Supplementary Information

Systematic In-Situ Hydration Neutron Reflectometry Study on Nafion Thin Films

*Hamish Cavaye[1], Rebecca Welbourn[1], Jan Glushke[2], Paul Hughes[3], Ky Nguyen[2], Adam Micolich[2], Paul Meredith[4,5], A. Bernardus Mostert[6]**

[1]ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Science and Technology Facilities Council, Didcot, OX11 0QX, United Kingdom.

[2]School of Physics, University of New South Wales, Sydney NSW 2052, Australia.

[3]Centre for Nano Health, College of Engineering, Swansea University, Swansea SA2 8PP, United Kingdom.

[4]Department of Physics, Swansea University, Singleton Park, SA2 8PP, Wales, United Kingdom.

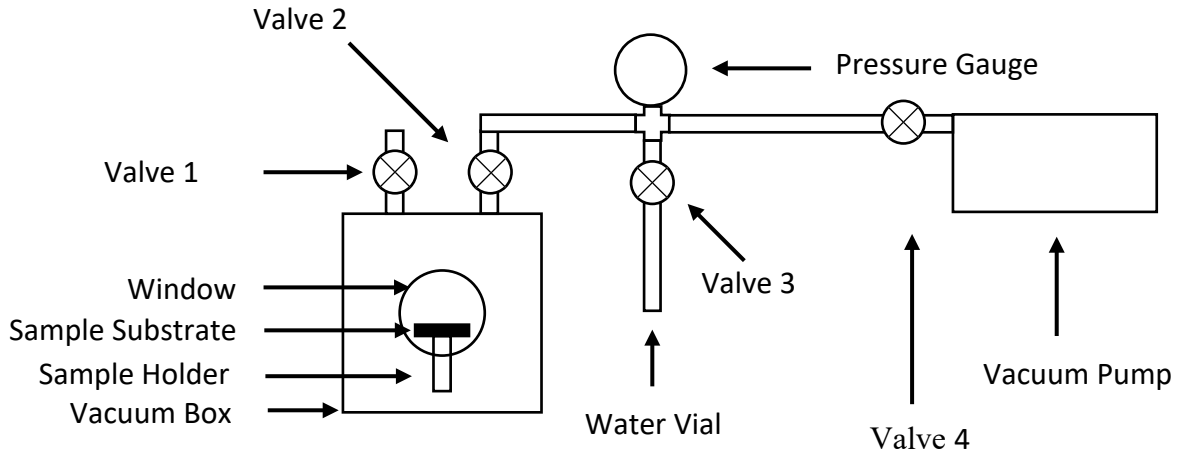
[5]School of Mathematics and Physics, University of Queensland, St Lucia Campus, Brisbane Queensland 4072, Australia.

[6]Department of Chemistry, Swansea University, Singleton Park, Swansea, SA2 8PP, United Kingdom.

Corresponding author:

a.b.mostert@swansea.ac.uk (A.B. Mostert).

Schematic



Scheme S1: A schematic of the experimental setup. A vacuum capable box with sapphire windows to permit neutrons to enter, houses a sample holder upon which the sample substrate is located. Vacuum is controlled using a pump (dry scroll) with valves that are operated manually to enable pumping of the entire system. Valve 1 is a vent vale to permit the box to reach atmospheric pressure. Valve 2 is an additional valve to enable control. Valve 3 controls the water vapour and valve 4 control direct access to the pump. Once vacuum is established, valve 4 is shut, and valve 3 is opened to water vapour to the desired pressure. Two such systems were employed, one for H_2O vapour and the other for D_2O vapour.

