chains. The 5% weight loss temperature ($T_{d5\%}$) of the PEC modified membrane was approximately 10 °C higher than that of SPA EK-C substrate membrane. Similar

results are shown in their DTG curves (Fig. 3). The desulfonation temperature of PEC modified membranes were observed slightly higher than that of pristine SPA EK-C, indicating that electrostatic forces and hydrogen bonding between the opposite charged polyelectrolyte improve the thermal stability of a membrane [28]. From these results, it can be concluded that the PEC modified membrane are thermal stable within the temperature range of fuel cell applications.

3.4. Water uptake, swelling ratio

Water molecules within a PEM have a profound effect on the proton conduction for a PEM [29]. Generally, improving proton conductivity always accompanies with increasing water uptake. However, the excessive water uptake results in the membrane weakness and dimensional change. Both the WU and SR of the PEC modified membranes are compared to the pristine SPA EK-C and

Table 1

The 5% weight loss ($T_{d5\%}$), water uptake, swelling ratio, oxidative stability, proton conductivity and methanol permeability of (Am-PEEK/SPA EK-C)_n membranes.

Number of bilayers	Td (°C)	WU (%)		SR (%)		σ (S cm ⁻¹)		Oxidative stability (min)	P ($\times 10^{-7}$ cm ² s ⁻¹)
		25 °C	80 °C	25 °C	80 °C	25 °C	80 °C		
0	269.44	32.53	48.46	7.08	11.47	0.0308	0.0923	75	3.80
2	274.54	33.29	48.19	9.83	14.41	0.0346	0.1027	53	3.57
5	272.58	30.82	42.88	8.11	10.95	0.0323	0.1021	45	3.50
15	273.87	31.30	48.10	7.20	9.86	0.0322	0.0938	73	3.43
c-PEC	274.04	29.17	42.60	5.34	7.24	0.0267	0.0825	96	2.99
Nafion	–	18.33	27.92	11.00	17.22	0.076	0.146	–	10.05

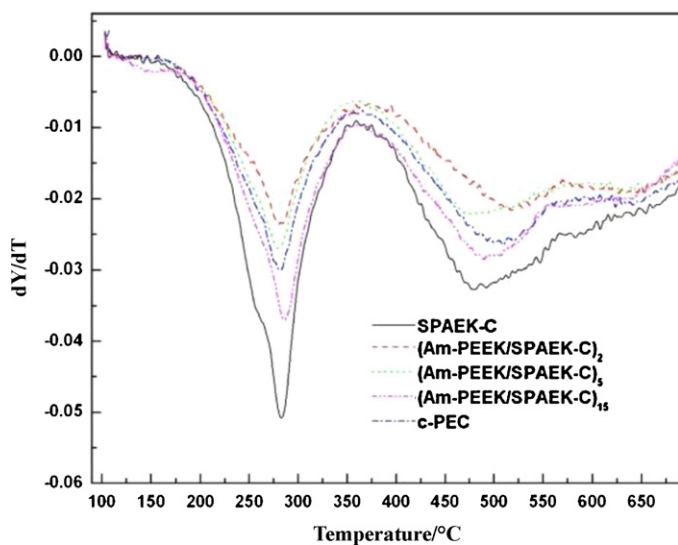
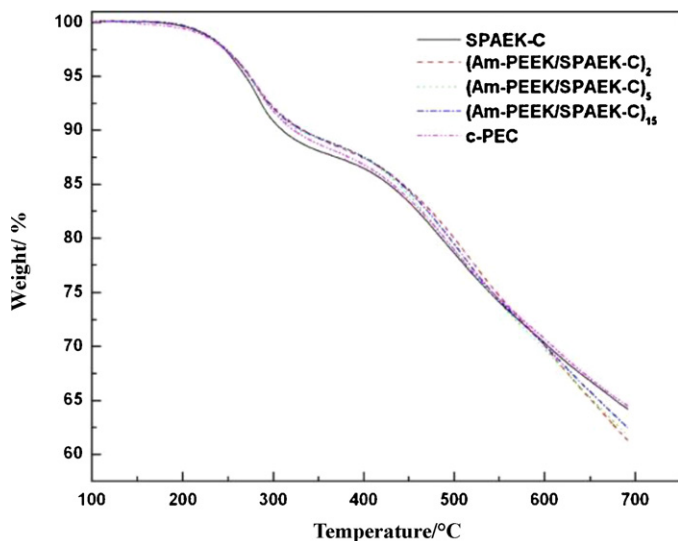


Fig. 3. TGA and DTG of SPAEK-C and (Am-PEEK/SPAEK-C)_n membranes in N₂.

