Supporting Information

1 SANS data analysis

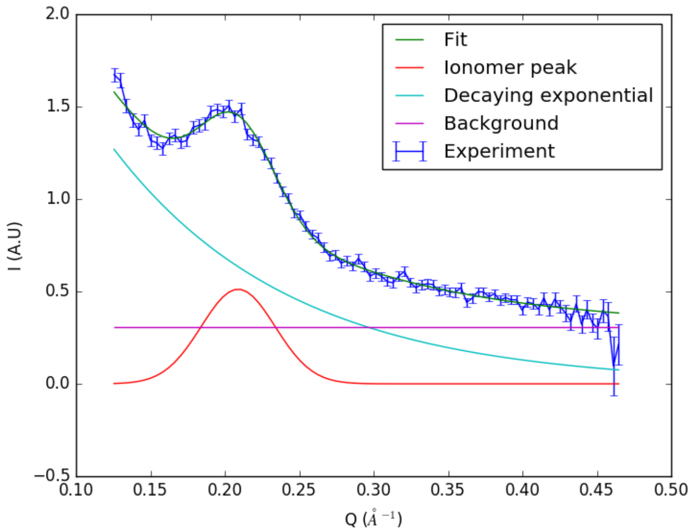

Figure S1: Example of a SANS spectrum with the fitted contributions.

The 1D radially averaged curves were fitted with the sum of a gaussian representing the ionomer peak, a decaying exponential representing the large scale polymer organization and a flat background accounting for incoherent scattering[3] (Fig. S1). The peak position Q_{iono} was further used to assess the hydration state of the membrane.

2 QENS data analysis

2.0.1 Low resolution data analysis

The low resolution data were fitted over the -1, +1 meV energy transfer range with a two lorentzian model according to[1]:

$$S(Q,\omega) = DW[P(Q) + A_{fast}(Q)L_{fast}(\omega) + A_{rot}(Q)L_{rot}(\omega)] * R(\omega) + B \quad (1)$$

where P(Q) represents the elastic contribution, L_{fast}, L_{rot} represent the 2 lorentzians, DW the Debye-Waller factor, Re(ω) the instrumental resolution function, and B a flat background. The first lorentzian L_{fast} Half Width Half Maximum (HWHM) followed a $D_{local}Q^2$ law, with D_{local} representing the local water diffusion coefficient, while the spectral width of the second component Lrot was fitted with a constant HWHM accounting for fast water rotations falling in the spectrometer window. The $A_{fast}(Q)$ amplitude of the diffusive component was fitted with a soft boundaries confinement model [5]:

$$A_{fast}(Q) = 1 - exp(-Q^2\sigma^2) \quad (2)$$

with σ being the confinement radius. This models describes well the behavior of water protons interacting with ionomer matrix [4] [2].

2.0.2 High resolution data analysis

High resolution data were fitted over the -30 +30 μeV range with 2 quasielastic components corresponding to water confined by the polymer (which is also visible on the low resolution data), but also another slow confined component corresponding to hydronium ion proton motions [4], similarly to the low resolution data:

$$S(Q,\omega) = DW[P(Q) + A_{nano}(Q)L_{nano}(\omega + A_{slow}(Q)L_{slow}(\omega))] * R(\omega) \quad (3)$$

Since the resolution is increased by approximatively two decades, we are resolving components that lie in the low resolution elastic peak. Accordingly, the L_{nano} represents the elastic contribution of the gaussian confinement model convolved with a long range translational term [4]. This component follows a $D_{nano}Q^2$ law with D_{nano} being a long range inter water droplet diffusion coefficient. The second component L_{slow} had a Q-constant linewidth corresponding to confined motion attributed to slow confined hydronium ion motions, which allow us to extract a τ_{slow} correlation time. In order to minimize the number of fit parameters, the amplitude A_{nano} was imposed to follow a gaussian confinement form factor with a radius σ imposed to the value found on the low resolution data. A similar approach was used for A_{slow}, with a confinement diameter of 3.7 Åtaken for Perrin et al [4].

References

[1] Quentin Berrod, Sandrine Lyonnard, Armel Guillermo, Jacques Ollivier, Bernhard Frick, and Gérard Gébel. Qens investigation of proton confined motions in hydrated perfluorinated sulfonic membranes and self-assembled surfactants. In *EPJ Web of Conferences*, volume 83, page 02002. EDP Sciences, 2015.

[2] Quentin Berrod, Sandrine Lyonnard, Armel Guillermo, Jacques Ollivier, Bernhard Frick, Abdelatif Manseri, Bruno Améduri, and Gérard Gébel. Nanostructure and transport properties of proton conducting self-assembled perfluorinated surfactants: A bottom-up approach toward pfsa fuel cell membranes. *Macromolecules*, 48(17):6166–6176, 2015.

[3] A Morin, G Gebel, L Porcar, Z Peng, N Martinez, A Guillermo, and S Lyonnard. Quantitative multi-scale operando diagnosis of water localization inside a fuel cell. *Journal of The Electrochemical Society*, 164(2):F9–F21, 2017.

[4] Jean-Christophe Perrin, Sandrine Lyonnard, and Ferdinand Volino. Quasielastic neutron scattering study of water dynamics in hydrated nafion membranes. *The Journal of Physical Chemistry C*, 111(8):3393–3404, 2007.

[5] Ferdinand Volino, Jean-Christophe Perrin, and Sandrine Lyonnard. Gaussian model for localized translational motion: application to incoherent neutron scattering. *The Journal of Physical Chemistry B*, 110(23):11217–11223, 2006.