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Supplementary Information

Resolve the Pore Structure and Dynamics of Nafion 117: Application of High Resolution ^{7}Li Solid State Nuclear Magnetic Resonance Spectroscopy

Cheng-Hua Chia, Zhen Wu, Cheng-Hsien Wu, Ren-Hao Cheng, Shangwu Ding*

In this Supplementary Information, the pore size distribution of Nafion obtained with NMR cryoporometery experiment is presnted. As can be seen from the results, there do exist three types of pores in the membrane we used.
Because the pore shape model (cylinder) used in NMR cryoporometry, the large pores may be overestimated. In this sample, we believe that the pore size around 2.0 nm may be overestimated. Although the quantitative accuracy of pore size distribution obtained with NMR cryoporometry is not as good as the results from our high resolution ^{7}Li MAS result shown in the main text, the number of pore types is trustworthy.

The experimental procedure is summarized as follows. The basic idea of NMR cryoporometry is the well-known phenomenon of melting/freezing point depression of a confined liquid (e.g., water). The change of phase transition temperature (melting/freezing point) depends on the size of the pore/channel where the probing liquid (water) is filled. By measuring the intensities of the water in different pores via, e.g., the ^{1}H NMR signal of water, the pore size distribution is obtained. A full review on the principle of NMR cryoporometry can be found in Ref. [1].

The depression of the phase transition temperature is given by Gibbs-Thompson equation:

$$\Delta T = T_0 - T = \frac{2\gamma T_0}{R\rho\Delta H} = K\frac{1}{R}, K = \frac{2\gamma T_0}{\rho\Delta H} = \text{constant} \qquad \text{(S1)}$$

where

R : the radius of the pore (pore size)
γ : crystal-liquid interfacil energy.
ρ : density of the frozen liquid
ΔH : bulk enthalpy of fusion

Suppose there are N types of pores with intensity (I_{0i}), inverse transition temperature X_{ci} ($=1000/T_{ci}$), the width of transition temperature (Δ_i), $i=1,2,\ldots N$. The total ^{1}H NMR signal is expressed as

$$I(X) = \sum_{i=1}^{N} \frac{I_{0i}}{\sqrt{\pi}} \int_{-\infty}^{\frac{(X - X_{ci})}{\sqrt{2}\Delta_i}} \exp[-u^2] du \qquad \text{(S2)}$$

By deconvoluting the NMR signal into different contributions (best fitting above euqation), the number of types of water and the relative proportion of each type of water can be obtained. T

The melting point distribution is given by differentiating equation S2, i.e., *dI/dX*.

The pore size distribution is given by *dI/dR*, which can be calculated from equations (S1, S2).

References

[1] Oleg V. Petrov, István Furó. Progr. NMR Spectrosc, 2009, 54, 97-122.

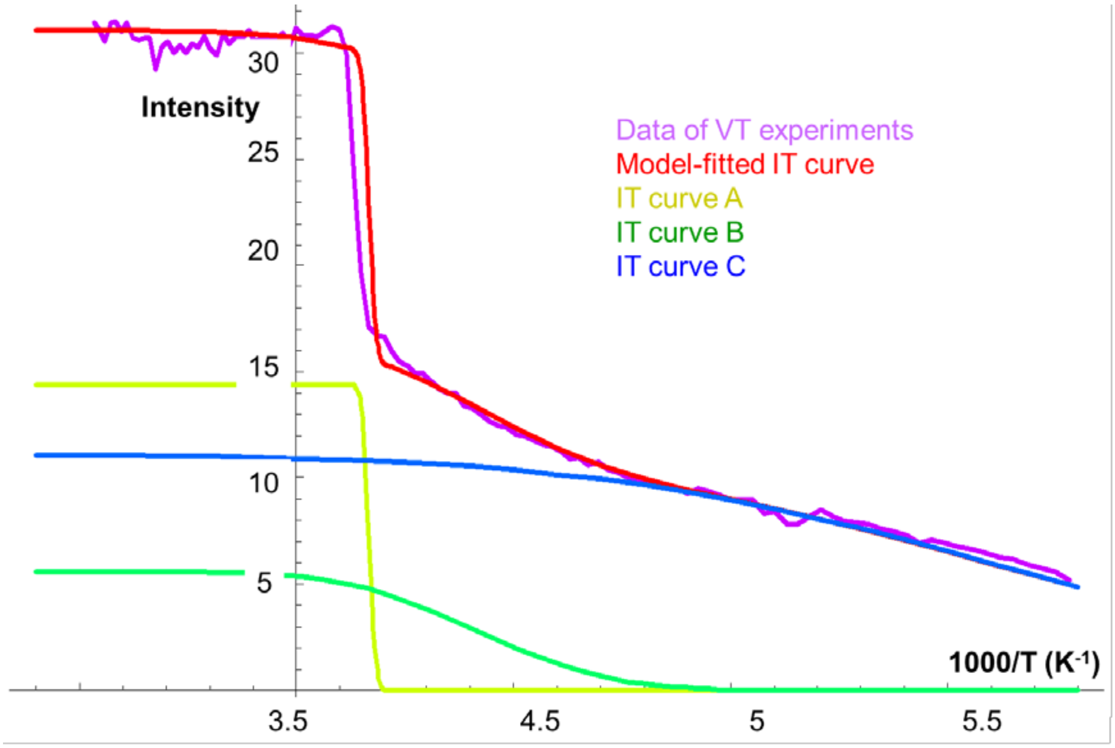

Fig. S1 The experimental (purple) and fitted (red) ^{1}*H of water NMR signal intensities as a function of inverse temperature. The signal can be deconvoluted into three types (yellow, blue and green), corresponding to water with different freezing/melting points.*