Nafion 117 (listed in Table 1 and shown in Fig. 4). Although the self-assemble action on the membranes can restrict the hydrophilic of the multilayered films, the water soluble SPAEK-C also results in high water uptake values. The restrict effect and the hydrophilic nature lead to the irregular of water uptake values. However, the WU is reduced after the cross-linking treatment. The SR of membranes also show a similar trend. It is obvious that the cross-linked bonds help to hold the polyelectrolyte together to restrict the hydrophilic domains and thus decrease the WU and SR.

3.5. Oxidative stability

The oxidative stability of the PEC modified membranes was examined by the Fenton's test, which is one of the standards for evaluating the oxidative stability of PEMs. Table 1 shows the elapsed time (*t*) when the membranes start to break into pieces. It can be seen that the elapsed time of the pristine membrane is 75 min. And the 2, 5 and 15 bilayered membranes were 53 min, 45 min, and 73 min, respectively, which indicated the oxidative stability of the bilayered membranes first decreased, and then increased. But after cross-linking, the elapsed time was up to 96 min. The result clearly demonstrated that the dense network formed by a cross-linking could restrict the molecular shedding,

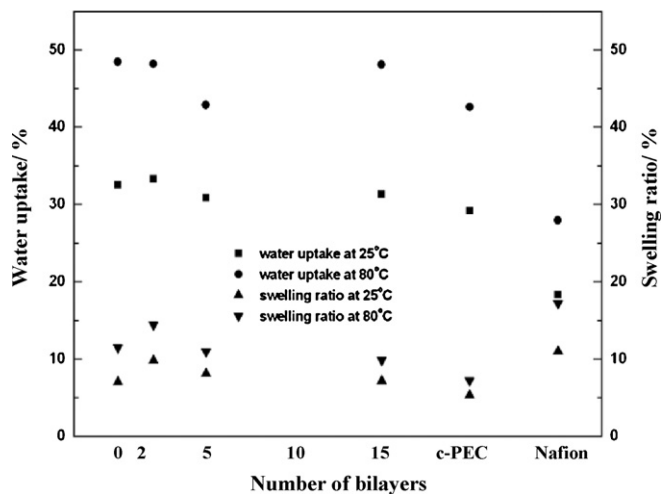


Fig. 4. Water uptake and swelling ratio of bilayers membranes.

and make the polymer chain to be less attacked by oxidizing radical species [30].

3.6. Proton conductivity, methanol permeability and selectivity

The proton conductivity is one of the crucial properties for determining the fuel cell performance. Higher levels of proton conductivity allow higher power densities to be achieved. The proton conductivities of membranes are listed in Table 1 and plotted as a function of temperature and bilayer number (Fig. 5).

It is interesting to observe that the proton conductivities at 80 °C of 2, 5 and 15 bilayered membranes are 0.103 S cm⁻¹, 0.102 S cm⁻¹ and 0.094 S cm⁻¹, respectively. They are both higher than that of the pristine membrane (0.0923 S cm⁻¹). Compared to the 10 wt.% SPAEK/phenoxy resin composite membrane as a promising candidate in DMFCs, the PEC modified membranes also show much higher conductivities [31]. As is well known, LBL self-assembled polyelectrolyte bilayers have some negative effect on the conductivity of membranes. However, the effect can be reduced into minimum by using a proper combination of polyanion and polycation. To assemble a highly conductive polymer is a good choice

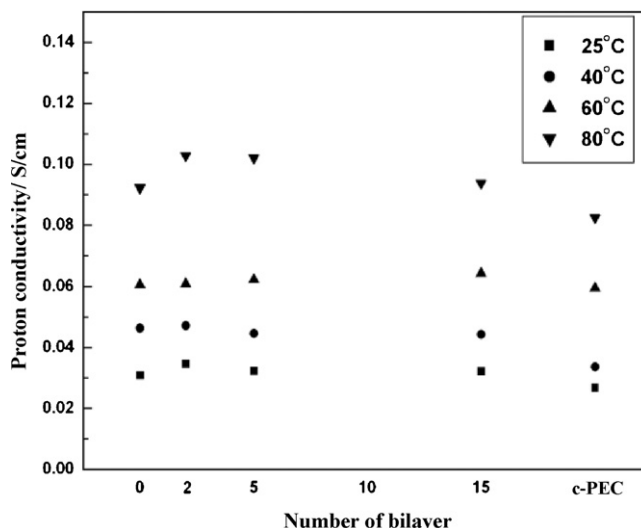


Fig. 5. Proton conductivity of the membranes.

