

## Supporting Information:

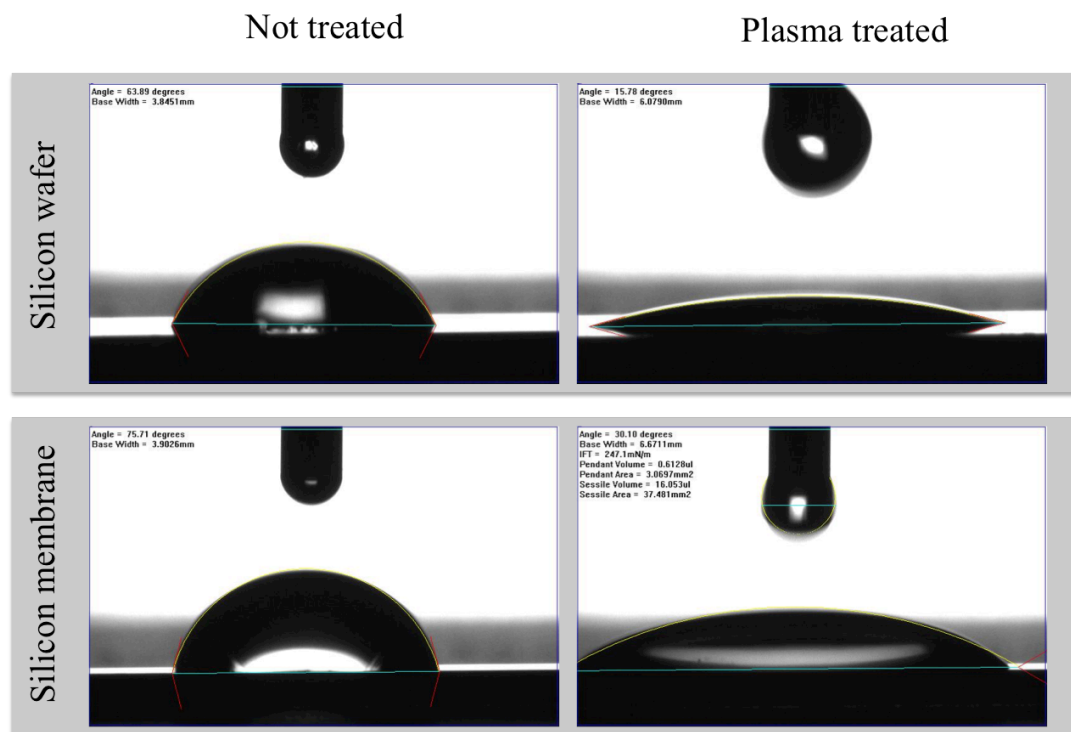
# **Three-dimensional Pulsed Field Gradient NMR measurements of self-diffusion in anisotropic materials for energy storage applications**

