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Layer-by-Layer Self-Assembly of Composite Polyelectrolyte– Nafion Membranes for Direct Methanol Fuel Cells**

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Perfluorosulfonic polymers such as Nafion are the most common membrane electrolytes used in polymer electrolyte and direct methanol fuel cells (PEFCs and DMFCs) owing to their high proton conductivity and good chemical and thermal stability. However, methanol readily migrates from the anode, through the Nafion membrane, to the cathode, reducing the open-circuit potential (OCP) by as much as 0.15-0.2 V and poisoning the electrocatalysts at the cathode.^[1] Methanol crossover seriously retards the technological development of DMFCs. Thus, there has been extensive research activity in the modification of Nafion-based membranes to reduce the methanol crossover through, for example, the in situ polymerization of Nafion with poly(1-methylpyrrole),^[2] and the development of composite membranes such as Nafion-silica,^[3,4] Nafion-zirconium phosphate,^[5] Nafion-cesium ions,^[6] and Nafion-poly(furfuryl alcohol) nanocomposite membranes.^[7] The modification of Nafion membranes reduces the methanol crossover and, in general, improves the performance of DMFCs. To achieve significant reduction in the methanol permeability, the oxide content has to be high (e.g., 20 wt % silica in the case of the Nafion-silica composite^[3]). This, in turn, reduces the proton conductivity and the mechanical properties are also seriously affected owing to the significant alteration of the membrane microstructure. Sandwiching a Pd thin film between Nafion membranes,^[8] depositing a Pd and/or Pd-Cu alloy thin film on the surface of a Nafion membrane,^[9-11] or depositing Pd nanoparticles through ion exchange followed by chemical reduction,^[12] have been shown to reduce the methanol crossover. Unfortunately, the Pd thin film increased the overall cell resistance. The dispersed Pd particles in the membrane altered its microstructure, resulting in reduced cell performance and stability.

Various multilayer membrane structures have also been investigated with the aim of suppressing methanol crossover. Yang and Manthiram studied the methanol crossover and conductivity of Nafion membranes with a thin barrier layer of sulfonated poly(ether ether ketone) (SPEEK).^[13] Si et al. de-

veloped trilayer membranes composed of one central methanol barrier layer and two conductive layers to suppress the methanol crossover.^[14] Casting non-conductive polymers such as poly(vinyl alcohol) (PVA) onto Nafion membranes can also reduce the methanol crossover.^[15] However, in all these cases, the proton conductivity also decreased significantly due to the addition of a relatively thick barrier layer.

The sequential adsorption of oppositely charged polyelectrolytes by layer-by-layer (LbL) self-assembly is an efficient method for obtaining multilayer thin films. This technique has progressed significantly since the pioneering work by Decher et al.^[16,17] In this technique, two oppositely charged polyelectrolytes dissolved in aqueous solution are alternately deposited on a support surface by means of electrostatic attraction. After each dipping cycle, the surface charge is reversed, which enables deposition of a subsequent layer. The process leads to the formation of a final multilayer structure that is stabilized primarily by strong electrostatic forces. The simplicity and efficiency of this technique has resulted in a wide range of applications of multilayer films for sensors,^[18] nonlinear optics,^[19] photoactive films,^[20] drug delivery,^[21,22] and selectivearea patterning.^[23] Recently, Farhat and Hammond reported the deposition of a polyelectrolyte multilayer on a porous support using the LbL technique to fabricate an extremely thin (10-16 µm) composite membrane.^[24] A fuel cell using a poly(ethylene oxide)-poly(acrylic acid) (PEO-PAA) composite membrane achieved a power density of 16.5 mW cm⁻² at a relative humidity of 55 %.

We have been able to prepare an effective multilayer methanol-blocking thin film on a Nafion membrane using LbL self-assembly of oppositely charged polyelectrolytes. The starting materials were poly(diallyldimethylammonium chloride) (PDDA, polycation), poly(sodium styrene sulfonate) (PSS, polyanion), poly(1-(4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido)-1,2-ethanediyl, sodium salt) (PAZO, polyanion), and a Nafion membrane (N1135, 89 µm). Figure 1 shows the molecular structures of the PDDA, PSS, and PAZO polyelectrolytes used in this study. The LbL self-assembly was carried out by alternate dipping of the Nafion membrane in polycation and polyanion electrolyte solutions, as illustrated by Decher.^[16] The LbL self-assembly of oppositely charged polyelectrolytes was followed by UV-vis spectroscopy and the methanol-crossover current was measured in a set-up similar to that described by Ren et al.^[25]

