Supporting Information

Nanoscale Distribution of Sulfonic Acid Groups Determines Structure and Binding of Water in Nafion Membranes

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1. Sample preparation

Nafion® 117 (DuPont, 183 µm thick, 360 g m⁻²) and Nafion® 212 (DuPont, 50.8 µm thick, 100 g m⁻²) membranes (named as N117 and N212, respectively), both of 1100 g equivalent weight, were cut into pieces (1 cm × 5 cm in size) and boiled for 0.5 h in each of the following solutions separately and subsequently: H₂O₂ (34.5-36.5%, SIGMA-ALDRICH Chemie GmbH), MilliQ H₂O, 0.5 M H₂SO₄ (95.0-98.0%, SIGMA-ALDRICH Chemie GmbH), and MilliQ H₂O again. Then all samples were washed with MilliQ H₂O until the pH of the waste water was about 7 (pH paper, dispenser 1.0-11.0). Samples were stored in MilliQ H₂O before measurements for a maximum of 5 days. D₂O (99.8 ATOM%D, SIGMA-ALDRICH Chemie GmbH) was used as received in diffusion experiment.

2. Coherent anti-Stokes Raman scattering (CARS) spectroscopy

Experimental

CARS is a nonlinear analogue of conventional linear Raman spectroscopy and is thus sensitive to the vibrational signature of the species under investigation. Molecules are coherently excited by pump, Stokes and probe beams to generate the coherent anti-Stokes output. We used a dual-output laser source (Leukos-CARS, Leukos, Limoges, France) to provide the pump and Stokes beams. The pump/probe beam (30 mW, 1064 nm) is a passively Q-switched microchip laser with <1-ns pulses at 32 kHz repetition rate. The Stokes beam is generated with help of a supercontinuum fiber resulting in a bandwidth from 1.05 µm to 1.6 µm (30 mW). The Stokes and pump/probe beams were overlapped at a dichroic mirror (LP02-1064RU-25, Semrock), and introduced into a modified inverted microscope (Eclipse Ti-U, Nikon). They were focused onto the sample by an air objective (LCPlan N, 100X / 0.85 IR, Olympus). The forward CARS signal was collected with a 10 X magnification, 0.25 NA air objective (Newport). The Nafion® membranes were mounted in a homebuilt microfluidic sample holder, and broadband CARS spectra obtained with a spectral acquisition time of 50 ms on a CCD (Newton DU920P-BR-DD, Andor). The CARS data were collected with custom software written in LabView (National Instruments) and saved for offline processing with Igor Pro (Wavemetrics).

Data processing

Each raw CARS spectrum was converted into a Raman-like spectrum using a modified Kramers-Kronig phase-retrieval transform, with the CARS spectrum from glass serving as the non-resonant background. After transformation, a third-order polynomial was used to fit a slowly varying error phase to regions
of the spectra without resonances. This fit was subtracted from the transformed data to yield the retrieved CARS (processed CARS) data shown in this work. For all data, the fingerprint (600-1850 cm\(^{-1}\)) and water (2850-3850 cm\(^{-1}\)) regions of the spectra were processed independently. This was done to minimize the error phase from the transformed CARS spectra. The result of this process is a Raman-like spectrum in which spectral intensities are directly proportional to the concentration of vibrational oscillators.

Regarding band intensities, we note that the variation of the Raman scattering cross section with frequency is relatively weak compared to infrared spectroscopy, i.e. \(\sim 20\%\) increase from 3000 to 3700 cm\(^{-1}\),\(^{17}\) in this region, the N117 spectrum blue-shifts to higher wavenumbers by less than 50 cm\(^{-1}\), and thus the effect of a change in Raman cross-section on the integrated signal intensity can be neglected when comparing total band intensities of N117 and N212.

Constrained classical least squares (CCLS) was carried out with Igor Pro 6.37 (Wavemetrics) using an iterative global fit to the OH region of the Raman-like spectrum for the average spectrum of N117 and N212 (N = 3 spectra from three sample preparations). The inputs to the CCLS were a common bulk water (bulkW) component and an additional common spectral component with unknown spectral shape: Unknown1. The total area of N212 and N117 were normalized to 1, as was each component (bulkW and Unknown1). This was done to ensure that each component was equally weighted in the fit. The only constraint for Unknown1 was that all spectral components were non-negative. The initial guess for Unknown1 was that all spectral components were non-negative. The initial guess for Unknown1 was either a constant value at all frequencies or the bulkW spectrum. In both cases, the fit converged successfully and yielded the same spectral response with a finite contribution, which we called non-bulk water (nonbulkW). Finally, the weight of bulkW and nonbulkW to each of the N = 3 spectra from each membrane was calculated. The average and standard deviation are shown in Figure 2.

3. Measurement of the apparent diffusion coefficient (ADC) for water

\textit{In situ}, real-time water transport in Nafion\textsuperscript{®} membranes was initiated by a hydrogen-deuterium exchange (HDX) in the microfluidic sample holder – D\(_2\)O was exchanged for H\(_2\)O. CARS spectra from a single voxel (500 nm x 500 nm x 3.5 µm) in the membrane were measured over time starting just before the HDX. We obtained a broadband CARS spectrum (700-4000 cm\(^{-1}\)) at time intervals of \(\sim 100\) ms. Using the data processing routine described above, we ultimately obtained quantitative Raman-like spectra whose band intensities are directly proportional to concentration of vibrational moieties. Therefore, we could directly measure OH and OD concentrations over time in fully hydrated membranes to quantify the effective water diffusion (Figure S1).
concentrations of OH/OD in membrane were obtained by integrating the corresponding OH/OD peaks (Figure S1, left).

