

## Slow 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<sub>2</sub>, OH, (COOH)<sub>2</sub>] 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. In this work, following the previous experiments on TOFTOF (FRM-II), we have measured the quasielastic neutron scattering (QENS) of MIL-53(Fe)-(COOH)<sub>2</sub>-2H<sub>2</sub>O and MIL-53(Fe)-(COOH)<sub>2</sub>-3NH<sub>3</sub> on HFBS (NIST) in the time range 10 ns to 0.1 ns which is longer than that of TOFTOF (0.1 ns to 1 ps).

We found clear QENS spectra also on HFBS. These data were fitted well with a combination of delta and Lorentzian functions and the relaxation times  $\tau$  were calculated from the relation  $\tau = 2\pi/\Gamma$ . Figure 1 shows the temperature dependence of the relaxation times for both H<sub>2</sub>O and NH<sub>3</sub> samples. Both data of TOFTOF and HFBS are plotted. Two relaxations with Arrhenius temperature dependence are found in each sample. It is of interest that their activation energies are smaller than those of bulk water (17 kJmol<sup>-1</sup>) and ammonia (8.7 kJmol<sup>-1</sup>) liquids. These small activation energies should be related to the high proton conductivities of the present materials. Another interesting aspect of these relaxation is that the relaxation intensity is small compared with those of

other PCP type proton conductors and increases with increasing temperature in both samples. This fact suggests that the water and ammonia molecules in excited (metastable) sites contribute to proton conduction mechanism. More detailed structural studies are required for further discussion.

### References

- [1] T. Yamada *et al.*, J. Phys. Chem. B **115**, 13563 (2011).
- [2] T. Yamada *et al.*, J. Phys. Soc. Jpn. **82**, SA010 (2013).
- [3] M. Tadokoro *et al.*, J. Phys. Chem. B **114**, 2091 (2010).
- [4] S. Miyatsu *et al.*, Phys. Chem. Chem. Phys. **16**, 17925 (2014).

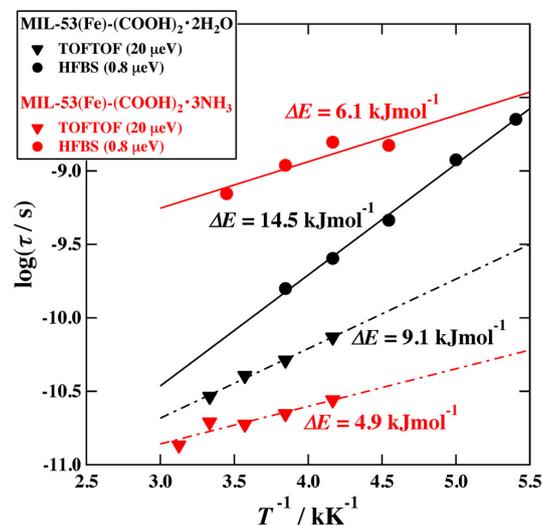


Fig. 1. Arrhenius plot for the relaxation times of MIL-53(Fe)-(COOH)<sub>2</sub>-2H<sub>2</sub>O and MIL-53(Fe)-(COOH)<sub>2</sub>-3NH<sub>3</sub>.