Neutron Reflectometry Modelling

D_2O Data

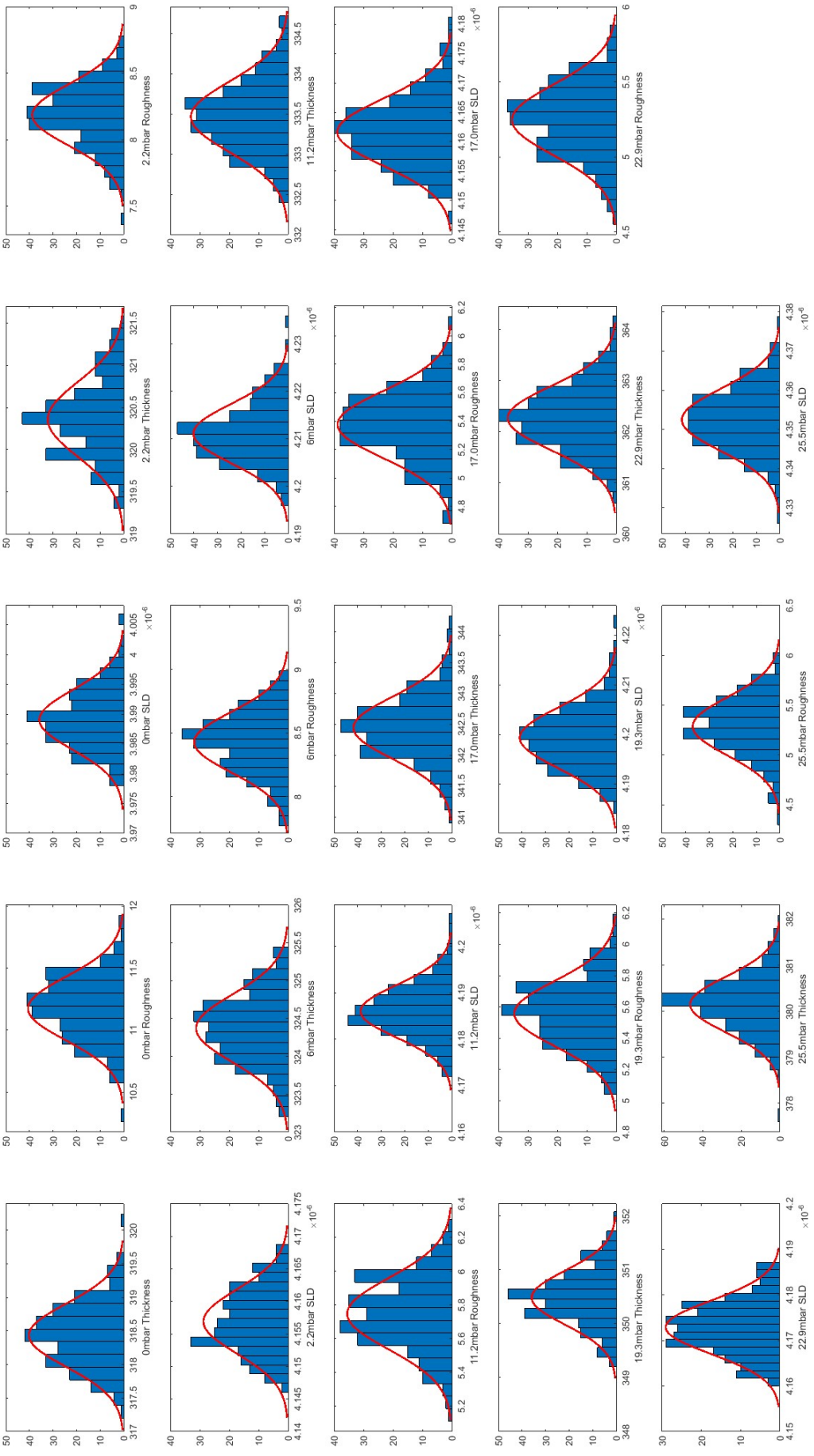


Figure S1. Histograms of the bootstrapping results for each fit parameter used when modelling the D_2O data. Subplots are labelled with the D_2O pres

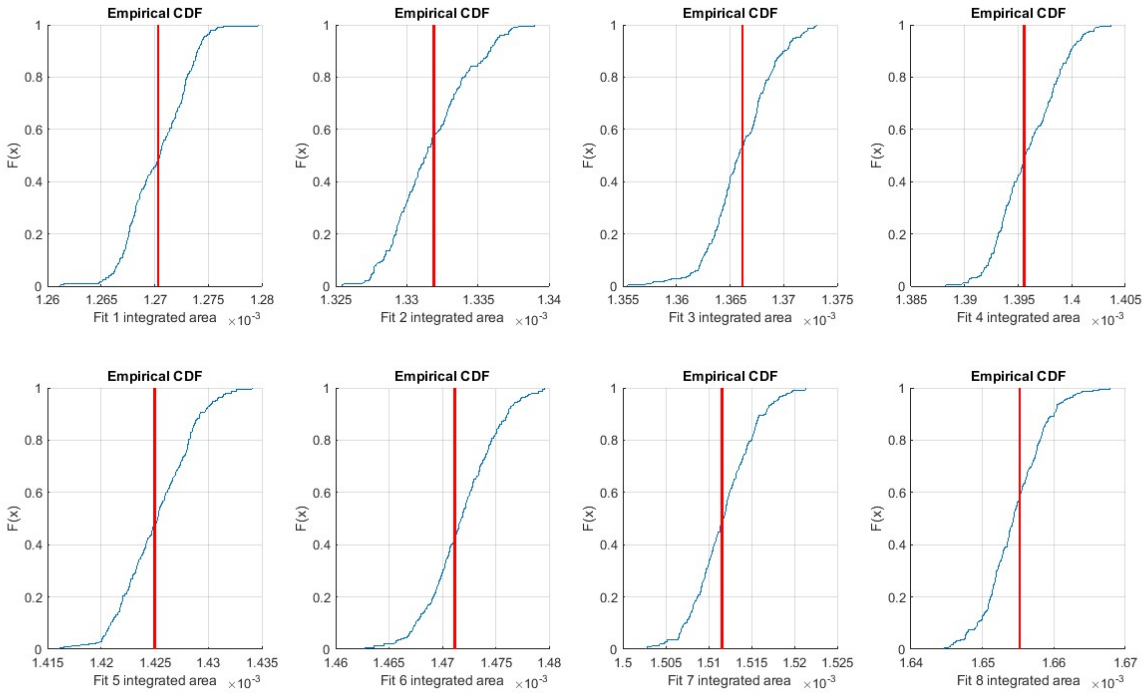


Figure S2. Bootstrapping result empirical cumulative distribution functions for the integrated areas of the SLD profiles for each D_2O dataset. The solid vertical line in each subplot represents the value from the full fit in each dataset. The RH values (from top left to bottom right) were 0, 9, 21, 40, 59, 72, 86, and 100%.

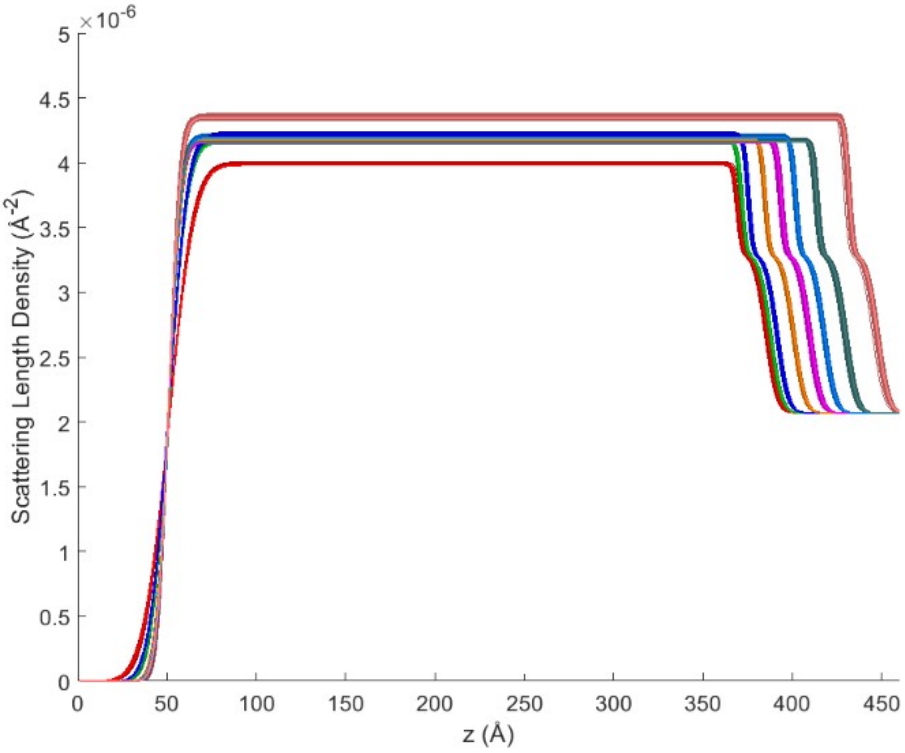


Figure S3. SLD profiles from the D_2O experiment. For each hydration point the SLD profile from the full fit (thick solid coloured line) is plotted along with the SLD profiles relating to all 250 bootstrapping fit results for each hydration point (thinner lines). Thus, the greatest uncertainty in each fit can be determined by the regions of the SLD profile with greatest spread between the thick and thin lines. Line colours match those used in the main manuscript (Figure 3b). The RH were 0, 9, 21, 40, 59, 72, 86, and 100%.