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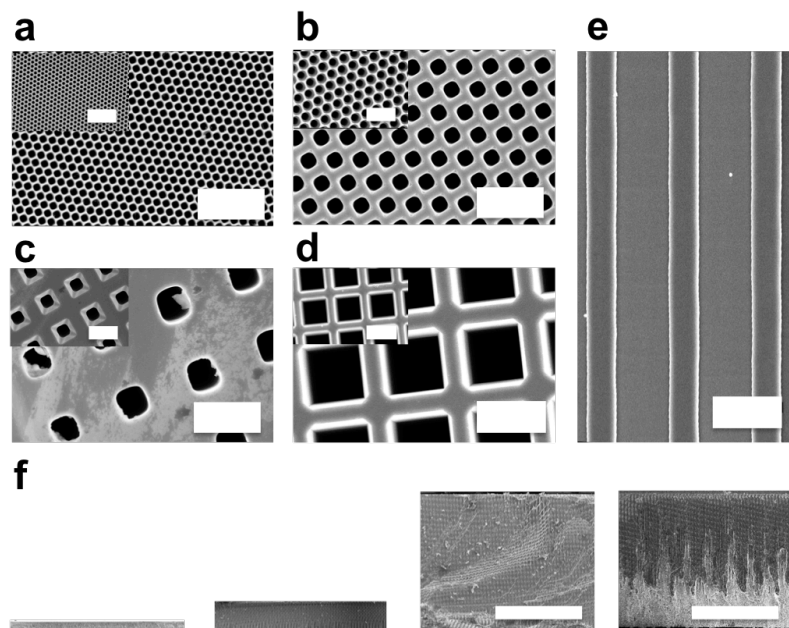
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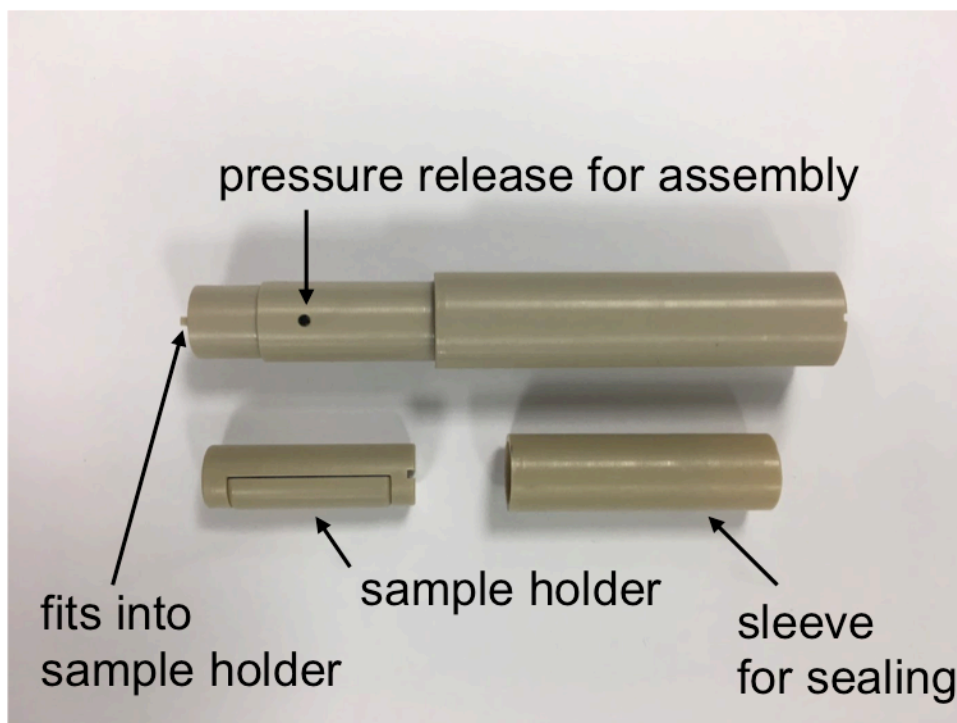
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**Figure S1.** Contact angle measurements for silicon and silicon membrane with and without plasma treatment

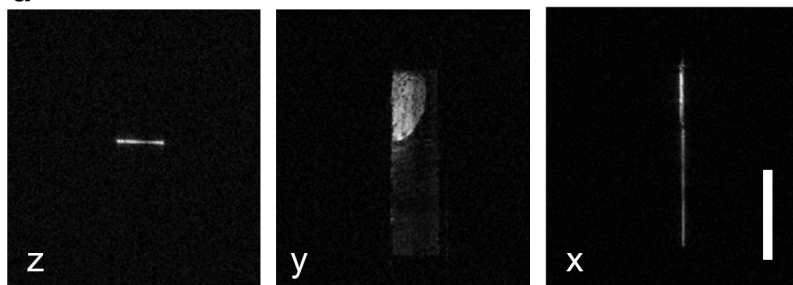


**Figure S2.** SEM images of silicon membrane surfaces taken from both sides of a) sample Si-47, b) sample Si-169, c) sample Si-500a, d) sample Si-500b, e) cross-section of sample Si-500b. 10  $\mu\text{m}$  scale bars, and f) cross-sections of samples Si-47, Si-169, Si-500a and Si-500b from left to right, with scale bars 300  $\mu\text{m}$ .

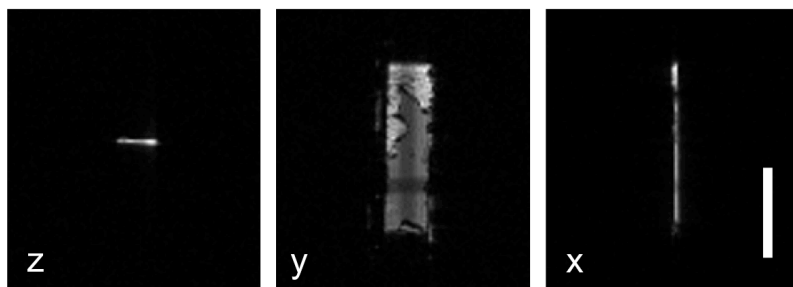


**Figure S3.** Sample holder with handle machined out of PEEK. The sleeve allows pressure to be applied on the sample holder and the handle with pin makes the alignment of the sample in the gradients easier.