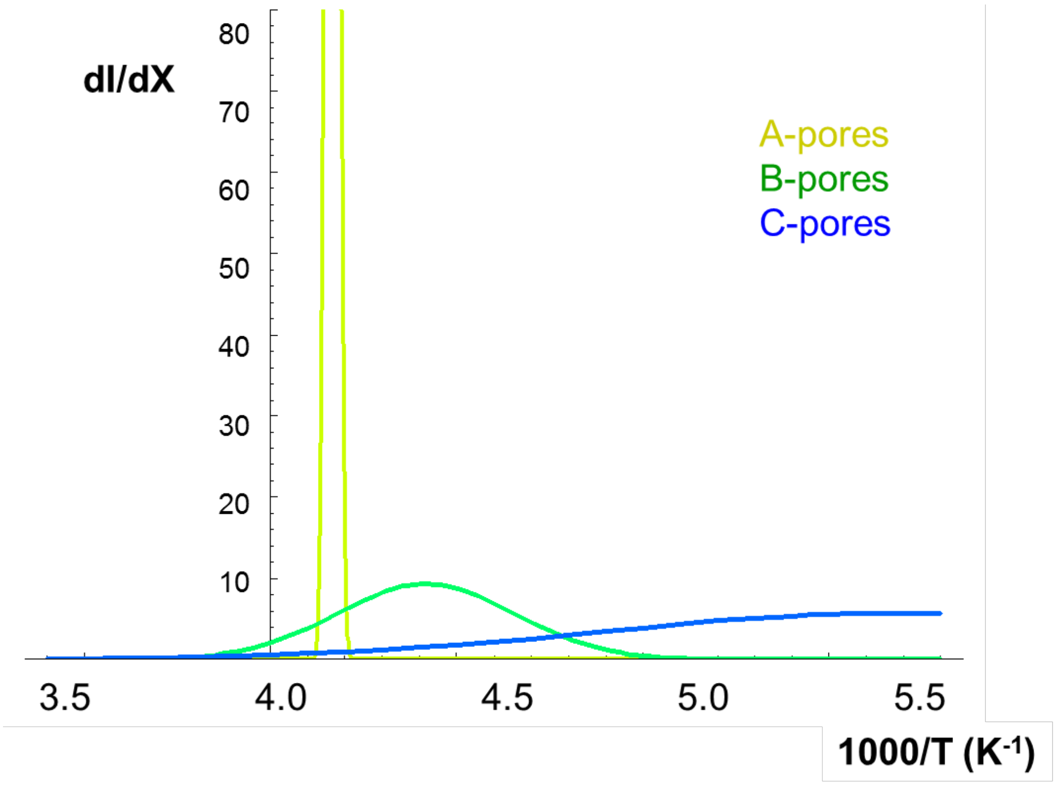

Fig. S2 The melting/freezing point distribution of water confined in Nafion 117, calculated from equation (S2).

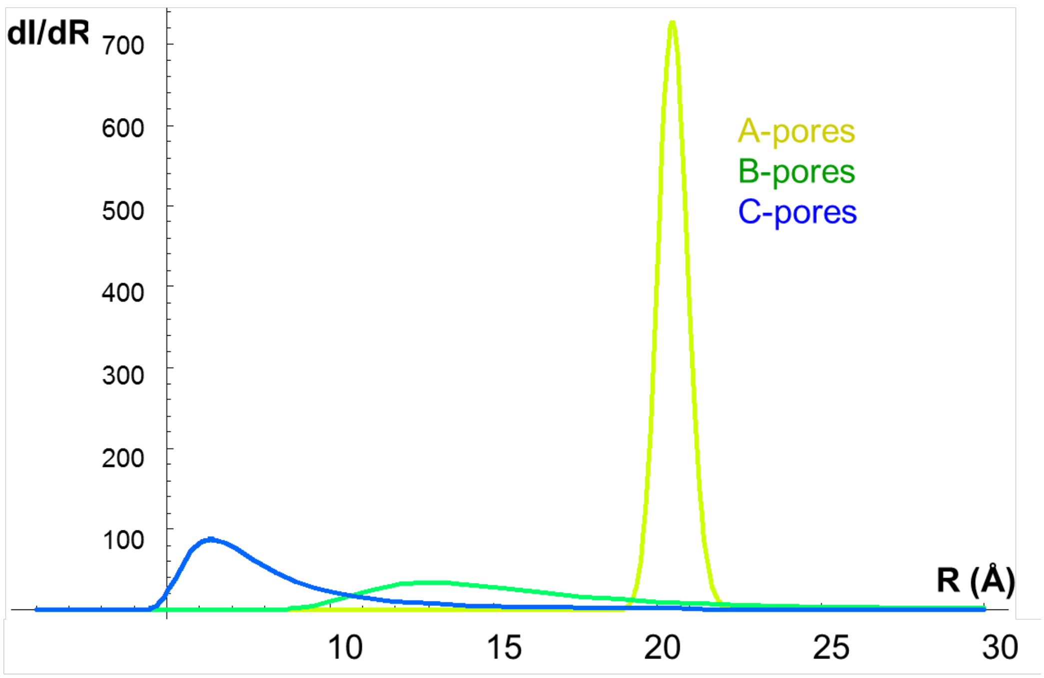

Fig. S3 The pore size distribution of Nafion 117 measured from NMR cryoporometry, calculated from equations (S1, S2).