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Multilayer Membranes Based on Sulfonated Poly(Ether Ether Ketone) and Poly(Vinyl Alcohol) for Direct Methanol Membrane Fuel Cells

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Abstract: Much work has been conducted on the substitutes for Nafion as proton exchange membrane materials. Some researches are focused on the heterogeneous multilayered membranes reported by R. Jiang [*J. Electrochem. Soc. 153 (2006) A1554*], B. Yang [*Electrochem. Commun. 6 (2004) 231*] and S. Ren [*J. Membr. Sci. 247 (2005) 59*]. However, just as the dependence of methanol crossover upon the layer with the lowest permeability, the proton transfer ability is major confined by the layer with the poorest conductivity. Moreover, various swelling ratio and contractibility of sub-layers will make the hidden problems of separation between catalyst layer and proton exchange membrane become more obvious. We present here a multilayered membranes containing five thin layers of sulfonated poly(ether ether ketone)(SPEEK) and five thin layers of poly(vinyl alcohol)(PVA). SPEEK layers and PVA layers were located alternatively in the composite membrane. The swelling behaviors of PVA layer are restrained by both sideward SPEEK layers. Methanol crossover is efficiently alleviated piece by piece without visible proton conductivity loss. The preliminary investigation in DMFC suggests its promising application as resisting methanol and proton exchange membrane.

Keyword: Multilayered membrane, Double-layer membrane, Methanol crossover, DMFC.

1. INTRODUCTION

Direct methanol fuel cells (DMFC) are attractive for transportation and portable application as they can offer important advantages such as high efficiency, compact structure and ease in refueling. Many breakthroughs in DMFC technology are obtained and some prototype fuel cells have been unveiled by now. However, several problems still need to be overcome before a general usage of the DMFC technology could be achieved. One of the major obstacles is the methanol crossover from the anode to the cathode through the typical Nafion membranes. This problem can be relieved by applying the dilute methanol. However, the dilute methanol can aggravate the drainage task of cathode. On the other hand, high methanol concentration is attractive to obtain high energy density. Therefore, the proton exchange membrane with low methanol permeation is particularly urgent for practical application.

In this regard, much work has been devoted to the development of fluorine-free alternative such as sulfonated poly(ether sulfones) [1, 2], sulfonated poly(arylene ether)s [3], sulfonated poly(*p*-phenylene) [4, 5], sulfonated polyimide [6, 7], sulfonated poly(arylene ether ketones) [8, 9, 10] and sulfonated aromatic poly(ether ether ketone) [11-14]. Among these membrane materials, SPEEK membranes are promising as they can offer adjustable proton conductivity [15, 16], excellent chemical and thermal stability [17]. Moreover, SPEEK membranes show lower methanol permeation than Nafion membrane due to their narrower and more branched hydrophilic channels [18]. Proton conductivity of this membrane is mainly dependent on sulfonation degree (DS) [19-20]. The DS of SPEEK can be adjusted by sulfonation time, temperature and concentration of sulfuric acid conveniently [21-24]. However, the introduction of $-SO_3$ groups can destroy the ordered structure of SPEEK molecular and promote the decomposition of SPEEK [18]. Moreover, SPEEK shows an increase in methanol crossover upon DS, which was induced by the severe membrane swelling in the methanol solution [25]. To maintain lower methanol permeability and suitable stability at high DS, many investigations have been conducted on the blend membranes based on SPEEK and crosslink additives such as poly(ether sulfone), poly(amide imide), polysulfone and poly(benzimidazole) [26-29]. However, the interactions between SPEEK molecules and additives are complex and indistinct, which might destroy the proton transfer channels and affect the cell performance negatively.

Recent years, a few researches have been conducted on the heterogeneous membranes such as multilayered membrane [25, 30, 31], which can offer satisfactory performance. Ren immersed SPEEK into Nafion containing casting solution to prepared Nafion-SPEEK-Nafion composite membranes. In Jiang's work [25], a thin layer of SPEEK with a lower DS (41 %) was used as the central methanol barrier layer; higher DS (60 %) SPEEK layers were applied on the two outer surfaces as the conductive layers. Yang [30] fabricated a multilayered membrane containing a thin central layer of SPEEK and two outer layers of recast Nafion. The investigation on the multilayered membranes suggests their promising application in DMFC. However, the self-governed characteristic of each layer should not be neglected. The multilayered membrane reported before contains only three layers, the thickness of each layers is ranging from 10~100 μm; each layers becomes one independent phase and presents the distinct characteristic of itself. Fox example, the various swelling ratio and mechanical strength of each layer

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make it difficult to maintain the tight contact among each other. Therefore, the separations in practical application might be an anxious problem. Moreover, the proton conductivity of the multilayered membrane might be restricted by the layer with poor proton transfer ability just as the major dependence of methanol crossover upon the layer with low methanol permeability [25, 30, 31]. In view of these problems, we present here a multilayered membrane containing five thin SPEEK layers and five thin PVA layers, above two kinds of layers were located alternatively. The thickness of each layer is about several microns. The thin layers of PVA are expected to block the methanol permeation piece by piece. The thin layers of SPEEK offer good mechanical strength and low swelling ratio. The multilayered membranes could thus alleviate the methanol crossover problem while offering good mechanical strength and cell performance.

