Supporting Information

Hot-Pressing Effects on Polymer Electrolyte Membrane Investigated by ^{2}H NMR Spectroscopy

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Received December 22, 2012, Accepted December 27, 2012

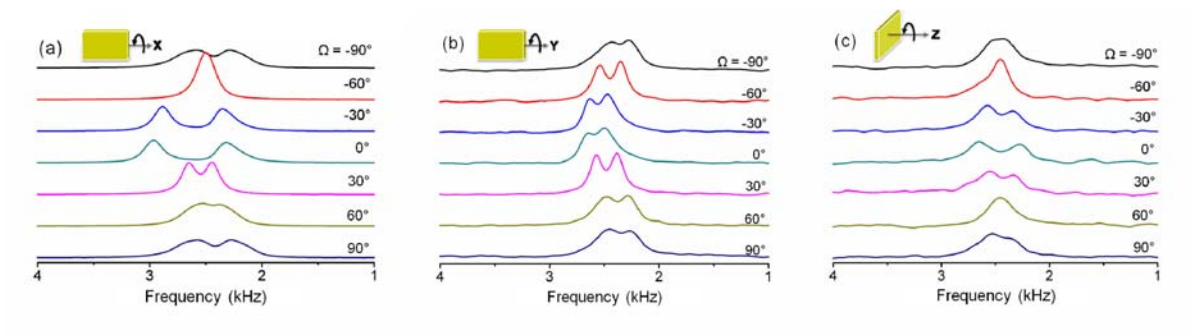


Figure S1. Representative spectra of the stretched Nafion 117 membranes obtained at 3 different rotation axes as designated in the spectra. The ^2H_2O contents were 13, 14, and 13 wt% for the membranes rotated along the (a) X, (b) Y, and (c) Z axes, respectively.

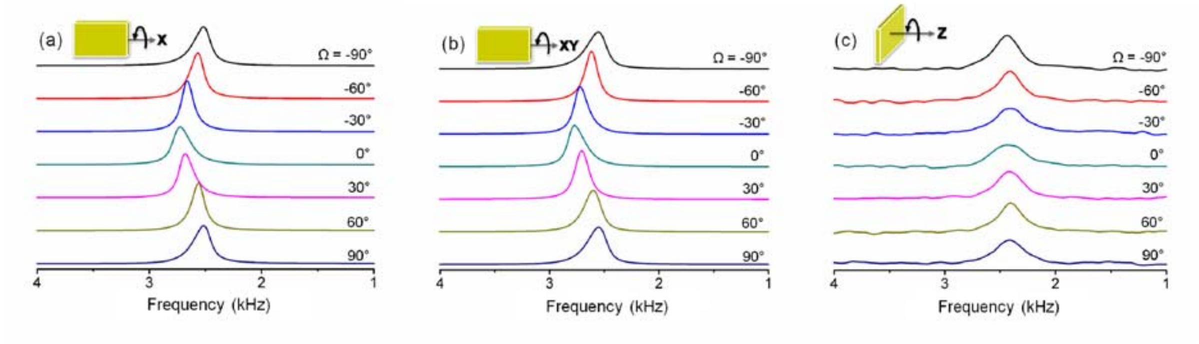


Figure S2. Representative spectra of the Nafion 117 membranes without any stress applied obtained at 3 different rotation axes as designated in the spectra. The ^2H_2O contents were (a) 23 wt% for the sample rotated along the X axis, (b) 29 wt% for the sample rotated along the XY axis, and (c) 3 wt% for the sample rotated along the Z axis.

[Relationships among θ, Ω, *α*, and β]

The average O-^{2}H director and H_0 can be expressed as vectors **A** and **B**, respectively, in the XYZ frame, adopting the method employed in reference S1. Using the vector product $\mathbf{A}\cdot\mathbf{B} = |\mathbf{A}||\mathbf{B}|\cos\theta$, the relationship between angles can be obtained if **A** and **B** were considered unit vectors.

