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Sub-second Morphological Changes in Nafion during Water Uptake Detected by Small-Angle X-Ray Scattering

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Abstract

The ability of Nafion[®] membrane to absorb water rapidly and create a network of hydrated interconnected water domains provides this material with an unmatched ability to conduct ions through a chemically and mechanically robust membrane. The morphology and composition of these hydrated membranes significantly affects their transport properties and performance. This work demonstrates that differences in interfacial interactions between the membranes exposed to vapor or liquid water can cause significant changes in kinetics of water uptake. *In-situ* small-angle X-ray scattering (SAXS) experiments captured the rapid swelling of the membrane in liquid water with nanostructure rearrangement on the order of seconds. For membranes in contact with water vapor, morphological changes are four-orders-of-magnitude slower than in liquid water, suggesting that interfacial resistance limits the penetration of water into the membrane. Also, upon water absorption from liquid water, a structural rearrangement from a distribution of spherical and cylindrical domains to exclusively cylindrical-like domains is suggested. These differences in water-uptake kinetics and morphology provide a new perspective into Schroeder's Paradox, which dictates different water contents for vapor- and liquid-equilibrated ionomers at unit activity. The findings of this work provide critical insights into the fast kinetics of water absorption of Nafion membrane, which can aid in the design of energy conversion devices that operate under frequent changes in environmental conditions.

KEYWORDS. Nafion, Water Sorption, Morphology, in-situ SAXS, Schroeder's Paradox.

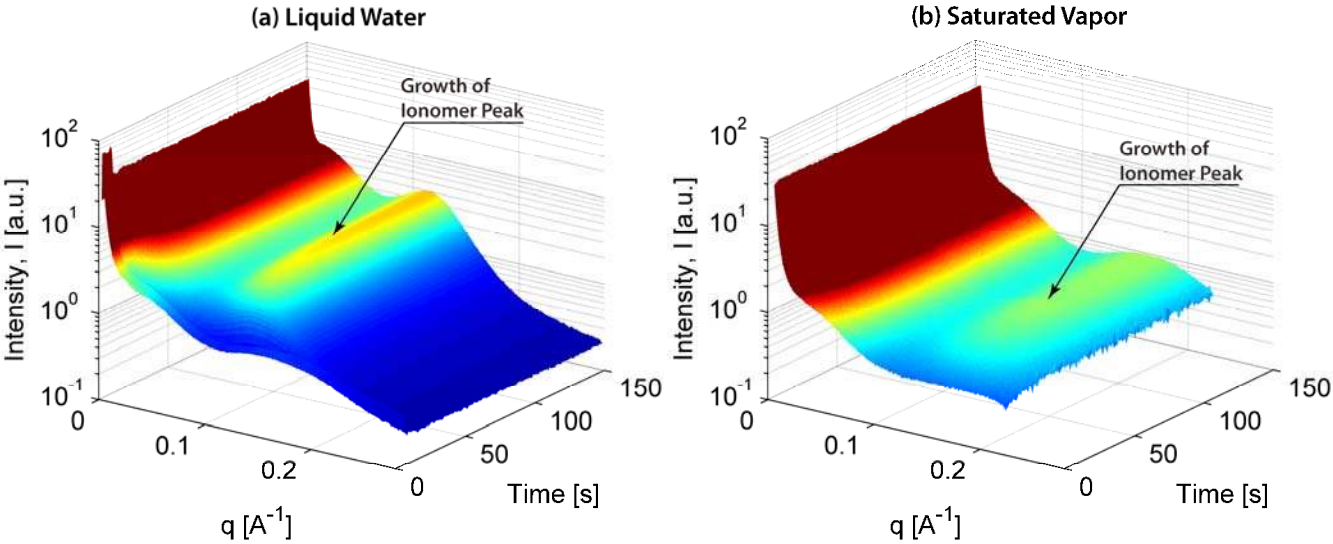
Nafion[®] is a widely studied perfluorinated sulfonic-acid (PFSA) ionomer where the sulfonic-acid (SO₃H) ionic groups are randomly tethered to the fluoropolymer backbone via side chains.¹ This PFSA membrane's good conductivity along with its structural integrity make it suitable for electrochemical applications such as polymer-electrolyte fuel cells and artificial-photosynthetic devices, which demand good durability, separation of reactants/products, and high conductivity. Water, which is a byproduct in a fuel cell, controls the proton mobility and therefore plays a key role in cell performance.^{2, 3} Understanding the water-absorption kinetics and mechanism in Nafion membranes is crucial in the design of more efficient energy-conversion devices and new proton-conductive materials. Due to the strong hydrophilicity of the ionic groups, Nafion can rapidly absorb water and undergo morphological rearrangements that affect transport properties. Furthermore, Nafion's water-absorption characteristics depend strongly on the environment in which the membrane is equilibrated. For example, Nafion membrane absorb up to 15 and 22 water molecules per ionic group in saturated vapor and in liquid water, respectively.^{1, 4-6} The difference in water uptake under saturated-vapor or liquid environments, both of which have unit water activity, is commonly referred to as Schroeder's Paradox.⁷ This phenomenon is observed in a wide-range of gels and ionomers, and its origin is still not fully understood. The differences observed between vapor- and liquid-contacted membranes have been attributed to metastable states, thermal history effects,⁴ and to the distinct processes for water uptake from liquid and vapor phases,^{2, 5, 8} where the latter involves overcoming the interfacial resistance arising from surface morphology.^{8, 9} These interfacial effects can be significant, and can arise from differences in the surface morphology between vapor- and liquid-contacted membranes due to surface-energy dissimilarities. The growth of water domains during sorption of an ionomer results in a phase-separated nanostructure, where water-swollen ionic domains facilitate water and ion transport through the hydrophobic polymer matrix.¹⁰⁻¹² Hence, the discrepancy in water content of a membrane exposed to water vapor or liquid affects not only its internal morphology but also its transport properties.^{1, 2, 4-6} The findings here provide new insights by revealing how the phase of water results in a four-orders-of-magnitude change in the timescale required to reach a steady-state structure, which is consistent with

