

# Supporting Information

## Unraveling Depth-Specific Ionic Conduction and Stiffness Behavior

### across Ionomer Thin Films and Bulk Membranes

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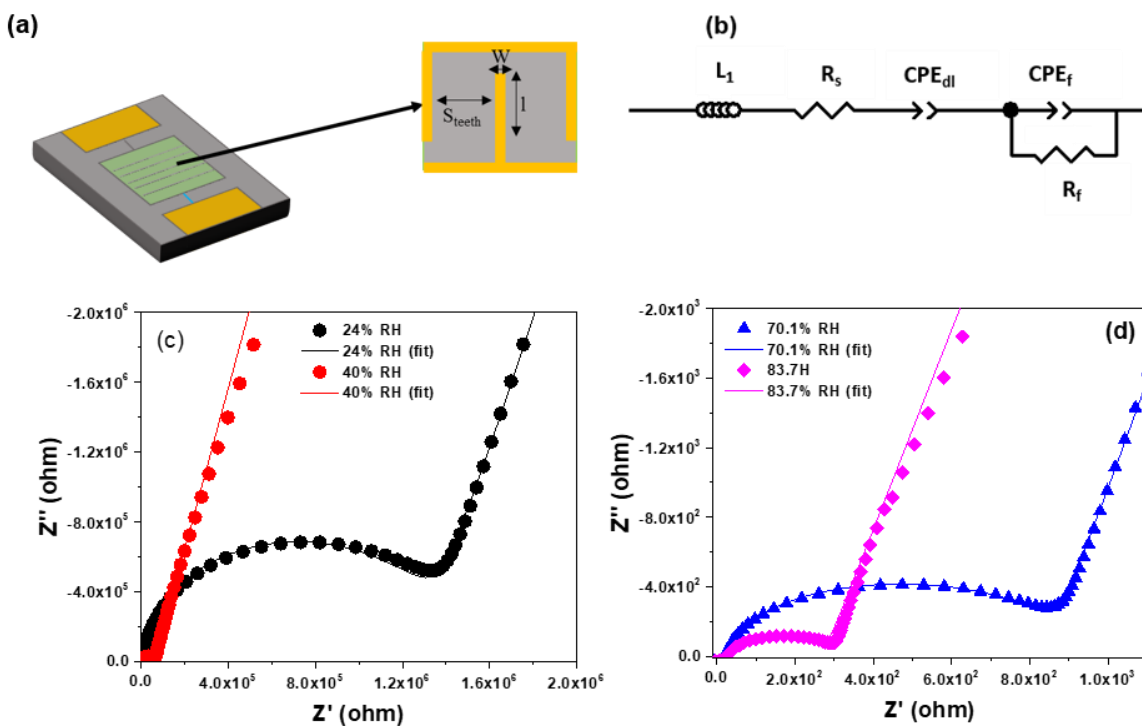
### Experimental Section.

**Materials.** Rotor probe, 9-(2-carboxy-2-cyanovinyl) julolidine (CCVJ), and 20 wt% Nafion solution (EW~1100) were purchased from Sigma-Aldrich (Milwaukee, WI). Photoacid probe, 8-hydroxypyrene-1,3,6-trisulonic acid (HPTS) were purchased from both Sigma-Aldrich (Milwaukee, WI) and Fisher Scientific (Somerville, NJ). Nafion membrane NR 212 (EW ~ 1100) was purchased from Ion Power (New Castle, DE). Ethanol and acetone were purchased from Fisher Scientific (Hampton, NH). Hydrochloric acid (ACS grade) was purchased from VWR (Radnor, PA). The coverslips (75 mm × 25 mm, thickness 170 μm, product no. 10812) were purchased from ibidi USA, Inc. (Fitchburg, WI) to spin-coat Nafion films or mount Nafion membranes. Silicon wafers coated with native silicon dioxide (n-SiO<sub>2</sub> wafers) were purchased from Wafer Pro (San Jose, CA) for film thickness measurements. The humidity chamber for CLSM imaging was purchased from ibidi USA, Inc. (Fitchburg, WI).