In our geometry, water can only diffuse into the membrane through the interface in contact with the microfluidic water flow channel, which allows us to treat the diffusion as a one-dimensional problem. Because the side opposite the water channel is a glass coverslip and the sample is physically constricted on all other boundaries, we use reflective boundary conditions in solving Fick’s second law. Furthermore, the water channel is effectively an infinite reservoir of diffusate since fresh water is constantly being supplied in the flow channel. As the membrane is equilibrated in pure water (or deuterium) before starting an experiment, we assume no diffusate to be present in the membrane before switching the fluid in the flow channel. With the given boundary and initial conditions, the analytical solution to Fick’s second law is given as:[4]

\[ c(t) = (1 - \frac{4}{\pi^2}) \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-\text{ADC} f^2 t \cos(fz)\right) \]  

(1)

where \( f = \frac{(2n+1)\pi}{2L} \), \( L \) is the thickness of membrane, \( t \) is the time after switching, ADC is the apparent diffusion coefficient, and \( z \) is the distance from the diffusate source, i.e. the distance from the membrane-channel interface to the measurement (focal) point. In this work, we use \( n = 3 \) terms of this infinite series as extra terms do not improve the fit quality. Since the initialization of flow after switching fluid reservoirs takes \( \sim 4 \) s, data between 0 and 4 s after switching are convoluted by both diffusion and channel dynamics. Therefore, the fit was performed only for those times greater than 5 s after switching, after the channel has stabilized. This leads to the deviation at early times between the fit and the experimental data, as expected. Nevertheless, using equation (1) with these constraints, we can accurately fit the concentration vs. time profiles of the diffusate moving into the membrane (Figure S1, right). The ADC of N212 is \( 3.6 \times 10^{-10} \) m\(^2\)/s and the ADC of N117 is \( 5.3 \times 10^{-10} \) m\(^2\)/s. The ADCs of N212 and N117 are presented in table S1 together with the measured proton conductivities. The mean ADC is an average of 5 ADC measured from 5 different membrane sections of the same batch and same pre-treatment.
**Figure S1.** H$_2$O diffuses from a microfluidic channel into D$_2$O saturated N212 membrane. CARS spectra are continuously collected from the same focal spot in the membrane. Left: Intensity of the OH stretching vibration (black) increases with time while intensity of the OD stretching vibration (blue) decreases. Right: the OH (black) and OD (blue) concentration changes vs. time obtained by integrating the respective spectral regions; solid red line is a fit to the Fickian diffusion model described in the eq. 1.
4. Proton conductivity

In-plane proton conductivity of the membranes was measured by impedance spectroscopy with a two-electrode geometry using an SI 1260 impedance/gain-phase analyzer and a Novocontrol broadband dielectric converter. The membranes were immersed in MilliQ H₂O in order to ensure they were fully saturated with water during the measurement. The measurements were carried out under room temperature. The resultant proton conductivity is calculated from the Cole-Cole and Bode plots.[5]

Table S1. Apparent water diffusion coefficients (ADC) and proton conductivities (σ). Errors are the standard deviation from 5 different measurements on different membrane sections from the same batch of membrane. * p < 0.05 using a Student’s t-test.

| Membrane | ADC×10⁻¹⁰ (m²/s)* | σ (S/cm)     |
|----------|-------------------|--------------|
| N212     | 3.6±0.4           | 0.033±0.008  |
| N117     | 5.3±0.3           | 0.072±0.010  |
5. Reference components for spectral decomposition

![Graph showing reference spectra](image)

**Figure S2** Reference spectra for CCLS fits: bulkW (blue) was collected from a water reservoir; nonbulkW (orange) was deduced in the decomposition process. Spectra were normalized to the total integrated intensity.
**Figure S3** Raman-like spectrum of nonbulkW (orange line), of water in perfluoro butane sulfonic acid (1:1 molar ratio perfluoro butane sulfonic acid:water, red line) and in dry Nafton® membrane (dried for 3 days at 25 °C, 30% relative humidity, black line) in the OH region. The main peak in the perfluoro butane sulfonic acid is located at 3498 cm⁻¹, very close to that in the nonbulkW at 3530 cm⁻¹ and for the air-dried spectrum. All spectra show a shoulder at 3628 cm⁻¹. Spectra were normalized to the total integrated intensity.
6. Shell thickness calculation for flat channel geometry

Assuming a flat channel geometry as suggested by Kreuer and Portale, [6] the calculation of the bulkW (core) and nonbulkW (shell) layers reduces to a linear one:

As stated in the main text, \( I_{\text{sw}} = \frac{V_{\text{total}} - V_{\text{core}}}{V_{\text{core}}} \). For the flat channel case, \( V = l \times d \)

where \( l \) is the channel length and \( d \) the channel thickness. It follows that

\[ I_{\text{sw}} = \frac{l \times (d_{\text{total}} - d_{\text{core}})}{l \times d_{\text{total}}} \]

If we assume that the SAXS/SANS data (references in main text) give \( d_{\text{core}} \), we can calculate \( d_{\text{shell}} \) for N212 to lie in the range of 0.4 nm, or 1 water molecule. The same calculation for N117 reveals a 42% thicker shell (about 1.5 water molecules), similar to the calculation for cylindrical channels.

Figure S4: Schematic sketches of a flat water channel geometry in Nafion consistent with the spectroscopic data presented in the main text, i.e. total Nafion and water content in the focal volume is the same for N117 and N212. Gray: Teflon backbone; black: sulfonic acid head groups; blue: (core) bulkW; white: (shell) nonbulkW.

References

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