the water phase controlling the surface morphological rearrangements, including domain orientation and size, which allow water ingress.

Despite the growing body of literature on structural properties of PFSA membranes upon water absorption, the kinetics of water uptake and associated morphological changes are still not fully characterized. The structural characterization of membranes during water absorption has remained a challenge due to the fast water-absorption kinetics of Nafion. This work aims to fill this gap by providing a window into the fast structural changes that occur during water uptake from vapor and liquid phases using small-angle X-ray scattering (SAXS) measurements with sub-second time resolution. Synchrotron SAXS experiments were carried out at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL), beamline 7.3.3, which is equipped with a 2D Dectris Pilatus 1M CCD detector (981 x 1043 pixels)¹³. The wavelength of the incident X-ray beam was 1.24 Å and the scattering wave vector, $q = 4\pi \sin(\theta)/\lambda$, where θ is the scattering angle, was in the range of 0.008 to 0.4 Å⁻¹. Nafion[®] 117 membranes, which were cleaned and dried prior to the tests (see supporting information for details), were placed into custom-made sample stage containing a small opening for the injection of water in both phases (Fig. S1). Images were taken with time resolution as low as 0.2 seconds during the membrane water sorption. At least 1000 images were recorded in each case. Static SAXS measurements were also performed on samples equilibrated for longer periods of time; the observed equilibrated SAXS profiles are consistent with those in the literature.^{1, 11, 12, 14-16}

