

Support Information

Layer-by-layer self-assembly of PDDA/PWA-Nafion composite membranes for direct methanol fuel cells

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Experimental

Poly(diallyldimethylammonium chloride) (PDDA) (35 wt% in water, $MW = 5000$, Aldrich-Sigma) and $H_3PW_{12}O_{40}$ (HPW, Aldrich-Sigma) were used without further treatment. Nafion solution (5 wt%) and Nafion membrane 212 were obtained from DuPont. Sulfuric acid (95–97 %), hydrogen peroxide (30 %), and methanol were obtained from Fluka. Milli-Q water (Millipore, $18.2 M\Omega cm$ at 25 °C) was used in the experiments.

Nafion 212 membranes were 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 . The membranes were stored in Milli-Q water before use. The LbL self-assembly of PDDA/HPW multilayers was carried out by alternate dipping of the pretreated Nafion membrane in PDDA (20 mM) and HPW (20 mM) solutions at room temperature for 15 min. After each dipping step, the membrane was rinsed with Milli-Q water to remove weakly bonded HPW or PDDA. The alternative self-assembly of PDDA and HPW was repeated to increase the number of bilayers. The LbL self-assembled membrane was finally cleaned with Milli-Q water.

The through-plane proton conductivity of the membranes was measured using a four-probe electrochemical impedance spectroscopy (Autolab) within the frequency range from 0.1 Hz to 100 KHz and amplitude of 10mV at room temperature in 1M H_2SO_4 solution. Methanol permeability was determined by using a diffusion cell. Methanol solution (2 M) and water were placed on different compartments of the diffusion cell and were separated by the membrane. Magnetic stirrers were used on each compartment to ensure uniformity. An Agilent GC 6890N with a HP-PLOT/U column was used for the methanol analysis, and the peak areas were converted to methanol concentration by using a calibration curve. The methanol diffusion

coefficient was calculated and obtained by analyzing the methanol flux with time as shown below:

$$C_{B(t)} = AP C_A(t-t_0) / V_B L \quad (1)$$

where C_B and C_A are the methanol concentration of permeated and feed side through the membrane, respectively. A , L and V_B are the effective area of membrane, the thickness and the volume of permeated compartment, respectively. P is the methanol diffusion coefficient.

The stability of the self-assembled PDDA-PWA bilayer structure was evaluated on a N212 membrane with 4 self-assembled PDDA-PWA bilayers at room temperature. The modified N212 membrane was immersed in Milli-Q water and the water was refreshed every hour. Then the conductivity of the modified N212 membrane was measured as a function of immersing time, using a four-probe electrochemical impedance spectroscopy (Autolab) within the frequency range from 0.1 Hz to 100 KHz and amplitude of 10mV at room temperature in 1M H₂SO₄ solution. After each measurement, the modified membrane was rinsed in Milli-Q water before the treatment in Milli-Q water.

To evaluate the performance of the DMFCs, a membrane-electrode-assembly (MEA) was made by sandwiching a LbL self-assembled composite PDDA/HPW-Nafion membrane between a PtRu/C anode and a Pt/C cathode. PtRu black (E-TEK) was as the anode and 40% Pt/C (E-TEK) was used as the cathode. The loading of Pt was 4 mgcm⁻² for the anode and 0.4 mg cm⁻² for the cathode. The Nafion in catalyst layer was ~15 wt% for anode and ~30 wt% for cathode. Carbon paper treated with poly(tetrafluoroethylene) was used as the gas diffusion layer. The MEA was hot-pressed at 132 °C for 60 s. Methanol (2 M) was fed to the anode at a flow rate of 5 mL min⁻¹. Pure oxygen was supplied to the cathode at 100 mL min⁻¹ at room temperature. Tests were carried out at room temperature with no back pressure.