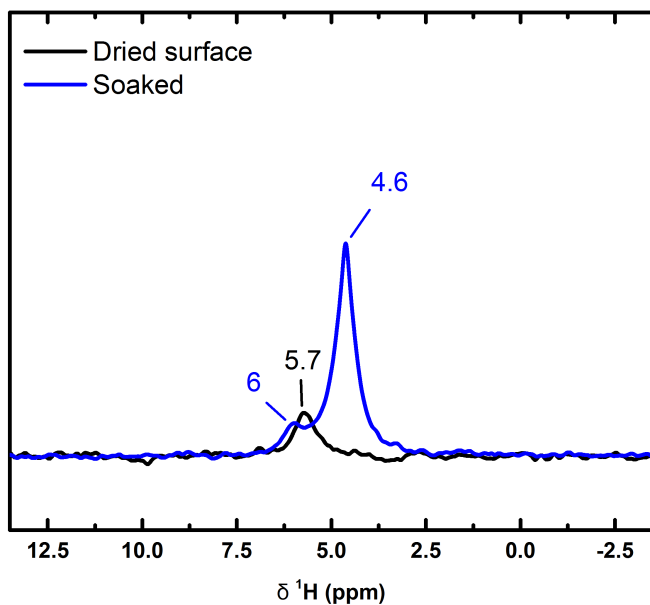
**a**



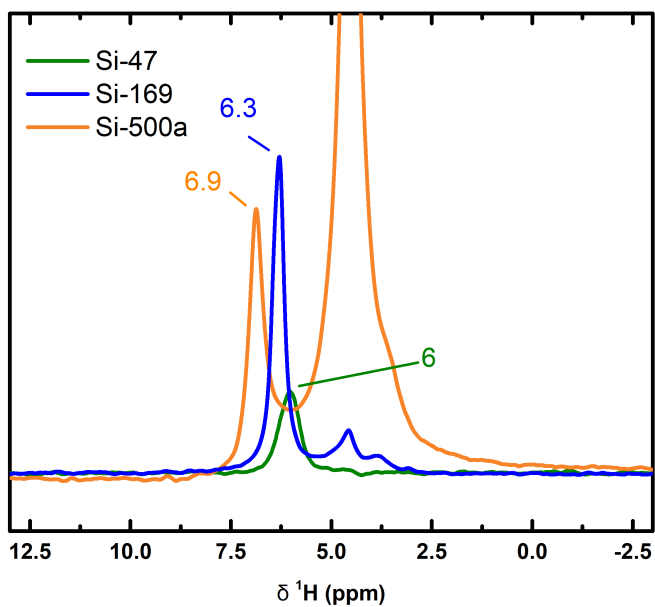
**b**



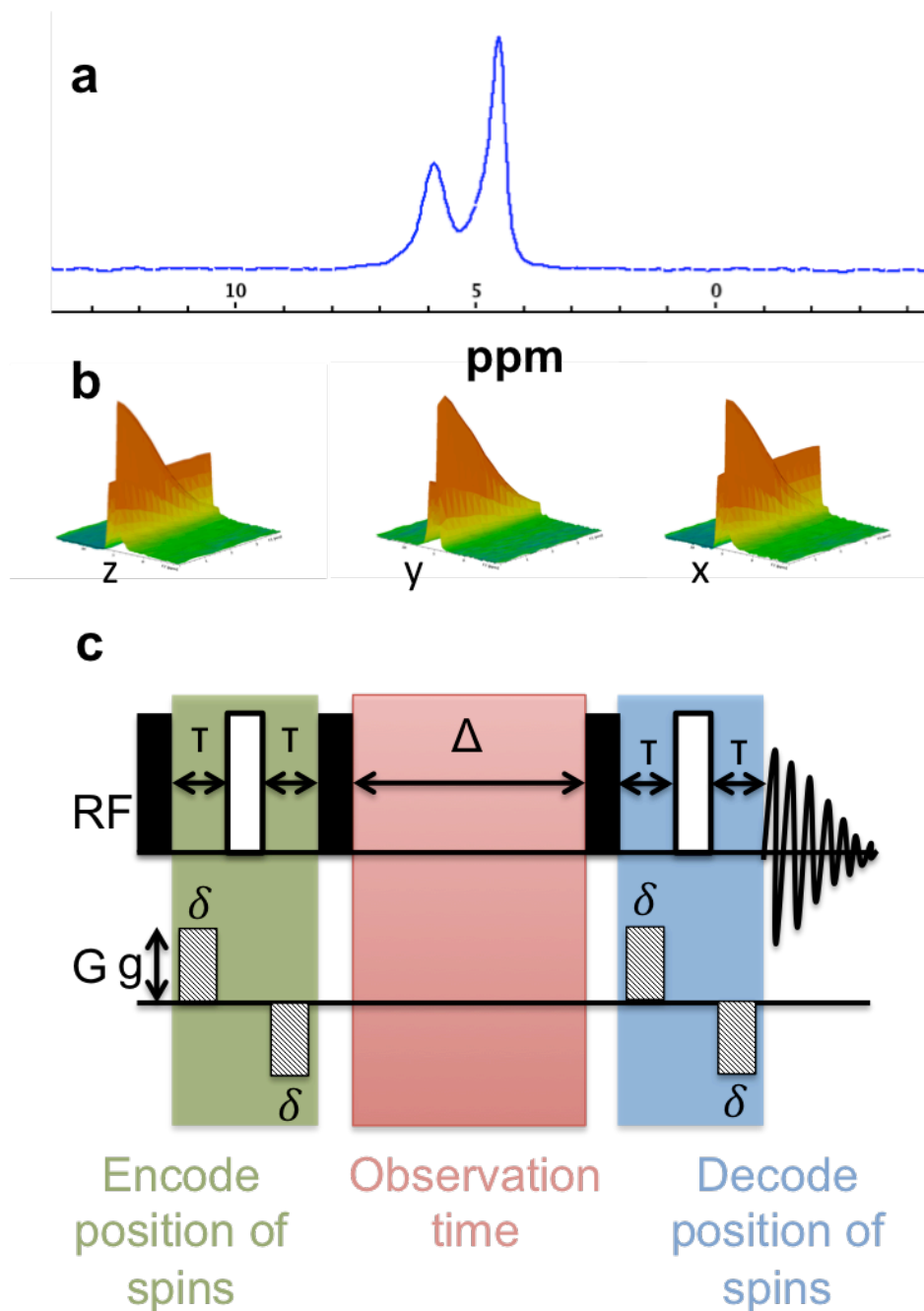
**Figure S4.** MRI images of a) the Si-47 and b) Si-169 samples both with excess liquid. The scale bars are 500 $\mu$ m.