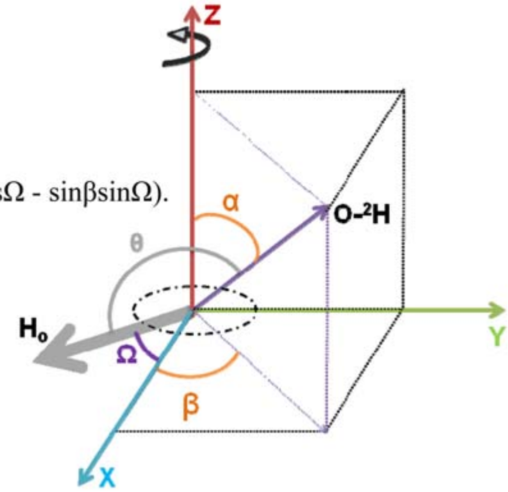
For the Z rotation

$\mathbf{A} = (\sin\alpha\cos\beta, \sin\alpha\sin\beta, \cos\alpha)$

$\mathbf{B} = (\cos\Omega, -\sin\Omega, 0)$,

resulting in

$\cos\theta = \sin\alpha\cos\beta\cos\Omega - \sin\alpha\sin\beta\sin\Omega = \sin\alpha(\cos\beta\cos\Omega - \sin\beta\sin\Omega)$.



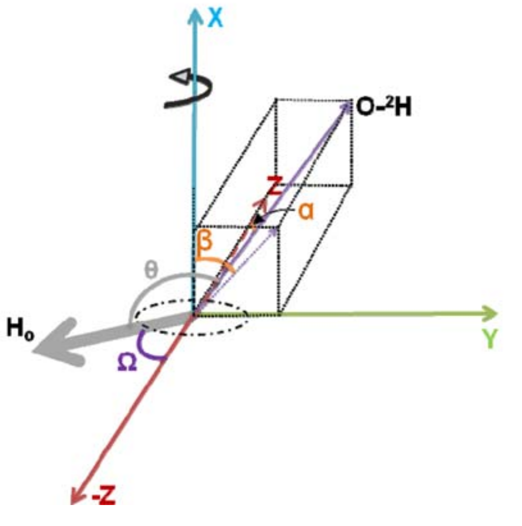
For the X rotation

$\mathbf{A} = (\sin\alpha\cos\beta, \sin\alpha\sin\beta, \cos\alpha)$

$\mathbf{B} = (0, -\sin\Omega, -\cos\Omega)$,

resulting in

$\cos\theta = -\sin\alpha\sin\beta\sin\Omega - \cos\alpha\cos\Omega$.



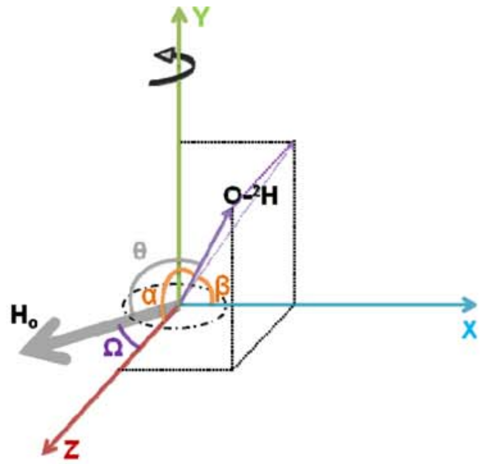
For the Y rotation

A = (sinαcosβ, sinαsinβ, cosα)

B = (-sinΩ , 0, cosΩ),

resulting in

cosθ = -sinΩsinαcosβ + cosΩ cosα.



For the XY rotation

A = (sinαcosβ, sinαsinβ, cosα)

B = (sinΩcos(45°), -sinΩ sin(45°), cosΩ) = (0.707sinΩ, -0.707sinΩ, cosΩ),

resulting in

cosθ = 0.707sinαcosβsinΩ - 0.707sinαsinβsinΩ + cosαcosΩ.

[Relationship between $\Delta\nu_0$ and water content]

The water content (in wt %) of polymer electrolyte membrane is proportional to the volume of water and therefore, to the channel volume filled with water in the membrane. $\Delta\nu_0$ values are proportional to surface-to-volume ratio (S/V) of hydrophilic channels due to the anisotropic ^{2}H interactions proportional to S/V.[S2,S3] Here each straight segment of channels is regarded as an individual channel so that channel tortuosity is reflected in the $\Delta\nu_0$ value.