### Methods and Relevant Results.

**Electrochemical Impedance Spectroscopy (EIS) measurement.** We used a Solartron 1260a Impedance/Gain-Phase analyzer coupled to Solartron 1296 Dielectric Interface (Solartron Analytical, Leicester, England) with four gold probes and an environmental chamber containing temperature stage and controller (Nextron, Busan, South Korea) for measuring the impedance spectra of the Nafion films. The proton conductivity measurements were done using two probe techniques according to the literature.<sup>1,2</sup> For EIS measurement, we purchased gold IDEs on a silicon wafer (110) with a thermally grown SiO<sub>2</sub> as an electrically insulating layer from Revtek Inc. (Torrance, CA). Each IDE had 150 gold teeth (N). The other IDE specifications were as follows (Figure S1a): width of each tooth (w): 8 μm; Teeth spacing (S<sub>teeth</sub>): 40 μm; overlapping length of teeth (l) coming from both sides of the IDEs: 4 mm. These IDEs were used as the substrate to make spin-coated Nafion films.

1 To make the ionomer films, we diluted 20 wt% Nafion solution to 10 wt% in ethanol to yield films with  
 2 different thicknesses. The spin-coated ionomer films on IDEs were then dried at 42 °C for 3 h, annealed  
 3 at 100 °C for 7 h, and cooled down to room temperature for 12 h inside a vacuum oven (Model #1415,  
 4 VWR, Radnor, PA). After annealing, the contact pads (i.e. where we place the probes) were cleaned. The  
 5 films were then placed inside a humidity-controlled chamber as mentioned in our previous work.<sup>2</sup> To  
 6 maintain specific relative humidity (% RH) inside this humidity chamber, we used saturated CH<sub>3</sub>COOK  
 7 (24%RH), K<sub>2</sub>CO<sub>3</sub> (40% RH), NaCl (70% RH), and Na<sub>2</sub>SO<sub>4</sub> (84% RH) solutions. A dry air stream with a  
 8 flow rate of 0.5 SCFH (~235 ccm) was passed through a saturated salt solution to create humid air with  
 9 specific %RH. The humidified air was then passed through our environmental chamber to perform RH-  
 10 based EIS measurements. We inserted a traceable humidity meter (Fisher Scientific, Somerville, NJ) to  
 11 probe and monitor %RH inside the environmental chamber. At each %RH, we ensured the equilibration  
 12 of the sample by measuring the impedance within the range of 1-10 kHz. Once the equilibrium was  
 13 achieved, we performed the impedance measurement over the range of 10MHz-10mHz at 100 mV AC  
 14 potential.

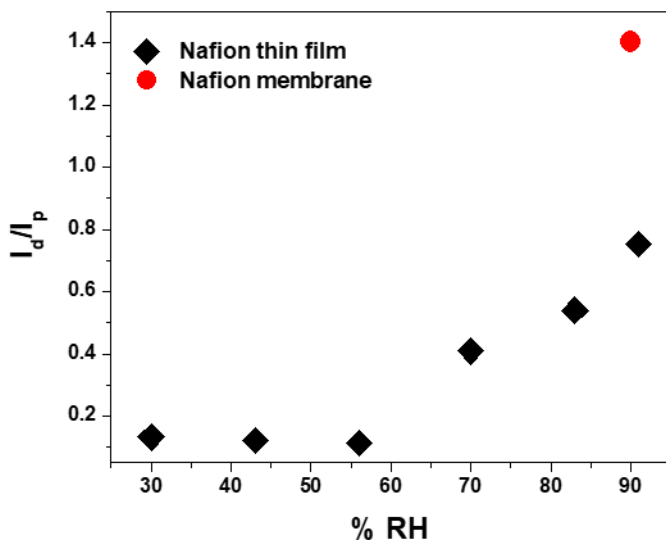


15 **Figure S1.** Specifications of the IDEs used in this work (a); equivalent circuit model used for fitting of  
 16 the data (b). The impedance data and corresponding fit for 575 nm thick Nafion film at different RHs (c,  
 17 d).

