Dynamics of hydrated anion exchange membrane

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The polymer electrolyte membranes used in polymer electrolyte fuel cells (PEFCs) are usually "proton-exchange" membranes that allow the permeation of protons. On the other hand, in anion exchange membrane fuel cells (AEMFCs), "anion exchange" solid polymers are used that allow hydroxide ions to permeate. One of the merits of AEMFC is to use non Pt metals, such as nickel and cobalt, as catalysts. However, AEMFCs do not have sufficient electrical conductivity. A major reason for their low power generation performance is that the anion-path is little known in the membrane. Continuing from 2021, QENS measurements of hydrated anion-exchange electrolyte membrane (QPAF-4) and Nafion were performed using AGNES spectrometer to reveal the localized fast motion of the side chain of the polymer and translational and rotational motions of adsorbed water. The list of the samples and measured temperatures is as follows:

1. QPAF-4 (H_2O, 60°C, 60%, 80%, and 90% RH)   288, 303, 318, 333, 348, and 363 K

2. QPAF-4 (D_2O, 60°C 60%, 80%, and 90 % RH)   333 K

3. Nafion (H_2O, 100°C, 80% RH)
   363, 373, 383, and 393K

The values in the parentheses indicate the temperature and relative humidity in adsorption equilibrium with H_2O or D_2O). For D_2O adsorbed hydrated membrane, polymer dynamics is mainly observed. The information of water dynamics is contained in H_2O adsorbed membrane.

The water adsorbed membrane was sealed in an aluminum cylindrical container. To observe a wide range of dynamics, QENS was measured with both 120 μeV (standard mode: ST) and 50 μeV (high-resolution mode: HR) energy resolutions. The Q range is 0.38-2.63 Å^{-1} (ST) and 0.29-2.03 Å^{-1}(HR). Dynamic structure factors obtained from quasi-elastic scattering measurements were fitted with one delta and one Lorentzian function. Q-dependence of the full-width half-width (FWHM) of the Lorentzian function is used to reveal the diffusion of protons, and the activation energy of the translation of the protons of the polymer film and water molecules is determined from the temperature dependence of the diffusion coefficient.

Figure 1 shows the Q-dependence of full-width half-maximum (FWHM) of the Lorentzian function for H_2O adsorbed QPAF-4. The FWHM is plateau at $Q^2 < 1.4$ Å^{-2} and increases over Q^2 of 1.4 Å^{-2}. This is a characteristic of confined diffusion of water molecule. The confinement size is estimated from the Q_0 value where the slope changes. The value is 5.3 Å ($=2\pi/Q_0$) at 303 K, and it increases with increasing temperature, indicating that the mobile space of water increases with temperature. On the other hand, the FWHM for D_2O adsorbed QPAF-4 is independent of Q. It could be assigned to the localized fast motion of the side chain of the polymer.

A molecular dynamics simulation of hydrated QPAF-4 is conduced to compare with the QENS result and extract the detailed information.
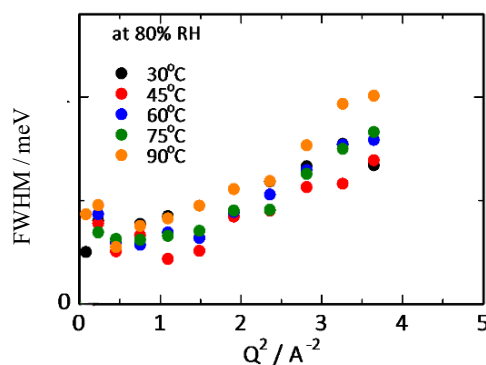

Fig. 1 Q-dependence of FWHM of the QENS componnet for QPAF-4 (60°C, 80% RH)