

Battery reaction mechanism of disulfide ligands in metal organic frameworks

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Molecular cluster battery (MCB) using a polynuclear metal complex molecule (molecular cluster) as a positive electrode active material exhibits higher discharge capacity than the conventional lithium-ion battery. This is because $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ which is one of molecular clusters reduces as much as 24 electrons for discharge reaction¹. To develop MCB, we prepared the metal organic framework (MOF) in which these clusters are connected with an organic ligand having redox active anthraquinone, and realized the stable cycle property and the high capacity due to the stable structure with the pore in MOF and dual redox reactions of metal ion and ligand². We further prepared the active material containing 4,4'-dipyridyl disulfide (4dpds) which is one of the disulfide ligands and Cu ion, DS-Cu-MOF, which improves the charge-discharge characteristic³. In this study, we prepare MOF-based active materials which contains 4dpds and Co ion (DS-Co-MOF). For the analysis of the charge-discharge mechanism in DS-Co-MOF, the S-S bond change is investigated by S *K*-edge X-ray absorption spectroscopy.

As the active materials of a positive electrode for lithium-ion battery, DS-Co-MOF was used. After the charged or discharged cells were disassembled in the glove box, the electrodes were fixed to the sample holder in the transfer vessel by using carbon tape. Then, the samples were transferred to the measurement chamber for S *K*-edge XAFS. The XAFS measurements in a fluorescence mode were performed at BL-13 in SR Center, Ritsumeikan University. KTP (011) was used as the monochromator crystal.

S *K*-edge XANES spectra for the pristine, discharged and charged DS-Co-MOF electrodes were measured. For the pristine sample, the two peaks were observed. One on the low energy side corresponds to $1s \rightarrow \sigma^*$ transition (S-S bond) and the other on the high energy side is attributed to $1s \rightarrow \sigma^*$ transition (S-C bond). For the discharged sample, one broad peak was observed. For the charged sample, the structure is almost same with the pristine. Because the 4dpds disulfide ligand in

the MOF has S-C and S-S bonds, the two peaks can be attributed to each bond. On the other hand, as the S-S bond was cleaved by two-electron reduction of this ligand by discharge, only one peak attributable mainly to S-C bond was observed after discharge. Because the XANES structure of the charged sample is similar to the pristine, the S-S bond was almost reversibly reformed by charging accompanied by two electron oxidation.

In the S *K*-edge EXAFS Fourier Transformation, the peak position observed at 1.8 Å in the pristine and charged samples was shifted to 2.0 Å for the discharged sample, which might be induced by the cleavage of S-S bond. For the discharge-charge cycle, the peak behavior exhibits the reversible change. In the case of only 4dpds ligand not included in the MOF structure, the change in the S *K*-edge XAFS in the charge-discharge reaction is not reversible. Therefore, for the charge-discharge reaction in DS-Co-MOF, two-electron redox reaction of disulfide ligand accompanied by reversible cleavage / formation of S-S bond occurs in the MOF structure. This result represents that incorporation of molecular cluster into the MOF structure can be a useful tool for achieving high capacity and stable cycle characteristics of disulfide compounds.

References

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