

# Supporting Information

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## Role of Mechanical Factors in Controlling the Structure-Function Relationship of PFSA Ionomers

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This supporting information details the water-vapor uptake experiment using the DVS, additional SAXS and WAXS profiles, and the derivation of the model equations.

## Uptake in Water Vapor

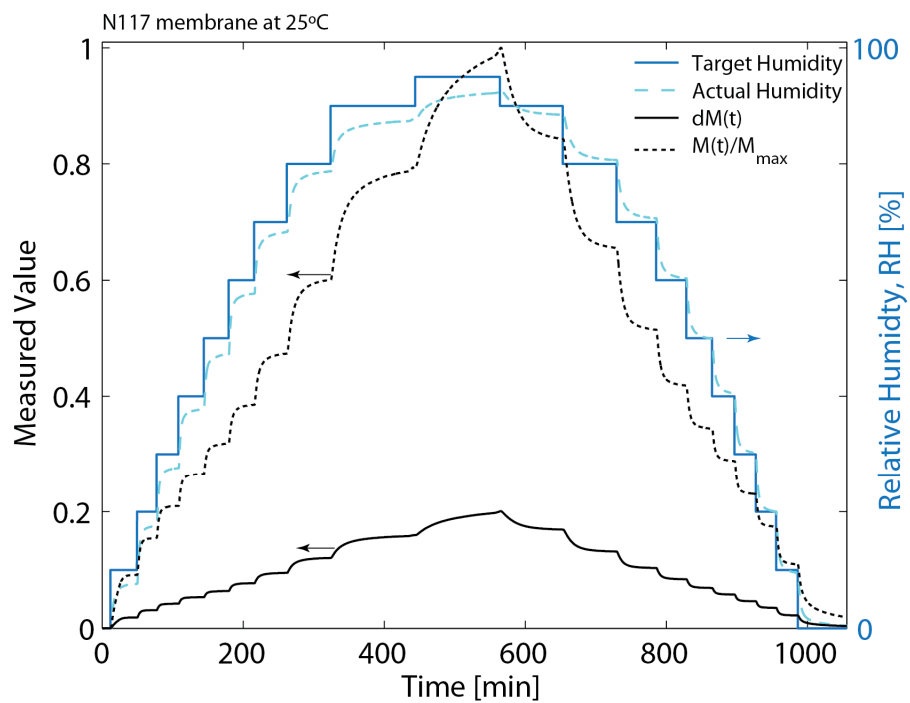
As mentioned, the uptake in water vapor for the various membranes was measured using DVS. In this test, as shown in Figure S1, the humidity was increased in steps of 10%, where the membrane was equilibrated at each RH step for at least 2 hours or until the change in the weight  $\Delta M/M_0$  was less than 0.005%/min. The weight of water absorbed by the sample,  $M_w$ , is determined from the measured weight of humidified sample,  $M$ , and the initial weight,  $M_0$ . The water content (or hydration number),  $\lambda$ , is determined at the end of each RH step from

$$\lambda = \frac{(M - M_0) / \bar{M}_w}{M_p^{\text{dry}} / EW} = \frac{M_w / \bar{M}_w}{M_p^{\text{dry}} / EW} \quad (\text{S1})$$

where  $M_p^{\text{dry}}$  is the weight of the polymer sample in reference dry state,  $EW$  [g/mol] is the equivalent weight of the ionomer (1100 g/mol) and  $\bar{M}_w$  is the molar weight of water (18 g/mol). After completion of a sorption-desorption cycle, samples were heated in DVS up to 120°C and weight measurement was continued for another hour. From the difference between 'dry' weight measured initially at 25°C (0% RH) and that at 120°C, residual water content,  $\lambda_{\text{res}}$ , is calculated:

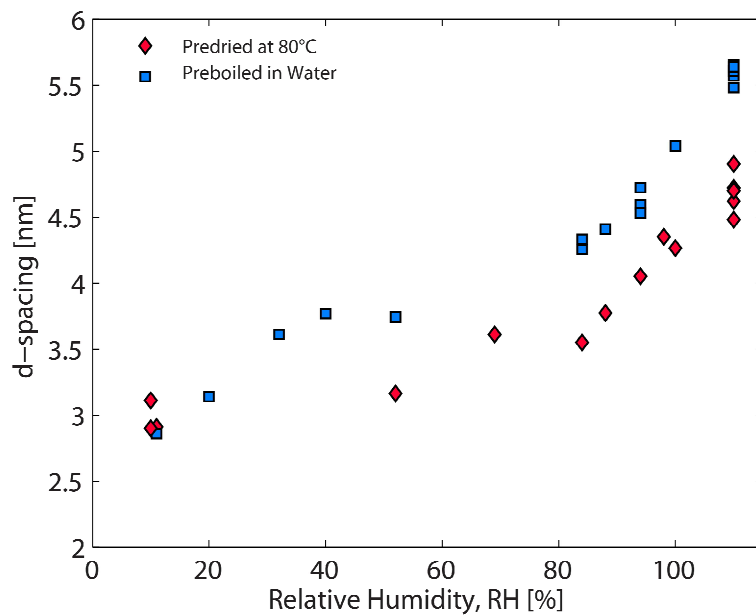
$$\lambda_{\text{res}} = \frac{(M_0^{(25^\circ\text{C})} - M_0^{(120^\circ\text{C})}) / \bar{M}_w}{M_p^{\text{dry}} / EW}. \quad (\text{S2})$$

Therefore, the reference dry state for weight  $M_p^{\text{dry}}$  shall be taken as the minimum weight measured for the sample during drying.