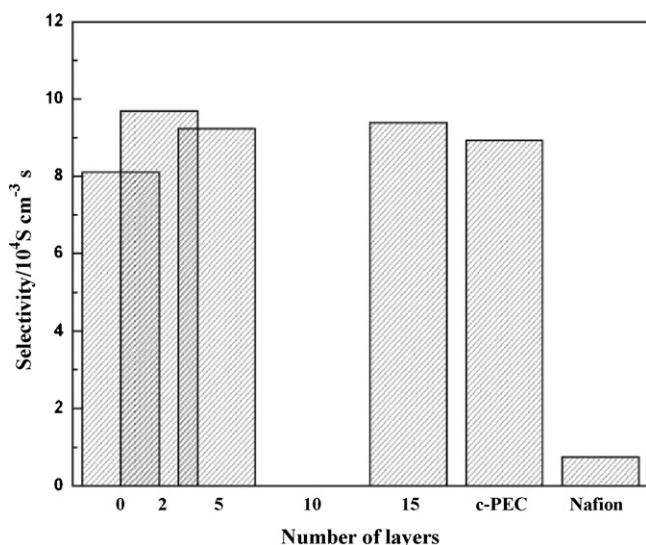


Fig. 6. Selectivity of SPAEK-C, (Am-PEEK/SPAEK-C)_n and Nafion 117.

to obtain the optimum properties. For this system, the slightly increase in conductivity may result from the fact that the highly sulfonated SPAEK-C contains numerous sulfonic acid and carboxylic acid groups, which may serve as a proton conductor. Since the soluble SPAEK-C has strong affinity towards water (this was also verified by the water uptake results), the multilayers can give rise to hydrophilic regions on the surface of membrane matrix. And the hydrophilic areas formed around the cluster of polycation and polyanion lead to the absorption of water, enabling easy proton conduction [32]. The increasing trend of proton conductivity corresponded well to the increasing trend of water uptake. Combining with the negative effect of LBL on the proton conduction, the conductivity takes on an increasing trend with the number of bilayer increasing; then it decreases. After the membrane was heated at 120 °C for 4 h, the proton conductivity of cross-linked 15-bilayer modified membrane decreased to some extent. The behavior correlated well with the reduced water uptake after the cross-linked treatment.

Table 1 also lists the methanol permeability of membranes at room temperature. Compared to the pristine SPAEK-C and Nafion 117 membranes, the methanol permeability of the Am-PEEK/SPAEK-C modified membranes was lower. The values decreased with an increase in the number of bilayers. The pristine SPAEK-C membrane showed the methanol permeability of $3.80 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, whereas, the Am-PEEK/SPAEK-C membranes containing 2, 5 and 15 bilayers showed the permeability of 3.57×10^{-7} , 3.50×10^{-7} and $3.43 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively. After cross-linking, the methanol permeability further decreased to $2.99 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. The results indicate that the electrostatic interactions or the cross-linking effects between the anion/cation pairs effectively block the methanol transport pathways.

Membranes intended for DMFCs must possess both high proton conductivity and low methanol crossover from the anode to the cathode compartment. Thus, selectivity (*S*), which is defined as the ratio of proton conductivity to methanol permeability, is a crucial selective factor for evaluating the potential performance of a DMFC membrane [33]. The higher selectivity value indicates the better performance in DMFCs [34,35]. Fig. 6 shows the *S* values of membranes. It can be noticed that the *S* of the multilayered membranes is one order of magnitude higher than that of Nafion 117, making these modified membranes a good alternative to be used in DMFCs.

4. Conclusions

Multilayered PECs were successfully prepared from Am-PEEK and SPAEK-C solutions by a LBL method. c-PEC was then obtained by a heat-induced cross-linking reaction between Am-PEEK and SPAEK-C via the formation of amide bonds. SEM results showed the presence of thin layers coated on the substrate. These thin multilayered films showed a significant effect on the reduction in methanol permeability. Two-bilayer of Am-PEEK/SPAEK-C modified membrane exhibited a high proton conductivity of 0.103 S cm^{-1} at 80 °C and a low methanol permeability of $3.57 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. And the cross-linked 15-bilayer modified membrane shows a remarkable reduction of WU, SR and methanol permeability compared to uncross-linked membranes. The selectivity of these multilayered PEC modified membranes is one order of magnitude higher than that of Nafion 117, which is attractive in DMFCs. Thus, LBL self-assembly of Am-PEEK/SPAEK-C bilayers on SPAEK-Cs is a convenient and effective method to prepare excellent PEMs for DMFC applications.

Acknowledgement

The authors thank the National Nature Science Foundation of China (grant no. 21074044) for financial support of this work.

