
Supporting Information

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Ageing protocol

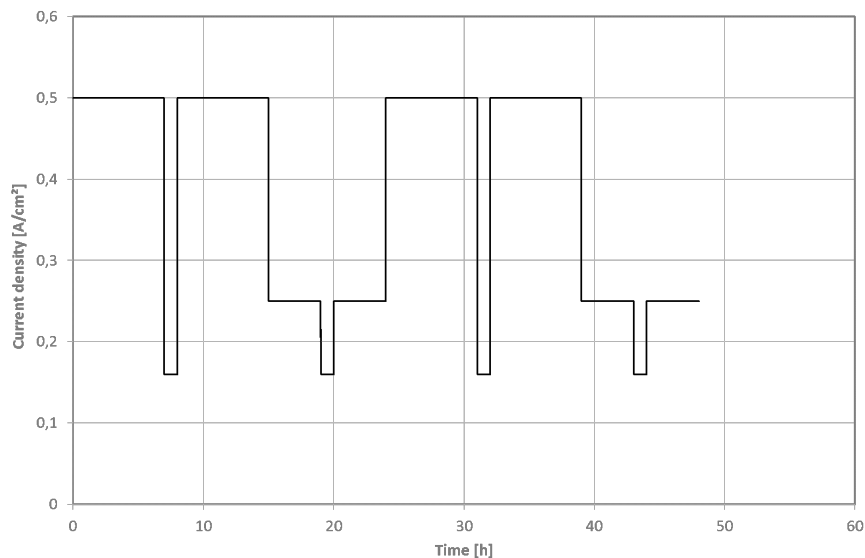


Figure S1: Scheme of the 24 hours cyclic load profile during the ageing procedure

The scheme of the 24 hours cyclic load profile of the cell during the 600h aging procedure is shown in fig S1. The drop in performance during the ageing protocol was monitored by

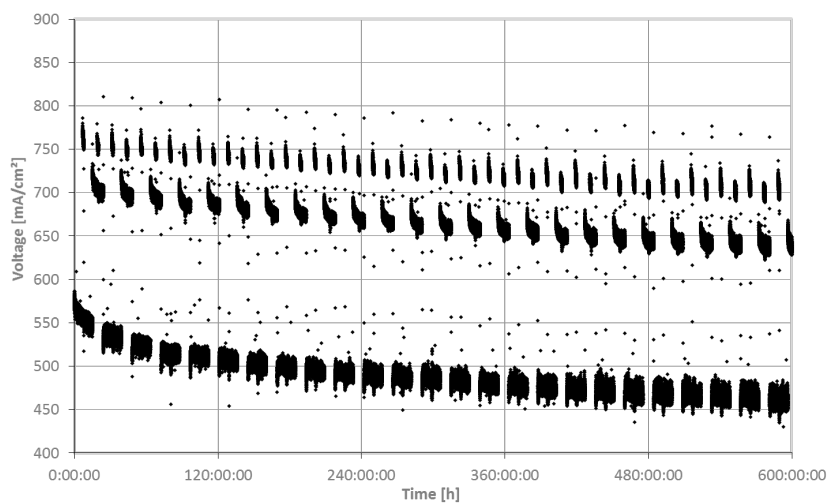


Figure S2: Voltage as a function of time during the ageing procedure

following the evolution in voltage as a function of time (fig S2). At the beginning and the end of the aging procedure, polarization curves were recorded in order to further quantify the effects of ageing in terms of performance drop (fig. S3).

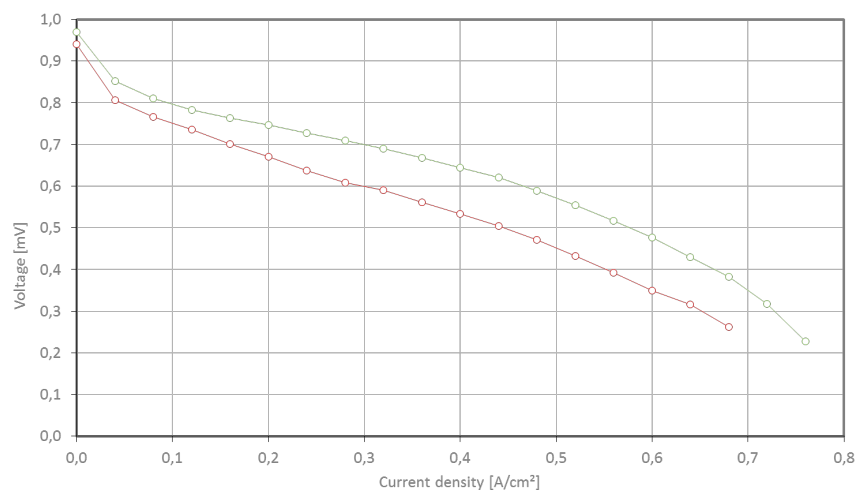


Figure S3: Polarization curves before (green) and after (red) the aging procedure