Figure 1 shows the time evolution of SAXS profiles during water uptake of Nafion[®] 117 membrane from dry to close to saturated vapor or liquid water (more traditional line plots (intensity vs. q) of selected data are shown in supporting information). Growth of the ionomer peak is clearly more pronounced for the liquid-contacted membrane, which exhibits higher intensity and movement of the peak to lower q_{peak} values. Spacing between the water domains, $d = 2\pi/q_{\text{peak}}$, is plotted as a function of time in Fig. 2. In less than a minute, d -spacing increases from 3.45 nm to 3.8 nm in saturated vapor, and to 5.2 nm in liquid water. Moreover, measured d -spacing after the membrane is equilibrated for 1 hour, 1 day, and 1 week are depicted in Fig. 2. Domain spacing of the membrane in liquid water does not

show any discernable change after the first 3 minutes of hydration suggesting that the membrane is close to equilibrium. However, for the membrane in saturated vapor, d-spacing continues to increase significantly for the first day and then slows down, although even after one week, d-spacing in liquid water is still slightly higher than that in vapor. This small difference can be attributed to both the slow kinetics for vapor-equilibrated samples as well as small deviations from saturation concentration that might arise over the long time of the equilibration. These results provide clear evidence that the phase of water has a significant effect on the kinetics of hydration of the ionic domains. This effect is consistent with the fact that differences in the surface structure of vapor- and liquid-contacted membranes result in drastic variations in the water-uptake mechanism. In liquid water, the membrane surface is covered with hydrophilic groups, and water uptake occurs within seconds. In water vapor, the presence of hydrophobic groups on the surface increases the interfacial resistance to water transport, resulting in a slower water uptake. This surface-limited concept is strengthened by the fact that the fast response in liquid water suggests that internal rearrangement of the microstructure may likewise be rapid; thus only the interface should be limiting. It also agrees with humidity-dependent interfacial resistances that have been observed with Nafion membranes.^{17, 18}



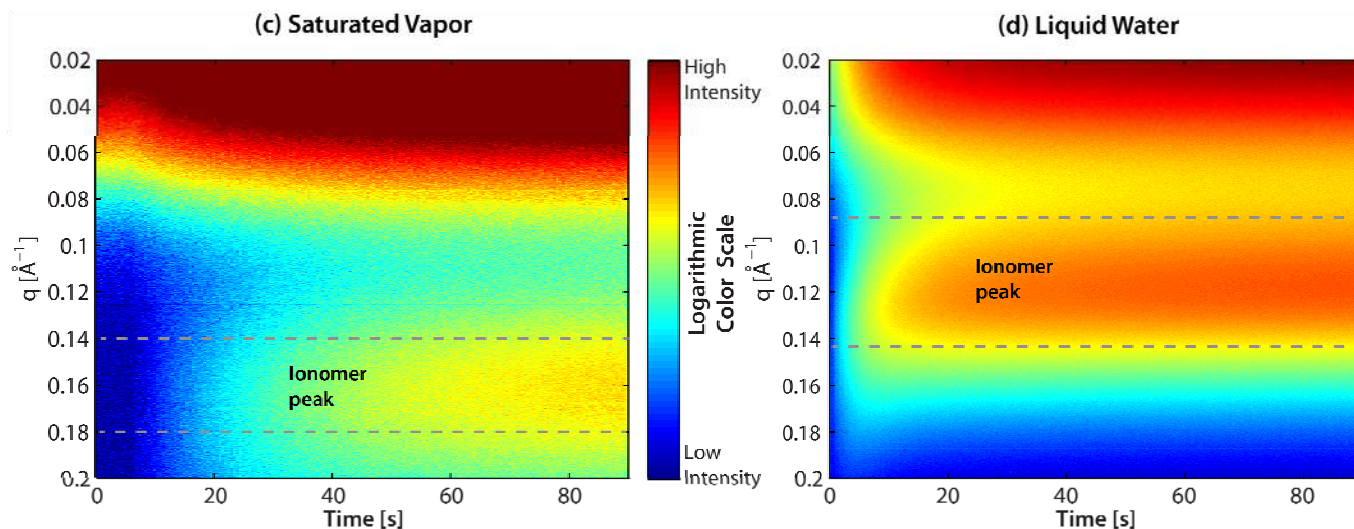


Figure 1 Radial average scattering profiles of Nafion membrane during water absorption from (a,c) saturated vapor and (b,d) liquid water. The arrows indicate the evolution of ionomer peak corresponding to an increase in domain spacing, i.e. the microscopic swelling of water domains. The q -range for the ionomer peak is also shown in b, d.

