

Proton conductivity in the dry membrane of poly(sulfonic acid) and polyamine layer-by-layer complex†

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A layer-by-layer assembled and molecular-complexed polymer membrane was prepared by the simple combination of poly(4-styrenesulfonic acid) and poly(allylamine) on a comb-shaped gold electrode: it displayed a very high proton conductivity of 10^{-3} S cm $^{-1}$ under a dry condition at 120 °C.

Proton-conducting polymer electrolyte membranes (PEMs) are the key material for the operation of a polymer electrolyte fuel cell (PEFC).¹ Perfluorosulfonic acid polymer membranes, such as Nafion[®], are presently the only practically applicable ones for the PEFCs. In Nafion[®], the pendant sulfonic acid group forms a hydrophilic water-containing protonic cluster among the hydrophobic perfluoroethylene backbone, which provides a proton mobility with a conductivity of 10^{-1} – 10^{-2} S cm $^{-1}$ under a hydrated condition.² However, since protons migrate as water-solvated ones, the proton conductivity decreases above 100 °C and below 0 °C, which is a major drawback for the development of the Nafion-based PEFC. A membrane-forming and hydrocarbon-based polyelectrolyte with a high proton conductivity even under an unhydrated or dry condition is the most desired material for the PEFC.^{3,4} The major approach among the hydrocarbon-based PEMs for the dry condition operation has focused on protonic acid-doped base polymers and base-doped acid polymers, such as poly(benzimidazole) doped or complexed with a phosphoric acid.⁵ Some of the acid-doped base polymers showed a proton conductivity as high as 10^{-2} – 10^{-3} S cm $^{-1}$ under a relatively low humidity of 5–30%, but the doped acid was water-soluble and eluted out during the FC operation.⁵ Additionally, the proton conductivity of the membranes under a dry condition remained on the order of 10^{-5} S cm $^{-1}$.

It is well known that the mixing of aqueous solutions of an acid polymer and a base polymer immediately produces a polyion complex of the acid polymer (polyanion) and the base polymer (polycation).⁶ The polyion complex contains a high proton concentration due to a salt-forming and cross-linked structure to yield a water-insolubility and thermostability. However, the polyion complex is a fibrous material, which lacks any molding capability and does not give a dense membrane both with a proton conductivity and a gas barrier property for use as PEMs.

In this paper, we focus on a membrane of a polyion complex prepared using a layer-by-layer adsorption method, as a potential

proton-conducting PEM. The layer-by-layer method is the alternative adsorption of an acid polymer and a base polymer to form a membrane of a multi-layered assembly of the polyion complex with a nm thickness based on the electrostatic complexation of oppositely charged polyelectrolytes.⁷ Hammond and co-workers reported the proton conductivity measurement on membranes of polyion complexes of poly(acrylic acid) and poly(ethylenimine) prepared using the layer-by-layer method.⁸ However, they concluded that the proton conductivity remained at 10^{-12} S cm $^{-1}$ for their polyion complex membranes under a dry condition.⁸ We presumed that the membranes prepared in their study were a layer-by-layer formed membrane but not composed of molecular-complexes of the acid and base polymers or that each polymer layer was not thin enough to efficiently form the polyion complexes: They noted that the average thickness of their polyion complex layer was 33 nm for the poly(acrylic acid) and poly(ethylenimine) bilayer. Additionally, the conductivity measurement procedure used in their study was not specifically designed for the layer-by-layer complexed membrane adsorbed on a substrate.

In our previous paper,⁹ we reported a molecular-based and nm-sized layer-by-layer membrane formation *via* the complexation of poly(sulfonic acids) and polyamines by carefully examining the preparation conditions such as the acid–base pairs of polymers, the solution concentration, and the dipping and rinsing periods. In this paper, for the first time, we describe the layer-by-layer polyion complex membrane formation of poly(4-styrenesulfonic acid) (PSS) and poly(allylamine) (PAA), with a nm thickness for each polymer bilayer, onto a silicon substrate fabricated with a μ m-sized and comb-shaped gold electrode¹⁰ and the proton conductivity of the polyion complex membrane under a dry condition.

The 100 bilayered PSS–PAA complex membrane illustrated in Fig. 1(a) was prepared on a silicone substrate fabricated with a comb-shaped gold electrode,¹¹ using the layer-by-layer method

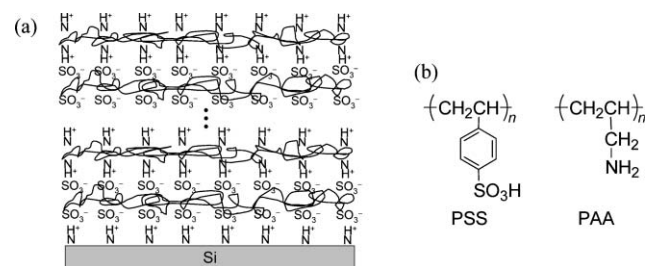


Fig. 1 Illustration of the layer-by-layer polyion complex membrane on the silicon substrate (a) and chemical structures of poly(4-styrenesulfonic acid) (PSS) and poly(allylamine) (PAA) (b).

