Supplemental Information
“Neutron Reflectometry Fitting Techniques for Under-determined, Multi-layered Structures: Lamellar Phase Segregation in Ultra-thin Nafion Films”

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Neutron Reflectivity Data Collection

For measurements in the range $0.5^\circ < \theta < 6.5^\circ$, the upstream slits were opened continuously at a rate of 0.4 mm/degree-$\theta$, to provide a constant $\Delta Q/Q$, a flux that increases as $Q^2$, and a constant 4.3 cm wide beam projection onto the plane of the sample. Below this range, the upstream slits were held constant at 0.05 mm (t42 at 0\% RH) or 0.1mm (for all other measurements.) This limits uncertainty in the incident intensity that would arise from repeated slit movements at narrow slit settings, where the constant slit motor uncertainty becomes larger relative to the total beam width. Above $\theta = 6.5^\circ$ the incident slits are held fixed at 2.6 mm in order to keep the final slit from exceeding the detector limit. The two downstream slits were held fixed at 0.6 mm and 0.8 mm below $\theta = 0.5^\circ$ and were opened at rates of 1.2 mm/degree of $\theta$ and 1.6 mm/degree of $\theta$, respectively, above this angle to accept the entire reflected beam while limiting additional background. Above $\theta = 6.5^\circ$ they are held fixed at 7.8 mm and 10.4 mm, respectively. A horizontal slit near the sample defined a roughly 25 mm footprint in the orthogonal direction.
The background signal was measured during two sets of scans with the slits and theta as in the specular scans, but with the detector offset slightly from the specular \((\theta \times 2)\) condition, to \(\theta \times 2.5\) and to \(\theta \times 1.5\). These two background scans were averaged to provide an approximation of the background scattering at the specular condition. Small deviations from this linear interpolation between background measurements were modeled when fitting the data by a residual background fitting parameter that is invariant with Q. The reflected intensity is normalized by the incident intensity as a function of slit settings, which is measured via a beam directed through the Al walls of the controlled-relative humidity (RH) sample environment (see below for a full description) that serves as the medium through which the incident and reflected beams pass during specular and background scans. In all scans a beam monitor after the first upstream slit is used to normalize the detector intensity against small temporal variations in neutron flux from the source. The full Q range was divided into several scans to allow for variations in the time per point and Q step size. Data were taken as several repeated series of these scans through the entire Q range of interest, to check for changes that might occur over time. Sample and instrument alignment are also re-checked periodically by scanning theta. If no statistically significant differences are seen in the various data sets they are combined for increased counts at each Q value, which decreases the relative uncertainty. The specular reflectivity is determined by subtracting the averaged background scans from the specular scans and then normalizing by the incident intensity. The counting statistics of these individual measurements are
propagated through the reduction to provide error bars on the data at plus and minus one standard deviation.

*Controlled RH Sample Environment*

Because the water uptake of Nafion varies considerably with small variations in RH at high humidity, care was taken to maintain stable and consistent control of the thermal environment and humidity. Samples were maintained at 29.6 ± 0.2 °C and 92.1 ± 1.5 % RH using a custom-built sample environment, shown schematically in Figure 1. Dry Ar carrier gas was first passed through a dew point generator, DPG, (*Li-Cor, Inc.*)[1], which itself was housed inside a controlled-temperature enclosure. The flow-rate was controlled at 240 ± 70 cm³/minute via a needle valve, based upon observations of a flowmeter positioned at the entrance of this DPG enclosure. From there, the humidified gas travelled through a controlled-temperature heated line to the sample environment, which is a temperature-controlled Al cylinder (Al transmits neutrons with very little attenuation) positioned on the goniometer stage of the instrument. Resistive heaters were attached above and below the neutron window to minimize temperature gradients. Control instrumentation, including gas inlet and outlet, an in-line RH sensor in the gas outlet, a flow meter at the gas outlet for leak detection, as well as electrical feedthroughs for temperature measurement and control, is housed on a flange which lies above and seals the sample cylinder. All temperatures in the carrier gas path other than the sample temperature are actively controlled at a constant temperature via K-type thermocouples and resistance heaters to maintain temperatures well above the dew point.
Up to four samples can be held in the sample environment at one time, and are kept in good thermal contact with the sample heater by polished aluminum clamps mounted to a Cu block at the top flange of the sample can. The samples are maintained at a precise and stable temperature via simultaneous heating, via a resistive cartridge heater, attached to the Cu block at the sample mount, which is actively controlled using a Pt thermometer, and cooling, via coolant loop filled with an ethylene glycol/water mixture maintained at a constant temperature by a water chiller.[2] The sample temperature is monitored via a calibrated Cernox sensor (Lakeshore Cryotronics, Inc.) attached to one of the samples by a clamp with a polished mating face placed outside of the neutron beam path. The RH at the sample was determined by two methods, which agreed to within the experimental uncertainty: (i) comparison of the specified dew point and the sample temperature, and (ii) via RH probe (Rotronics) positioned within the sample can, which is properly adjusted for the difference in temperatures between the sample and the exit port. The dew point generator maintains the set point to within ± 0.2 °C and the sample temperature is controlled to within ±0.2 °C of the set point (the Cernox sensor is accurate to within ±0.04 °C; the additional uncertainty accounts for the ability of the active temperature control to maintain the system at a constant temperature), giving an overall RH uncertainty of 1.5% for this experiment.

