

In situ XAFS studies on Mn12 Molecular Cluster Batteries

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Introduction

To achieve next generation batteries with both high capacities and fast charging/discharging, we have recently proposed molecular cluster batteries (MCBs), where polynuclear metal complex clusters (molecular clusters) that undergo multi-step redox reactions were used as cathode active materials and lithium metal was used as an anode. So far we fabricated the MCBs of Mn12Ac [Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄], exhibiting an extremely high capacity of ca. 200 Ah/kg, which is higher than that of the usual lithium ion batteries.^{[1],[2]}

In the present study, we performed in situ Mn *K*-edge XAFS measurements of the Mn12 MCBs, developing a battery reaction cell, and investigated the valence state and local structure of the Mn ions in the battery reaction to reveal the microscopic mechanisms of their battery performance.

Experimental

We developed a battery reaction cell for in situ XAFS studies. In situ Mn *K*-edge XAFS spectra were recorded in a transmission mode at the beam line BL-12C of the Photon Factory in KEK, Tsukuba, Japan. The in situ cell was placed between two transmission ion chambers. During in situ XAFS measurements, the area of the cathode subjected to X-ray, was ca. 1 mm × 1 mm. To avoid chemical decomposition of Mn12 by X-ray, a Quick-XAFS (QXAFS) method was adapted, by which one spectrum was obtained within 60 sec. During the charging/discharging reaction (2.0 – 4.0 V) in the first two cycles, we performed the measurements with an interval of 15 mins.

Results and discussion

Figure 1 shows the XANES spectra for the second charging/discharging processes. They exhibit a systematic change with an isosbestic point at 6555eV. The neutral Mn12 molecule consists of eight Mn³⁺ and four Mn⁴⁺ ions, and the presence of the isosbestic point means that only one of the Mn³⁺ or Mn⁴⁺ ions exhibits a valence change in this battery reaction.

The averaged valence N_v of the Mn ions in Mn12 was obtained from the edge energy. The initial value of N_v before the first charging is 3.3, which agrees with that of the neutral Mn12 (3.33). After the first charging, N_v shows only a slight increase to 3.5, which is consistent with the small changes in voltage and capacity in the first

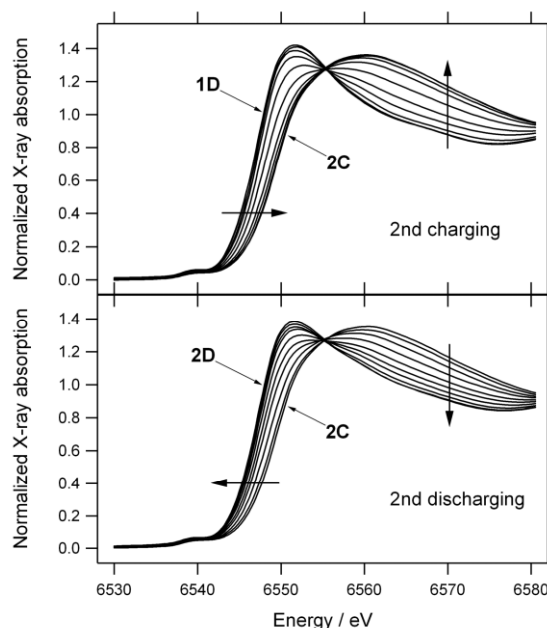


Figure 1. Evolution of the normalized in situ Mn *K*-edge XANES spectra for Mn12 MCBs during the first two cycles.

charging. The first discharging brings about a quick decrease in N_v , and the value reaches 2.5 at $V = 3.0$ V. Unexpectedly, N_v becomes constant in the range of 3.0–2.0 V, though the discharging curve still exhibits a capacity. The second charging increases the value of N_v from 2.5 to 3.3 after a plateau in the range of 2.0–3.0 V. This behavior is consistent with that in the discharging process. The N_v change by 0.9 during the first discharging indicates an approximately ten-electron reduction per one Mn12 molecule, and corresponds to a battery capacity of ca. 100 Ah/kg. Another half of capacity in the voltage range of 2.0–3.0 V can be explained by not a redox change of the Mn ions but a capacitance effect such as electrical double layers at the interface between microcrystals of Mn12 and carbon materials.

EXAFS analyses suggested that the Mn12 core structure is maintained in the charging/discharging (oxidation/reduction) processes.

References

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