1 After measuring the impedance spectra, we used the ZView software (Scribner Associates, Southern  
 2 Pines, NC) and an equivalent circuit model (Figure S1b) to obtain the resistance of the films. In the  
 3 equivalent circuit model (Figure S1b),  $L_1$  represents the inductance in connecting cables,  $R_s$  accounts for  
 4 the resistance of the connecting cables and probes,  $CPE_{dl}$  accounts for the imperfect capacitor-like  
 5 behavior of the double-layer (interface of the ionomer and IDE). In addition,  $CPE_f$  and  $R_f$  account for the  
 6 imperfect capacitor-like behavior of the film and resistance of the ionomer, respectively. The impedance  
 7 spectra and the fits using the equivalent circuit model are shown in Figure S1c, d. Additional details of the  
 8 equivalent circuit model we used are available in our previous paper.<sup>2</sup> We then calculated the ion  
 9 conductivity ( $\sigma$ ) of the ionomer films using the following equation:

$$\sigma = \frac{1}{R_f} \frac{S_{teeth}}{l(N-1)d}$$

11 Here,  $R_f$  is the resistance of the film,  $d$  is the ionomer film thickness,  $S_{teeth}$  is the spacing between IDE's  
 12 teeth,  $l$  is the overlapping length of each tooth, and  $N$  is the number of teeth of IDEs.



23 **Figure S2.** Deprotonation ratio ( $I_d/I_p$ ) as a function of %RH in 600 nm thick Nafion film on an n-SiO<sub>2</sub>  
 24 wafer and a 50  $\mu$ m thick bulk, free-standing Nafion (NR212) membrane.  $I_d/I_p$  values for this plot are  
 25 measured using steady state fluorescence spectroscopy.

26 **Steady-state fluorescence measurement.** Steady-state fluorescence measurements of HPTS in Nafion thin  
 27 films and membranes were done following the procedure we described in our previous work.<sup>3</sup> First, the  
 28 dye was incorporated into the ionomer samples. The Nafion membranes (~2 cm  $\times$  2 cm) were soaked into  
 29 1 M HCl for 1 h followed by rinsing with DI water to remove excess acid. The membranes were dipped

1 into 0.1 M HPTS (in water) for 24 h with continuous stirring followed by quick rinsing thrice with DI  
2 water. To make HPTS-incorporated Nafion film, 20 wt% Nafion solution was diluted first to 10 wt%  
3 using ethanol. An appropriate volume of stock solution of HPTS (38 mM) in DI water was then added to  
4 this diluted Nafion solution to yield a final dye concentration of 0.75 mM. This Nafion-HPTS mixed  
5 solution was spin-coated over the n-SiO<sub>2</sub> substrate to yield ~600 nm thick Nafion film. The Nafion  
6 membranes and films were then dried at 42 °C for 3 h, annealed at 100 °C for 7 h, and cooled down to  
7 room temperature for 12 h inside a vacuum oven (Model #1415, VWR, Radnor, PA).

8 To measure the steady-state fluorescence of HPTS in these thin films and membranes, we used PTI  
9 QuantaMaster 400 steady-state fluorimeter (Horiba, NJ) (excitation/emission slit width = 1 nm; step size  
10 = 10 under excitation correction and zero bias) for the measurements. A custom-built glass humidity  
11 chamber and a salt solution-based RH control system (described in the EIS measurement section) were  
12 used. HPTS was excited at 370 nm ( $\lambda_{exc}$ ) and the emission was collected in the wavelengths ranging from  
13 390-590 nm ( $\lambda_{em}$ ). The deprotonation ratio ( $I_d/I_p$ ) was calculated from the intensities of emission maxima  
14 of protonated ( $I_p$ ,  $\lambda_{em, max} \sim 430$  nm) and deprotonated states ( $I_d$ ,  $\lambda_{em, max} \sim 510$  nm) of HPTS. The  $I_d/I_p$  values  
15 were plotted as a function of RH as can be seen in Figure S2.

