多孔性配位高分子を用いた新しいプロトン伝導体の中性子散乱研究

Neutron scattering study on new proton conductors based on porous coordination polymers

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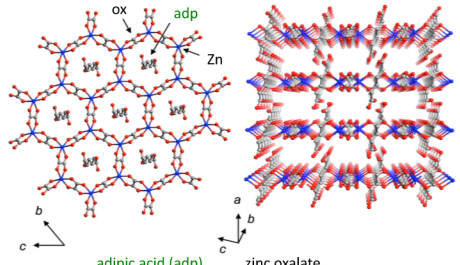
1. Introduction

Crystal Structures

Sadakiyo et al., J. Am. Chem. Soc. 131, 9906 (2009).

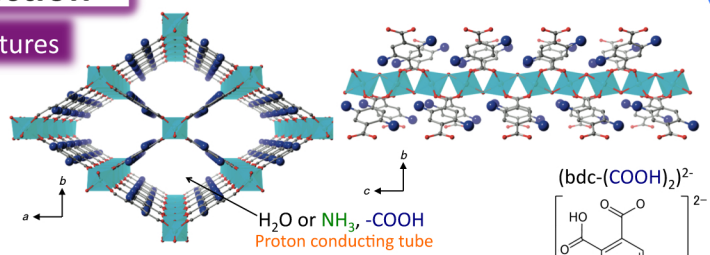


$(NH_4)_2[HOOC(CH_2)_4COOH][Zn_2(C_2O_4)_3]\cdot 3H_2O$ → ZnADP, $\sigma = 1.0\times10^{-2}$ Scm^{-1}

Proton carrier — Proton supplier — Proton carrier

substituted by K^+ → ZnKADP, $\sigma = 1.2\times10^{-4}$ Scm^{-1}

Shigematsu et al., J. Am. Chem. Soc. 133, 2034 (2011).



$Fe(OH)(bdc\text{-}(COOH)_2)\text{-}2H_2O$ → MIL-53(Fe)-$(COOH)_2$-$2H_2O$, $\sigma \sim 10^{-6}$ Scm^{-1}

Proton supplier — Proton carrier

$Fe(OH)(bdc\text{-}(COOH)_2)\text{-}3NH_3$ → MIL-53(Fe)-$(COOH)_2$-$3NH_3$, $\sigma \sim 10^{-5}$ Scm^{-1}

Proton carrier

Purpose To clarify proton dynamics and conduction mechanism by QENS

2. Neutron Spectrometers

Wide dynamic range!
0.1 ps - 10 ns (5 orders)

AGNES (TOF direct), ISSP, JRR-3
Energy resolution:
120 or 49 μeV (0.1 ps - 50 ps)
Energy window:
$-3 < E < 20$ meV

IRIS (TOF inverted), ISIS
Energy resolution:
17.5 μeV (10 ps - 500 ps)
Energy window:
$-1.3 < E < 4$ meV

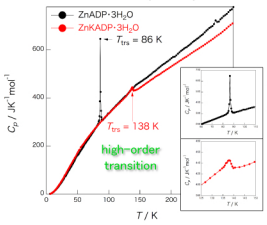
TOFTOF (TOF direct), FRM-II
Energy resolution:
20 μeV (10 ps - 500 ps)
Energy window:
$-1 < E < 0.6$ meV

HFBS (back scattering), NCNR
Energy resolution:
0.8 μeV (100 ps - 10 ns)
Energy window:
$-0.017 < E < 0.017$ meV