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with the specified preparation conditions⁹ of dipping the substrate in a 0.15 unit mM PSS aqueous solution for 15 min, following by rinsing with distilled water for 10 min, then dipping in a 0.30 unit mM PAA aqueous solution for 15 min, followed by water rinsing for 10 min. We repeated this cycle 100 times which required 4 days to yield the membrane and then dried it *in vacuo* at 120 °C for 3 days. A field emission scanning electron microscopic (FE-SEM) image of the 100 bilayered PSS–PAA complex membrane on the substrate clearly showed a smooth, dense, and pinhole-free membrane formation (Fig. 2). The membrane formation of PSS (without PAA) resulted in brittle and cracked samples after the drying process (see ESI,† Fig. S4). The layer-by-layer complexation of PSS and PAA enhanced the membrane formability of the protonic acid polymer. The thickness of the 100 layer-by-layer PSS–PAA membrane was 112 nm (see Fig. 2), in which one polyion complex bilayer was estimated to have a thickness of *ca.* 1 nm: This agreed with the mass amount determined by a quartz crystal microbalance measurement on the layer-by-layer adsorption process.⁹ X-Ray photoelectron spectroscopy and infrared reflection–absorption spectroscopy of the PSS–PAA complex membrane prepared on the substrate supported an acid–base polyion complex formation on the substrate by the layer-by-layer adsorption without any contamination (see ESI,† Fig. S5 and S6). Diffusible ions, such as Na⁺ and Cl[−], other than protons, were not detected in the membrane. The PSS–PAA membrane prepared on the substrate absorbed 0.3 wt% of water per membrane (estimated by a microbalance measurement) after immersing it in water for 1 week. However, the membrane was completely insoluble in water even after 1 month, while the PSS immediately dissolved. The water insolubility of the layer-by-layer membrane could be realized by the molecular-based complexation or cross-linking between the acid and base polymers. Water content in the PSS–PAA membrane was less than 0.1 wt% per membrane even after the proton conductivity measurement under the dry condition.

Proton conductivity of the 100 bilayered PSS–PAA complex membrane on the substrate with the comb-shaped gold electrode was measured along with control data of the Nafion[®] membrane

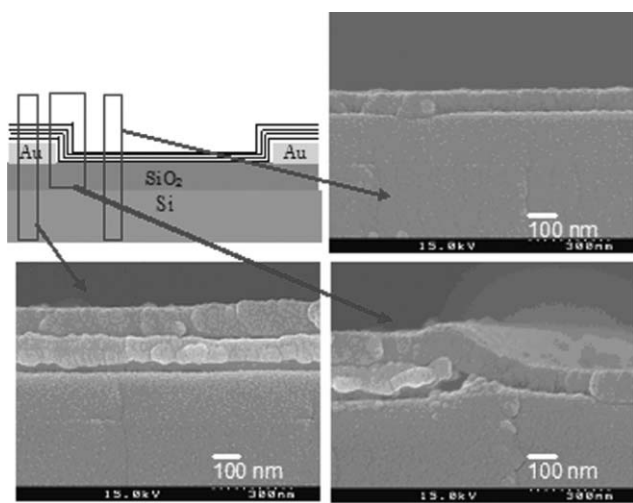


Fig. 2 FE-SEM images of the 100 bilayered PSS–PAA complex membrane assembled on the silicone substrate fabricated with the comb-shaped gold electrode.

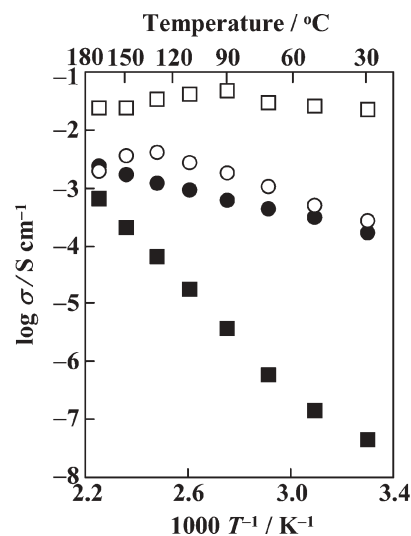


Fig. 3 Proton conductivity of the dry (●) and hydrated (○, water content = 0.3 wt%) PSS–PAA complex membrane, and the dry (■) and hydrated (□, water content = 12 wt%) Nafion[®] membrane on the silicone substrate fabricated with the comb-shaped gold electrode.

