

Controlling Nafion Structure and Properties via Wetting Interactions (Supporting Information)

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1. Transmission Electron Microscopy Measurements of Nafion Films

The TEM images presented in Figure S1 correspond to Nafion thin-film samples (a) as-cast and (b) post-annealing at 200 °C. Nafion side chains were stained for 45 min with Ruthenium (IV) oxide to provide a dark contrast to the areas corresponding to ionomer domains. The TEM images show the phase-separated structure of Nafion, with a low degree of order. Upon annealing, the unstained perfluorinated domains form bigger aggregates with a lengthscale that correspond to the ones arising from periodic crystalline domains observed in GISAXS measurements.

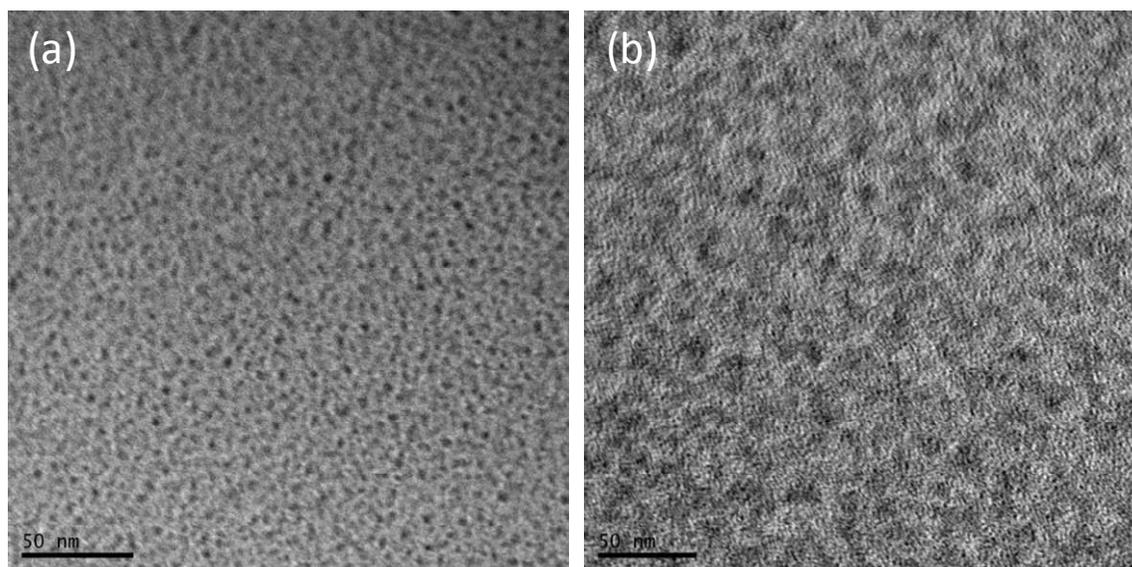


Figure S1. Transmission electron micrographs of films cast on Si substrates (a) before and (b) after thermal annealing at 200 °C. The films were stained with Ruthenium (IV) oxide.

2. Secondary-Ion Mass Spectrometry Measurements

The SIMS traces presented in Figure S2 were acquired for a 100 nm Nafion film cast on a thermally grown 300 nm SiO₂ substrate and annealed at 200 °C at high vacuum. A thick SiO₂ layer was used in this case to prevent charge compensation in the interface of the polymer and the substrate during SIMS measurements. For this experiment, a buffer layer of deuterated polystyrene (d-PS) was spin-cast on top of the polymer film from a toluene solution. The measurements were acquired on a Physical Electronics 6650 Dynamic SIMS system using a 2 kV oxygen beam and a 50 nA current. In Figure S2 we present deuterium, carbon and silicon normalized counts traces across the thickness of the film, which show a

small increase in the concentration of carbon at the interface of Nafion with the substrate. This increase in carbon density can be attributed to a larger presence of crystallites near the substrate interface.

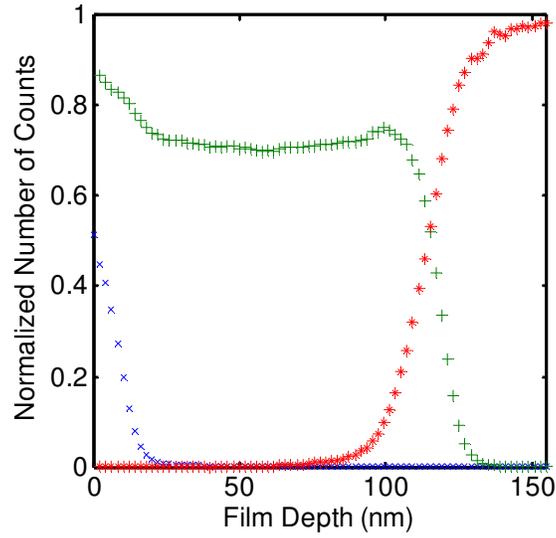


Figure S2. Deuterium (x), Carbon (+), and Silicon (*) traces as a function of film depth in thermally annealed Nafion films. An increase in carbon density is observed near the SiO₂ interface, potentially attributed to the presence of crystallites near the substrate.