Results

Figure S1 shows UV-vis spectra of the LbL self-assembled Nafion 212 membranes as a function of the number of PDDA-PWA bilayers. The absorbance exhibits a characteristic absorption peak at 265nm and increases with an increasing number of the self-assembled PDDA-PWA bilayers. PWA has a characteristic absorption peak at 265 nm, while PDDA is basically transparent in the

UV-vis spectral range. Thus, the increase in the absorbance at 265 nm was attributed to the adsorption of PWA molecules on the previously deposited PDDA layer. The inset graph in Fig. 1 shows the absorbance at 265 nm as a function of the number of PDDA-PWA bilayers, which increased almost linearly with the number of LbL self-assembled PDDA-PWA bilayers. The linear relationship indicates that similar amount of PDDA or PWA was deposited in every dipping cycle and the multilayer was formed in a regular manner. The results show that HPW molecules are incorporated in the multilayer structure.

Figure S1. UV-vis spectra of the N212 membrane as a function of the number of self-assembled PDDA-PWA bilayers. The inset is the plot of the absorbance at 265 nm against the number of PDDA-PWA bilayers.

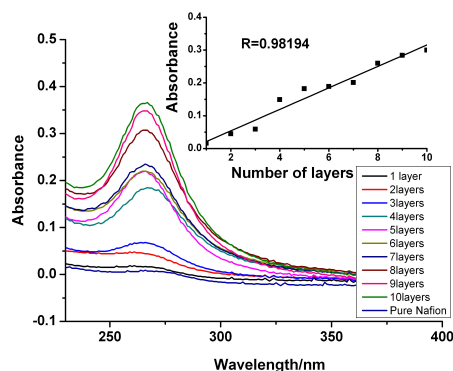


Figure S2 shows the conductivity stability of a 4 PDDA-PWA bilayers self-assembled N212 membrane as a function of immersing time. The results indicate that the conductivity of the self-assembled PDDA-PWA nafion membrane is stable with the water immersing treatment. If the PWA molecules in the self-assembled PWA/PDDA bilayers leak out from the bilayer structure, the conductivity of the sample would increase as the PDDA-PWA bilayers would collapse due to the absence of the electrostatic force between the negative charged PWA and positively charged PDDA. The reduction in the PDDA-PWA bilayers would lead to the increase in the conductivity

as shown in Figure 2a. Thus, the stability of the proton conductivity of the self-assembled PWA/PDDA bilayers indicates that PWA in the self-assembled PWA/PDDA bilayers is stable and does not leach out in water probably due to the strong electrostatic force. This indicates that the self-assembled PDDA-PWA bilayer structure is stable in water.

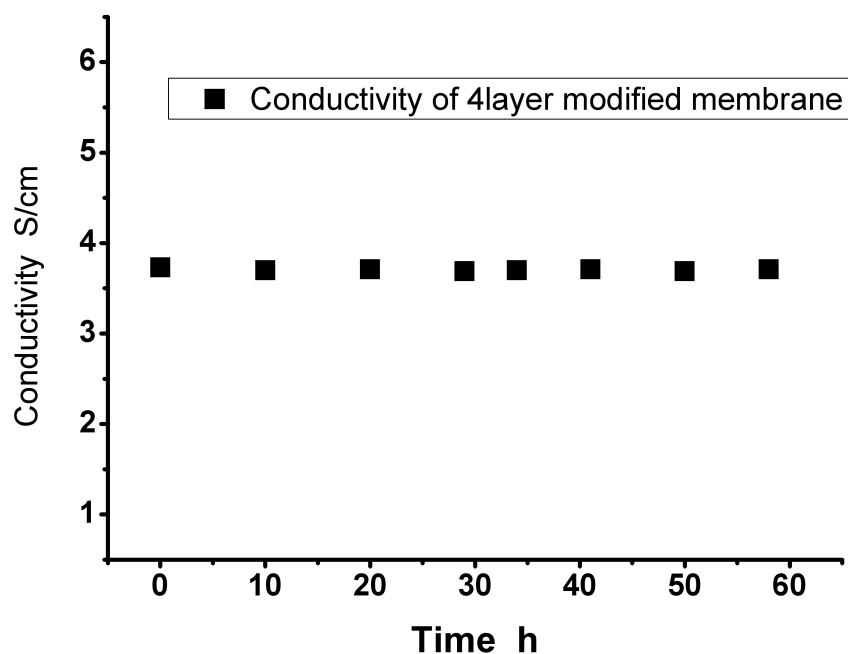


Figure S2. Plot of the conductivity of the 4 PDDA-PWA bilayer assembled N212 membrane as a function of immersing time.