References

- [1] B. Smitha, S. Sridhar, A.A. Khan, *J. Membr. Sci.* 259 (2005) 10–26.
- [2] G. Wegner, *Polym. Adv. Technol.* 17 (2006) 705–708.
- [3] R.G. Rajendran, *MRS Bull.* 30 (2005) 587–590.
- [4] S.S. Kocha, *Handbook of Fuel Cells—Fundamentals, Technology, and Applications*, vol. 3, Wiley, Chichester, UK, 2003.
- [5] A.S. Arico, S. Srinivasan, V. Antonucci, *Fuel Cells* 1 (2001) 133–161.
- [6] N. Jia, M.C. Lefebvre, J. Halfyard, Z. Qi, P.G. Pickup, *Electrochem. Solid-State Lett.* 3 (2000) 529–531.
- [7] N. Miyake, J.S. Wainright, R.F. Savinell, *J. Electrochem. Soc.* 148 (2001) A905–A909.
- [8] P. Staiti, A.S. Arico, V. Baglio, F. Lufrano, E. Passalacqua, V. Antonucci, *Solid State Ionics* 145 (2001) 101–107.
- [9] C. Yang, S. Srinivasan, A.S. Arico, P. Creti, V. Baglio, V. Antonucci, *Electrochem. Solid-State Lett.* 4 (2001) A31–A34.
- [10] V. Tricoli, *J. Electrochem. Soc.* 145 (1998) 3798–3801.
- [11] J. Liu, H. Wang, S. Cheng, K.-Y. Chan, *J. Membr. Sci.* 246 (2005) 95–101.
- [12] Z.G. Shao, X. Wang, I.M. Hsing, *J. Membr. Sci.* 210 (2002) 147–153.
- [13] B. Yang, A. Manthiram, *Electrochem. Commun.* 6 (2004) 231–236.
- [14] X. Zhang, M.L. Gao, X.X. Kong, Y.P. Sun, J.C. Shen, *J. Chem. Soc. Chem. Commun.* (1994) 1055–1056.
- [15] K. Ariga, Y. Lvov, T. Kunitake, *J. Am. Chem. Soc.* 119 (1997) 2224–2231.
- [16] G. Decher, *Science* 277 (1997) 1232–1237.
- [17] G. Decher, M. Eckle, J. Schmitt, B. Struth, *Colloid Interface Sci.* 3 (1998) 32–39.
- [18] S.P. Jiang, Z. Liu, Q. Tian, *Adv. Mater.* 18 (2006) 1068–1072.
- [19] H.D. Lin, C.J. Zhao, W.J. Ma, H.T. Li, H. Na, *J. Membr. Sci.* 345 (2009) 242–248.
- [20] C.J. Zhao, H.D. Lin, Z.M. Cui, X.F. Li, H. Na, W. Xing, *J. Power Sources* 194 (2009) 168–174.
- [21] J. Wang, C.J. Zhao, G. Zhang, Y. Zhang, J. Ni, W.J. Ma, H. Na, *J. Membr. Sci.* 363 (2010) 112–119.
- [22] J.J. Harris, P.M. Derose, M.L. Bruening, *J. Am. Chem. Soc.* 121 (1999) 1978–1979.
- [23] H.D. Lin, C.J. Zhao, Z.M. Cui, W.J. Ma, T.Z. Fu, H. Na, W. Xing, *J. Power Sources* 193 (2009) 507–514.
- [24] M.M. Guo, B.J. Liu, Z. Liu, L.F. Wang, Z.H. Jiang, *J. Power Sources* 189 (2009) 894–901.
- [25] M. Gil, X.L. Ji, X.F. Li, H. Na, J.E. Hampsey, Y.F. Lu, *J. Membr. Sci.* 234 (2004) 75–81.
- [26] D. Yoo, S.S. Shiratori, M.F. Rubner, *Macromolecules* 31 (1998) 4309–4318.
- [27] G. Socrates, *Infrared Characteristic Group Frequencies*, John Wiley & Sons, New York, 1980.
- [28] Y. Wan, K.A.M. Creber, B. Peppley, V.T. Bui, *J. Appl. Polym. Sci.* 94 (2004) 2309–2323.
- [29] K.D. Kreuer, A. Rabenau, W. Weppner, *Angew. Chem. Int. Ed.* 21 (1982) 208–209.
- [30] C. Perrot, L. Gonon, M. Bardet, C. Marestin, A. Pierre-Bayle, G. Gebel, *Polymer* 50 (2009) 1671–1681.
- [31] 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.
- [32] K. Miyatake, K. Oyaizu, E. Tsuchida, A.S. Hay, *Macromolecules* 34 (2001) 2065–2071.
- [33] B.S. Pivovar, Y.X. Wang, E.L. Cussler, *J. Membr. Sci.* 154 (1999) 155–162.
- [34] J. Shen, J. Xi, W. Zhu, L. Chen, X. Qiu, *J. Power Sources* 159 (2006) 894–899.
- [35] Y. Shen, X. Qiu, J. Shen, J. Xi, W. Zhu, *J. Power Sources* 161 (2006) 54–60.