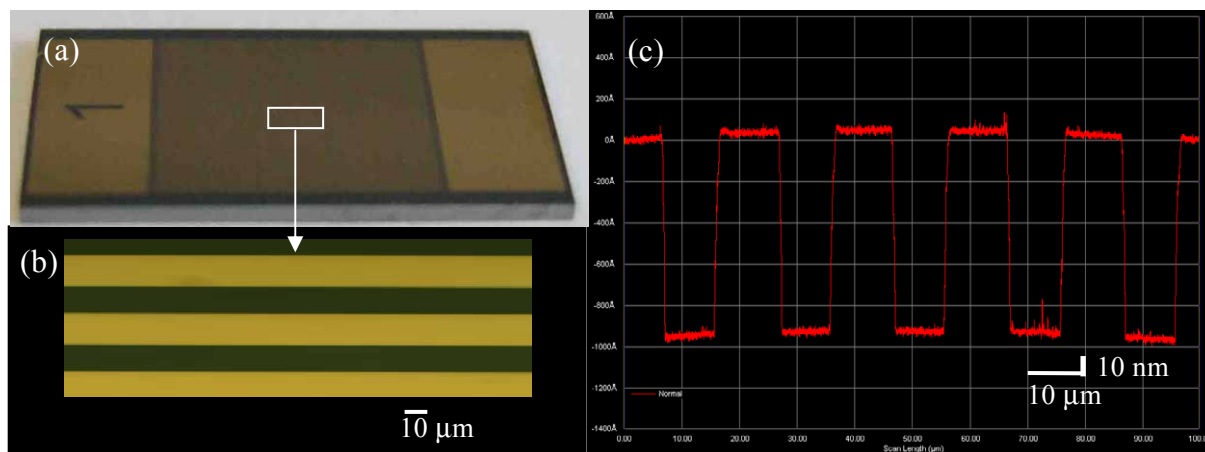


**Proton Conductivity in the Dry Membrane of  
Polysulfonic Acid and Polyamine Layer-by-Layer Complex**

Takahiro Tago, Hirokazu Shibata and Hiroyuki Nishide

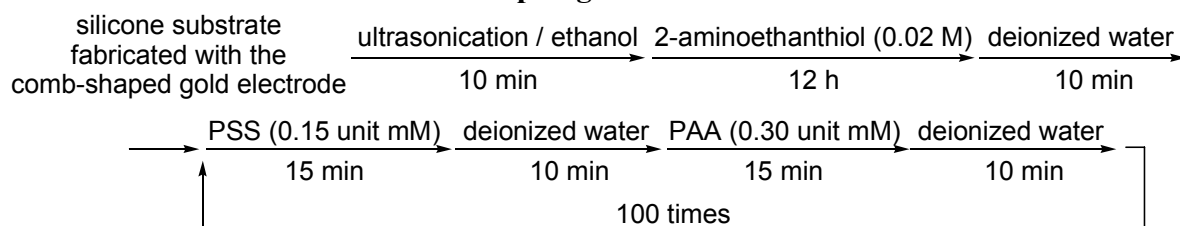
*Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan*

**1. Fabrication of the comb-shaped gold electrode.** Comb-shaped gold electrode with a micrometer length between the two electrodes and the long total electrode length was fabricated to measure the proton conductivity of the layer-by-layer polyion complex membrane. Hexamethyldisilazane and an ethyl lactate solution of a positive photoresist resin (TSMR-v90, 10cp) purchased from Tokyo Ohka Kyogyo, Co. and a solution of cyclopentanone and tetrahydrofurfuryl alcohol of poly(dimethylglutarimide) purchased from Micro Chem, Corp. were spin-coated onto a SiO<sub>2</sub> surface of the silicon substrate and exposed to UV light through a photomask. After the UV-exposure, the photoresist resin was chemically developed using a tetramethylammonium hydroxide solution, and the substrate was cleaned by oxygen plasma etching. Titanium (30 nm) and gold (70 nm) layers were electro-deposited onto the resist-patterned substrate. The metal-coated photoresist resin was removed by ultrasonication in acetone and by immersion in methanol, isopropylalcohol, and water. The width and total length of the obtained comb-shaped gold electrode were 10 μm and 2.2 m, respectively, and the two electrodes were 10 μm apart. The surface roughness of the comb-shaped gold electrode was measured as ±5 nm using the P-15 contact stylus profilometer (KLA-Tencor Co.).

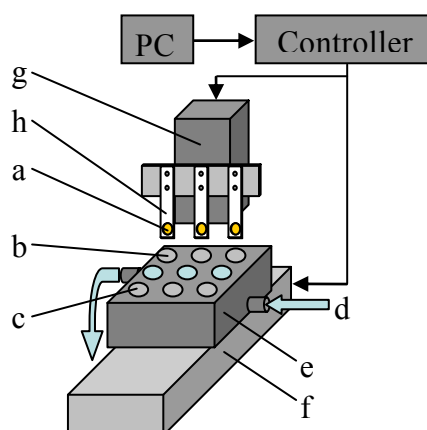


**Fig. S1** Photograph (a), optical image (b), and surface profiler chart (c) of the comb-shaped gold electrode.

## 2. Preparation of the layer-by-layer PSS–PAA complex membrane on the silicone substrate fabricated with the comb-shaped gold electrode.