H_2O Data Analysis, Single Layer Model

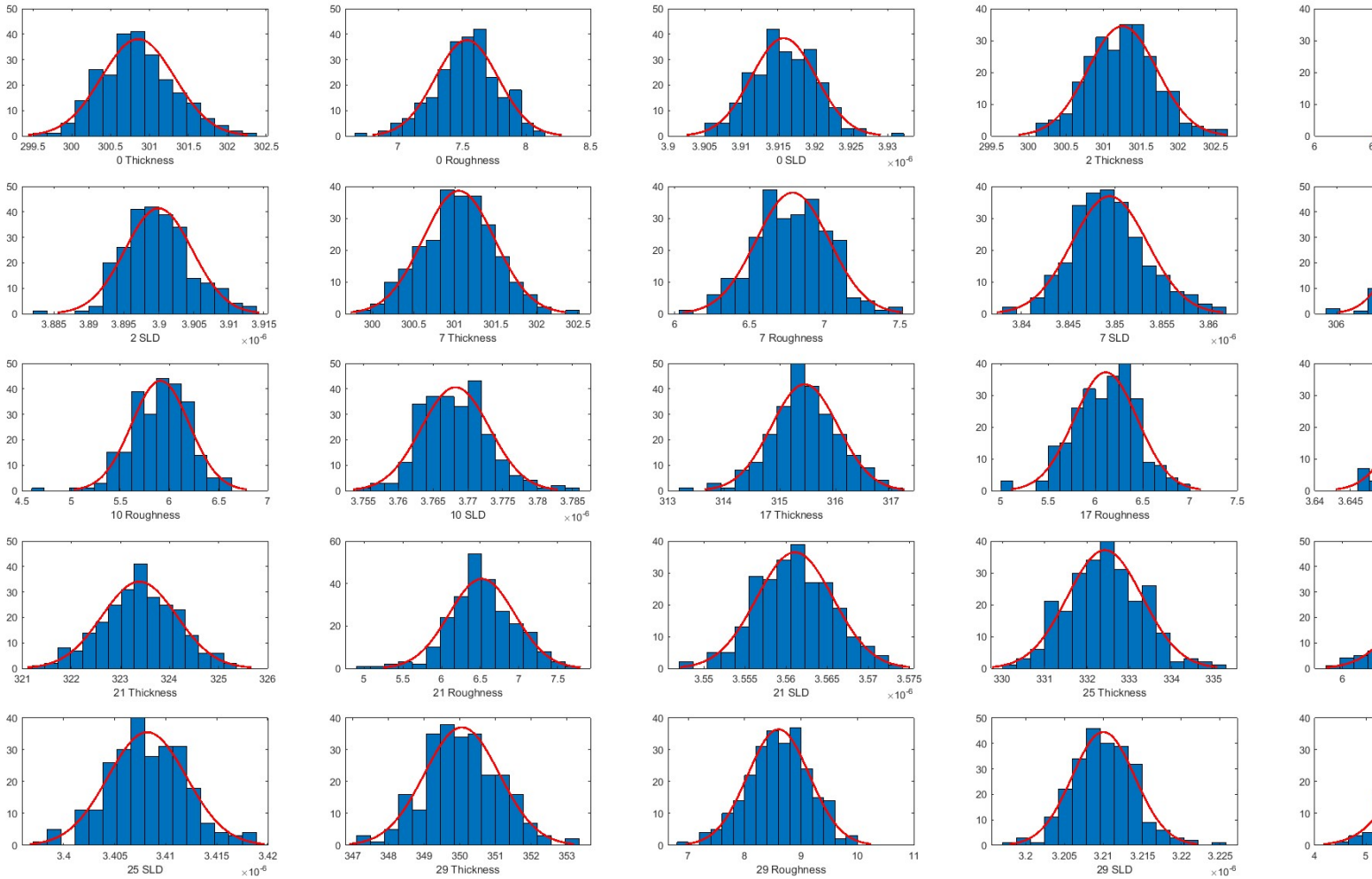

0 Thickness
0 Roughness
0 SLD
2 Thickness
2 SLD
7 Thickness
7 Roughness
7 SLD
10 Roughness
10 SLD
17 Thickness
17 Roughness
21 Thickness
21 Roughness
21 SLD
25 Thickness
25 SLD
29 Thickness
29 Roughness
29 SLD

Figure S4. Histograms of the bootstrapping results for each fit parameter used when modelling the H_2O (single layer) data. Subplots are labelled wit