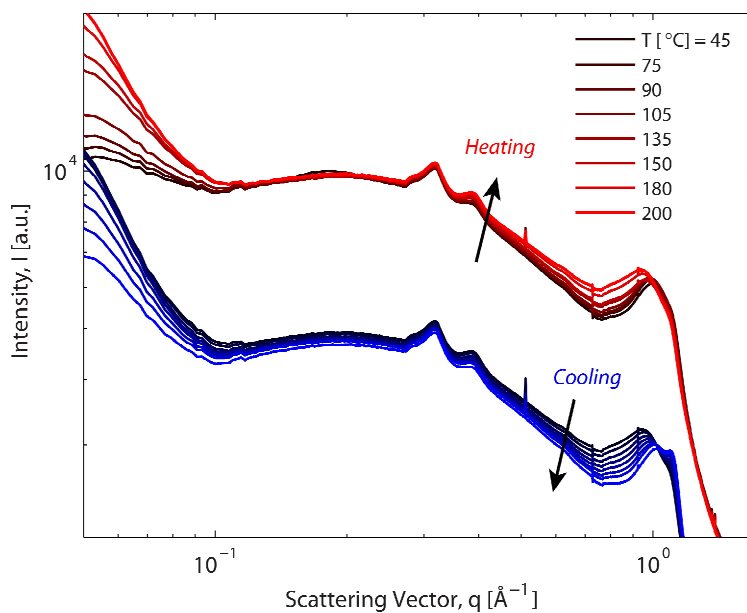


**Figure S1 DVS data showing RH and mass gain as a function of a sorption/desorption cycle.**

## SAXS Profiles

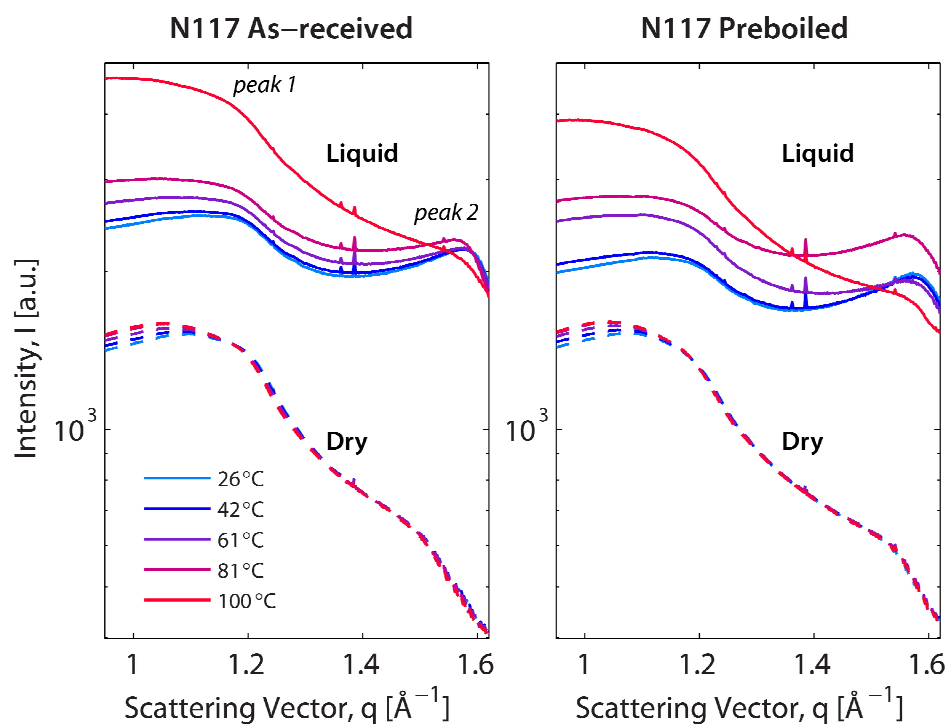


**Figure S2** Domain spacing of predried and preboiled Nafion 117 membrane as a function relative humidity and in liquid water at 25°C.



**Figure S3** Unprocessed scattering profiles in for Nafion 117 during a heating/cooling cycle. The peak around 0.3 Å<sup>-1</sup> is due to the kapton window in the stage. The profiles in the main text are corrected for background and plotted in the higher q range.





