QENS study on dynamics of Mg-ion-conducting hydrous MOF

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There is strong demand for non-lithium-ion solid-state batteries, promising candidates of which are Mg ion batteries [1]. However, Mg ion exhibits suppressed conductivity in solids due to its strong electrostatic interactions with nearby anions.

MIL-101 is a kind of metal organic framework (MOF) with porous structure. Recently, Taniguchi et al. [2] reported that MIL-101 incorporating $Mg(TFSI)_2$ (TFSI: bis(trifluoro methanesulfonyl)imide) exhibits superionic conductivity of the order of 10^{-3} S cm^{-1} after absorbing water (WT) vapor. To understand the role of WT molecules in Mg-ion conduction, we investigated the WT molecular dynamics using quasielastic neutron scattering (QENS).

Three samples, bulk WT/$Mg(TFSI)_2$, MIL-101•52WT(WT-MOF), and MIL-101•1.6 $Mg(TFSI)_2$•47WT (WT-Mg-MOF) were measured on AGNES using the standard mode (energy range: $-4 < E < 20$ meV, Q range: $0.2 < Q < 2.7$ Å^{-1}, energy resolution: 140 μeV). The measurement temperatures are 300, 280, 260, 240, 220, 3 K for bulk WT/$Mg(TFSI)_2$, and 300, 280, 260, 240, 220, 200, 180, 3 K for WT-MOF and WT-Mg-MOF. The measurement time for each temperature is 3 h for bulk WT/$Mg(TFSI)_2$, and 6.5 h for WT-MOF and WT-Mg-MOF. Fixed window scan (FWS) was conducted for the three samples using the standard mode.

Figure 1 shows the temperature dependence of the normalized QENS spectra of the three samples. The spectra for all samples become broader with increasing temperature due to QENS broadening. The QENS spectra are fitted to the sum of a Lorentz function (rotational mode), a Fourier-transformed (FT) Kohlrausch-Williams-Watts (KWW) function (α-relaxation) and an elastic component (hydrogens in the MIL-101 framework). Figure 2 shows the fitting result for the WT-MOF sample.

The translational diffusion coefficients become smaller in order of bulk WT, bulk WT/$Mg(TFSI)_2$, WT-MOF and WT-Mg-MOF, indicating that WT diffusion is slowed down by the interaction with MIL-101 pore walls and Mg-ions. This is consistent with the proposed Mg^{2+} conduction mechanism, in which the diffusion of Mg^{2+} ions is assisted by the diffusion of WT molecules [2]. In future work, QENS experiments with higher energy resolution, dielectric relaxation measurements, and ionic conductivity measurements will be performed to clarify the relationship between WT molecular motion and Mg-ionic conduction.

[1] Hyun Deog Yoo, et al., *Energy Environ. Sci.* **2013,** 6, 2265-2279.
[2] Kaori Taniguchi, et al., 73rd conference of Japan Society of Coordination Chemistry (2023)

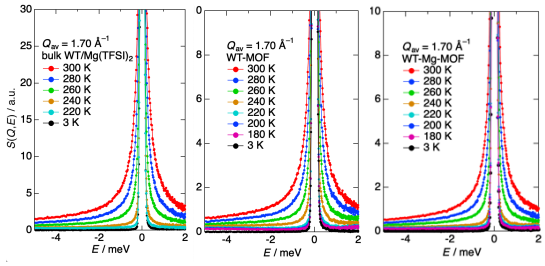

Fig. 1. Temperature dependence of QENS spectra of bulk WT/$Mg(TFSI)_2$, WT-MOF and WT-Mg-MOF.

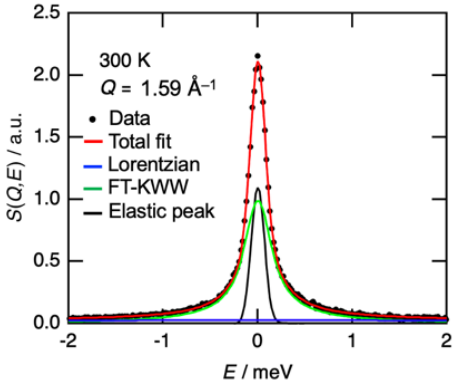

Fig. 2. Fit result of a QENS spectrum of WT-MOF, 300 K, Q = 1.59 Å^{-1}.