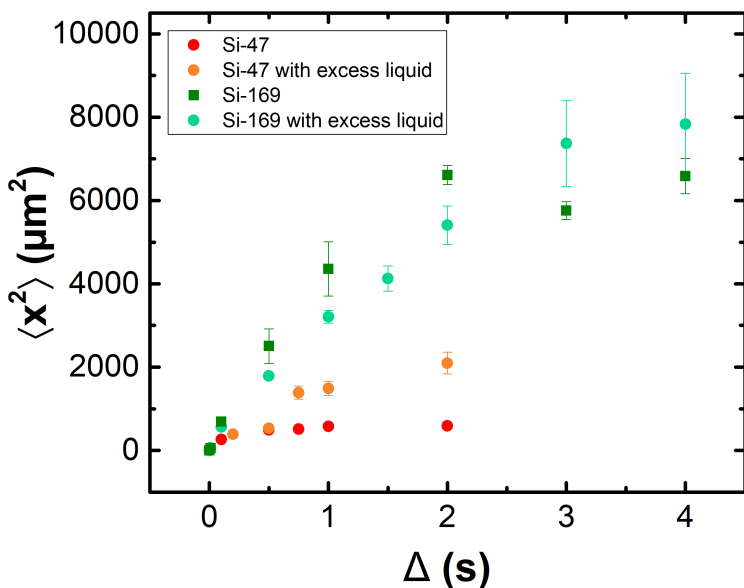
**Figure S5.**  $^1\text{H}$  NMR spectra of the Si-47 sample soaked in electrolyte (blue) and after drying the surface (black).