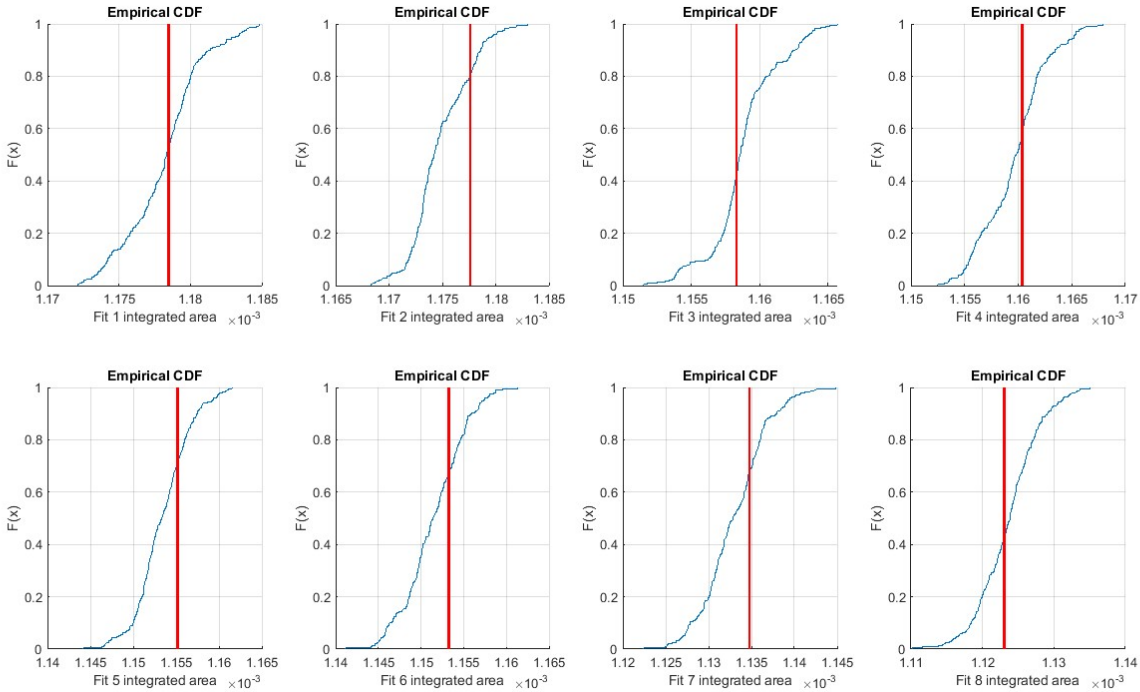


Figure S5. Bootstrapping result empirical cumulative distribution functions for the integrated areas of the SLD profiles for each H_2O (single layer model) dataset. The solid vertical line in each subplot represents the value from the full fit in each dataset. The RH values (from top left to bottom right) were 0, 8, 22, 35, 56, 69, 80, and 100%.

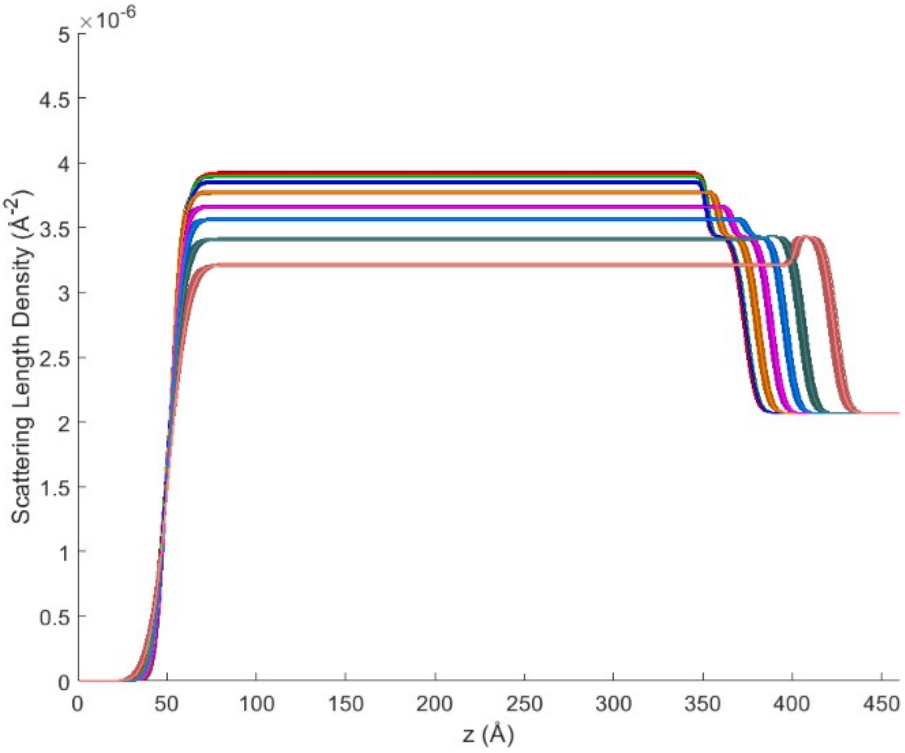


Figure S6. SLD profiles from the H_2O (single layer model) experiment. For each hydration point the SLD profile from the full fit (thick solid coloured line) is plotted along with the SLD profiles relating to all 250 bootstrapping fit results for each hydration point (thinner lines). Thus, the greatest uncertainty in each fit can be determined by the regions of the SLD profile with greatest spread between the thick and thin lines. Line colours match those used in the main manuscript (Figure 5 b). The RH were 0, 8, 22, 35, 56, 69, 80, and 100%.