Time series measurements

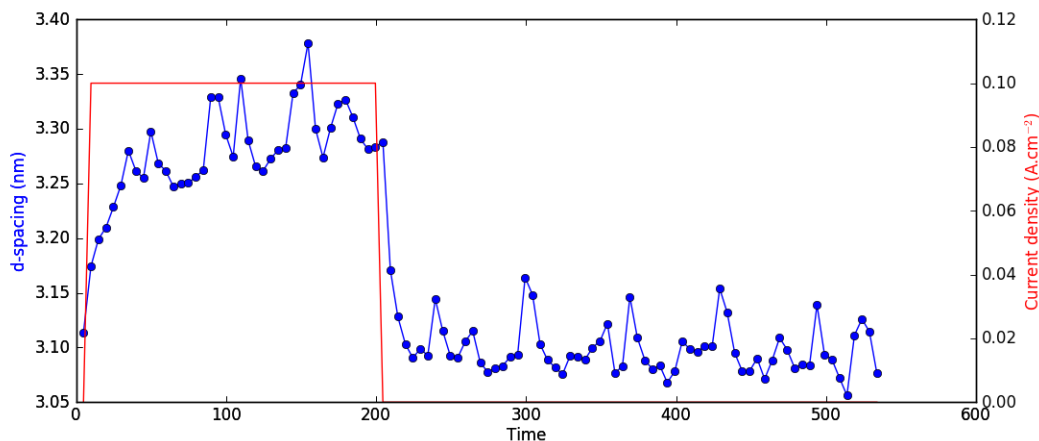


Figure S4: Time evolution of the d-spacing at startup (from OCV to 0.2 A.cm⁻²) on the pristine cell, at the air outlet channel.

Kinetics measurements were also performed on the pristine membrane at start-up. The time evolution of the d-spacing is shown in fig. S4. We observe a rapid increase of the d-spacing in the first 20 s, followed by a stabilization regime (not achieved during this measurement). The stabilization is attained typically within 200 s, in agreement with the time previously measured by SANS¹.

Analysis of SAXS spectra

The 1D SAXS data were fitted using a combination of 3 components representative of the classical characteristics of PFSA membranes²: i) The ionomer peak, representative of the average distance of the water/hydrophobic phase separation was fitted with a gaussian function, ii) The matrix peak, which is a low angle correlation peak present in PFSA membranes was also fitted with a gaussian, and iii) the large scale upturn in intensity at very low-angles representing the interface of very large objects which was fitted with a power law decay. The expression used was thus the following:

$$I(Q) = Y_0 + BQ + I_{ion} \exp\left(-\frac{Q-Q_{ion}}{\sigma_{ion}}\right) + I_m \exp\left(-\frac{Q-Q_m}{\sigma_m}\right) + I_p Q^{-a}$$

where the first two terms account for a linear background and the last 3 terms for components i), ii) and iii) respectively. Q_{ion} and Q_m stand for the positions of the ionomer and matrix peaks, respectively, σ_{ion} and σ_m being the variance of the Gaussians, I_{ion} and I_m their amplitude. a is the exponent of the low angle intensity power law (equal to -4 in case of a Porod behavior), and I_p its amplitude. The Porod's law states that the scattered intensity of a two phase system scales as $\delta\rho\phi(1-\phi)SQ^{-(6-D_f)}$, with $\delta\rho$ the squared two phase contrast, ϕ the volume fraction, S the surface area of the particles, and D_f the fractal dimension of the surface. An example of the fitted data with the components is illustrated in fig S6.