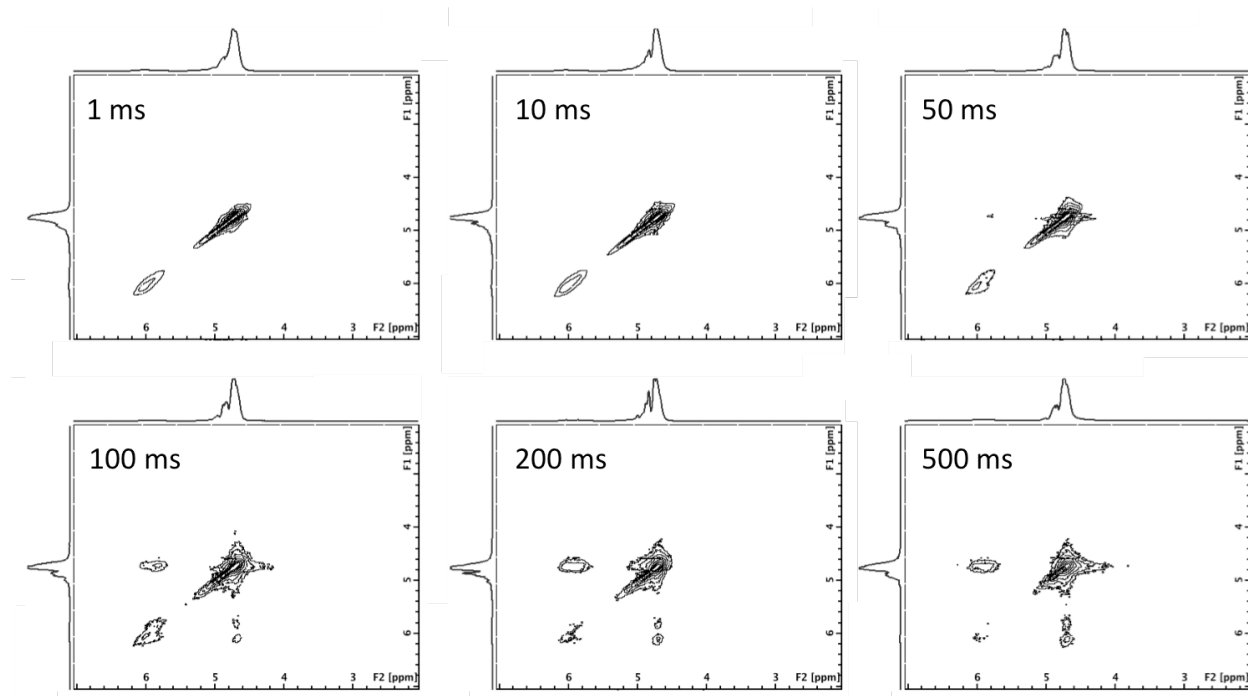
**Figure S6.** Spectra for samples Si-47 (dried surface), Si-169 (with excess liquid) and Si-500a (with excess liquid).



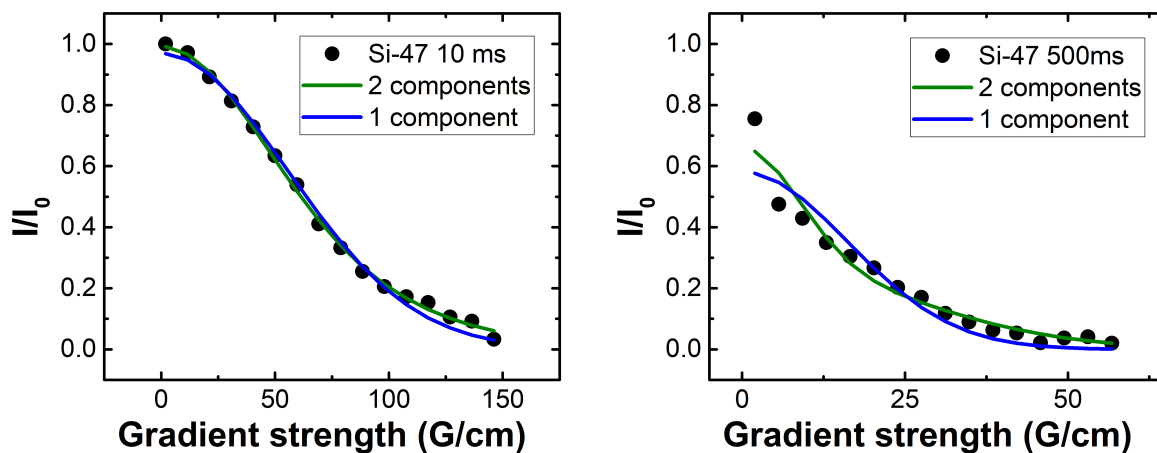
**Figure S7** a) 1D slice of a  $^1\text{H}$  diffusion measurement for  $\Delta = 10$  ms with the soaked Si-47 sample and b) stack plots of peak intensities with increasing gradient strength along the X, Y and Z directions, c) pulse sequence used for the all the PFG measurements reported in this paper. Figure c is adapted from <sup>1</sup>. The 13-interval sequence, a stimulated echo bipolar phase (PGSTEBP) <sup>2</sup>, is a type of stimulated-echo pulse-frequency sequence (PGSTE) and preferred for  $T_1 \gg T_2$ , whereby the maximum diffusion is limited  $T_1$ . This is because in PGSTE, and other pulse sequences based on that sequence (e.g. PGSTEBP), there is a z-filter  $\pi/2$  pulse storing the magnetization along z during  $\Delta$ , so there is no significant loss during the diffusion time.



