Fast proton dynamics in porous coordination polymer MIL-53

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The development of high-performance proton conductors is of great importance for hydrogen storage and fuel cell technology. We have developed proton conductors based on porous coordination polymers (PCPs) and investigated their physical properties by means of neutron scattering techniques [1, 2, 3, 4]. Recently, a new type PCP, M(OH)(bdc-R) [M = Fe, Al, bdc = 1,4-benzenedicarboxylate, R = NH_2, OH, $(COOH)_2$] was developed by Materials of Institut Lavoisier and named "MIL-53" (MIL = Materials of Institut Lavoisier). We have found that MIL-53 can be a good proton conductor by adsorbing not only water molecules but also ammonia molecules from their gas phases.

MIL-53(Fe)-$(COOH)_2$-$2H_2O$ and MIL-53(Fe)-$(COOH)_2$-$3NH_3$, which have the highest proton conductivity in the series, were measured on the TOFTOF spectrometer (FRM II, Germany) with an energy resolution of 16 μeV in the temperature range between 240 and 330 K. The peak broadening due to the quasielastic neutron scattering (QENS) was observed in the temperature range between 240 and 330 K for both samples. Figure 1 shows the QENS spectra of both the H_2O and NH_3 samples at $Q = 0.8$ Å^{-1} and $T = 300$ K. All of the QENS data were fitted well with a combination of delta and Lorentzian functions. The half width at half maximum (Γ) of the Lorentzian function does not depend much on Q, suggesting that the relaxations are of local motions and the proton conduction of is due to the Grotthuss mechanism. The temperature dependence of the relaxation times and the activation energy of the relaxation will be discussed after the QENS measurement on the slower time region.

References

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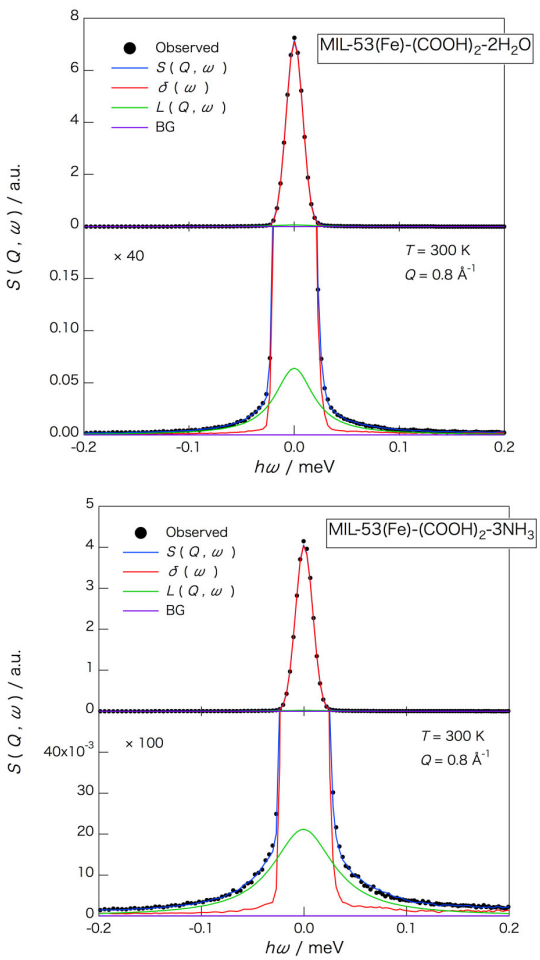

Fig. 1. QENS spectra of MIL-53(Fe)-$(COOH)_2$-$2H_2O$ and MIL-53(Fe)-$(COOH)_2$-$3NH_3$ measured on the TOFTOF spectrometer.