If the channel shape is assumed to be a cylinder with a radius of r and a length of l, the volume of the cylinder is $\pi r^2 l$, and the inner surface area of the cylinder is $2\pi rl + 2\pi r^2$. Consequently, S/V of the cylinder becomes $2/r + 2/l$. For the closed cylinders, the inner surfaces for the cylinder top and bottom are orthogonally oriented to that of the cylinder body. Thus, the anisotropic interaction proportional to the surface area of a closed cylinder requires a vector sum of $2\pi rl$ and $2\pi r^2$ and not a scalar sum. However, it would be more realistic to regard hydrophilic channels as cylinders with open ends. Therefore, S/V for a channel in a cylinder shape can be approximated as $2/r$. For rectangular columns with a length of l and widths of r_1 and r_2, S/V = $(2lr_1 + 2lr_2 + 2r_1r_2)/(lr_1r_2) = 2/r_2 + 2/r_1 + 2/l$. If the rectangular columns have open ends, S/V = $2/r_1 + 2/r_2$ and S/V = $4/r$ for $r = r_1 = r_2$. Here it can be recognized that S/V is proportional to κ/r, and that the proportional constant, κ, depends on the channel shape. If the channel shape is close to a sphere, S/V is close to $3/r$. But spherical shapes nullify any anisotropy, and $\Delta\nu_0$ becomes zero. Even if the channel shape is not spherical, the completely randomly oriented channels can result in zero $\Delta\nu_0$ under the condition that the structures ^2H_2O probed are interconnected enough for ^2H_2O to sense all of the structures and exchange deuterons in the NMR time scale. The $\Delta\nu_0$ values at the same water content would differ according to the degree of channel alignments. Therefore, κ is also a function of channel alignment or ordering degree.

When the channel volume is reduced by water content change, at least one dimensional length of the channel, for example, r, can be smaller than the anisotropic interaction length at some points. Then $\Delta\nu_0$ changes to a larger value than κ indicates. This can be expressed such that κ can also be a function of the smallest dimensional length of a channel relative to the anisotropic interaction length. Here, the diffusion path lengths can be taken as an example of anisotropic interaction lengths.

The plot of $\Delta\nu_0$ versus water content in wt% can be replaced with the plot of S/V of hydrophilic channels (κ/r) versus the hydrophilic channel volume ($V = n\pi r^2 l$, where n is the number of channels) if $\Delta\nu_0 = \kappa'/r$ and κ' is a proportional constant including the conversion constant for S/V to $\Delta\nu_0$. For simplicity, the same shape and size for all the channels were assumed. Increased r of a channel induces increased length of a neighboring channel not parallel to the channel. In addition, if the channel shape is not changed during swelling or shrinking, the ratio of r and l should be constant. Therefore, l can be replaced with εr, where ε is a proportional constant. This results in $V = n\pi r^2 l = n\pi\varepsilon r^3$. The expression can be rearranged to $r = (V/n\pi\varepsilon)^{1/3}$ and then $\Delta\nu_0 = \kappa'/r$ becomes $\Delta\nu_0 = \kappa'/(V/n\pi\varepsilon)^{1/3} = \kappa'(n\pi\varepsilon)^{1/3}V^{(-1/3)}$. Thus, the plot of $\Delta\nu_0$ versus water content is in the form of $Y = \delta X^{(-1/3)}$ where δ is a proportional constant. $\delta = \delta_1\delta_2\delta_3\delta_4$, where δ_1 is a proportional constant related with channel alignments; δ_2 is a proportional constant related with channel shapes; δ_3 is a proportional constant related with the smallest dimensional channel length relative to the anisotropic interaction length; and δ_4 is a proportional constant related with the ratio of l to r. Among δ_n (n = 1, 2, 3, and 4), only δ_3 can be a function of water content. When δ is not a function of water content, the plots of $\Delta\nu_0$ versus water content for different δ values would result in the same curve shapes with different slopes.

References

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(S2) Li, J.; Wilmsmeyer, K. G.; Madsen, L. A. *Macromolecules* **2009**, *42*, 255.

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