

Supporting Information

Assembly of unbalanced charged polyampholyte onto Nafion[®] to produce high-performance composite membranes

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Experimental

Materials:

SPES-NH₂ was synthesized according to a similar procedure in our previous report.¹ Other chemicals and solvents were used as received. Milli-Q water (Millipore, 18.2 MΩcm at 25 °C) was used in the experiments.

Characterization:

UV-vis spectra of the thin films were collected on a Shimadzu UV-2450 spectrophotometer.

The proton conductivities of the composite membranes were evaluated through electrochemical impedance spectroscopy in the temperature range of 30 to 80 °C by a four-point probe method. The impedance measurements were carried out on a Solartron 1255B Frequency Response Analyzer and a Solartron 1470 Battery Test Unit (Solartron, UK) coupled with a computer. Membrane samples, with 1 cm² surface areas were sandwiched between two Au blocking electrodes. The samples were allowed to equilibrate at the desired temperature for 0.5 h. The impedance spectra were then recorded with the help of a ZPlot/ZView software (Scribner Associates) under an ac perturbation signal of 10 mV in the frequency range of 100 mHz to 100 KHz.

Layer-by-Layer Assembly:

The Nafion[®] 117 membrane was treated according to the standard procedure of 30 min immersed in a 5 wt% H₂O₂ solution at 80 °C, 30 min in Milli-Q water at 80 °C, and 30 min in an 8 wt% H₂SO₄ solution at 80 °C. The membrane was rinsed in Milli-Q water three times to remove traces of H₂O₂ and H₂SO₄ after each treatment. The membrane was then stored in Milli-Q water before use.

The prepared Nafion[®] membrane was alternately dipped in each SPES-NH₂ (2 mg/mL) and GA solutions (2.5 wt%, pH~4) at room temperature for 20 min to deposit multilayer films on Nafion[®] support. After each dipping step, the membrane was rinsed with Milli-Q water to remove weakly bonded polyelectrolyte molecules. Finally all prepared LbL composite membranes in Na⁺ form were inverted into H⁺ form by immersing into 1N HCl for 48 h. The LBL self-assembled membrane was finally cleaned with Milli-Q water and stored in Milli-Q water before use.

A homemade quartz crystal microbalance (QCM) was used to detect the mass of the deposited layers using a 9 MHz quartz electrode coated with Ag on both sides. The QCM frequency shifts were monitored with a Protek C3100 universal frequency counter.

Methanol diffusion coefficients were determined using an H's test cell with a solution containing 1 N methanol in water on one side and pure water on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. Methanol concentration within the water cell was monitored by SHIMADZU GC-1020A series gas chromatograph.

The methanol diffusion coefficients were calculated by the following equation:

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

Where C_A and C_B are the methanol concentration of feed side and permeated through the membrane, respectively. A , L , and V_B are the effective area, the thickness of membrane, and the volume of permeated compartment, respectively. DK is defined as the methanol permeability. t_0 is the time lag.

Ion exchange capacity (IEC) values H^+ form of self assembled composite membranes were determined by titration method. A sample membrane in proton form was soaked in saturated NaCl solution for 48 h at room temperature to exchange H^+ with Na^+ . Then, H^+ released into the solution was titrated with a 0.01 N NaOH solution using phenolphthalein as the indicator. IEC value was calculated by using the following formula:

$$IEC = \frac{MV}{m_{dry}}$$

where IEC is the ion exchange capacity expressed in mequiv.g⁻¹; V is the added titrant volume at the equivalent point expressed in mL, M is the molar concentration of the titrant and m_{dry} is the dry mass of the sample expressed in g.

The water uptake and water swelling of membranes were determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously.²

The cross-sectional morphology of SPES-NH₂/GA modified Nafion[®] membrane was characterized by an XL30 ESEM FEG field emission scanning electron microscope (FE-SEM, FEI Company with 20 kV operating voltage). Cross-sectional

analysis by scanning electron microscopy (SEM) revealed that the multilayer was formed on both sides of surface modified Nafion[®] membrane homogeneously. The thickness of 30 bi-layers of SPES-NH₂/GA deposited Nafion[®] composite membrane is about 60 nm. In other words, one deposition cycling of SPES-NH₂/GA gives a deposited layer roughly in 2 nm thickness.

Performance tests for a single cell

The Pt-Ru/C with 40 wt.% Pt + 20 wt.% Ru/C and the Pt/C catalyst with 20 wt.% Pt were used as the anodic and cathodic catalysts, respectively. Nafion[®] 117 and the composite membrane prepared were used as the electrolyte. The fabrication of the membrane electrode assembly (MEA) is the same as that in the literature.³ The catalyst loading was 4 mg cm⁻² for both the anode and the cathode and the effective electrode area of the single cell was 9 cm². The performance of the single cell was measured at 25 °C with a Fuel Cell Test System (Arbin Co.). 2.0M CH₃OH solution with a flow rate of 5 mL min⁻¹ and oxygen with a flow rate of 100 L min⁻¹ at 0.05 MPa were used. Each single cell was operated for three times.