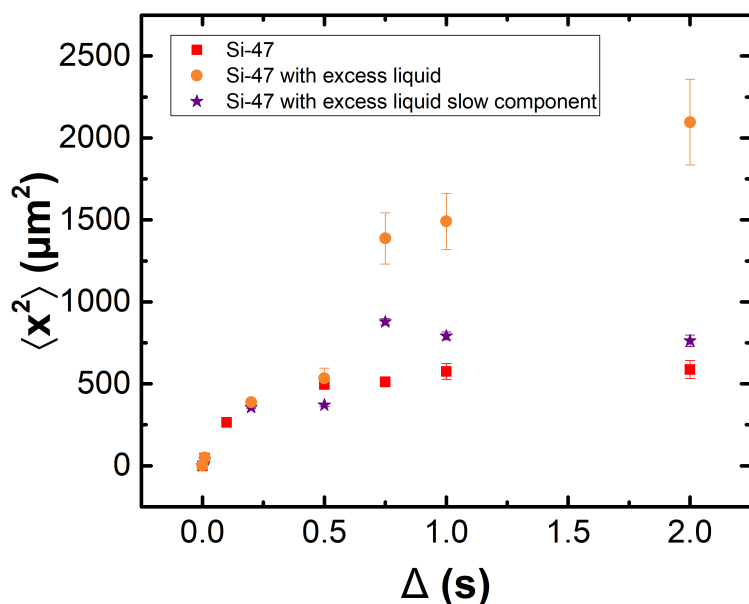
**Figure S8.** Square displacements for Si-47 and Si-169, dried and with excess H<sub>2</sub>O. The obtained values can be found in Table S3. For the fit of the plateau the last four data points are used for samples without the added excess liquid and the last three data points for samples with excess liquid (for the excess liquid those ones are underestimating due to the continuing increase).



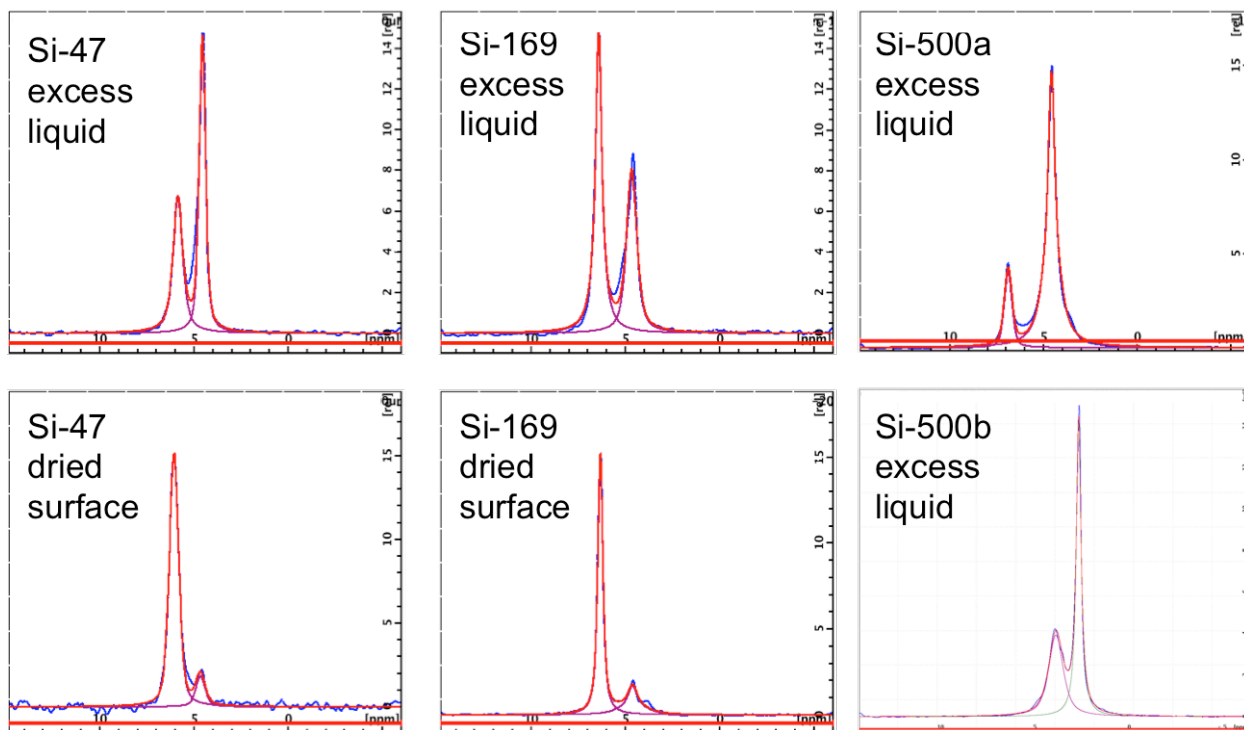
**Figure S9.** Example <sup>1</sup>H 2D NMR exchange spectroscopy spectra for sample Si-47 with excess liquid (water). Spectra are shown for different mixing times,  $\tau_{\text{mix}}$ . Measurements were taken with the micro 5 probehead used for the PFG measurements.