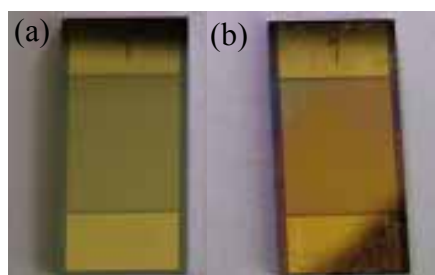
**Scheme 1**



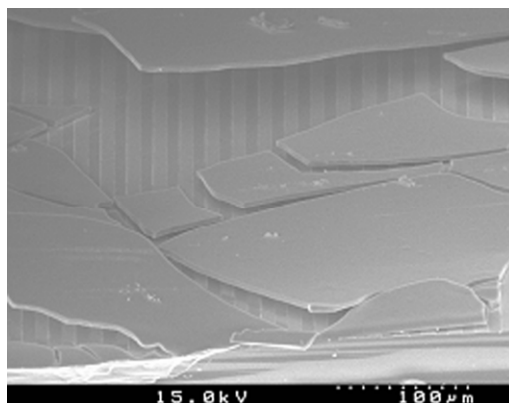
**Fig. S2** Apparatus for the layer-by-layer adsorption experiment: a) silicone substrates with the comb-shaped gold electrode ( $14 \times 7$  mm), b) vials ( $\phi = 40 \times 75$  mm) for the acid polymer solution, c) vials ( $\phi = 40 \times 75$  mm) for the base polymer solution, d) distilled water flow for rinsing, e) a Teflon-coated working stage ( $20 \times 20 \times 8.5$  cm), f) an auto X-stage, g) an auto Z-stage, and h) Teflon holders.

Poly(4-styrenesulfonic acid) (PSS; weight-average molecular weight  $M_w = 7 \times 10^4$ ) was purchased from the Aldrich Co. Poly(allylamine) (PAA;  $M_w = 6 \times 10^4$ ) was from the Nitto Boseki Co., Japan. The layer-by-layer PSS–PAA complex membrane on the silicone substrate fabricated with the comb-shaped gold electrode was prepared as shown in Scheme 1. The gold electrode surface was modified by soaking in an aqueous 2-aminoethanethiol solution (0.02 M), followed by rinsing with distilled water. The apparatus for automatic dipping the substrate in the polymer and rinse solutions was designed and set up (Fig. S2). The layer-by-layer adsorption experiment was carried out by dipping the substrate in the 0.15 unit mM PSS aqueous solution for 15 min, following by rinsing with distilled water for 10 min, then dipping in the 0.30 unit mM PAA aqueous solution for 15 min, following 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. The 100 bilayered PSS–PAA complex membrane was obtained as a transparent, smooth, and dense membrane (Fig. S3). 10 specimens were replicated to provide the following membrane characteristic and conductivity measurement.

The 3000 bilayered PSS–PAA complex membrane was also prepared by operating 3000 cycles under the same fabrication conditions, which took 4 months. The thickness of the membrane was 3  $\mu\text{m}$ , and the membrane showed a proton conductivity of  $10^{-3} \text{ S cm}^{-1}$  at 120°C. However, even the 3  $\mu\text{m}$ -thickness membrane could not be released from the substrate as a self-standing membrane.



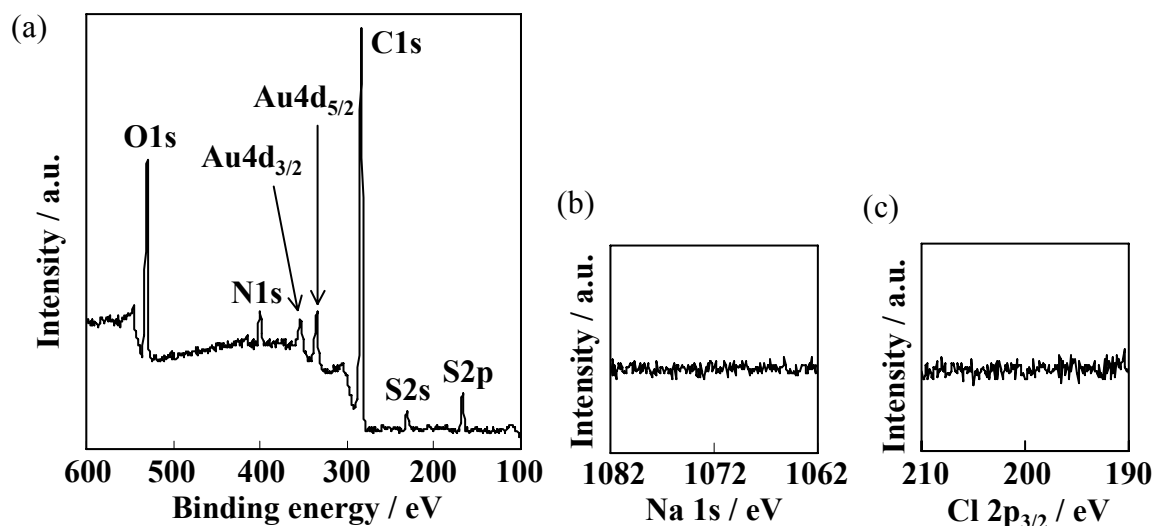
**Fig. S3** Photographs of the silicone substrate with the comb-shaped gold electrode (a) and the substrate after the preparation of the PSS–PAA complex membrane (b).



