

Morphology of Water Transport Channels and Hydrophobic Cluster with Nafion Films Visualized with the AFM-IR Spectroscopy and Imaging Techniques

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The nanoscale distribution of distinctly different water molecules within a perfluorinated sulfonic acid polymer Nafion film has been chemically imaged for the first time [1]. By utilizing the newly developed AFM-IR microspectroscopy method [2], a direct chemical visualization was achieved of the water molecule domains based upon their characteristic water molecular OH-stretching vibrations.

The water structure within Nafion films has been the subject of numerous studies [3] in particular Fourier transform infrared (FT-IR) spectroscopic studies have been performed to look at the chemical structure of Nafion. Hydration FT-IR studies have shown that hydrated free (bulk-like) water, bH_2O , within the Nafion matrix has a peak IR absorbance at 3482 cm^{-1} . On the other hand, water bound to the hydronium ion, iH_2O , of which the OH-stretching vibrational mode is constrained due to interaction with the sulfonate ionic group has a peak absorbance at the lower wavenumber of 3211 cm^{-1} [4].

However, above-mentioned "traditional" FT-IR methods are unable to visualize water structure at such high resolution, as the nanoscale, because the spatial resolution is limited by the wavelength of the probe light which is $\sim 10\text{ }\mu\text{m}$ at best. AFM-IR which utilizes the photothermal induced resonance phenomena [5] allows for chemical infrared spectra to be obtained at spatial resolutions near 40 nm .

Figure 1 shows the AFM-IR chemical maps of the two OH-stretching peaks at 3482 and 3211 cm^{-1} measured at the same sample location. Clear distinctions in the distribution of the different water structural states were obtained. In Figure 1(a), the free (bulk-like) water, bH_2O , distribution showed thin string-like channels that elongate towards the lower right of the image. On the other hand, the bound water, iH_2O , peak shown in Figure 1(b), revealed an aggregated cluster structure that differed in distribution from that of the free water. The bound water was clustered at opposite ends of the free water channels. Figure 1(c) shows the AFM-IR spectra obtained at the two points, C1 and C2, which clearly confirms the intensity of the bound peak at C1 is lower than that of the clustered area at C2.

These AFM-IR chemical imaging results have revealed ionic bound water molecules, (3211 cm^{-1}) that were clustered in domains, while the hydrated free bulk-like water molecules, bH_2O , (3482 cm^{-1}) were found within transportable channels that linked these clusters.

Further work is planned to look at the hydration effect of these channels and clusters, which should provide invaluable information in understanding the proton exchange membrane through these water channels that are essential for development of more efficient fuel cells.

References

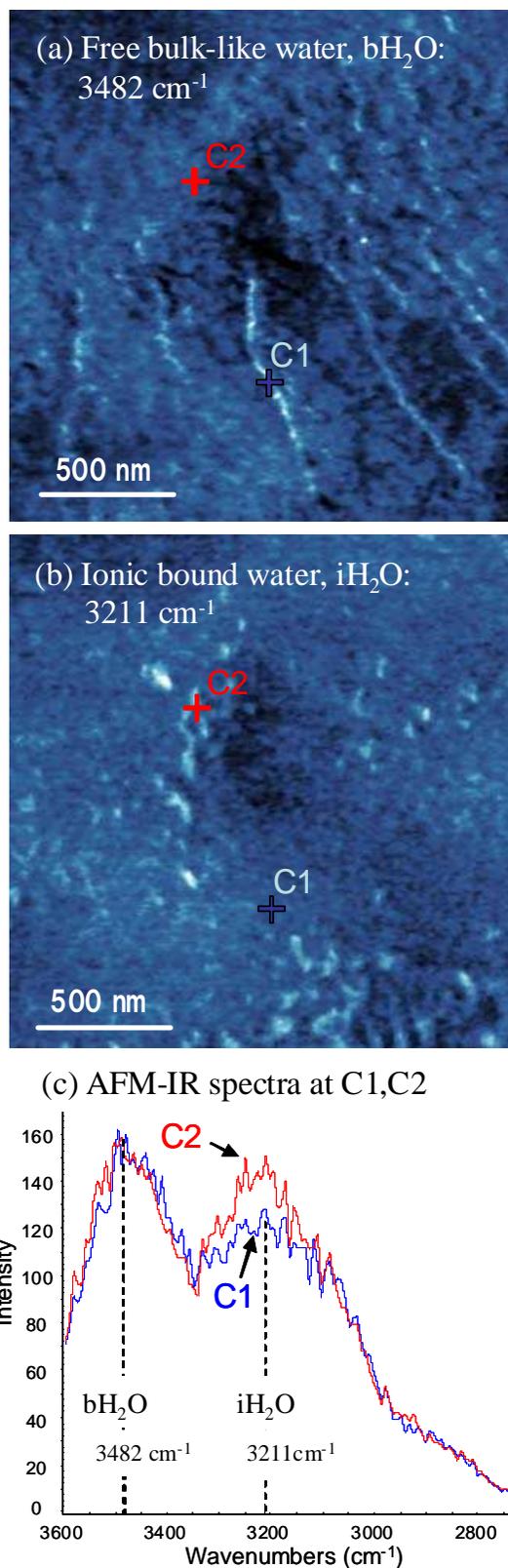
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Figure 1: AFM-IR chemical images of water within Nafion film. (a) free (bulk-like) water at 3482 cm^{-1} , bH_2O (b) bound ionic water at 3211 cm^{-1} , iH_2O (c) AFM-IR

spectra obtained at point C1 and C2.