Supporting Information

Visualization of ion transport in Nafion using electrochemical strain microscopy

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Experimental Section

ESM imaging was performed under a water environment using commercial atomic force microscopy (MFP-3D, Asylum Research) combined with a closed fluid cell (Asylum). We used Pt/Ir coated ESM tips (ATEC-CONTPt, spring constant: 0.2 N/m). We used Dual AC Resonance Tracking (DART) mode for our ESM operation near a frequency range of 100 ~ 110 kHz, which enhances the sensitivity of the measurement without significant cross-talk between the topography and the electromechanical response. We used a Nafion 117 membrane (thickness: 178 µm, Dupont, Inc), which we attached to the stainless steel holder using double-sided carbon tape for electrical connection to the ground. Both ac voltage (1 V at ~ 100 kHz) and +2 V_{dc} or -2 V_{dc} were applied to the ESM tip to measure the electromechanical response of the Nafion membrane. We scanned the tip at a rate of 1 Hz over areas of 3 µm × 3 µm and 5 µm × 5 µm. For Figs. 4 and 5, we subtracted the background to observe the contrast ESM amplitude and facilitate a comparison between different regions using the ImageJ program (National Institute of Health). The raw images for Figs. 4 and 5 are presented in Figs. S4 and S5.



Fig. S1 ESM of Nafion in an ambient condition; (a) topography (b) amplitude, and (c) phase of ESM

response.



Fig. S2 Topography (upper), ESM amplitude (middle), and ESM phase (lower) images under different ac voltages of (a) 0.5 V_{ac} , (b) 1 V_{ac} , (c) 1.5 V_{ac} , and (d) 2 V_{ac} ; supplementary information of Fig. 2.



Fig. S3 Topography (upper), ESM amplitude (middle), and ESM phase (lower) images of pristine state (a, c) and while applying (b) +2 V_{dc} , and -2 V_{dc} (d) to tip ; Nafion in an ambient condition.



Fig. S4 Topography (upper), ESM amplitude (middle), and ESM phase (lower) images of (a) pristine state and after applying +2 V_{dc} for (b) 5 min, (c) 10 min, (d) 15 min, and (e) 20 min (red box: the region where we applied +2 V_{dc}); supplementary material of Fig. 4.



Fig. S5 Topography (upper), ESM amplitude (middle), and ESM phase (lower) images of (a) pristine state and after applying -2 V_{dc} for (b) 5 min, (c) 10 min, (d) 15 min, and (e) 20 min (red box: the region where we applied -2 V_{dc}); supplementary material of Fig. 5.



Fig. S6 Schematic plot of the ESM amplitude and phase as a function of ac drive frequency where ω_0 indicates the contact resonance frequency whereas ω_1 and ω_2 represent the ac drive frequencies of DART ESM. The dotted line is obtained from the surface with low damping constant while the solid line is obtained from the surface with high damping constant. Higher energy dissipation (high damping constant) corresponds to smaller quality factor (Q), which increases the bandwidth (B_m) of the contact resonance peak, leading to decrease in the ESM amplitude and increase in the ESM phase at ω_1 .