H_2O Data Analysis, Including Lamellae

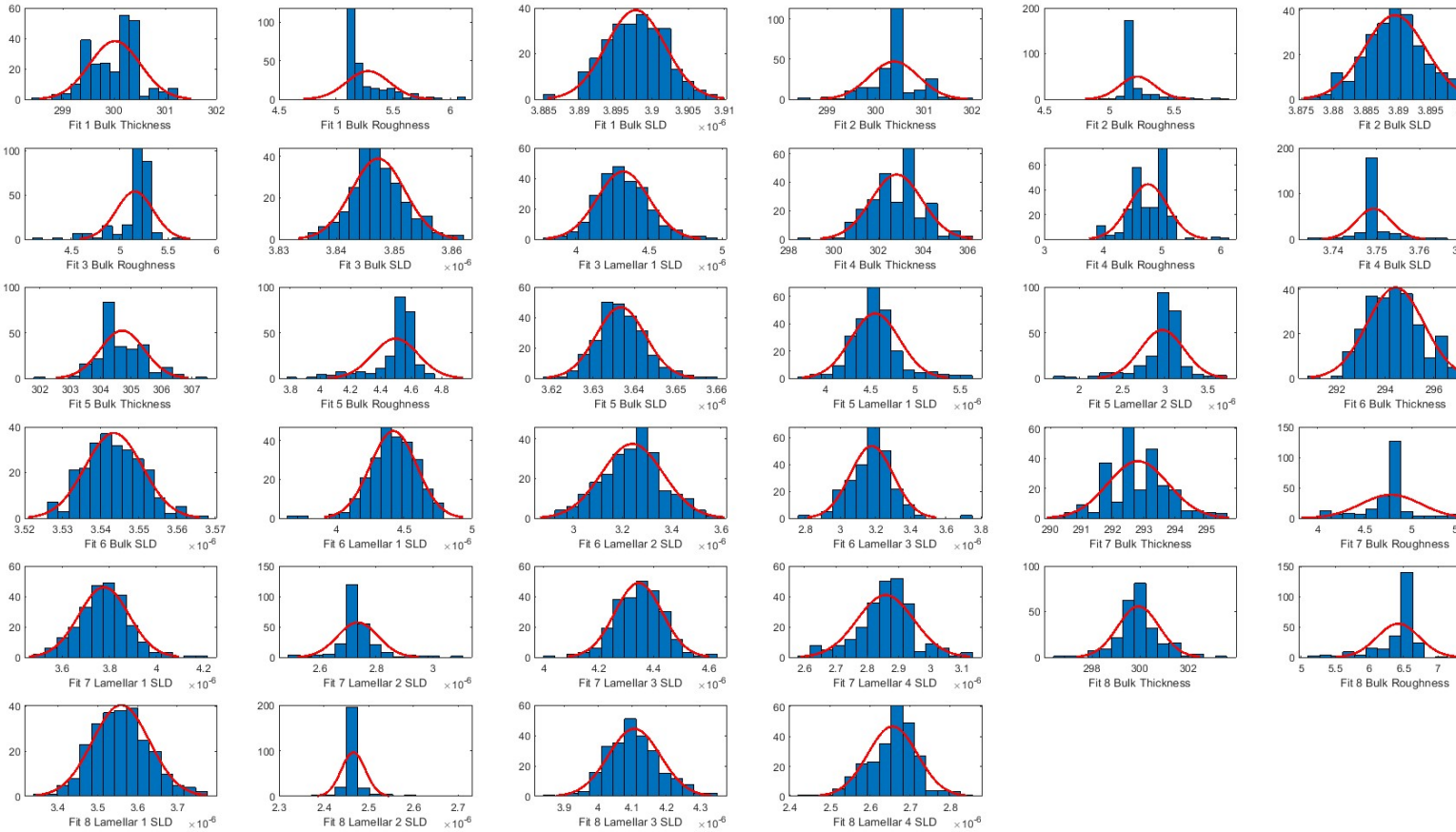

Fit 1 Bulk Thickness
Fit 1 Bulk Roughness
Fit 1 Bulk SLD
Fit 2 Bulk Thickness
Fit 2 Bulk Roughness
Fit 2 Bulk SLD
Fit 3 Bulk Roughness
Fit 3 Bulk SLD
Fit 3 Lamellar 1 SLD
Fit 4 Bulk Thickness
Fit 4 Bulk Roughness
Fit 4 Bulk SLD
Fit 5 Bulk Thickness
Fit 5 Bulk Roughness
Fit 5 Bulk SLD
Fit 5 Lamellar 1 SLD
Fit 5 Lamellar 2 SLD
Fit 6 Bulk Thickness
Fit 6 Bulk SLD
Fit 6 Lamellar 1 SLD
Fit 6 Lamellar 2 SLD
Fit 6 Lamellar 3 SLD
Fit 7 Bulk Thickness
Fit 7 Bulk Roughness
Fit 7 Lamellar 1 SLD
Fit 7 Lamellar 2 SLD
Fit 7 Lamellar 3 SLD
Fit 7 Lamellar 4 SLD
Fit 8 Bulk Thickness
Fit 8 Bulk Roughness
Fit 8 Lamellar 1 SLD
Fit 8 Lamellar 2 SLD
Fit 8 Lamellar 3 SLD
Fit 8 Lamellar 4 SLD

Figure S7. Histograms of the bootstrapping results for each fit parameter used when modelling the H_2O (lamellae model) data. Subplots are labelled

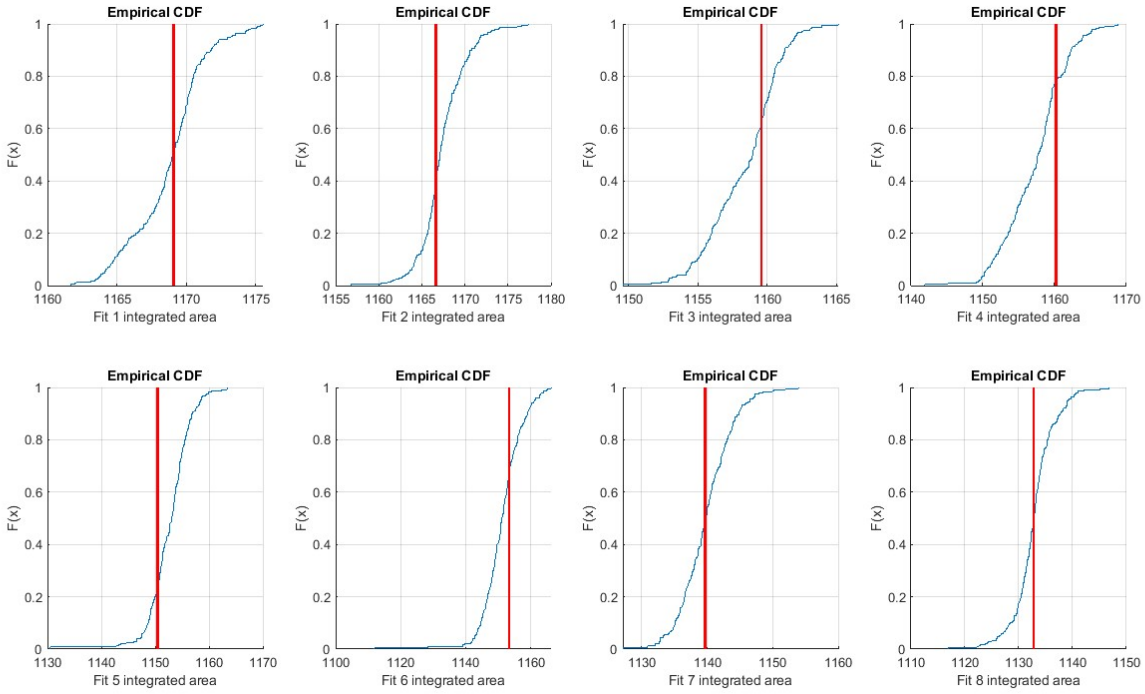


Figure S8. Bootstrapping result empirical cumulative distribution functions for the integrated areas of the SLD profiles for each H_2O (lamellae model) dataset. The solid vertical line in each subplot represents the value from the full fit in each dataset. The RH values (from top left to bottom right) were 0, 8, 22, 35, 56, 69, 80, and 100%.

