

## Relationship between structures and battery performances of MOFs with disulfide moiety-containing ligands

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Lithium-sulfur batteries using sulfur as cathode are interesting because of their high theoretical energy density. However, lithium polysulfide formed by the cleavage of the S-S bond during discharge tends to dissolve in the electrolyte solution, resulting in poor cycle capability. It is essential to realize the reversible redox reaction of the S-S bond which is the minimum unit of sulfur. In this study, we propose to use a metal organic framework (DS-MOF), in which disulfide ligands are coordinated to metal ions, as a cathode material. The purpose of this study was to clarify the correlation between the structure and the battery performance by examining the reversibility in the electrochemical reaction of the S-S bond by S K-edge X-ray absorption fine structure (XAFS) analyses.

Lithium metal batteries using DS-MOFs ( $[\text{Cu}_4(\text{HCO}_2)_6(\text{OH})_2(4\text{dpds})_2]_n$  [1],  $[\text{Mn}_5(2\text{dtba})_4(\text{OH})_2]_n$  [2],  $[\text{Co}(\text{NCS})_2(4\text{dpds})_2]_n$  [3], and  $[\text{Mn}_2(6\text{dtna})_2(\text{H}_2\text{O})_2]_n$  [4]) as cathodes were charged-discharged for 50 cycles. S K-edge XAFS measurements of cathodes before and after charge/discharge were performed by using the partial fluorescence mode or the total electron yield mode at Ritsumeikan University SR Center BL-13.

DS-MOFs:  $[\text{Cu}_4(\text{HCO}_2)_6(\text{OH})_2(4\text{dpds})_2]_n$ , and  $[\text{Mn}_5(2\text{dtba})_4(\text{OH})_2]_n$  with small pores show lower capacities than the theoretical values. On the other hand, DS-MOFs having a large pore size:  $[\text{Co}(\text{NCS})_2(4\text{dpds})_2]_n$ , and  $[\text{Mn}_2(6\text{dtna})_2(\text{H}_2\text{O})_2]_n$  exhibited capacities close to the theoretical value. It is suggested that lithium ions are easily inserted into DS-MOFs having a large pore and that a redox reaction of metal ion and S-S bond occurs. In addition, the capacity retention after 50 cycles is 49% for  $[\text{Co}(\text{NCS})_2(4\text{dpds})_2]_n$ , whereas it is 75% for  $[\text{Mn}_2(6\text{dtna})_2(\text{H}_2\text{O})_2]_n$ . This result indicates that the three-dimensional DS-MOFs suppresses the dissolution of DS-MOFs, resulting in stabilization of the cycle performances of the S-S bond.

In S K-edge XAFS of DS-MOFs having a small pore, the peak attributed to  $\sigma^*$  (S-S bond, 2472 eV) was observed before/after charge/discharge, and did not change in the discharge process. The S-S bond didn't undergo a redox reaction because the insertion of lithium ions does not occur in the discharge process when the pore volume is small. In  $[\text{Co}(\text{NCS})_2(4\text{dpds})_2]_n$ , the peak derived from the NCS ligand was observed after the discharge, but the peak

from  $\sigma^*$  (S-S bond) was not observed. After charging, a spectrum is similar to that before charging/discharging. In  $[\text{Mn}_5(2\text{dtba})_4(\text{OH})_2]_n$ , the peak intensity of  $\sigma^*$  (S-S bond) becomes small in the discharge process, and the spectrum after recharging is similar to that before and after charge/discharge. The reversible change of the spectra indicates the reversible cleavage/reformation of the S-S bond. The reversible change of S-S bond in charge/discharge process is due to our reported electrochemical change of S-S bond in MOFs [5], and then the capacity is close to the theoretical value.

It was found that the presence of pores promotes the redox reaction of the S-S bond, and the dimensionality of the structure becomes a factor that determines the cycle performances of the S-S bond. Also, it was clarified that high capacity and stable cycle performances can be realized by the reversible redox reaction of S-S bond in DS-MOFs with a large pore.

### References

- [1] T.-W. Tseng, T.-T. Luo, Y.-R. Shih, J.-W. Shen, L.-W. Lee, M.-H. Chiang and K.-L. Lu, *CrystEngComm*, **2015**, 17 (14), 2847-2856.
- [2] S. M. Humphrey, R. A. Mole, J. M. Rawson and P. T. Wood, *Dalton Trans.*, **2004**, 0 (11), 1670-1678.
- [3] N. D. Pinta, L. Fidalgo, G. Madariaga, L. Lezama, and R. Cortés, *Cryst. Growth Des.*, **2012**, 12(10), 5069-5078.
- [4] R. Carballo, B. Covelo, N. F.-Hermida, A. B. Lago and E. M. V.-López, *CrystEngComm*, **2009**, 11(5), 817-826.
- [5] T. Shimizu, H. Wang, N. Tanifuji, D. Matsumura, M. Yoshimura, K. Nakanishi, T. Ohta, H. Yoshikawa, *Chem. Lett.*, **2018**, 47(5), 678-681