**Figure S4 Wide-angle scattering profiles for as-received and preboiled Nafion 117 membrane during heating in liquid water.**

## Model

The water activity within the polymer is described as<sup>1</sup>

$$\ln a_p = \ln(1 - \phi'_p) + \left[ \left( 1 - \frac{1}{\bar{V}_p / \bar{V}_w} \right) \phi'_p + \chi \phi'^2_p \right], \quad (\text{S3})$$

where  $\chi$  is Flory–Huggins interaction parameter,  $\phi_p$  is the volume fraction of the polymer, which may also include the bound water,  $\lambda^B$ , strongly attached to ionic groups as part of the polymer. Fraction of the polymer including the bound water can be written as

$$\phi_p = (\bar{V}_p + \lambda^B \bar{V}_w) / (\bar{V}_p + \lambda \bar{V}_w), \quad (\text{S4})$$

Bound water in the membrane can be determined from various methods as explained in references.<sup>2-4</sup> One of the key parameters characterizing the chemical energy is the interaction parameter, which was reported to be between 0.9 and 2.2 from sorption analysis<sup>2, 5, 6</sup> and simulations<sup>7, 8</sup>, at various levels of hydration. In this work, we adopted the following expression from our earlier work<sup>9</sup>

$$\chi(\phi_p, T) = \chi_s \phi_p^{1.5} + \chi_T \left( 1 - \frac{T}{T_{\text{ref}}} \right) \quad (\text{S5})$$

where  $\chi_s$  and  $\chi_T$  are the components of the interaction parameter controlling the swelling and temperature effects, respectively. The parameter  $\chi_T$  was attributed to the interactions arising from the change in the phase of water and the associated changes in membrane morphology.

Figure 11 in the text shows the model predictions, and the parameters used in the model are  $\chi_s = 1.9$ , and  $\chi_T = 0$  (as the membrane is in vapor phase at room temperature). A higher backbone modulus,  $E_b$ , is used for the dried membrane, which is calculated from the modulus of the dry membrane,  $E_{\text{dry}}$ , using the mechanics model explained in references<sup>10, 11</sup> which is simply a scaling approach in the following form

$$E_b \propto \frac{E_{\text{dry}}}{1 - \phi_{\text{SO}_3}^m} \quad (\text{S6})$$

where  $m$  is a geometric parameter based on the shape of the ionic groups which is assumed to be spherical as the membrane is in dry state. Details of the calculations and determination of scaling parameters can be found in reference.<sup>11</sup> This model assumes, from a mechanistic perspective, that the backbone excludes the ionic groups (and also the bound water) and therefore uses the fraction of sulfonic acid ( $\text{SO}_3$ ) ionic groups in the dry membrane to determine the contribution of the polymer backbone to the measured modulus of the membrane. Fraction of  $\text{SO}_3$  groups in the membrane can be easily calculated from the equivalent weight (EW) and density of the dry membrane, i.e.:

$$\phi_{\text{SO}_3} = \frac{EW}{\rho_{\text{dry}}} \quad (\text{S7})$$

In this study, EW is 1100 g/mol and density of the dry membrane is taken to be 2.05 g/cm<sup>3</sup>. Finally, backbone modulus of the membrane is taken to be ~320 MPa and 420 MPa for the preboiled and dried membrane, respectively. These values are determined from the modulus of the dry membrane which is measured by means of the compressive stress-strain curves discussed in the text. Compressive modulus of the membrane is determined from the slope of the initial linear portion of the stress-strain curve for strains below 0.02.

## References

1. Flory, P. J., *Principles of polymer chemistry*. Cornell University Press: Ithaca, 1953; p 672.
2. Choi, P.; Jalani, N. H.; Datta, R. *Journal of the Electrochemical Society* **2005**, 152, (3), E123-E130.
3. Choi, P. H.; Datta, R. *Journal of the Electrochemical Society* **2003**, 150, (12), E601-E607.
4. Takata, H.; Mizuno, N.; Nishikawa, M.; Fukada, S.; Yoshitake, M. *International Journal of Hydrogen Energy* **2007**, 32, (3), 371-379.
5. Futerko, P.; Hsing, I. M. *Journal of the Electrochemical Society* **1999**, 146, (6), 2049-2053.
6. Yeo, R. S. *Polymer* **1980**, 21, (4), 432-435.
7. Wu, D. S.; Paddison, S. J.; Elliott, J. A. *Energy & Environmental Science* **2008**, 1, (2), 284-293.
8. Paddison, S. J.; Wu, D. S.; Elliott, J. A.; Hamrock, S. J. *Langmuir* **2010**, 26, (17), 14308-14315.
9. Kusoglu, A.; Kienitz, B. L.; Weber, A. Z. *Journal of the Electrochemical Society* **2011**, 158, (12), B1504-B1514.
10. Kusoglu, A.; Karlsson, A. M.; Santare, M. H. *Polymer* **2010**, 51, (6), 1457-1464.
11. Kusoglu, A.; Santare, M. H.; Karlsson, A. M.; Cleghorn, S.; Johnson, W. B. *Journal of Polymer Science Part B: Polymer Physics* **2008**, 46, (22), 2404-2417.