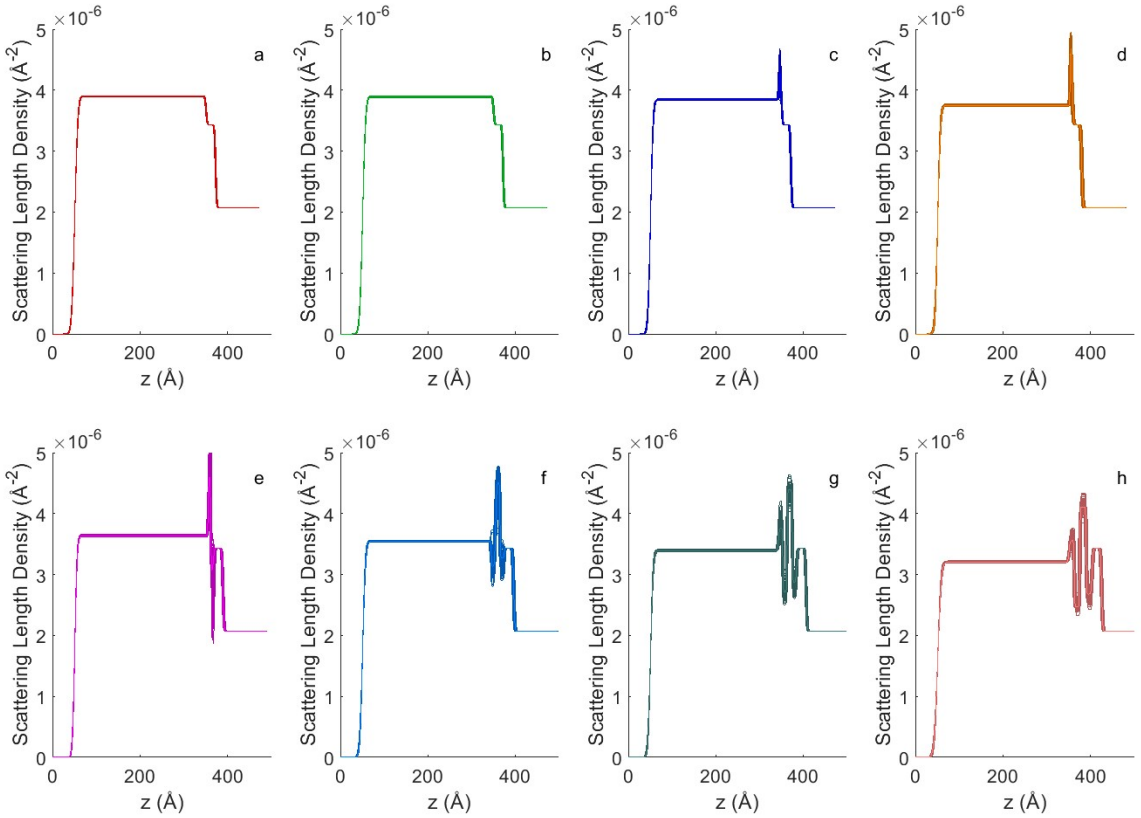


Figure S9. SLD profiles from the H_2O (lamellae model) experiment. For each hydration point the SLD profile from the full fit (thick solid coloured line) is plotted along with the SLD profiles relating to all 250 bootstrapping fit results for each hydration point (thinner lines). Thus, the greatest uncertainty in each fit can be determined by the regions of the SLD profile with greatest spread between the thick and thin lines, and is mostly concentrated in the lamellae region for each fit, i.e. these models confirm the lamellar structure, but show some uncertainty in the precise details of these lamellae. Line colours match those used in the main manuscript (Figures 6 and 7). The RH were a) 0%, b) 8%, c) 22%, d) 35%, e) 56%, f) 69%, g) 80%, and h) 100%.

Other Figures

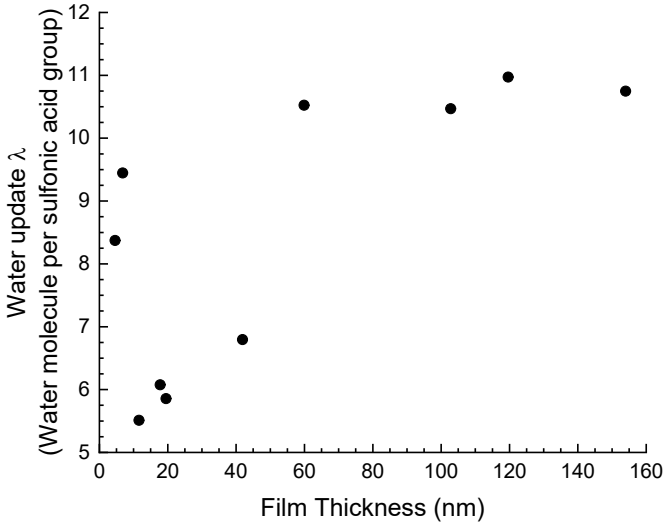


Figure S10. The λ data calculated from DeCaluwe *et al.*[1] using their average water volume fraction in the supplementary information and their equation 5. Data was obtained using a molecular weight for Nafion of 1100 g/mol, molecular weight for water 18.015 g/mol, water density of 0.9970474 g/cm^3 and Nafion density of 1.98 g/cm^3 as per their report.