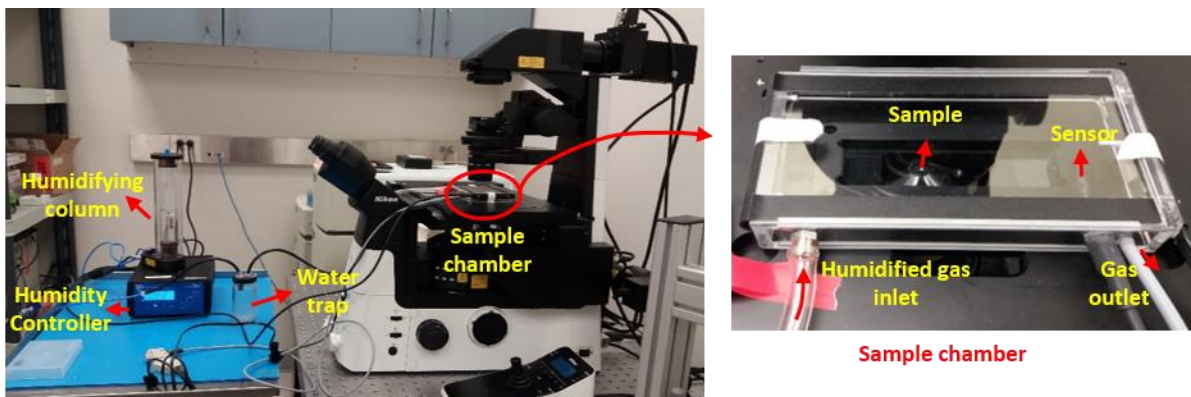
16 **Sample preparation and CLSM imaging: Nafion membrane.** HPTS was incorporated into Nafion  
17 membranes following the same procedure used for steady-state fluorescence measurements. After that,  
18 the membranes were annealed (same as before) and stored inside plastic containers with silica gel to keep  
19 them dry while transferring to the microscope facility and until the measurement is done.

20 CLSM image collection was carried using a Nikon A1R advanced imaging system on a Nikon-Ti2  
21 inverted fluorescence microscope with the Nikon NIS Element-C image acquisition program (Nikon  
22 Corporation-USA). We used 405 and 488 nm laser lines for capturing the emission of protonated and  
23 deprotonated states of HPTS across the samples, respectively. We also used a 20x lens (dry) and 1  $\mu$ m z-  
24 interval between xy-plane images.

25 In one set of CLSM experiments, an HPTS-incorporated and annealed Nafion membrane was imaged at  
26 ambient condition first (Figure 3a, 3d). Before imaging, a membrane sample was placed over a coverslip  
27 for CLSM-imaging. Please note that we did not mount the membrane samples using glycerol (as typically  
28 done) since we wanted to image the membranes at a dry state and compare those with the images obtained  
29 at a hydrated state. Since we did not use glycerol (which also makes the specimen adhere to and lay flat  
30 on a surface), the membrane samples were wrinkly at some places (as expected). We, therefore,  
31 selectively imaged the flat regions of the membranes.

1 After imaging at ambient condition, this membrane was quickly dipped in water in a petri dish to hydrate  
2 both sides of the membrane only and then pat-dried using Kim wipe. The hydrated membrane was then  
3 placed over a coverslip again to take another CLSM image (Figure 3b-d).

4 In another set of hydration experiments, the HPTS-incorporated Nafion membrane was placed inside a  
5 humidity-controlled chamber specially designed for the CLSM system (Figure 3e-h). The imaging was  
6 carried out at 20% and 90% RH. The experimental set-up of the humidity-based CLSM imaging is shown  
7 in Figure S3 and discussed in the next section.



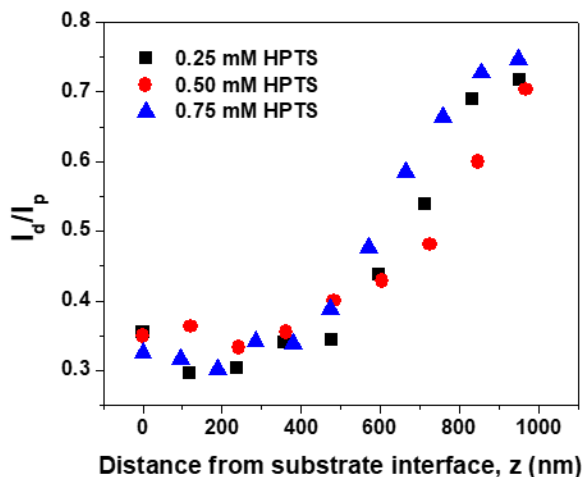
8 **Figure S3.** Experimental setup for performing humidity-based CLSM measurements of ionomer films  
9 and membranes (left). A zoomed view of the sample chamber (right).