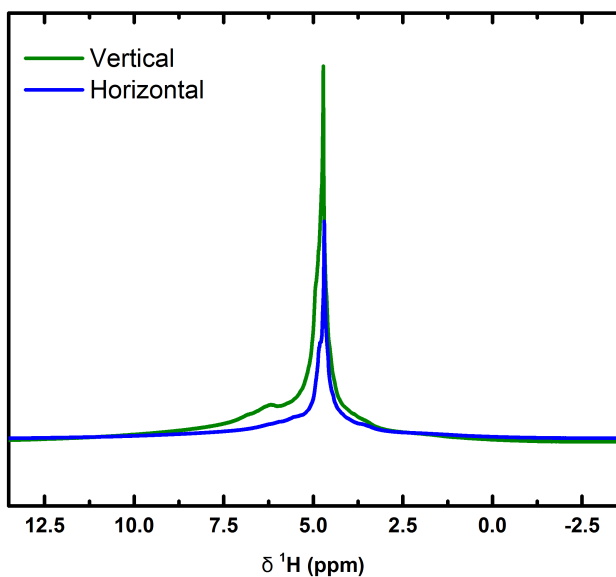
**Figure S10.** Peak intensity as a function of gradient strength for sample Si-47 with excess liquid. The fits with one and two components are shown for  $\Delta$  values of 10 and 500 ms. The standard deviations are 0.0256 and 0.0140 ( $\Delta = 10$ ) and 0.0591 and 0.0426 ( $\Delta = 500$ ) for the single and two component fits, respectively.



**Figure S11.** Square displacements for sample Si-47, dried and with excess liquid. For the sample with excess liquid, the diffusion coefficients were also fit with a two-component fit (see Figure S10) and the slower diffusion coefficient root mean square (rms) displacements are depicted here. The component fit rms displacement results in  $53 \pm 7 \mu\text{m}$  what is closer to the measurements of sample Si-47 with dried surface. The single component fit (dark blue) is shown as reference and resulted in  $110.6 \pm 33.5 \mu\text{m}$ .

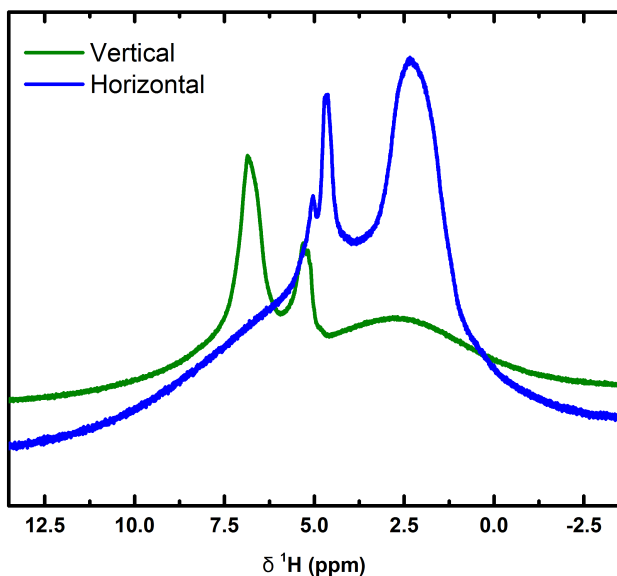


**Figure S12.** Peak fitting of the  $^1\text{H}$  NMR spectra obtained from samples with excess liquid and dried surfaces. The resultant values can be found in Table S4. Samples Si-47, Si-169 and 500a are with water and Si-500b is with DMSO.

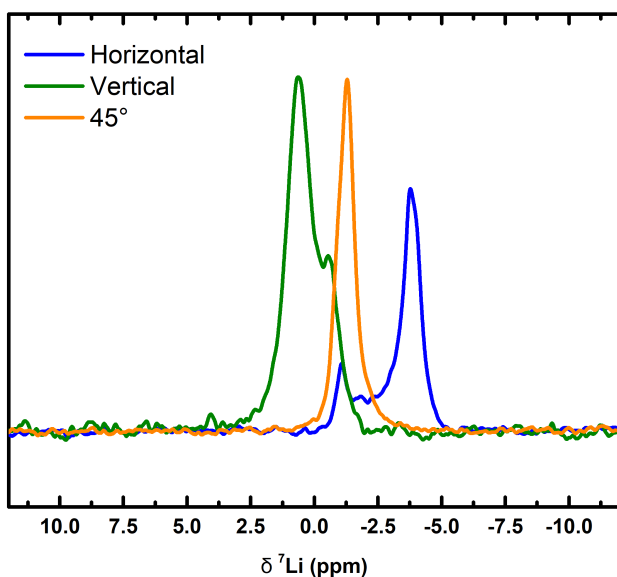


**Figure S13.**  $^1\text{H}$  one pulse NMR spectra of a  $\text{H}_2\text{O}$  confined in the PEEK holder, where the holder is oriented in a vertical and horizontal direction (using a standard Bruker static probe with a solenoid coil). For consistency, in our diffusion measurements, the sample in the PEEK holder was oriented vertically with respect to  $B_0$  and the pores oriented along the Y gradient (see MRI Fig 3A).