Sub-optimal Fits to t42 Data for Models With Too Few Lamellae

As described in the manuscript, NR data sets taken on sample t42 in 92% and 0% RH environments were best fit by models with 6 and 3 lamellae, respectively, at the
Nafion-substrate interface. Models with greater numbers of lamellae fit the data with roughly equal $\chi^2$ to these models, or else the improvement in the fit was not enough to justify the extra model complexity. For models with fewer lamellae than the best fits, the goodness-of-fit $\chi^2$ statistics increased rapidly, characterized by a poor fit to the data in the region of the high-Q peak that is attributed to the lamellar structure. In generally, fits with too few lamellae could not reproduce the high amplitude of this peak. This is shown in Figure S1 for models with $n < 6$ lamellae fit to the 92% RH data, and in Figure S2 for models with $n < 3$ lamellae fit to the 0% RH data.

*Fits to t5 Data Without Isotope Contrast Variation*

For sample t5, NR data was initially taken in 92% RH with the carrier gas humidified by H$_2$O. Initial fits to this data resulted in numerous models with disparate SLD profiles that all gave suitable fits to the data (as characterized by low $\chi^2$ values), as demonstrated in Figure S3. Figure S3a shows a collection of representative SLD profiles (offset on the y-axis for ease of visualization) that all gave suitable fits to the data. As can be seen, these profiles appear to be related by combinations of symmetry operations on sections and re-arrangements of these sections. Figure S3b shows the simulated NR data from these profiles, overlaid on the measured NR data, demonstrating that the piecewise symmetry related models gave very similar fits to the data. Because the NR data taken in H$_2$O vapor was incapable of distinguishing between these disparate models, the sample was re-measured in 92% RH where D$_2$O was the humidifying isotope. As described in the
manuscript, subsequent simultaneous fitting to the two data sets was capable of distinguishing between these models, and identified a single model that gave a suitable fit to the data and was also consistent with the lamellar SLD profile as identified previously[3] and in fits to sample t42.
Figure S1. Fits to NR data taken on sample t42, 92% RH, with varying numbers of lamellae. As the number of lamellae increases, the fit in the region of the high-Q lamellar peak centered at $Q_z \sim 2.0 \text{ nm}^{-1}$ improves noticeably. The inset focuses on this high-Q peak.
**Figure S2.** Fits to NR data taken on sample t42, 0% RH, with varying numbers of lamellae. As the number of lamellae increases, the fit in the region of the high-Q peak associated with the remnant lamellar structure, centered at $Q_z \sim 2.2$ nm$^{-1}$, improves noticeably. The inset focuses on this high-Q peak.
Figure S3. Multiple fits to NR data on taken sample t5 exposed to 92% RH humidified by H₂O vapor. (a) Various and disparate SLD profiles (offset on the y-axis for ease of visualization) that all produced suitable fits to the NR data; (b) simulated NR data from the SLD profiles overlaid on the measured NR data, demonstrating the inability of the NR data to differentiate between the various models.
References

(1) Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