2. EXPERIMENTAL

The details on sulfonation of poly(ether ether ketone) have been report elsewhere [12]. Based on our previous study and reports by Yang [30], SPEEK membrane with a sulfonation level above 50 % could obtain reasonable proton conductivity and suitable mechanical properties. Hereby, a DS of 55 % was used in this study to demonstrate the concept. The homogenous SPEEK solution (10 %, dissolved in DMSO) and PVA (10 %, H_3PO_4 2 %, dissolved in DMSO,) solution was obtained beforehand by thermal dissolving. The multilayered membrane was fabricated by the sample casting method repeatedly. 1 mL SPEEK solution was firstly dropped on the tailor-made plate (diameter: 75 mm) and evaporated at 60 ˚C. 1 mL PVA solution was then dropped onto the as formed SPEEK membrane and evaporated at 60 ℃. Subsequently, 1 mL SPEEK solution was again dropped on the PVA surface and evaporated at 60 ˚C. The above process was repeated until five SPEEK layers and five PVA layers were obtained alternately. With the aim of comparison, double-layer membrane and blend membrane were fabricated too. Double-layer membrane was fabricated by dropping 5 mL SPEEK solution on the customized plate and dried at 60 ˚C, 5 mL PVA solution was then dropped onto the SPEEK surface and evaporated at 60 ˚C. Blend membrane was formed by mixing 5 mL SPEEK solution and 5 mL PVA solution homogenously, the mixed solution was then casted onto the tailor-made plate and dried at 60 ℃. The three composite membranes above was finally dried under vacuum at 80 ˚C for 12 h and 110 ˚C for 3 h. The as formed multilayered membrane, double-layer membrane and blend membrane are designated, respectively, as MM, DM and BM.

Liquid uptake of the membranes in water and 10 M methanol solution was calculated by determinating the change in weight and dimensions under dry and wet status [32]. Ionic exchange capacity was obtained by classical titration method [12]. Methanol permeability was measured using a homemade glass diffusion cell. The structure and the process were similar to the report [32]. The proton conductivity was measured by AC impedance spectroscopy over a frequency range of 1-10^6 Hz. The performances of the cells with MM, DM and BM membranes were compared. The above experiments were all carried at 80 ˚C.

3. RESULTS AND DISCUSSION

3.1. Swelling Behavior in Water and 10 M Methanol Solution

Table **1** summarizes the water uptake and swelling ratio of the three composite membranes at 80 ℃. The swelling ratio in the direction of plane is far lower than that in thickness direction, which might be beneficial to the practical DMFC. In DMFC applications, thickness swelling might reinforce the contact between current collectors and membrane electrolyte assembly. In contrary, the swelling in plane can loosen the contact between electrolyte membrane and catalyst resulting in the increase in resistance of MEA and separations in the later applications. The water uptake for the MM membrane is lower than those of DM and BM membranes. Especially, the dimensional stability of MM membrane is much higher than the other two membranes. The higher swelling behavior of thin PVA layers was restrained by both sideward SPEEK layers. DM membrane shows the highest uptake and swelling ratio due to the higher uptake of PVA layer. BM membrane shows the middle swelling behavior on account of some interaction between SPEEK and PVA molecules, which will be discussed in other paper. The similar results in 10 M methanol solution are presented in Table **2**.

Table 1. Swelling Behavior in Water

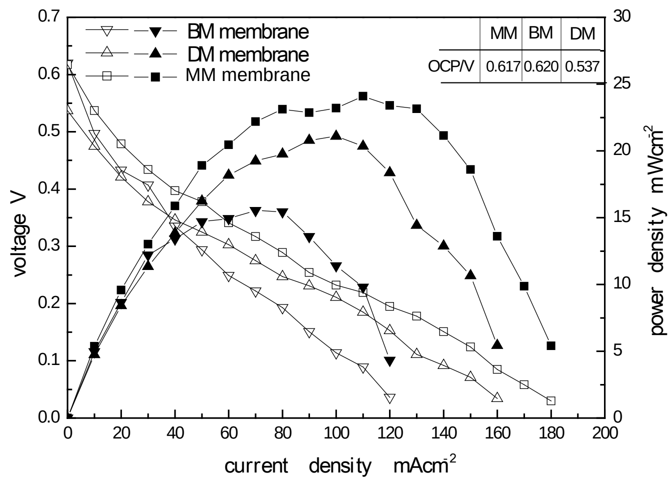
Membrane Samples	Uptake (%)	Thickness Swelling (%)	Planar Swelling (%)
Multilayer membrane (MM)	30.5	28.4	5.3
Double-layer membrane (DM)	76.2	67.1	16.8
Blend Membrane (BM)	46.8	30.2	12.4