**Figure S14.**  $^1\text{H}$  one pulse NMR spectra of Si-500a with  $\text{H}_2\text{O}$  in vertical and horizontal orientation (peak holder in static probe). In the static  $^1\text{H}$  measurements the sample pores are oriented parallel (horizontal orientation) and orthogonal (vertical orientation) to  $B_0$ .



**Figure S15.**  $^7\text{Li}$  NMR spectra of Si-500b with LP30 electrolyte in vertical,  $45^\circ$  and horizontal orientation (PEEK holder in static probe). In the static  $^7\text{Li}$  measurements the sample pores are oriented parallel (horizontal orientation) and orthogonal (vertical orientation) with respect to  $B_0$ . The out-of-pore peak is less intense than observed in the diffusion measurements as this sample was dried more.

As can be seen in the static measurements, the holder produced a background in the single scan for  $^1\text{H}$ , which is due to the Viton O-ring. Nevertheless, for the diffusion measurements this background is not observed (it decays rapidly) since the protons in the polymer are rigid. For the  $^7\text{Li}$  measurements no background due to the holder and O-ring could be observed because no lithium is present in either of these materials.

**Table S1:  $^1\text{H}$   $T_1$  and  $T_2$  values for  $\text{H}_2\text{O}$** 

Sample	$T_1 > 4.7$ ppm (s)	$T_2 > 4.7$ ppm (s)	$T_1 \leq 4.7$ ppm (s)	$T_2 \leq 4.7$ ppm (s)
$\text{H}_2\text{O}$	-	-	3.2	2.1
Si-47 dried surface	0.5	0.6	-	-
Si-47 excess liquid	0.8	0.1	1.1	0.1
Si-169 dried surface	1.7	0.2	-	-
Si-169 excess liquid	1.5	0.1	1.4	0.2
Si-500a excess liquid	1.9	0.2	1.9	0.4
Si-500b excess liquid	1.8	0.02	1.5	0.6

**Table S2:  $^7\text{Li}$   $T_1$  and  $T_2$  values for  $\text{LiPF}_6$** 

Sample	$T_1 > 0$ ppm (s)	$T_2 > 0$ ppm (s)	$T_1 \leq 0$ ppm (s)	$T_2 \leq 0$ ppm (s)
$\text{LiPF}_6$	-	-	2.6	1.8
Si-169 + $\text{LiPF}_6$	1.1	0.1	0.9	0.3

**Table S3:** rms displacement at the plateau for Si membranes with and without excess liquid (Fig. S7)

Sample ( $\mu\text{m}$ )	rms displacement at plateau ( $\mu\text{m}$ ), $\pm$ standard deviation from fit
Si-47 dried surface	$57.1 \pm 10.3$
Si-47 excess liquid	$94.6 \pm 36.4$
Si-169 dried surface	$194.6 \pm 31.3$
Si-169 excess liquid	$215.6 \pm 29.3$

**Table S4:** Peak integrations for samples with sola in Topspin. “Best overlap” from fitting in TopSpin whereby above 70% is classified as a “good agreement” between the experimental and calculated spectrum. .

Sample	Best overlap (%)	Left integral	Right integral	Left / right
Si-47 excess liquid	92.3	1	1.4	0.7
Si-47 dried surface	89.6	1	0.1	7.8
Si-169 excess liquid	92.3	1	0.7	1.4
Si-169 dried surface	94.7	1	0.3	3.1
Si-500a excess liquid	95.2	1	5.3	0.2
Si-500b excess liquid	95.5	1	0.7	1.4

- 1 A. C. Forse, J. M. Griffin, C. Merlet, J. Carretero-Gonzalez, A.-R. O. Raji, N. M. Trease and C. P. Grey, Direct observation of ion dynamics in supercapacitor electrodes using in situ diffusion NMR spectroscopy, *Nat. Energy*, 2017, **2**, 16216.
- 2 P. T. Callaghan, *Translational dynamics and magnetic resonance : principles of pulsed gradient spin echo NMR*, Oxford University Press, 2011.