# Investigation of Local 3*d* Electronic States for Porous Coordination Polymers Studied by Soft X-ray Absorption Spectroscopy

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The dehydrate two dimensional porous coordination polymers (PCP) of $[M(H_2O)_2\{Ni(CN)_4\}]\cdot 4H_2O$ (***M*Ni-H₂O**; *M* = Mn, Fe, Co, Ni): $[M\{Ni(CN)_4\}]$ (***M*Ni**) have a chemical nature of the gate open pressure for water molecules. This nature may be correlated with the local symmetry of *M* ions between ***M*Ni-H₂O** and ***M*Ni** since the crystal structure can be changed due to the heating and cooling in the air [1]. However, it is difficult to determine the local symmetry of ***M*Ni** because of the amorphous PCP.

In this study, we carried out the $L_{2,3}$-edge X-ray absorption spectroscopy (XAS) to determine the local symmetry of *M* ions for ***M*Ni**.

The XAS measurements were carried out at BL-11 of Synchrotron Radiation Center in Ritsumeikan University, Japan. The $L_{2,3}$-edge XAS spectra of *M* ions were taken simultaneously in the total electron yield (TEY), partial fluorescence yield (PFY), and partial electron yield (PEY) modes with a photon energy resolution of ~500 meV.

These micro-crystal samples of ***M*Ni-H₂O** and ***M*Ni** were thinly expanded on the conductive carbon tape attached on the sample holder in the air for ***M*Ni-H₂O** and the Ar atmosphere for ***M*Ni** before transferring them into the vacuum chamber, respectively. We repeatedly measured the spectra on the same and different sample positions, confirming the data reproducibility with neither serious radiation damage nor sample-position dependence of the $L_{2,3}$-edge XAS spectra. Photon energy was calibrated by the top of the $L_3$-edge peak of $Mn_2O_3$ (641.5 eV), $\alpha$-$Fe_2O_3$ (709.7 eV), $LiCoO_2$ (780.2 eV), and NiO (854.0 eV) respectively. All measurements were performed at room temperature.

Figure 1 shows the $L_{2,3}$-edge XAS spectra of *M* ions in the PEY mode which is the most reliable for the quantitative discussion even though it is relatively surface sensitive reported by the previous XAS studies [2]. The sample color of ***M*Ni-H₂O** has been changed to ***M*Ni** when due to the high vacuum (Vacuum in the Fig.1). Actually, since the spectra of ***M*Ni-H₂O** have the same spectra as those of ***M*Ni** (Heated in the Fig.1), we consider that the water molecule in ***M*Ni-H₂O** was dehydrated into a vacuum.

What an interesting point is the different dehydration time by vacuum between ***M*Ni-H₂O** with *M* = Mn, Fe, Co and **NiNi-H₂O**. The change in the shape of the XAS spectra, it was found that while ***M*Ni-H₂O** with *M* = Mn, Fe, Co were completely hydrated in ~30 minutes under high vacuum, **NiNi-H₂O** took as long as ~5 hours. we consider that this different dehydration time is due to the electronic state of *N*-coordinating *M* ions coordinated with water molecules.

## References

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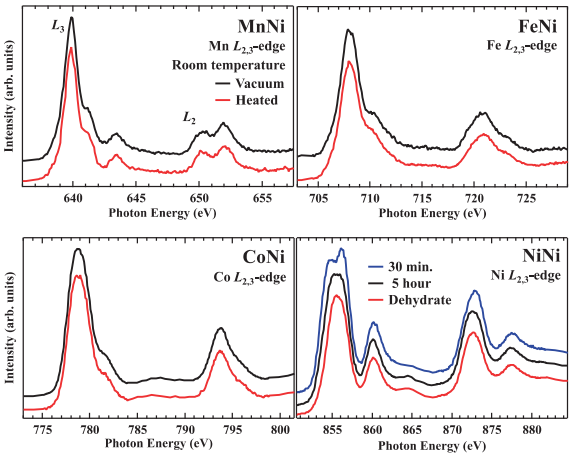


**Fig. 1** The $L_{2,3}$-edge XAS spectra of *M* ions in the PEY mode at room temperature.