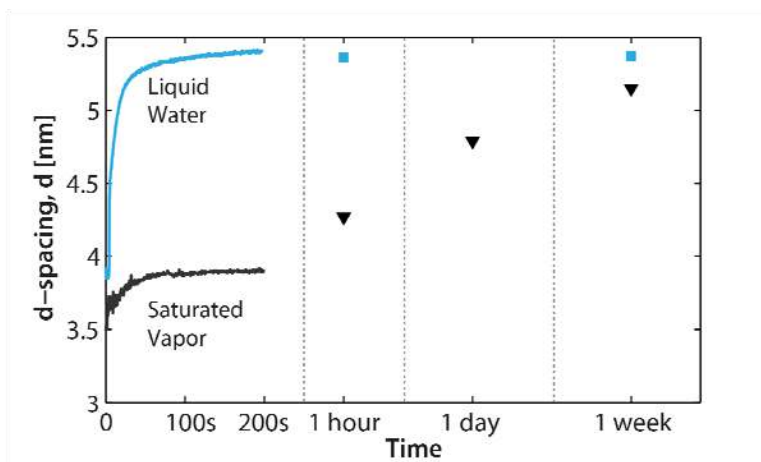


Figure 2 Increase in domain spacing with time for membrane equilibrating in saturated vapor and liquid water. (Note the difference in time scale and see Fig. S2 for a close up of initial stage, and Fig. S3 for the line profiles at 2 minutes and 1 week).

The sorption kinetics at the nanoscale is described using a two-term diffusion equation to model the change in d -spacing corresponding to the microscopic swelling of water domains (See Fig S2 and supporting information for details). Best-fit model parameters are given in Table 1. Multiple time

constants are generally attributed to the polymer relaxation^{6, 18} or swelling processes occurring at multiple scales, but have not been investigated with such short times. In liquid water, steady-state swelling is reached almost instantly, where the first time constant, τ_1 , is 2 seconds. In vapor, however, in addition to the time constant (20 to 30 s) for short-term swelling, a long-term equilibrium is observed with time constants in the order of 10^4 seconds, which is closer to macroscopic diffusion time constants.^{2, 6, 18} Thus, swelling from vapor continues at a slower rate at the nanoscale due to the polymer-relaxation mechanisms accommodating the growth of water domains and the interfacial effects that limit water diffusion into the polymer.^{9, 18} However, when the membrane is in liquid water, sub-second morphological changes are observed, suggesting that structural changes occur first in the liquid-contacted surface which accelerates the absorption of water into the bulk of the membrane. In the case of vapor experiments, the surface characteristics seem to evolve at a much slower rate, and the measured timescale for swelling exhibits the characteristics of macroscopic water diffusion.

Furthermore, low- q scattering from the obtained SAXS profiles can provide information related to the shape of the hydrated domains,^{11, 15, 16} provided that one is far enough away from any influence of scattering due to the crystalline component. Nanostructured materials show a power-law decay in intensity at low q values, $I(q) \sim q^{-\alpha}$, with $\alpha = -4$ for spherical domains and $\alpha = -1$ for long cylindrical domains.¹⁹ Fig. 3 shows the evolution of α as the membranes absorb water from vapor or liquid environments. For the case of membranes in contact with liquid water, the rapid evolution of α from -2.3 to -1 suggests a structural rearrangement from a distribution of spherical and cylindrical domains to exclusively cylindrical-like domains upon absorption. The changes in α for samples equilibrated in water vapor are not pronounced even after a day (only changing from -2.3 to -1.9). These observations are consistent with previous work where water domains of PFSA have been described as interconnected spheres^{10, 11, 14} and cylinders¹⁶ embedded in the polymer matrix, or pools surrounding polymeric rods,^{15, 20} all of which depend on the membrane's water content.