prepared on it (the circle and square plots in Fig. 3, respectively). The proton conductivity of the hydrated Nafion[®] membrane (water content = 12 wt%) on the substrate with the comb-shaped gold electrode was on the order of 10^{-2} S cm^{−1}, which agreed with values² previously reported using a conventional electrode. The proton conductivity of the hydrated PSS–PAA complex membrane (water content = 0.3 wt%) was on the order of 10^{-3} – 10^{-4} S cm^{−1} and gave a maximum conductivity at 130 °C. Under the dry condition,¹² the conductivity of the Nafion[®] membrane was very low, as has been previously reported (the closed square plots in Fig. 3). On the other hand, the PSS–PAA complex membrane almost maintained the proton conductivity on the order of 10^{-3} – 10^{-4} S cm^{−1} even under the dry condition (the closed circle plots), which was surprisingly higher than that of the Nafion[®] membrane (10^{-4} – 10^{-8} S cm^{−1}). The proton conductivity of the PSS–PAA complex membrane reached 1.1×10^{-3} S cm^{−1} at 120 °C and 2.1×10^{-3} S cm^{−1} at 170 °C which was the highest proton conductivity among those previously reported⁴ under a dry condition for the membranes without the addition of any low-molecular acid and base molecules such as phosphoric acid and imidazole. The high conductivity at 170 °C of the PSS–PAA membrane was maintained even after a month, supporting both the high thermal stability¹³ of the polyion complex membrane and also the proton conduction without any humidity.

Proton conductivity of the 30 bilayered PSS–PAA complex membrane with an *ca.* 30 nm membrane thickness was on the order of 10^{-4} – 10^{-6} S cm^{−1} (30–170 °C). This lower proton conductivity in comparison with that of the 100 bilayered PSS–PAA membrane was probably due to the poor membrane formability or a disordering in the complexation during the initial stage of the 20 adsorption cycles. On the other hand, the 80 bilayered PSS–PAA complex membrane had a conductivity of 10^{-3} – 10^{-4} S cm^{−1} (30–170 °C). A control PSS–PAA membrane with a 1.3 μm total membrane thickness and 6–7 nm thickness for each PSS and PAA alternate polymer layer was prepared on the

same substrate by 100 alternative adsorptions using a concentrated polymer solution (20 unit mM PSS and 40 unit mM PAA). The membrane was turbid, supporting the fact that PSS and PAA did not form a molecular-based polyion complex in this membrane. The proton conductivity of this control membrane was very low ($<10^{-11}$ S cm $^{-1}$). The PSS membrane (without PAA) prepared on the substrate was cracked (see ESI,† Fig. S4) and did not show any proton conductivity.

Fig. 3 also shows the temperature-dependency of the proton conductivity. The conductivity under the dry condition, which increased with temperature, obeyed an Arrhenius type plot and did not have any break point (around 100 °C). The slope of the plots provided an activation energy of 20 kJ mol $^{-1}$ for the PSS–PAA complex membrane. This activation energy for the proton conductivity in the PSS–PAA membrane was significantly low in comparison with that for the Nafion[®] membrane (79 kJ mol $^{-1}$). A high conductivity and low activation energy for the PSS–PAA complex membrane was considered to be caused by the high proton concentration (ion exchange capacity = 4.1 meq. g $^{-1}$) and proton mobility *via* the layer-by-layer and molecular-based complexation structure of the acid polymer and base polymer in the membrane.

The results indicate the layer-by-layer polyion complex membrane is a potential candidate as a high-temperature PEM. The layer-by-layer complex membranes composed of some other acid and base polymers could display a similar high proton conductivity.¹⁴

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- 10 The proton conductivity of the 100 bilayered PSS–PAA complex membrane with a thickness of 100 nm on a gold substrate was first vertically checked to the substrate by carefully depositing gold or aluminum on the membrane. However, the measured resistance was zero due to penetration of the deposited metal through the thin organic membrane.
- 11 For the fabrication of the comb-shaped gold electrode on the silicone substrate, see ESI†.
- 12 Before the proton conductivity measurement, the membrane was kept in a temperature-controlled chamber at 170 °C with relative humidity of 0% for one day. The conductivity measurement was carried out in the same chamber.
- 13 Thermogravimetry on the PSS–PAA membrane prepared on the substrate did not show any weight loss around 100 °C. The 10% weight loss ($T_{d10\%}$) or the thermal degradation temperature of the PSS–PAA membrane itself was 380 °C, which was 115 °C higher than that of PSS. This significantly high thermostability of the layer-by-layer membrane suggests an effective network formation through the polymer complex formation.
- 14 A dry layer-by-layer complex membrane of PSS and poly(ethylenimine) prepared on the substrate was turbid and did not show any proton conductivity. On the other hand, the complexation of the poly(vinylphosphoric acid) and PAA gave a smooth and transparent membrane which had a proton conductivity of 10^{-4} – 10^{-6} S cm $^{-1}$ (30–170 °C). It is suggested that a good membrane formability in the layer-by-layer complexation realized the proton conductivity.