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XAFS Studies on Charging-Discharging Processes in Molecular Cluster Batteries

Hirofumi YOSHIKAWA* [1], Shun HAMANAKA [1], Yasuhito MIYOSHI [1],
Toshihiko YOKOYAMA [2] and Kunio AWAGA [1]

[1] Research Center for Materials Science & Department of Chemistry, Nagoya University, Furo-cho,
Chikusa, Nagoya, 464-8602, Japan
[2] Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Introduction

Recently, much attention has been focused on the creation of new energy systems, such as high-performance rechargeable batteries, as a solution to the global energy and environmental crises. Redox active molecular materials are good candidates for a high-performance cathode active material. To achieve both high capacity and fast charging/discharging, we have previously proposed the use of polynuclear metal complex clusters (molecular clusters that are small aggregates of metal ions connected by organic ligands) that undergo multi-step redox reactions as a cathode active material for lithium batteries In our previous paper,[7] we reported the fabrication of a molecular cluster battery (MCB) in which the cathode active material is $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (abbreviated as Mn12Ac).

Here we carried out ex situ XAFS analyses on the charging/discharging processes of the Mn12-MCBs to reveal the microscopic mechanisms of their battery performance. XAFS analysis is an appropriate technique for observing valence changes and local structures of nanoscale or highly disordered compounds such as battery active materials.

Experimental

We performed XAFS measurements on the cathode material after the 1st charging (**1C**)/discharging (**1D**) and after the 2nd charging (**2C**)/discharging (**2D**). These samples were prepared separately; after the charging/discharging operation, each sample was taken from the coin cell and was subjected to the ex situ XAFS.

Results and discussion

Figure 1 shows the Mn K-edge XANES spectra of **1C**, **1D**, **2C**, **2D** and as-prepared Mn12Pe^t. The spectrum of **1C** is similar to that of Mn12Pe^t, but, after the first discharging, the spectrum of **1D** is significantly different from that of **1C**. The spectra of **2C** and **2D** are nearly the same as those of **1C** and **1D**, respectively. From the absorption edges of Mn12Pe^t, **1C**, **1D**, **2C**, and **2D**, which are defined as the point of the largest gradient of the absorption curve, their average Mn valences are calculated, as shown in Figure 1. There is no significant valence change between Mn12 Pe^t and **1C**, which is in agreement with the small voltage change in the first charging. It is considered that Mn12Pe^t in the as-prepared battery is in the neutral state. The average valence shows
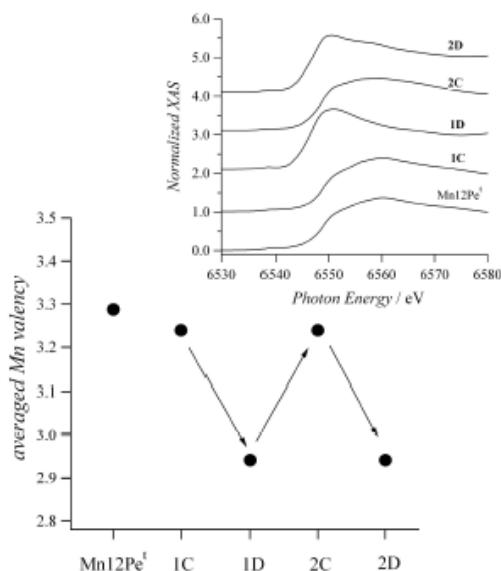

Figure 1. Averaged Mn valence (Inset : Normalized Mn K-edge XANES spectra)

a decrease of 0.34 after the first discharging (**1D**), and returns to the original value after the second charging (**2C**). A good repeatability is observed in the change from **2C** to **2D**. The valence change of 0.34 per Mn atom indicates that one Mn12Pe^t molecule exhibits a valence change of ca. 4 in the discharging/charging processes. Based on this value, the theoretical value of the battery capacity is predicted to be ca. 40 Ah/kg, which is much smaller than the large capacity (ca. 150 Ah/kg) in the first run, but is comparable to those after the eighth cycle. It is hard to explain the large capacity in the first cycle, but a possible reason for the excess capacity is the formation of electrical double layers at the interface between microcrystals of Mn12.

EXAFS analyses were also performed in order to reveal structural changes in the Mn12Pe^t molecule. The EXAFS spectra suggest a significant structural change of Mn12Pe^t which is, however, repeatable in the redox process.

Reference

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

* yoshikawah@mbox.chem.nagoya-u.ac.jp