10 **Humidity set-up for CLSM imaging.** The environmental chamber, used for the CLSM system, was  
11 purchased from ibidi USA, Inc. (Fitchburg, WI). Ambient air was passed through a humidifying column  
12 connected to a humidity controller to generate humid air (flow rate 40 L/h (667 ccm)) with varied % RH  
13 (20-90% RH). The generated humid air, before entering the sample chamber, was passed through a water  
14 trap to avoid any accidental jump of liquid droplets or condensation inside the sample chamber. The  
15 acting %RH inside the sample chamber was monitored using two independent RH probe (or sensor)  
16 systems simultaneously: one was connected as a part of the feedback loop of ibidi humidity controller  
17 system, and the other probe was an independent one (Fisher Scientific (Somerville, NJ)) inserted  
18 manually inside the sample chamber.

19 **Sample preparation and CLSM imaging: Nafion films.** For CLSM imaging, we made dye-Nafion films  
20 over coverslips. The coverslips were a better choice than n-SiO<sub>2</sub> wafers as the substrate for CLSM  
21 imaging since the coverslips were transparent, at the same time, had SiO<sub>2</sub> on the surfaces (like n-SiO<sub>2</sub>  
22 wafers).

23 To make Nafion solution containing HPTS, a certain volume of HPTS stock solution (38 mM) in DI  
24 water was added to 2-10 wt% Nafion solutions to attain a final dye concentration of 0.75 mM. Please note

1 that when the HPTS concentration was varied within a certain range (~0.25-0.75 mM), the absolute  
 2 intensities of the two states of HPTS ( $I_d$  and  $I_p$ ) varied. But the ratio of emission intensities of these two  
 3 states ( $I_d/I_p$ ) remained unchanged (Figure S4). Hence, in this report, we chose a concentration of HPTS  
 4 within this range (i.e. 0.75 mM) while making all ionomer films to eliminate any effect of dye  
 5 concentration on the CLSM measurements.



14 **Figure S4.** Effect of HPTS concentration on  $I_d/I_p$  profile of 850 nm thick Nafion film at 90% RH. The  
 15 results showed a negligible effect of dye concentration on the ratiometric response of HPTS.

16 For CCVJ-based CLSM experiments, a certain volume of CCVJ stock solution (18.6 mM, 5 mg/mL) was  
 17 added to the same Nafion solutions (2-10wt%) first. Here, we maintained a constant CCVJ: ionomer ratio  
 18 (0.03:1, w/w) while making films with different thicknesses. This allowed us to (i) eliminate the CCVJ  
 19 concentration effect on its fluorescence response ( $I_z$  or  $I_{z/d}$ ) and (ii) attribute the observed changes in  $I_z$  or  
 20  $I_{z/d}$  solely to mobility/stiffness changes within the films (Figure 5).

21 The dye (HPTS or CCVJ)-Nafion mixed suspensions were then spin-coated over the glass coverslips. The  
 22 rpm during spin-coating was adjusted to obtain Nafion films with thickness ranging between 65-1000 nm.  
 23 The films were annealed (as described earlier) and stored inside plastic containers with silica gel as  
 24 mentioned earlier.

