Supporting information

Multistep Thickening of Nafion Thin Films in Water

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Surface morphology of Nafion® films in air and water

The surface morphology of Nafion® thin films with a thickness of approximately 50 nm on silver and quartz substrates was examined by atomic force microscopy (AFM, E-sweep with an SPI3800 controller, SII NanoTechnology Inc.) using an intermittent contact mode at room temperature. A Si cantilever tip with a radius of approximately 10 nm was used and a spring constant of the lever was 1.6 $N \cdot m^{-1}$.

Figure S1 shows AFM images of Nafion® films on silver and quartz substrates observed in air and water, respectively. The root-mean-square roughness (R_q) of all the samples was less than 1 nm.

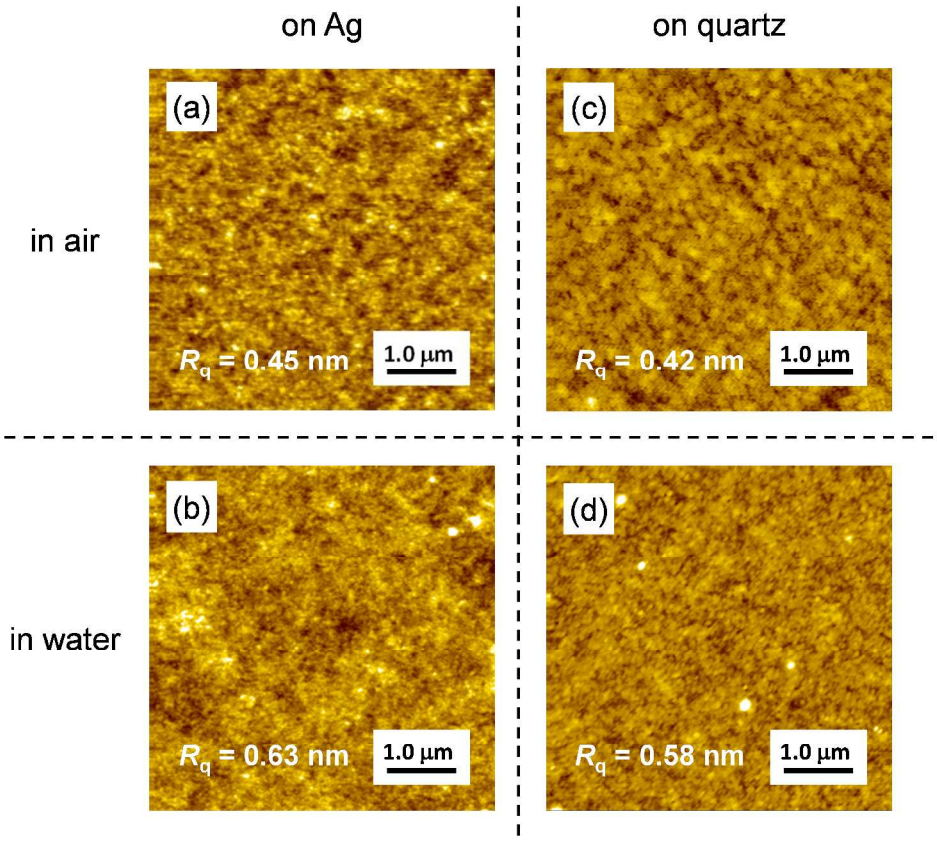

Figure S1. AFM images of Nafion® films on silver in (a) air and (b) water and on quartz in (c) air and (d) water, respectively. Each root-mean-square roughness (R_q) is shown.

Swelling ratio for different-thick Nafion® films

Swelling behavior was also examined for Nafion® films with different thicknesses. Figure S2 shows the time dependence of the swelling ratio for Nafion® films with initial thicknesses (h_o) of 20 nm and 80 nm on silver (red) and SiO_x (blue) substrates. The films thickened in three steps. Dotted lines correspond to the borders between the regimes; 1.05 for between regimes I and II and 1.26 for between regimes II and III. At a given thickness, water diffusion into Nafion® films is slower than on the SiO_x substrate that on the silver one.

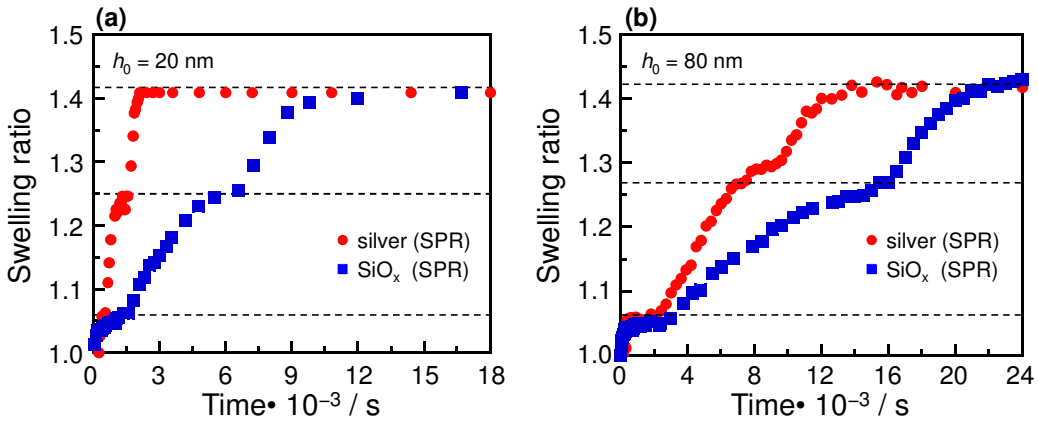

Figure S2. Time dependence of swelling ratio for Nafion® films on silver (red) and SiO_x (blue) substrates with an h_o of (a) 20 nm and (b) 80 nm, respectively.