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Unlocking the Observation of Different Proton Populations in Fluorinated Polymers by Solid-state ^{1}H and ^{19}F Double Resonance NMR Spectroscopy

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Electronic Supplementary Information

S1. Cross-Polarization NMR

Nafion is a fluorinated polymer with an interconnected network of hydrophilic domains, so large ^{1}H and ^{19}F spin baths are available for magnetization transfer. Even though standard cross-polarization (CP) NMR is no quantitative technique, CPMAS NMR spectra showed too low signal-to-noise ratios (S/N) compared to equivalent direct excitation and Hahn-echo spectra. Additionally, in $^{19}F \rightarrow \mathbf{^{1}H}$ CPMAS NMR, every new spectrum was out of phase, while in $^{1}H \rightarrow \mathbf{^{19}F}$ CPMAS NMR, drastic decay of signal intensity was already apparent after a contact time of only 250 µs. Figure S.1 depicts this behaviour. For $^{19}F \rightarrow \mathbf{^{1}H}$ and $^{1}H \rightarrow \mathbf{^{19}F}$ CPMAS NMR spectra, strong apodizations by exponential multiplication with 40 Hz and 500 Hz, respectively, were needed to reach a reasonably good signal-to-noise ratio. The CPMAS NMR spectra for recast and cryomilled Nafion samples showed a similar behavior to those of pristine Nafion, also yielding little information.

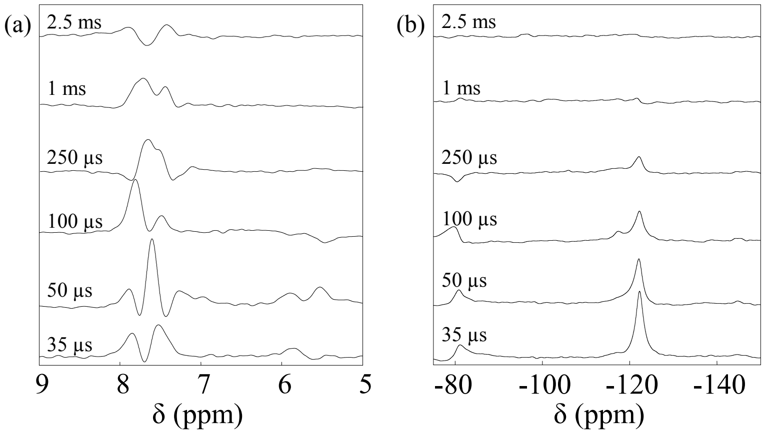

Figure S1. (a) $^{19}F \rightarrow \mathbf{^{1}H}$ CPMAS and (b) $^{1}H \rightarrow \mathbf{^{19}F}$ CPMAS NMR spectra recorded for pristine Nafion at indicated contact times.

S2. Multiple Cross-Polarization NMR

Build-up curves shown in Figure S.3 plot relative signal intensities of the most intense peak of $^{1}H \rightarrow \mathbf{^{19}F}$ CPMAS and MC-CP NMR spectra of pristine Nafion against contact time. While the $^{1}H \rightarrow \mathbf{^{19}F}$ CPMAS NMR signal has completely disappeared, the signal intensity of $^{1}H \rightarrow \mathbf{^{19}F}$ MC-CP NMR spectra increases with contact time until a plateau is reached after a contact time of about 5 ms. This shows the effectiveness of the MC-CP pulse sequence when dealing with relatively mobile species.

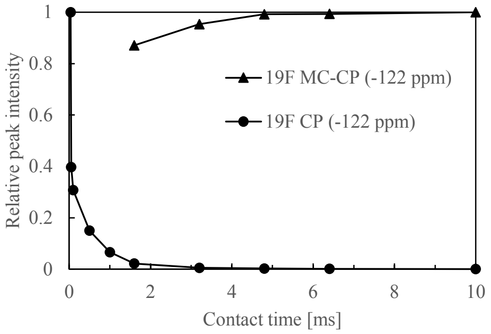

Figure S2. Build-up curves plotted for the most intense peak of $^1H \rightarrow \mathbf{^{19}F}$ CPMAS and MC-CP NMR spectra of pristine Nafion.