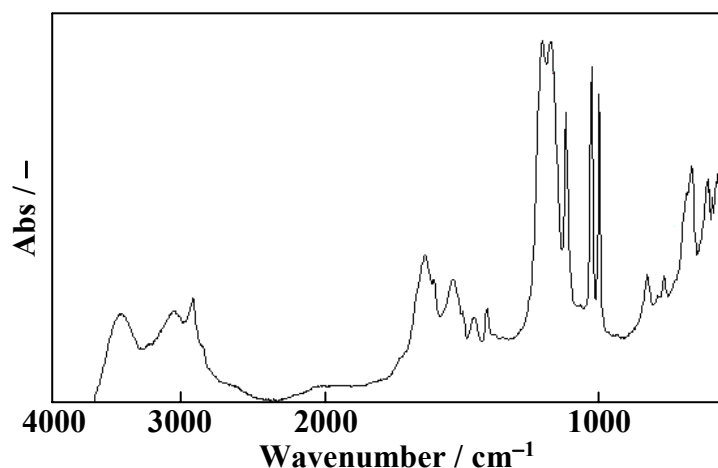
**Fig. S4** FE-SEM image of the PSS (without PAA) membrane assembled on the silicone substrate fabricated with the comb-shaped gold electrode.

**3. Characterization of the layer-by-layer PSS–PAA complex membrane on the silicone substrate fabricated with the comb-shaped gold electrode.** X-Ray photoelectron spectroscopy and infrared reflection-absorption spectroscopy were used to analyze the surface composition of the membrane prepared on the silicone substrate with the comb-shaped gold electrode. X-Ray photoelectron spectra were obtained using a JEOL JPS-9010TR spectrometer with an Al K $\alpha$  line source. All spectra were calibrated with respect to the position of the carbon 1s peak at 284 eV. Fig. S5 shows a survey scan of the 100 bilayered PSS–PAA membrane on the silicone substrate fabricated with the comb-shaped gold electrode: This identified the presence of the following elements: C (1s, 284 eV), N (1s, 400 eV), O (1s, 530 eV), S (2s, 230 eV; 2p 167 eV), and Au (4p<sub>3/2</sub> 546 eV; 4d<sub>5/2</sub> 335 eV; 4d<sub>3/2</sub> 353 eV; 4f<sub>5/2</sub> 84 eV; 4f<sub>3/2</sub> 88 eV). The peak of Na (1s, 1070 eV), Cl (2p<sub>3/2</sub>, 200 eV), and no other metal ions were detected.

Infrared reflection-absorption spectroscopy (JASCO FT/IR-6100 spectrometer with a RAS PRO 410-H grazing angle reflection attachment) on the same PSS–PAA membrane showed an absorption ascribed to the sulfonate (1036 and 1212 cm<sup>-1</sup>) and the amine (1633, 3042, and 3448 cm<sup>-1</sup>) groups (Fig. S6). These analytical results supported an acid-base polyion complex formation on the substrate by the layer-by-layer adsorption without any contamination.



**Fig. S5** XPS spectrum of the PSS–PAA complex membrane on the silicone substrate with the comb-shaped gold electrode over the region from 600 to 100 eV (a), the regions of Na 1s (b) and Cl 2p<sub>3/2</sub> (c).



**Fig. S6** IR-RAS spectrum of the PSS–PAA complex membrane on the silicone substrate with the comb-shaped gold electrode.

**4. Proton conductivity measurement of the layer-by-layer polyion complex membrane prepared on the substrate.** The proton conductivity of the membranes prepared on the silicone substrate fabricated with the comb-shaped gold electrode was measured by the two-probe method using an Eco Chemie Autolab PGSTAT30 AC impedance analyzer over the frequency and temperature ranges from 1 Hz to 1 MHz and from 30 to 170°C, respectively, at

intervals of 20°C in a temperature-controlled chamber (ESPEC ST-110). We measured the conductivity by using the 5 membrane specimens to check reproducibility of the data (within the experimental error of <10 %).