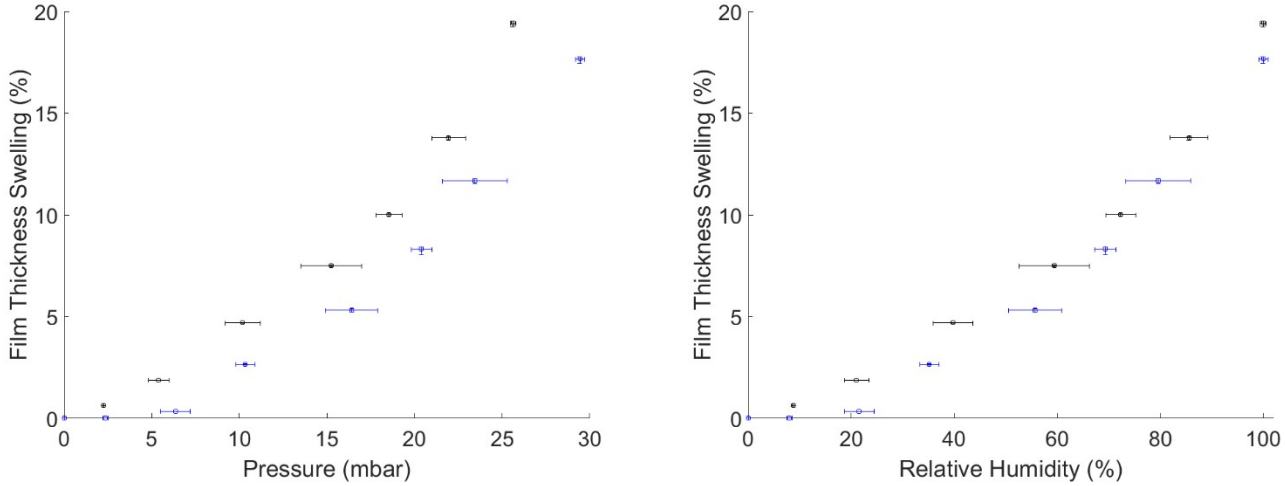


Figure S11. Film thickness swelling results plotted as a function of a), absolute vapour pressure, and b), relative humidity for both the H_2O (blue) and D_2O (black) data sets.

Fitting Parameters

The authors would like to note that the following tables represent the fit parameters used in the analysis of the reflectivity data in this study. However, they are not reported here as specific details of individual layers within the samples. Rather, for each sample, the SLD profile as a whole must be considered. The values reported here are for completeness only. This is particularly relevant for the fit parameters used in the lamellar models in Table S3.

Parameter	**Dataset**	**Value**	**Units**
Resolution	All	4.39	%
Substrate roughness	All	4.99	Å
Oxide thickness	All	16.0	Å
Oxide roughness	All	2	Å
Oxide SLD	All	3.29	E-6 Å^2
Background	0 mbar	6.7E-7	-
Background	2.3, 5.4, & 10.2 mbar	3.0E-7	-
Background	15.3, 18.6, 22.0, & 25.7 mbar	5.0E-8	-
Nafion Thickness	0 mbar	318.9	Å
Nafion Roughness	0 mbar	11.2	Å
Nafion SLD	0 mbar	3.98	E-6 Å^2
Nafion Thickness	2.3 mbar	320.8	Å
Nafion Roughness	2.3 mbar	8.2	Å
Nafion SLD	2.3 mbar	4.15	E-6 Å^2
Nafion Thickness	5.4 mbar	324.8	Å
Nafion Roughness	5.4 mbar	8.5	Å
Nafion SLD	5.4 mbar	4.20	E-6 Å^2

Nafion Thickness	10.2 mbar	333.9	Å
Nafion Roughness	10.2 mbar	5.8	Å
Nafion SLD	10.2 mbar	4.18	E-6 Å^2
Nafion Thickness	15.3 mbar	342.9	Å
Nafion Roughness	15.3 mbar	5.4	Å
Nafion SLD	15.3 mbar	4.16	E-6 Å^2
Nafion Thickness	18.6 mbar	350.8	Å
Nafion Roughness	18.6 mbar	5.6	Å
Nafion SLD	18.6 mbar	4.19	E-6 Å^2
Nafion Thickness	22.0 mbar	362.7	Å
Nafion Roughness	22.0 mbar	5.3	Å
Nafion SLD	22.0 mbar	4.16	E-6 Å^2
Nafion Thickness	25.7 mbar	380.6	Å
Nafion Roughness	25.7 mbar	5.3	Å
Nafion SLD	25.7 mbar	4.34	E-6 Å^2

Table S1. Fitting parameters used to fit the D_2O data.

Parameter	**Dataset**	**Value**	**Units**
Resolution	All	3.53	%
Background	All	6.14E-7	-
Substrate roughness	All	5	Å
Oxide thickness	All	21.6	Å
Oxide roughness	All	2	Å
Oxide SLD	All	3.43	E-6 Å^2
Nafion Thickness	0 mbar	301.1	Å
Nafion Roughness	0 mbar	7.5	Å
Nafion SLD	0 mbar	3.92	E-6 Å^2
Nafion Thickness	2.4 mbar	301.6	Å
Nafion Roughness	2.4 mbar	7.2	Å
Nafion SLD	2.4 mbar	3.90	E-6 Å^2
Nafion Thickness	6.4 mbar	301.4	Å
Nafion Roughness	6.4 mbar	6.8	Å
Nafion SLD	6.4 mbar	3.85	E-6 Å^2
Nafion Thickness	10.4 mbar	308.0	Å
Nafion Roughness	10.4 mbar	5.9	Å
Nafion SLD	10.4 mbar	3.77	E-6 Å^2
Nafion Thickness	16.4 mbar	315.8	Å
Nafion Roughness	16.4 mbar	6.1	Å
Nafion SLD	16.4 mbar	3.66	E-6 Å^2
Nafion Thickness	20.4 mbar	323.6	Å
Nafion Roughness	20.4 mbar	6.5	Å
Nafion SLD	20.4 mbar	3.56	E-6 Å^2
Nafion Thickness	23.5 mbar	332.8	Å
Nafion Roughness	23.5 mbar	7.1	Å

Nafion SLD	23.5 mbar	3.41	E-6 Å^2
Nafion Thickness	29.5 mbar	350.4	Å
Nafion Roughness	29.5 mbar	8.6	Å
Nafion SLD	29.5 mbar	3.20	E-6 Å^2

Table S2. Fitting parameters used to fit the H_2O (single layer) data.