Table 2. Swelling Behavior in 10 M Methanol

Membrane Samples	Uptake (%)	Thickness Swelling (%)	Planar Swelling (%)
Multilayer membrane (MM)	15.2	11.1	3.3
Double-layer membrane (DM)	40.6	28.8	12.4
Blend Membrane (BM)	28.7	19.5	7.1

Table 3. IEC, Proton Conductivity and Methanol Permeability

Membrane Samples	IEC (mmol g^{-1})	Proton Conductivity (S cm^{-1})	Methanol Permeability (cm^2 s^{-1})
Multilayer membrane (MM)	1.01	5.5×10^{-2}	3.0×10^{-6}
Double-layer membrane (DM)	0.92	1.7×10^{-2}	5.5×10^{-6}
Blend Membrane (BM)	0.35	4.4×10^{-3}	2.9×10^{-6}



Current density mA cm^{-2}	Voltage V			Power density mW cm^{-2}		
	BM	DM	MM	BM	DM	MM
0	0.62	0.537	0.617	0	0	0
10	0.497	0.475	0.537	4.97	4.75	5.37
20	0.433	0.421	0.479	8.66	8.42	9.58
30	0.407	0.378	0.434	12.21	11.34	13.02
40	0.335	0.346	0.397	13.4	13.84	15.88
50	0.294	0.325	0.378	14.7	16.25	18.9
60	0.249	0.303	0.341	14.94	18.18	20.46
70	0.222	0.275	0.317	15.54	19.25	22.19
80	0.193	0.247	0.289	15.44	19.76	23.12
90	0.151	0.231	0.254	13.59	20.79	22.86
100	0.114	0.211	0.232	11.4	21.1	23.2
110	0.089	0.185	0.219	9.79	20.35	24.09
120	0.036	0.153	0.195	4.32	18.36	23.4
130		0.111	0.178		14.43	23.14
140		0.092	0.151		12.88	21.14
150		0.071	0.124		10.65	18.6
160		0.034	0.085		5.44	13.6
170			0.058			9.86
180			0.03			5.4

	MM	BM	DM
OCP/V	0.617	0.620	0.537

Fig. (1). Polarization curves of cells with different membranes.

3.2. IEC, Proton Conductivity and Methanol Permeability

Ionic exchange capacity (IEC) is usually considered to correspond to the proton transfer property in homogenous proton exchange membrane. However, it is only a referenced factor offering contributions to the proton conductivity in multilayered and double-layer membranes. In heterogenous membranes, the proton conductivity of the double-layer membrane is restricted by the sub-layer with larger proton resistance. IEC, proton conductivity and methanol crossover results are shown in Table **3**. Compared to DM membrane, MM membrane achieved more than three times proton conductivity in despite of the similar IEC value. The proton transfer ability of DM membrane was confined by the large block of PVA layer. BM presents the lowest IEC and proton conductivity due to some interaction between SPEEK and PVA molecule.

MM membrane gives equivalent methanol permeability to that of BM. In our test, it also means that the methanol resistance piece by piece in multilayered membrane is much efficient than the double-layer membrane.

3.3. Open Circuit Potential and Polarization of the Cells

Fig. (**1**) compares the open circuit potential (OCP) and polarization curves of cells assembled with MM, DM and BM membranes. BM membrane exhibits larger polarization losses than the MM membrane due to the poor proton conductivity. The inset-table shows the similar OCP value of BM and MM membrane. DM membrane presents lower OCP than the other membranes due to the slightly larger methanol permeability. However, DM membrane gives better performance than BM membrane. The results in Fig. (**1**) suggest the promising application of multilayered membrane in DMFC.

CONCLUSION

We have demonstrated a multilayered membrane concept to alleviate methanol crossover and maintain high proton conductivity. This concept was based on the performance difference between homogenous membrane and heterogenous membrane reported in [25, 30, 31]. Multilayered membranes containing five thin layers of SPEEK are found to significantly reduce the swelling ratio and maintain high proton transfer ability; five thin layers of PVA are determined to block methanol crossover piece by piece efficiently. We believe that this multilayered approach to membrane fabrication is a promising attempt to develop the good proton exchange membrane. Further investigations on long-term stability in DMFC, the effect of thickness and layers number are currently underway in our laboratory. Multilayered membranes based on other materials will also be studied in our following research.

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