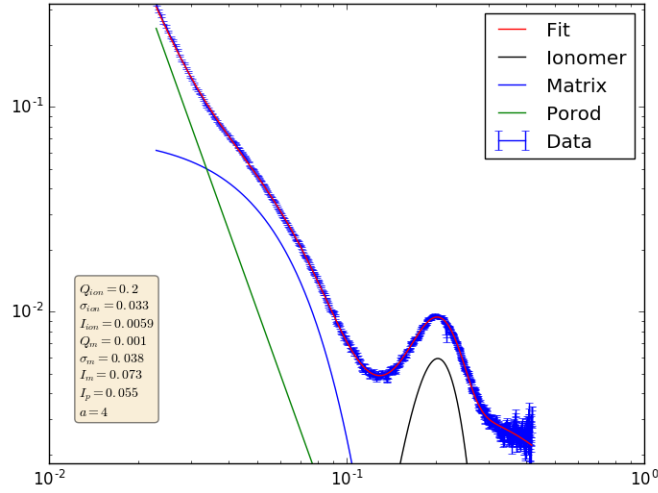


Figure S5: Example of the fitted data using three components, e.g. two Gaussian functions (ionomer peak, matrix knee) and a power law (low-Q signal).

Note that the high brilliance of the synchrotron and exceptional Q -resolution achieved on the beamline, combined with a clearly defined ionomer peak, allowed us to have an excellent accuracy on the determination of peak position. Errors calculated from the fitting procedure on this parameter were found to be less than 1%, and therefore they are not shown in the figures representing variations of d -spacings.

d-spacing vs peak integral representation

The values of d-spacings in function of ionomer peak integral, represented in Figure 5 of the main text, are gathered all together to highlight the master curve behavior of the (d,I) correlation. Additional data are also provided (in purple), corresponding to different operating conditions where the membrane is much more hydrated. Accordingly, much higher values of d-spacings are obtained in both aged and pristine cells in this case. The results show that the proportionality between d-spacings and peak integral (indicated by the dashed line) is a general property independent of positions in the cell and operating conditions.

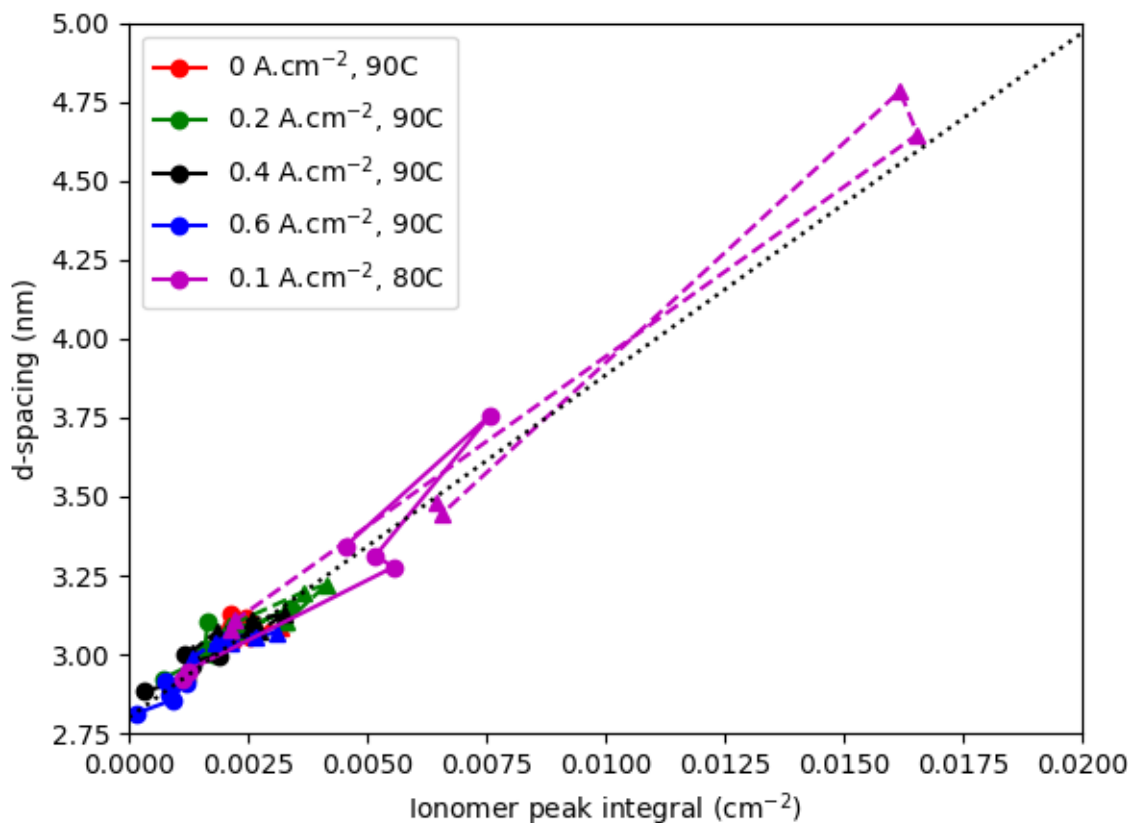


Figure S6: Variations of d-spacings as a function of the integral of the ionomer peak in a broad range of operating conditions on aged (triangles) and pristine (circles) membranes, for all 6 probed positions (not indicated for clarity), including high membrane hydration measurements (purple). The black dotted line serves as a guide to the eye, emphasizing the correlation between the two parameters.