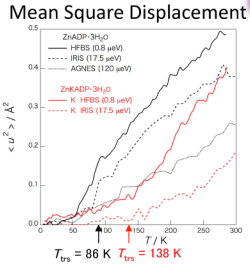
3. Results & Discussion

Phase Transitions

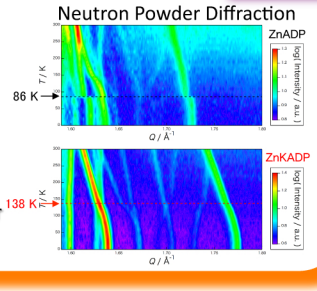
Heat Capacity



Mean Square Displacement



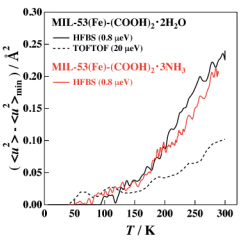
Neutron Powder Diffraction



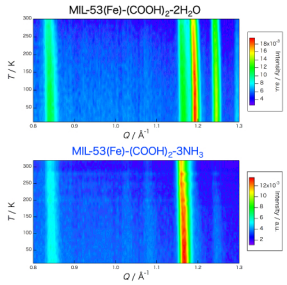
ZnADP $\Delta_{trs}S = 5.2$ JK^{-1}mol^{-1} → order-disorder

ZnKADP $\Delta_{trs}S = 1.9$ JK^{-1}mol^{-1} → displacive

Mean Square Displacement

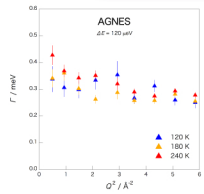


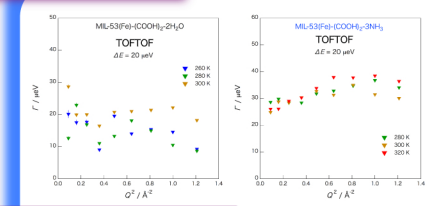
Neutron Powder Diffraction



No transition!

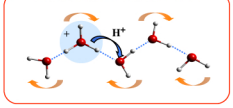
Q-dependence of HWHM



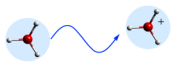


Independent of Q → local mode

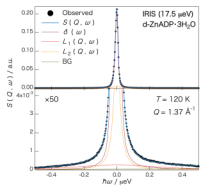
Grotthuss mechanism

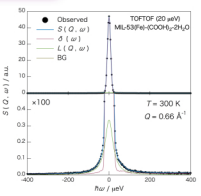


cf. Vehicle mechanism



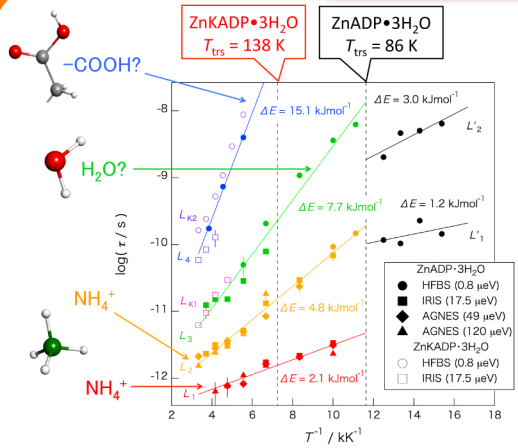
QENS Analysis



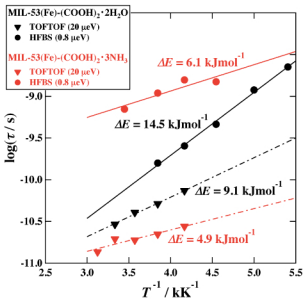


$$S(Q,\omega) = R(Q,\omega) \otimes \left[\delta(\omega) + \sum_i L_i(Q,\omega)\right] + \mathrm{BG}$$

Arrhenius Plots of Relaxation Times



Two fast relaxation modes of NH_4^+ with very small activation energy!!



$\frac{\text{QENS}}{\text{elastic} + \text{QENS}}$ is 7%(H_2O) & 11%(NH_3)

→ very small

cf. proportion of H atoms of H_2O and NH_3

MIL-53(Fe)-$(COOH)_2$-$2H_2O$ 44%

MIL-53(Fe)-$(COOH)_2$-$3NH_3$ 64%

4. Conclusion

ZnADP

High-order transitions associated with H atoms
ZnADP : 86 K ZnKADP : 138 K

Four relaxation modes found by QENS

Two fast relaxational motions of NH_4^+ with very small activation energy

MIL-53

Local motions of H_2O and NH_3 found by QENS

Number of moving molecules is small

Protons are carried by Grotthuss mechanism with not only H_2O but also NH_4^+, NH_3 molecules (ions)

→ New proton conduction mechanism