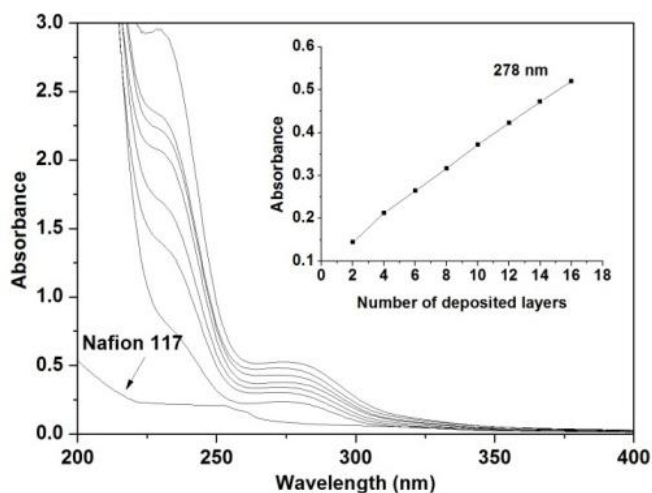


Fig. S1 UV-vis spectra of SPES-NH₂/GA multilayer with varying numbers of bilayers.

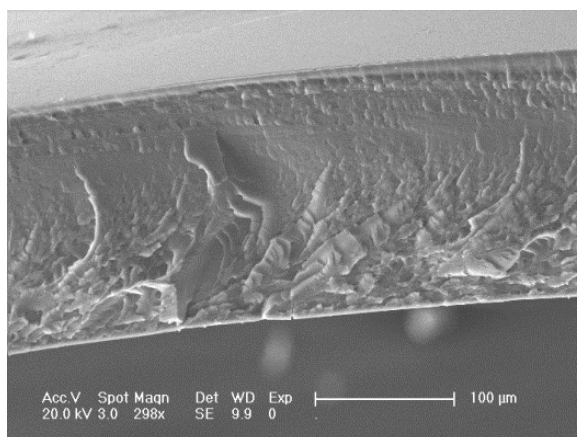


Fig. S2 SEM image of 30 bi-layers of SPES-NH₂/GA modified Nafion[®] membrane.

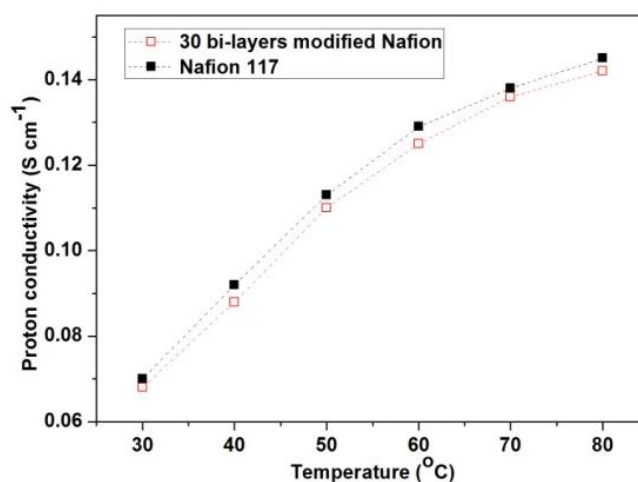


Fig. S3 Temperature dependence of the proton conductivity of SPES-NH₂-GA -coated Nafion[®] membranes.

Table S1. IEC, proton conductivity, water uptake, and methanol permeation of Nafion[®]-SPES-NH₂-GA composite membranes.

Membrane	Number of bi-layer	IEC	(S cm ⁻¹)σ	WU	PM ×10 ⁻⁶ cm ² s ⁻¹
Nafion [®] -SPES-NH ₂ -GA	5	0.91±0.02	0.068±0.005	19.9%±0.1%	2.0±0.1
	10	0.95±0.05	0.068±0.004	20.3%±0.3%	1.1±0.1
	15	0.97±0.03	0.067±0.005	20.5%±0.3%	0.86±0.05
	20	0.99±0.02	0.066±0.008	21.0%±0.2%	0.71±0.04
	25	1.02±0.04	0.067±0.008	21.3%±0.4%	0.66±0.03
	30	1.04±0.02	0.066±0.006	21.8%±0.5%	0.57±0.04
	50	1.12±0.03	0.065±0.01	22.1%±0.2%	0.41±0.05
Nafion [®] 117		0.89±0.05	0.070±0.01	19.6%±0.3%	2.4±0.2

SPES-NH ₂ -GA		2.42±0.07	0.27±0.012	33.5%±0.5%	
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Some of the results and discussion

The multilayer growth was also verified by quartz crystal microgravimetry (QCM). Fig. 2b plots the QCM frequency shift, proportional to the mass of the deposited layer, vs. the deposition cycle. As can be seen, the QCM frequency decreased regularly with the successive deposition of SPES-NH₂ and GA “layers” on the substrate. The average frequency decrease for the deposition of one SPES-NH₂ layer and one GA layer was about 65 Hz and 8 Hz, respectively, corresponding to a layer thickness of about 2 nm, assuming a layer density of 1 g cm⁻³. The linear increase of SPES-NH₂ with the number of the deposited bi-layers indicates a regular growth of a molecular-level and nm-sized layer-by-layer membrane.

To further prove the content of free -SO₃H in the composite membrane, the ion exchange capacity (IEC) of the H⁺ form of the assembled composite membranes was determined by titration and the results are listed in Table S1. The IEC values of the composite membrane were higher than those of unmodified Nafion[®] 117, and were increased with the number of the deposited bilayers. This result further confirms that the assembly process introduced more free -SO₃H groups onto the composite membrane.

Reference

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