Supplementary Information

Cross-Correlated Humidity Dependent Structural Evolution of Nafion Thin Film Confined on Platinum Substrate

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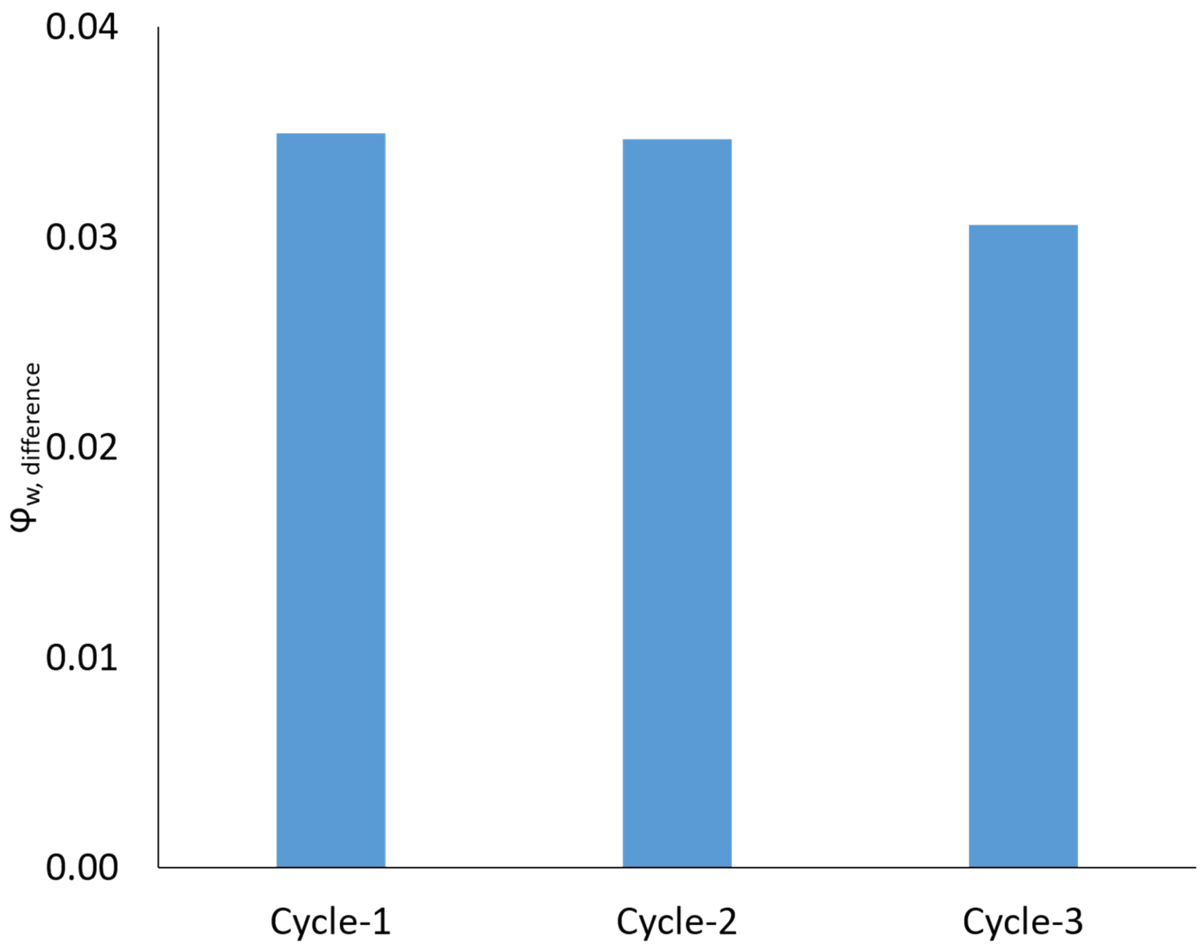

Figure S1. The difference in volume fraction estimated from ellipsometry and QCM at 25 °C for a sample cycled three times between 0% and 90% RH. Note mass of water on the bare Pt is deducted from QCM measurement.

a) Volume fraction estimation from direct mass uptake measured by QCM

$$\Delta m = \Delta F / CF \quad (1)$$

$$L_w = \Delta m / \rho_w \quad (2)$$

$$\Phi_w = {}^{L_w}\!/_{L} \quad (3)$$

Where, Δm is the water mass uptake measured from QCM in ng/cm^2, ΔF the frequency change upon water uptake in Hz, CF the conversion factor 56 Hz/ng, L_w and L the thickness of water and dry ionomer layer in nm, ρ_w the density of water in g/cm^3, and φ_w is the water volume fraction.

b) Volume fraction estimation from measurement of unidirectional film expansion in Z direction (Ellipsometry and NR).

$$\Phi_w = {}^{\Delta L}/_{L} \quad (4)$$

where, *ΔL* is change in thickness of the dry film in nm upon water uptake.

c) Volume fraction estimation from SLD measured by NR.

$$\varphi_w(z) = {}^{(SLD_{ion} - SLD_{ion+w}(z))}/_{(SLD_{ion} - SLD_w)} \quad (5)$$

$$\varphi_w = {}^{\int \varphi_w(z).dz}/_{L} \quad (6)$$

where SLD_{ion} is the SLD of the dry ionomer, SLD_{ion+w} is the SLD of water containing ionomer, SLD_w is the SLD of water, and L is thickness of ionomer