Measurements of the disorder of the water/hydrophobic phase separation

The disorder inherent to the formation of a phase separation can be accessed by measuring the relative full width at half maximum (FWHM= ΔQ) of the scattering peak. This $\Delta Q/Q_0$ can be seen as the spreading of the distribution of d-spacings in the material, larger values meaning broader distributions, e.g. increased disorder. The variations of $\Delta Q/Q_0$ versus the d-spacing are shown in fig S7. Similarly to what is observed when plotting the d-spacing

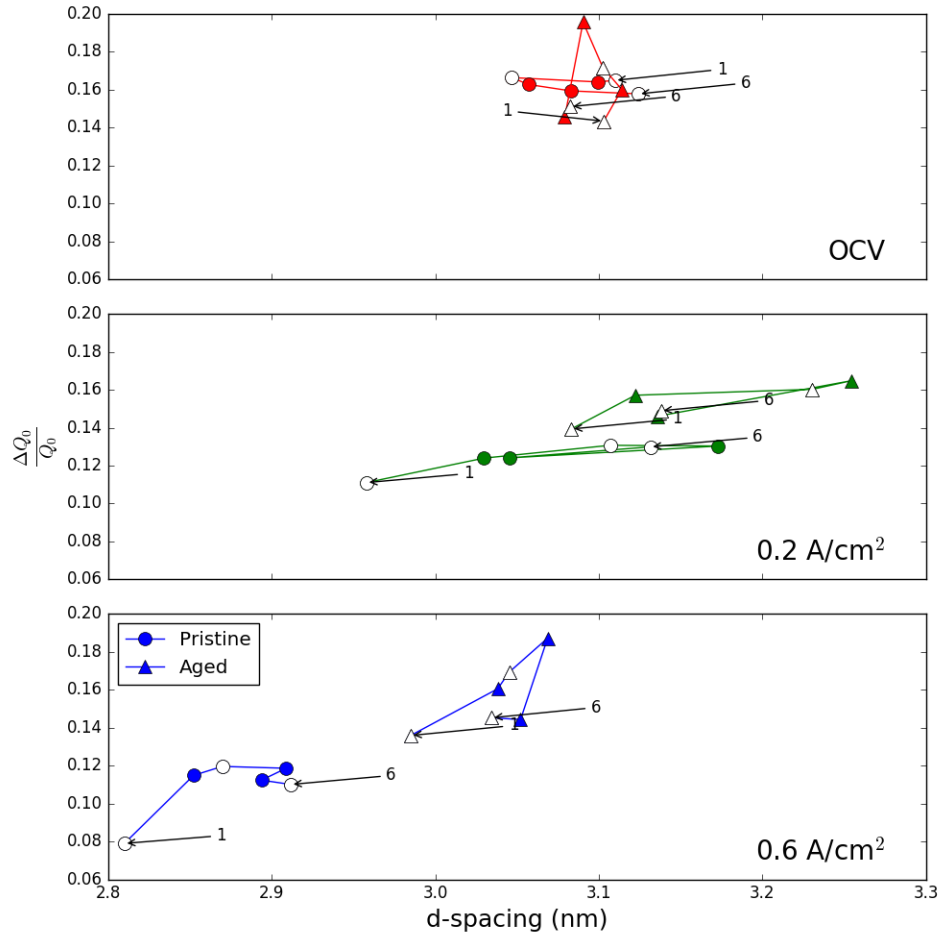


Figure S7: Normalized FWHM as a function of the d-spacing

versus the ionomer peak integral (Figure 5 in the main text), we observe a correlation between the normalized FWHM and the d-spacing, meaning that disorder (distribution of d-spacings)

is increased as the phase separation distance increases.

References

- (1) Martinez, N.; Peng, Z.; Morin, A.; Porcar, L.; Gebel, G.; Lyonnard, S. *Journal of Power Sources* **2017**, *365*, 230–234.
- (2) Kusoglu, A.; Weber, A. Z. *Chemical reviews* **2017**, *117*, 987–1104.