Table 1. Model parameters and time constants for the microscopic swelling of membrane during sorption from saturated vapor and liquid water.

Model Parameters	Vapor	Vapor	Liquid	liquid
	Short-term	Long-term	Short-term	Long-term
1 st Time Constant, τ_1 [s]	21	25	2.3	2.3
2 nd Time Constant, τ_2 [s]	36	1.0×10^4	37	37
A	0.83	0.19	0.46	0.46

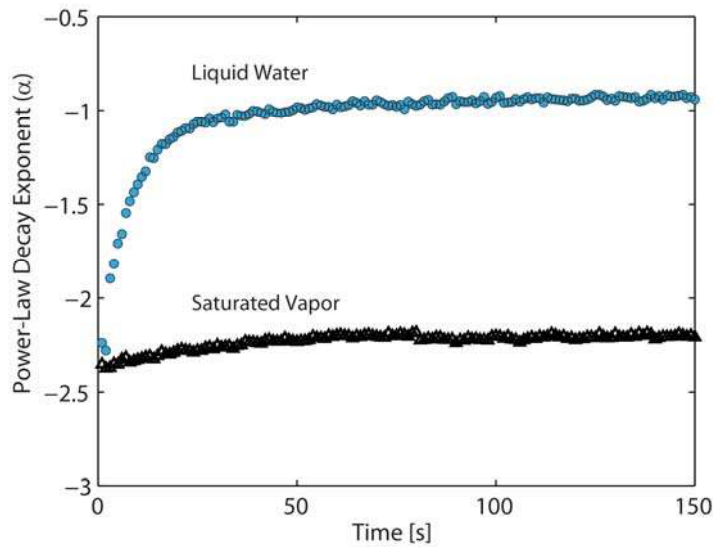


Figure 3 The slopes of the small-angle upturn as a function of time were plotted for vapor and liquid-equilibrated membrane.

The results presented in this work provide a detailed description of Nafion membrane’s structural evolution at very short times during water absorption. Also, this study provides evidence of different kinetics depending on contacting phase of water. The results are consistent with an interfacial resistance at the membrane/vapor surface that limits the water uptake in vapor, but which is significantly reduced at the membrane/liquid surface where the surface becomes instantly hydrophilic allowing water molecules to easily diffuse into the membrane. This lower resistance allows membranes contacted with water to reach steady-state in a few seconds as opposed to more than 24 hours for membranes equilibrated in vapor. The presented observations suggest that the phase of water with which the

membrane is in contact alters the surface nanostructure via interfacial interactions,^{9, 20} and, more importantly, controls the sorption kinetics and the morphological evolution during water uptake. The insights provided on fast structural changes that occur upon water absorption can provide guidelines to optimize device operations and help interpret experiments in which Nafion is in contact with water. The time-resolved *in-situ* SAXS techniques described in this study can also be extended to other systems with fast structural rearrangements and aid in the understanding and hence development of alternative ion-conducting materials.

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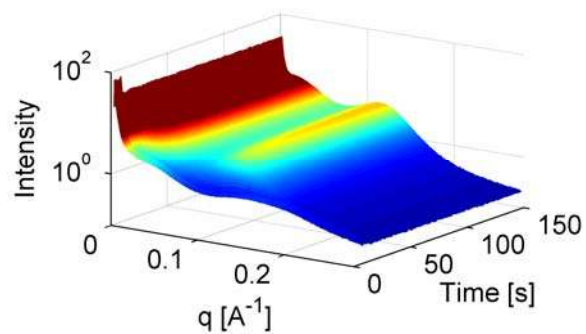
Supporting Information Available. Material about the details of experimental setup, interpretation and modeling of change in domain spacing, and select SAXS line plots are available free of charge via the Internet at <http://pubs.acs.org/journal/amlccd>.

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