Figure 2 shows UV-vis spectra of the LbL self-assembled N1135 membrane as a function of the number of PDDA–PSS and PDDA–PAZO bilayers. For PDDA–PSS multilayers, al-

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Figure 1. Molecular structure of a) PDDA, b) PSS, and c) PAZO.

though the absorbance peak at 225 nm was not shown clearly, the absorbance increased with an increasing number of PDDA-PSS bilayers (Fig. 2a). Absorbance at 225 nm is most likely related to the characteristic wavelength of 228 nm for the sodium styrene sulfonate mers.^[20] Since PDDA is almost transparent in the UV-vis spectral range, the increase in absorbance was attributed to the adsorption of PSS on the previously deposited PDDA layer. The inset graph of Figure 2a shows the absorbance at 225 nm as a function of the number of PDDA-PSS bilayers, which increased linearly with the number of LbL self-assembled PDDA-PSS bilayers. This linear relationship indicates that the same amount of polymer was deposited in every dipping cycle and the multilayer was formed in a regular manner. A linear dependence of the absorbance on the number of bilayers was also observed for LbL self-assembly of PDDA-PAZO bilayers on Nafion (Fig. 2b). The absorption peaks at 269 and 355 nm in the LbL self-assembled films are characteristic of the PAZO polyelectrolyte.

To evaluate the effect of PDDA–PSS and PDDA–PAZO multilayers on the proton conductivity of the N1135 membranes, the conductivity was measured at 30 °C. The results are given in Table 1. The conductivity of an unmodified N1135 membrane was 0.124 S cm^{-1} . With an increase in the number of self-assembled PDDA–PSS bilayers, the conductivity of the membrane decreased. However, the decrease in the proton conductivity appears to be small. After the self-assembly of eight PDDA–PSS bilayers, the proton conductivity was 0.106 S cm^{-1} , a decrease of 15 % compared with that of a pristine Nafion membrane. On the other hand, with the self-assemble of the self-assemble o

sembly of five PDDA–PAZO bilayers, the conductivity decreased to 0.071 S cm⁻¹, a reduction in conductivity of 43 %. The reduction in the proton conductivity of a Nafion membrane modified with PDDA–PAZO bilayers is significantly higher than that with PDDA–PSS bilayers. Since PAZO is a comblike polymer, its layer thickness is greater than that of PSS, which contains



Figure 2. UV-vis spectra of the N1135 membrane as a function of the number of layers self-assembled: a) PDDA–PSS and b) PDDA–PAZO bilayers.

smaller monomeric blocks.^[26] The much smaller decrease in the conductivity in the case of self-assembled PDDA–PSS bilayers could also result from the fact that PSS contains a sulfonic acid group, which may serve as a proton conductor. The LbL self-assembled polyelectrolyte bilayers have some negative effect on the conductivity of the membrane. However, this effect appears to depend on the nature of the polyelectrolyte bilayers and can be reduced to a minimum by using a proper combination of polycation and polyanion, as shown in the case of PDDA–PSS bilayers.

 Table 1. The proton conductivity, limiting methanol-crossover current, and maximum power density of N1135 membranes as a function of the number of PDDA-PSS and PDDA-PAZO bilayers.

Number of PDDA-PSS bilayers	0	1	2	4	8	5 PDDA– PAZO bilayers
Conductivity [S cm ⁻¹]	0.124	0.113	0.109	0.107	0.106	0.071
OCP [V]	0.540	0.558	0.552	0.560	0.554	0.560
Limiting methanol-crossover current [mA cm ⁻²]	98 ± 4.0	92 ± 3.2	90 ± 2.7	78 ± 2.8	69 ± 2.0	76 ± 2.7
Maximum power density [mW cm ⁻²]	26	30	36	37	33	29



Figure 3 shows the limiting-current curves for the oxidation of methanol that has crossed over from the anode to the cathode through N1135 membranes, for various self-assembled PDDA–PSS and PDDA–PAZO multilayers. The methanol-



Figure 3. Methanol-crossover current of an MEA with LbL self-assembly of PDDA–PSS and PDDA–PAZO bilayers on N1135 membranes. The methanol-oxidation current was measured at 30 °C.