25 The dye-incorporated Nafion films were then placed inside the humidity chamber (substrate-side facing  
 26 the laser) for CLSM imaging. To capture the images of thin films, we used 70-120 nm z-steps. According  
 27 to Abbe's diffraction limit, light with excitation wavelength ( $\lambda_{exc}$ ), traveling in a medium with refractive  
 28 index (n), and converging to a spot of half-angle ( $\theta$ ), will have a minimum resolvable distance  
 29 ( $=\lambda_{exc}/(2\sin\theta)$ ), roughly  $\sim\lambda_{exc}/2$ . Based on this, the z-interval between xy-plane images should be  $\geq 185$   
 30 nm (since  $\lambda_{exc}=370$  nm for HPTS) to achieve high resolution. However, in our approach, we were not

1 concerned about the finer details (e.g. features) of the images or the absolute intensities of each channel  
2 ( $I_d$ ,  $I_p$ ). Rather, we were more interested to image the films even thinner than 300 nm. In order to create a  
3 decent  $I_d/I_p$  profile, we needed a reasonable number of xy-scans across the films. For that, we had to lower  
4 the z-interval below 185 nm. Before doing so, we did some imaging of Nafion films by varying the z-  
5 interval below and above 185 nm ( $z = 100$  to 300 nm). With a  $\pm 30\%$  overlap, this allowed us to achieve a  
6 z-interval as low as  $\sim 70$  nm. We saw that within this range of z-interval, our  $I_d/I_p$  profile for a specific  
7 film was negligibly impacted by the value of z-intervals (Figure S5). This suggested that even if there was  
8 a resolution loss at smaller z-intervals, that might have happened for both channels to a similar extent so  
9 that the  $I_d/I_p$  ratios remained unaffected. Thus, making measurements with z-interval as low as 70 nm did  
10 not invalidate our proton conduction profiles, rather allowed the measurement of relatively thinner films.  
11 For the very thin film (i.e. 65 nm thick one), instead of doing the automated z-scanning, we manually  
12 focused the topmost and bottommost fluorescent xy-planes and the emission intensities obtained from  
13 those planes were taken as our HPTS response at the air and substrate interfaces, respectively.

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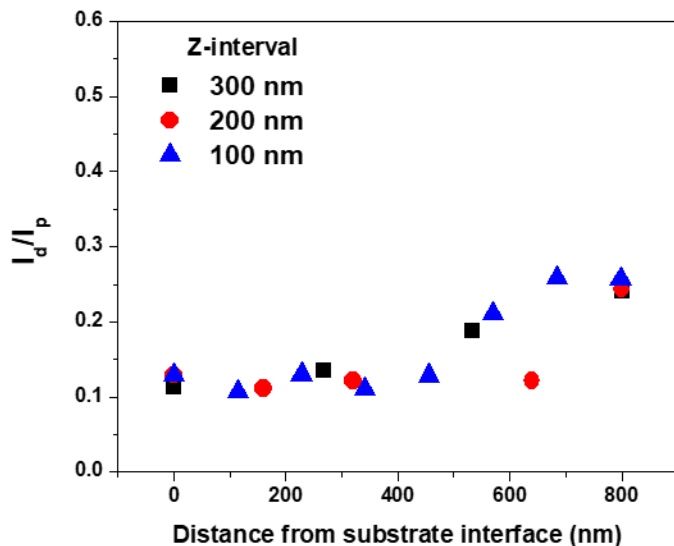
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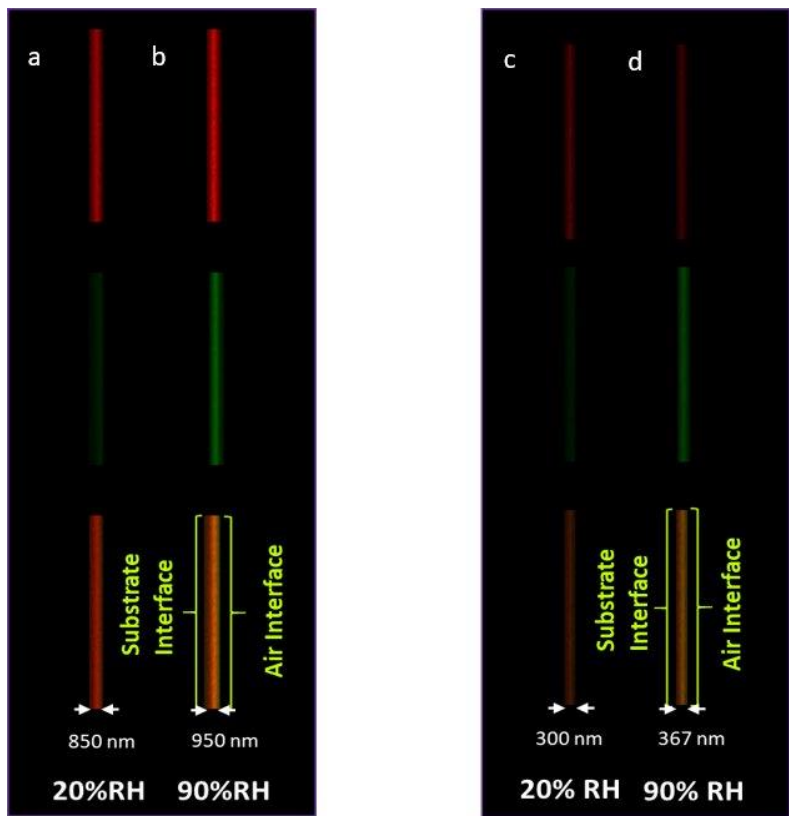
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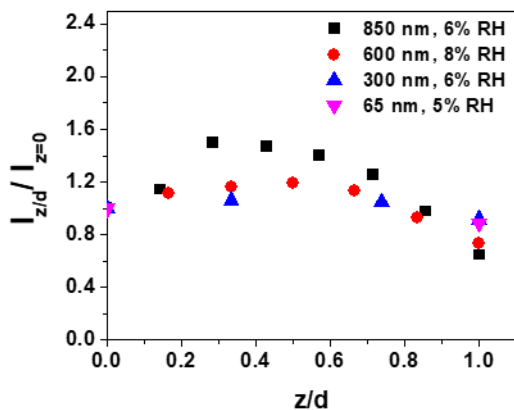
24 **Figure S5.** Effect of the z-interval on  $I_d/I_p$  profile of 800 nm thick Nafion film at 18% RH. The results  
25 showed a negligible effect of z-interval on the trend of  $I_d/I_p$  profile.