Parameter	**Dataset**	**Value**	**Units**
Substrate roughness	All	2	Å
Oxide thickness	All	21.6	Å
Oxide roughness	All	2	Å
Oxide SLD	All	3.43	E-6 Å^2
Background	0 mbar	3.31E-7	-
Resolution	0 mbar	3.44	%
Nafion Thickness	0 mbar	300.3	Å
Nafion Roughness	0 mbar	5.2	Å
Nafion SLD	0 mbar	3.90	E-6 Å^2
Background	2.4 mbar	5.96E-7	-
Resolution	2.4 mbar	3.13	%
Nafion Thickness	2.4 mbar	300.4	Å
Nafion Roughness	2.4 mbar	5.2	Å
Nafion SLD	2.4 mbar	3.89	E-6 Å^2
Background	6.4 mbar	4.79E-7	-
Resolution	6.4 mbar	3.62	%
Nafion Thickness	6.4 mbar	295.4	Å
Nafion Roughness	6.4 mbar	5.3	Å
Nafion SLD	6.4 mbar	3.84	E-6 Å^2
Lamella 1 Thickness	6.4 mbar	5	Å
Lamella 1 Roughness	6.4 mbar	2	Å
Lamella 1 SLD	6.4 mbar	4.45	E-6 Å^2
Background	10.4 mbar	5.94E-7	-
Resolution	10.4 mbar	4.53	%
Nafion Thickness	10.4 mbar	302.5	Å
Nafion Roughness	10.4 mbar	5.1	Å

Nafion SLD	10.4 mbar	3.75	E-6 Å^2
Lamella 1 Thickness	10.4 mbar	5	Å
Lamella 1 Roughness	10.4 mbar	1	Å
Lamella 1 SLD	10.4 mbar	4.81	E-6 Å^2
Background	16.4 mbar	5.42E-7	-
Resolution	16.4 mbar	4.24	%
Nafion Thickness	16.4 mbar	304.5	Å
Nafion Roughness	16.4 mbar	4.6	Å
Nafion SLD	16.4 mbar	3.63	E-6 Å^2
Lamella 1 Thickness	16.4 mbar	6	Å
Lamella 1 Roughness	16.4 mbar	1	Å
Lamella 1 SLD	16.4 mbar	4.60	Å
Lamella 2 Thickness	16.4 mbar	6	E-6 Å^2
Lamella 2 Roughness	16.4 mbar	1	Å
Lamella 2 SLD	16.4 mbar	3.04	E-6 Å^2
Background	20.4 mbar	7.56E-7	-
Resolution	20.4 mbar	4.96	%
Nafion Thickness	20.4 mbar	294.8	Å
Nafion Roughness	20.4 mbar	5.0	Å
Nafion SLD	20.4 mbar	3.54	E-6 Å^2
Lamella 1 Thickness	20.4 mbar	10	Å
Lamella 1 Roughness	20.4 mbar	1	Å
Lamella 1 SLD	20.4 mbar	3.15	Å
Lamella 2 Thickness	20.4 mbar	10	E-6 Å^2
Lamella 2 Roughness	20.4 mbar	2	Å
Lamella 2 SLD	20.4 mbar	4.49	Å
Lamella 3 Thickness	20.4 mbar	10	Å
Lamella 3 Roughness	20.4 mbar	1	E-6 Å^2
Lamella 3 SLD	20.4 mbar	3.27	E-6 Å^2
Background	23.5 mbar	5.92E-7	-
Resolution	23.5 mbar	4.74	%
Nafion Thickness	23.5 mbar	293.2	Å
Nafion Roughness	23.5 mbar	4.8	Å
Nafion SLD	23.5 mbar	3.39	E-6 Å^2
Lamella 1 Thickness	23.5 mbar	10	Å
Lamella 1 Roughness	23.5 mbar	2	Å
Lamella 1 SLD	23.5 mbar	3.79	E-6 Å^2
Lamella 2 Thickness	23.5 mbar	10	Å
Lamella 2 Roughness	23.5 mbar	1	Å
Lamella 2 SLD	23.5 mbar	2.71	E-6 Å^2
Lamella 3 Thickness	23.5 mbar	12	Å
Lamella 3 Roughness	23.5 mbar	1	Å
Lamella 3 SLD	23.5 mbar	4.38	E-6 Å^2
Lamella 4 Thickness	23.5 mbar	10	Å
Lamella 4 Roughness	23.5 mbar	1	Å
Lamella 4 SLD	23.5 mbar	2.90	E-6 Å^2
Background	29.5 mbar	3.70E-7	-
Resolution	29.5 mbar	4.24	%
Nafion Thickness	29.5 mbar	299.8	Å
Nafion Roughness	29.5 mbar	6.6	Å
Nafion SLD	29.5 mbar	3.21	E-6 Å^2
Lamella 1 Thickness	29.5 mbar	11.9	Å
Lamella 1 Roughness	29.5 mbar	2	Å
Lamella 1 SLD	29.5 mbar	3.56	E-6 Å^2
Lamella 2 Thickness	29.5 mbar	12.5	Å
Lamella 2 Roughness	29.5 mbar	1	Å
Lamella 2 SLD	29.5 mbar	2.47	E-6 Å^2
Lamella 3 Thickness	29.5 mbar	14.8	Å
Lamella 3 Roughness	29.5 mbar	1	Å
Lamella 3 SLD	29.5 mbar	4.11	E-6 Å^2
Lamella 4 Thickness	29.5 mbar	13.6	Å
Lamella 4 Roughness	29.5 mbar	1	Å
Lamella 4 SLD	29.5 mbar	2.68	E-6 Å^2

Table S3. Fitting parameters used to fit the H_2O (lamellae) data.

References

1. DeCaluwe, S. C.; Baker, A. M.; Bhargava, P.; Fischer, J. E.; Dura, J. A., Structure-property relationships at Nafion thin-film interfaces: Thickness effects on hydration and anisotropic ion transport. *Nano Energy* **2018,** *46*, 91-100.