oxidation current was measured at 30 °C. For simplicity, only the limiting-current data for the methanol crossover on a N1135 membrane with five PDDA-PAZO bilayers is shown in the figure. With one self-assembled PDDA-PSS bilayer, the limiting methanol-crossover current density was 92 mA cm⁻², a decrease of 6 % in comparison to 98 mA cm⁻² measured for an unmodified N1135 membrane. This indicates that the LbL self-assembly of the PDDA-PSS bilayer reduces the methanol-crossover current. When the number of PDDA-PSS bilayers was increased to four, the limiting methanolcrossover current decreased further to 78 mA cm⁻², which is similar to the value of 76 mA cm^{-2} observed for a N1135 membrane with five PDDA-PAZO bilayers. With eight PDDA–PSS bilayers, the crossover current was 69 mA cm⁻², a decrease in methanol permeability of 30 %, when compared with an unmodified N1135 membrane. The methanol crossover decreased with an increase in the number of LbL self-assembled oppositely charged polyelectrolyte bilayers.

The cell performance of DMFCs prepared with an unmodified N1135 membrane and N1135 membranes modified with PDDA–PSS and PDDA–PAZO bilayers at 30 °C is shown in Figure 4. The OCP was 0.540 V for the cell with an unmodified N1135 membrane. With an increasing number of PDDA– PSS bilayers, the OCP increased slightly to 0.56 V, most likely owing to a reduction of the methanol crossover. The best performance was observed for the DMFC that used an N1135 membrane with four self-assembled PDDA–PSS bilayers, achieving a power density of 37 mW cm⁻². This is an increase of 42 % in power output when compared to the cell using an unmodified N1135 membrane (26 mW cm⁻²).



Figure 4. Polarization curves and power output of a DMFC using an unmodified N1135 membrane, and N1135 membranes modified with self-assembled PDDA–PSS and PDDA–PAZO bilayers, measured at 30 °C. Operating conditions: $2 \le OH_3OH$, 0 psi; cathode, oxygen, 10 psi.

However, on further increasing the number of PDDA-PSS bilayers to eight, the maximum power density decreased to 33 mW cm^{-2} . This could be due to the observation that increasing the number of PDDA-PSS bilayers also decreases the proton conductivity of the membrane (see Table 1), thus increasing the overall cell resistance. This could result in a decease in the cell performance. Therefore, there is a delicate balance between the reduction in the methanol crossover and the decrease in proton conductivity for self-assembled multilayer thin films. The relatively small increase in the power density of the cell with a Nafion membrane modified with five PDDA-PAZO bilayers (29 mW cm⁻², an increase of 12 % in comparison to the cell with the unmodified Nafion membrane) is most likely due to the significant reduction of the proton conductivity of the composite PDDA-PAZO-Nafion membrane (see Table 1).

It is known that Nafion has a dual structure with a hydrophobic region interspersed with ion-rich hydrophilic domains, and that methanol diffuses primarily through the hydrophilic water-rich domains.^[27,28] Thus, blocking the water-rich domains, which are primarily associated with $-SO_3^-$ clusters on the Nafion-membrane surface, would effectively inhibit methanol crossover. Owing to the existence of a negatively charged sulfonic acid group, SO3-, on the surface of the Nafion membrane, self-assembly of positively charged polycations occurs as the result of electrostatic interactions. PDDA is a strong polycation and thus, with the self-assembly of a positively charged PDDA monolayer, charge inversion would take place on the Nafion surface.^[29] Dipping of the self-assembled PDDA-Nafion layer in a negatively charged polyanion solution, such as PSS or PAZO, would lead to the self-assembly of a polyanion monolayer. Figure 5 shows schematically the





Figure 5. Schematic diagram of the structure of a LbL self-assembly of oppositely charged polycations and polyanions on a Nafion electrolyte membrane, showing blocking of the methanol crossover.

structure of LbL self-assembled polycation and polyanion multilayers on a Nafion membrane, which inhibit methanol crossover.

The LbL self-assembly of oppositely charged polyelectrolytes on a Nafion membrane shows a significant effect on the reduction in methanol crossover and on the enhancement of the performance of DMFCs (Figs. 3,4). In the case of a DMFC using a Nafion membrane self-assembled with four PDDA-PSS bilayers, the power density increased by 42%, when compared to a cell with an unmodified Nafion membrane; this result shows a significant enhancement in the performance of DMFCs. Most importantly, the LbL self-assembly approach appears to have a much smaller detrimental effect on the proton conductivity and chemical and thermal stability of the Nafion membrane, a significant advantage compared to other modification approaches.^[2-15] LbL self-assembly of composite polyelectrolyte multilayer thin films offers a potentially very effective technique to minimize the methanol-crossover problem in DMFCs. Nevertheless, a significant amount of work is still needed to optimize the LbL self-assembly process of the oppositely charged polyelectrolytes and to understand the effect of interaction between the polycation and polyanion on the proton conductivity and methanol-crossover process.