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14 **Figure S6.** Pseudocolored CLSM images of HPTS incorporated in 850 nm thick (a, b) and 300 nm thick  
 15 (c, d) Nafion films at 20%RH (a, c) and 90% RH (b, d). The red (top row) and green (mid-row) colors  
 16 represent protonated and deprotonated state emissions of HPTS, respectively. The bottom row is the  
 17 superposition of both colors.

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25 **Figure S7.**  $I_{z/d}/I_{z=0}$  of CCVJ (i.e. mobility or stiffness relative to substrate interface) across Nafion films at  
 26 dry state (~5-8% RH).



1 **Thickness measurement.** Spectroscopic ellipsometry ( $\alpha$ -SE<sup>TM</sup>, J.A. Woollam Co., Inc., Lincoln, NE) with  
2 a spectral wavelength range of 381-893 nm and variable angle (65°-75°) was used to measure the  
3 thickness of ionomer films at ambient condition. The thickness of the native oxide layer on the silicon  
4 wafer (~1.77 nm) was measured before measuring the thickness of ionomer films and was used as a  
5 reference for ellipsometric modeling. Cauchy's model was used to obtain the thickness of all the ionomer  
6 films.

7 **Surface chemical mapping of ionomer films (Scanning electron microscopy (SEM)).** Energy-dispersive  
8 X-ray (EDX) analysis was performed for surface chemical mapping of fluorine, carbon, oxygen, and  
9 sulfur on the surface of ionomer thin films on n-SiO<sub>2</sub> wafers by using FEI Nova NanoSEM 450 at an  
10 acceleration voltage of 20 kV and 5 mm working distance. EDX detector was used to collect  
11 characteristic x-rays of different elements into an energy spectrum and EDX software was used to analyze  
12 the energy spectrum in order to determine the specific elements and construct the chemical mapping of  
13 the corresponding SEM image. Before the measurement, the samples were coated with a thin layer of  
14 gold (5 nm) to avoid an electron cloud on the sample.

#### 15 **References.**

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