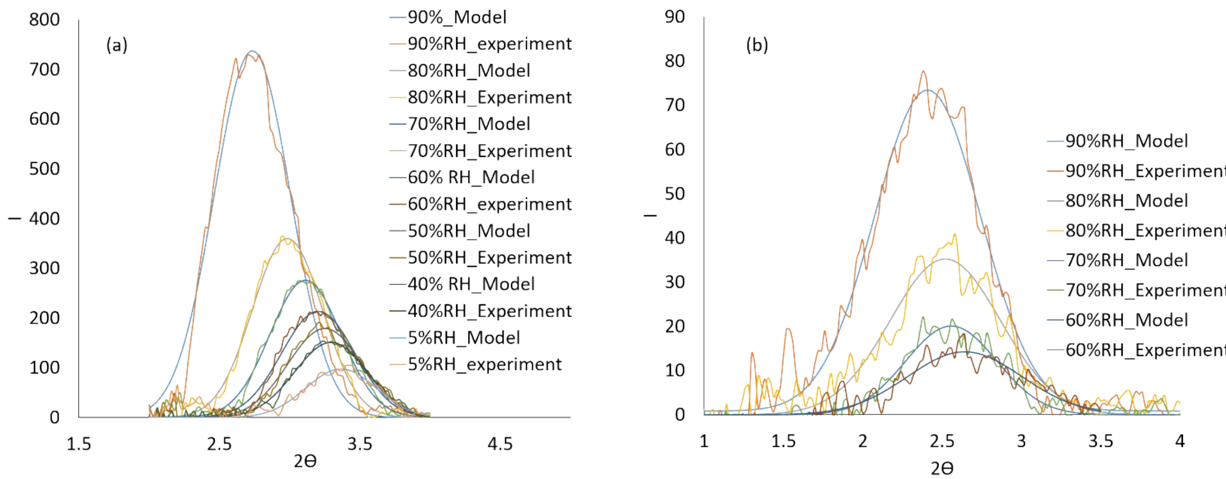

Figure S2. Fitting of the GISAXS peaks using a Gaussian curve for a) Out-of-plane intensity b) In-plane intensity

d) Fitting of Reflectivity data using different models

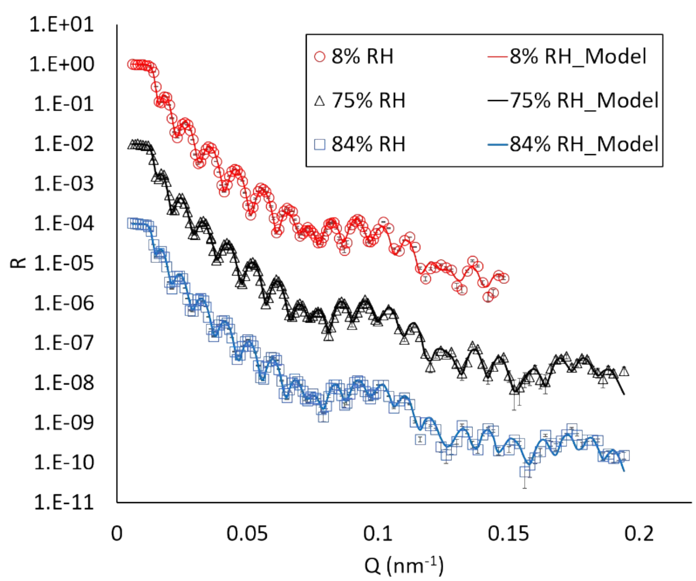

Figure S3. Reflectivity data obtained for water containing 55 nm EW1100 film on Pt in 8% RH, 75% RH, and 84% RH at 25 °C fitted with a four-layer model.

Table S1: Comparisons of Figure of Merits (FOM) for data fitted with different # of layers

RH	Layers	FOM	Chi2	BIC
8%	1	0.07	5.62	807.18
75%	1	0.09	54.98	7372
	2	0.079	46.85	6165
	3	0.074	37.06	4796
	4	**0.065**	**13.83**	**1819**
	5	0.064		
84%	1	0.095	24.9	3371
	2	0.085	21.81	2910
	3	0.08	18.69	2463
	4	**0.07**	**10.54**	**1411.5**
	5	0.07		

Where $$FOM = \frac{1}{n-p}\sum_{n=1}^{n} |\log(R) - log(S)|$$

Where $$chi2 = \frac{1}{n-p}\sum_{n=1}^{n} \left(\frac{R-S}{E}\right)^2$$ and $BIC = (n-p).chi2 + pln(n)$

Where

n is the number of data points, p the number of parameters, R the experimental reflectivity, and S is the simulated reflectivity, and E is experimental error. BIC is Bayesion information criterion.

FOM is the figure of merit indicates the goodness of the fit.

4-layer model is chosen to represent the structure of water contained ionomer thin film because compare to 3-layer model FOM change is more than 10%. We find that adding another layer doesn’t change FOM much (< 10%) therefore 4-layer model is most suitable.