Experimental

PDDA (35 wt % in water, weight-average molecular weight $(M_W) = 5000$ to 40 000, Aldrich), PSS $(M_W = 70\,000$, Sigma), and PAZO $(M_W = 65\,000$ to 100 000, Aldrich) were used without further treatment. The Nafion solution (5 wt %) and Nafion membrane (N1135, 89 µm) were obtained from DuPont. Sulfuric acid (95–97 %), hydrogen peroxide (30 %), and methanol were obtained from Fluka. Milli-Q water (Millipore, 18.2 M Ω cm at 25 °C) was used in the experiments.

The Nafion 1135 membrane was treated according to the standard procedure of 30 min in a 5 wt % H_2O_2 solution at 80 °C, 30 min in Milli-Q water at 80 °C, and 30 min in an 8 wt % H_2SO_4 solution at 80 °C. After each treatment, the membrane was rinsed in Milli-Q water three times to remove traces of H_2O_2 and H_2SO_4 . The membrane was stored in Milli-Q water before use.

The LbL self-assembly of PDDA–PSS multilayers was carried out by alternate dipping of the pretreated Nafion membrane in PDDA (20 mM) and PSS (20 mM) solutions at room temperature for 5 min. After each dipping step, the membrane was rinsed with Milli-Q water to remove weakly bonded polyelectrolyte molecules. The alternate self-assembly of polycation and polyanion was repeated to increase the number of bilayers [16]. The LbL self-assembled membrane was finally cleaned with Milli-Q water, followed by protonation treatment in 1 M H₂SO₄ at 80 °C for 30 min, and then rinsed again with Milli-Q water. The LbL self-assembly of the PDDA–PAZO multilayer on the Nafion-membrane surface followed the same procedure as that for the LbL self-assembly of the PDDA–PSS multilayers.

Characterization: The LbL self-assembly of PDDA–PSS and PDDA–PAZO multilayers on Nafion membranes was monitored using UV-vis spectroscopy (HP 8350) as a function of the number of bilayers. The conductivity of the LbL self-assembled Nafion membrane was measured using a modified four-probe dc conductivity cell, based on that described by Slade et al. [30]. The measurement was carried out at 30 °C in a 1 M H₂SO₄ solution.

To evaluate the methanol crossover and the performance of the DMFCs, a membrane–electrode assembly (MEA) was made by sandwiching a LbL self-assembled composite polyelectrolyte–Nafion membrane between a Pt–Ru anode and a Pt–C cathode. Pt–Ru black (Johnson Matthey) was used for the anode and 40 % Pt–C (Johnson Matthey) was used for the cathode. The loading of Pt in the catalyst layer was about 0.8 mg cm⁻² for both anode and cathode layers. Carbon paper treated with poly(tetrafluoroethylene) was used as the gas-diffusion layer. The MEA was hot-pressed at 140 °C and 4 MPa for 90 s.

Methanol crossover the self-assembled N1135 membrane was measured using an MEA with an electrode area of 5 cm² at 30 °C. Methanol (2 M) was fed to the anode at 7.5 mL min⁻¹ and humidified nitrogen was fed to the cathode side at 20 mLmin^{-1} with 10 psi (ca. 6.89 kPa) back pressure. The potential was scanned from 0.1 to 0.9 V at a scan rate of 0.5 mV s⁻¹ and the methanol that crossed over through the membrane was oxidized at the cathode. The limiting methanol-crossover current was obtained by measuring the transportcontrolled limiting current of the methanol electrooxidized at the membrane/Pt catalyst interface. The cells were made from the same batches of electrocatalysts and diffusion layers. In this case typical standard deviation in the methanol-crossover current density was in the range 4–5 % (Table 1). The power output of the DMFCs was evaluated on MEAs based on LbL self-assembled N1135 membranes. The catalyst and catalyst loading of the MEAs were the same as those for the methanol-crossover current measurements. Methanol (2 M) was fed to the anode at a flow rate of 7.5 mL min⁻¹. Oxygen was supplied to the cathode with humidification at 30 °C at a flow rate of 50 mL min⁻¹. The tests were carried out at 30 °C with 10 psi back pressure on the cathode side. Details of the measurement can be found elsewhere [31].

