

Electronic states and structures of Mn12 molecular cluster batteries

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Introduction

To innovate novel batteries with high efficiency and capacity, we have recently developed a rechargeable molecular cluster battery^[1] using a cathode consisting of Mn12 cluster $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ (abbreviated as Mn12Ac), a well-known material as a single molecule magnet (SMM). This battery exhibited a repeatable charging/discharging process with a capacity of ca. 100 Ah/kg, after the anomaly in the first discharging showing an extremely high value of 200-250 Ah/kg, that was higher than that of a usual lithium ion battery (ca. 180 Ah/kg). In the present research, we performed X-ray absorption fine structure (XAFS) analyses on the cathode materials of the molecular cluster batteries, leading to the elucidation of the battery reaction mechanism.

Experimental

The cathode materials were prepared by mixing conductive carbon fiber (VGCF) with 30wt% Mn12Ac. Then we fabricated the molecular cluster batteries with Li metal as an anode, and tested their charging-discharging properties. Before and after the battery tests, the cathode materials were examined by XAFS measurements with a conventional transmission mode at 30 K.

Results and discussion

From the Mn *K*-edge XANES spectra of the cathode materials, the oxidation state of Mn in Mn12Ac was estimated using a relationship that the threshold energy position of the absorption edge is proportional to the Mn oxidation state. When the Mn12Ac battery is fully charged, the average valence is obtained to be 3.2, which is smaller than 3.5 for the neutral Mn12Ac. After discharging, the value decreases to be 2.9 and return to the original value by charging. Since Mn12 includes twelve Mn ions, so that the difference of 0.3 suggests 3 or 4 electrons reduction/oxidation per one molecule during charging/discharging. This value can roughly explain the capacity of ca. 100Ah/kg.

The local structures such as Mn-Mn and Mn-O bond distances in Mn12Ac were estimated by EXAFS. Figure 1 shows the results of the Fourier transforms of the raw data. The neat Mn12Ac (bottom) exhibits the peaks at 2.4 and 3.2 Å, which are attributable to short and long Mn-

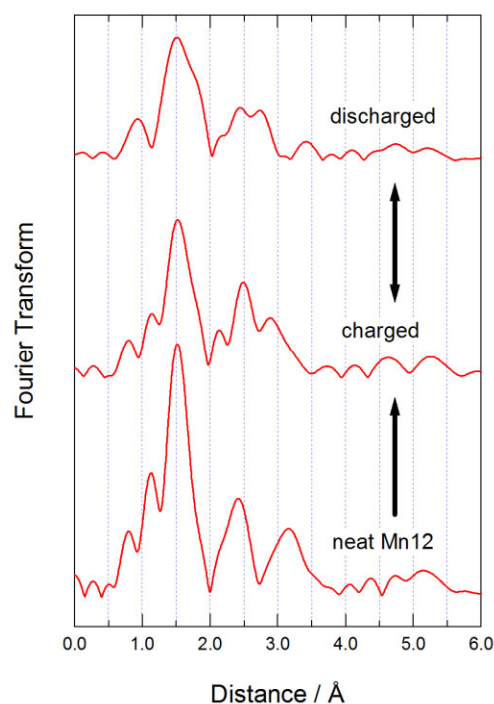


Figure 1. Fourier transforms of Mn *K*-edge EXAFS functions for the neat Mn12Ac and the cathode materials.

Mn distances, respectively. The intermediate curve shows the results for the charged state, which are different from that of the neat Mn12; the peak at 2.4 Å is slightly shifted to the longer distance side, and the peak at 3.2 Å disappeared. The top curve indicates the results for the discharged state, which is obviously different from neither those for the neat Mn12Ac nor those in the charged state

In summary, XAFS studies revealed that Mn12Ac in the cathode materials exhibits a reversible redox reaction through the charging/discharging process.

Reference

[1] H. Yoshikawa et al., *Chem. Commun.*, 3169-3170, (2007)

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