3. GISAXS depth penetration analysis

Following an analysis previously reported,^[40] the critical angle for Nafion thin-films was determined to be $\alpha_c = 0.154$. Using properties for Nafion, the penetration depth (Λ) can then be calculated as,^[44]

$$\frac{1}{\Lambda(\alpha_i)} = -2k_0 \operatorname{Im} \left(\alpha_i^2 - \alpha_c^2 - 2i \frac{\lambda\mu}{4\pi} \right)^{\frac{1}{2}}$$

Where $k_0 = 2\pi/\lambda$, and λ is the X-ray wavelength and μ is the linear absorption coefficient of Nafion.

Using this formalism, the penetration depth for Nafion films can be calculated at different incident angles (α_i) as presented in Figure S3.

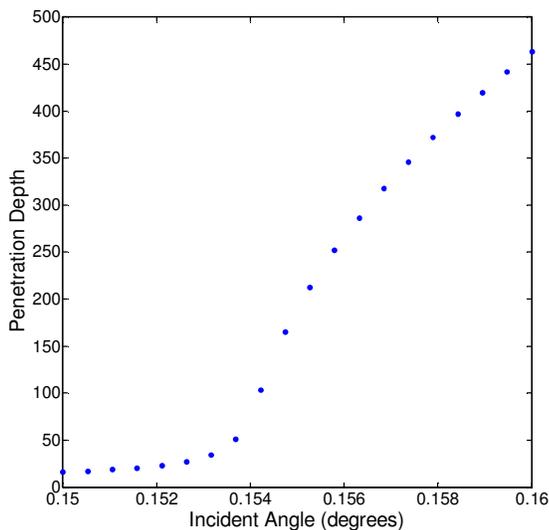


Figure S3. X-ray penetration depth for Nafion thin-films as a function of incident angle.

4. Kinetic analysis of macroscopic swelling of thin-films

The thickness-evolution data was fitted to a two-term exponential equation (Equation 1) commonly used to describe macroscopic swelling and dynamic water transport in Nafion[®] membranes.^[10, 45]

$$\frac{T(t)}{T_{\infty}} = 1 - A \exp\left(-\frac{t}{\tau_1}\right) + (1 - A) \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

In this equation, $T(t)$ and T_{∞} are the fractional thickness changes as the film absorbs water and the final recorded value. Furthermore, A is a fitting parameter and τ_1 and τ_2 are two time constants. Figure S4 presents traces of normalized thickness increase as a function of time during swelling. In this graph, it can be clearly observed that all the samples follow a similar behavior as they evolve towards their ultimate swelling value, with not much variation on their kinetics. The calculated values for each of the time constants for samples prepared on different substrates and undergoing different thermal treatments are presented in **Table S1**. All the fitted time-constant values are comparable between samples, although the OTS ones are consistently faster. Overall, there are not significant discrepancies which indicate that kinetics are more-or-less independent of the sample preparation condition even when the maximum water uptake is clearly affected.

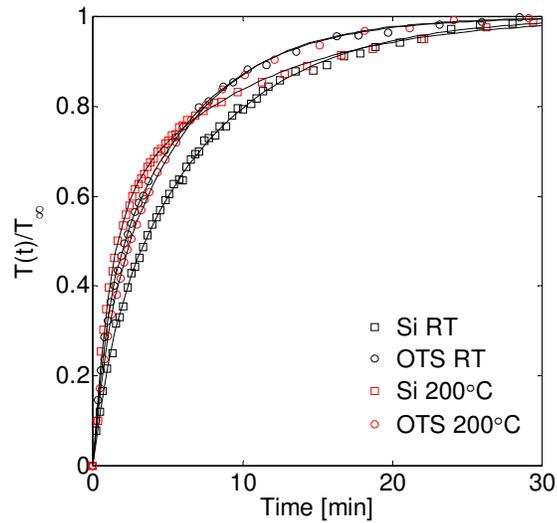


Figure S4. Time constants calculated from film-thickness swelling measurements. The first time constant, τ_1 (related to the water-absorption process) is relatively unaffected by processing conditions of the thin-films. The larger time constant, τ_2 (related to polymer-chain relaxation) is more strongly affected by the orientation and crystallinity of the domains in the film.

Table S1. Fitted time constant values for thin-film samples prepared on different substrates and under different thermal treatments.

Thin-film Sample	τ_1 [min]	τ_2 [min]
Si, Unannealed	1.20	7.48
OTS, Unannealed	0.84	5.97
Si, Annealed 200 °C	1.07	9.51
OTS, Annealed 200 °C	0.88	5.66