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- [1] A. S. Arico, S. Srinivasan, V. Antonucci, Fuel Cells 2001, 1, 133.
- [2] N. Jia, M. C. Lefebvre, J. Halfyard, Z. Qi, P. G. Pickup, *Electrochem. Solid-State Lett.* 2000, 3, 529.
- [3] N. Miyake, J. S. Wainright, R. F. Savinell, J. Electrochem. Soc. 2001, 148, A905.
- [4] P. Staiti, A. S. Aricò, V. Baglio, F. Lufrano, E. Passalacqua, V. Antonucci, *Solid State Ionics* 2001, 145, 101.
- [5] C. Yang, S. Srinivasan, A. S. Aricò, P. Creti, V. Baglio, V. Antonucci, *Electrochem. Solid-State Lett.* 2001, 4, A31.
- [6] V. Tricoly, J. Electrochem. Soc. 1998, 145, 3798.
- [7] J. Liu, H. Wang, S. Cheng, K.-Y. Chan, J. Membrane Sci. 2005, 246, 95.
- [8] C. Pu, W. Huang, K. L. Ley, E. S. Smotkin, J. Electrochem. Soc. 1995, 142, L119.
- [9] S. R. Yoon, G. H. Hwang, W. I. Cho, I.-H. Oh, S.-A. Hong, H. Y. Ha, J. Power Sources 2002, 106, 215.



- [10] J. Prabhuram, T. S. Zhao, Z. X. Liang, H. Yang, C. W. Wong, J. Electrochem. Soc. 2005, 152, A1390.
- [11] T. Hejze, B. R. Gollas, R. K. Sauerbrey, M. Schmied, F. Hofer, J. O. Besenhard, J. Power Sources 2005, 140, 21.
- [12] Y. J. Kim, W. C. Choi, S. I. Woo, W. H. Hong, *Electrochim. Acta* 2004, 49, 3227.
- [13] B. Yang, A. Manthiram, Electrochem. Commun. 2004, 6, 231.
- [14] Y. Si, J.-C. Lin, H. R. Kunz, J. M. Fenton, J. Electrochem. Soc. 2004, 151, A463.
- [15] Z.-G. Shao, X. Wang, I.-M. Hsing, J. Membrane Sci. 2002, 210, 147.
- [16] G. Decher, *Science* **1997**, 277, 1232.
- [17] G. Decher, M. Eckle, J. Schmitt, B. Struth, Current Opin. Colloid Interface Sci. 1998, 3, 32.
- [18] Y. Sun, X. Zhang, C. Sun, B. Wang, J. Shen, *Macromol. Chem. Phys.* 1996, 197, 147.
- [19] J. L. Casson, D. W. McBranch, J. M. Robinson, H. L. Wang, J. B. Roberts, P. A. Chiarelli, M. S. Johal, *J. Phys. Chem. B* **2000**, *104*, 11996.

- [20] S. Zapotoczny, M. Golonka, M. Nowakowska, Macromol. Rapid Commun. 2005, 26, 1049.
- [21] A. J. Chung, M. F. Rubner, *Langmuir* 2002, 18, 1176.
- [22] X. Shi, F. Caruso, Langmuir 2001, 17, 2036.
- [23] P. T. Hammond, G. M. Whitesides, Macromolecules 1995, 28, 7569.
- [24] T. R. Farhat, P. T. Hammond, Adv. Funct. Mater. 2005, 15, 945.
- [25] X. Ren, T. E. Springer, S. Gottesfeld, J. Electrochem. Soc. 2000, 147, 92.
- [26] M. S. Johal, J. L. Casson, P. A. Chiarelli, D.-G. Liu, J. A. Shaw, J. M. Robinson, H.-L. Wang, *Langmuir* 2003, 19, 8876.
- [27] J. Divisek, M. Eikerling, J. Electrochem. Soc. 1998, 145, 2677.
- [28] M. W. Verbrugge, J. Electrochem. Soc. 1989, 136, 417.
- [29] J. Kim, G. Kim, P. S. Cremer, J. Am. Chem. Soc. 2002, 124, 8751.
- [30] S. Slade, S. A. Campbell, T. R. Ralph, F. C. Wash, J. Electrochem. Soc. 2002, 149, A1556.
- [31] S. P. Jiang, L. Li, Z. Liu, M. Pan, H. L. Tang, *Electrochem. Solid-State Lett.* 2005, 8, A574.