S3. Decomposition Parameters

The ^1H NMR difference spectrum of cryomilled Nafion, acquired after subtraction of the bulk water signal observed in MC-CP-BABA NMR from the MC-CP NMR spectrum and recorded at a total contact time of 10 ms, effectively shows protons that exhibit no ^1H-^1H dipolar interactions (i.e. unpaired protons with only ^1H-^{19}F dipolar interactions). The MC-CP-BABA NMR spectrum and the difference spectrum were both decomposed into, respectively, 3 and 5 significant, highly distinct resonances of ^1H distributions. The decomposition parameters are listed in Table S3. For each decomposition peak, these parameters are: isotropic chemical shift (δ_{iso}), integral (with the total sum amounting to 100%), amplitude (with the highest intensity signal of the experimental difference spectrum set to 100%) and width at half height.

	Peak #	δ_{iso} (ppm)	Integral (%)	Amplitude (%)	Width (ppm)
MC-CP-BABA	1	6.00	9.2	34.6	0.23
	2	6.41	5.2	84.7	0.16
	3	6.70	41.6	65.3	0.35
difference spectrum	1	5.74	14.2	76.7	0.23
	2	6.21	7.8	59.3	0.23
	3	7.04	8.2	60.5	0.21
	4	7.32	15.7	72.1	0.35
	5	7.76	22.6	55.2	0.43

Table S3. Parameters for the decomposition of proton distributions of cryomilled Nafion observed in $^{19}F \rightarrow \mathbf{^1H}$ MC-CP-BABA NMR and in the difference spectrum that was acquired after subtraction of the 1D $^{19}F \rightarrow \mathbf{^1H}$ MC-CP-BABA NMR spectrum from the $^{19}F \rightarrow \mathbf{^1H}$ MC-CP NMR spectrum.

S4. Reproducibility of Samples

Solution-cast Nafion membranes are also frequently prepared using different solvents, especially when making composite membranes,[1,2] but these casting procedures affect chemical and thermal stability as well as the proton conductivity of the membranes. As milling[3] or heat treatment at water boiling temperatures also influence the state of the sample, further studies about different types of Nafion samples are required for a detailed description of modifications of the water and acid proton reorganizations observed by NMR spectroscopy (Figure 2.a in the main article). Remarkably, Nafion is a constantly evolving polymer.[4] This effect is also observed in Figure S4, as attested by the evolution of the averaged water signal of cryomilled Nafion observed in ^1H MAS NMR spectra over time, while spinning at a MAS frequency of 25 kHz. As MAS causes a slight heating of the sample and also creates a centrifugal force that acts on the sample, Nafion is expected to evolve quite fast until an equilibrium state has been reached.[5] This equilibration of the sample is irreversible, but the sample state is reproducible. This is why NMR experiments of Nafion samples have always been performed after a MAS equilibration time of at least 10 minutes.

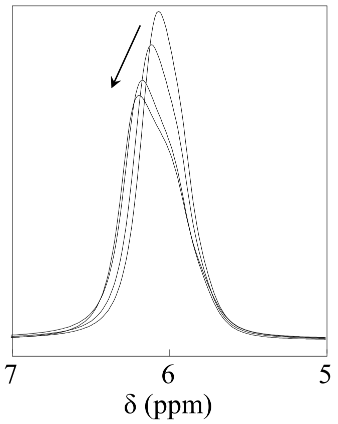

Figure S4. Evolution of shape and absolute intensity of the averaged water peak of cryomilled Nafion during magic angle spinning in ^{1}H MAS NMR over the course of 10 minutes.

S5. Experimental outlook

Future work would include the use of electrochemical impedance spectroscopy (EIS) for macroscopic proton conductivity measurements. By correlating NMR and EIS results, a physical model for interpretation of proton conduction can be developed. Also, physical modification of Nafion, such as cryomilling, drastically changes the water channel network inside the polymer. Further study of sample preparation and processing procedures will need to be performed and studied to enable more elaborate assignment and quantitation of NMR spectral features. The mechanism of proton conduction in such polymers as a function to water content and sulfonic group spatial distribution and its dynamics seems within reach. These new eyes on Nafion membranes will assist further optimization of proton exchange membranes for a variety of applications.

References

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