

In Situ Seamless Magnetic Measurements for Solid-State Electrochemical Processes in Prussian Blue Analogues

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1 Introduction

Recently, we have developed a novel rechargeable battery, "molecular cluster battery (MCB)", in which the cathode comprises polynuclear metal complexes (molecular clusters) such as polyoxometalates (POMs). It was found that these MCBs can exhibit higher battery capacities than conventional lithium ion batteries. In operando XAFS studies on MCBs of Mn12 and POMs revealed that they exhibit 8 and 24 electron reductions in their discharge, respectively. This means that such super-reduced species ($[\text{Mn}_{12}]^{8-}$ and $[\text{POM}]^{27-}$) are new materials that can be obtained only by solid-state electrochemistry, and it is expected that such electrochemically super-reduced compounds would exhibit novel physicochemical properties. In the present work, we developed an in situ magnetic measurement system under solid-state electrochemical reactions, and applied it to a mixed-valent chromium PBA ferrimagnet with a high T_c of 215 K. Herein, we describe a seamless change in magnetism during a solid-state electrochemical reduction of this compound.

2 Experiment

The quartz battery cell for in situ magnetic measurements with the size of $15 \times 7 \times 5$ mm was fabricated, to fit inside a commercial SQUID susceptometer. This small battery cell consists of an anode (Li), a separator, and a cathode including the Cr PBA. The cathode was prepared as follows: the PBA (10 wt%) and conductive carbon black (70 wt%) were mixed with polyvinylidene difluoride (20 wt%) as a binder. The cell was connected to a charge/discharge device, and then inserted into the SQUID. In situ magnetic measurements were performed as follows: the battery of the PBA was charged or discharged by leading or taking out, respectively, a constant current density of 0.1 mA in the SQUID at room temperature (3.5-1.7 V). At specific voltages versus lithium, we opened the circuit to keep the voltage constant and carried out variable-temperature magnetic measurements under a field of 10 kOe.

This electrochemical processes were examined by in operando Cr K-edge XANES measurements during the charging/discharging, using a special battery cell with an X-ray window in the center, which we developed previously, with a transmission mode at room temperature at the BL-9C of the Photon Factory in KEK.

3 Results and Discussion^[1]

Figure 1 shows the evolution of the temperature dependences of the magnetization for the PBA as a function of voltage. These magnetization values were obtained by subtracting the background contributions

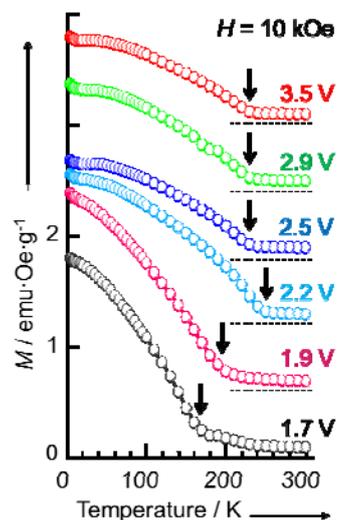


Fig. 1 Temperature dependences of the magnetization for the Cr PBA at various voltages in the discharge.

from the quartz cell and lithium metal. The temperature dependence of the magnetization in the voltage range of 3.5-2.5 V exhibits a quick rise below 215 K. This behavior is the same as that of the initial sample, and the change at 215 K is assigned to a ferrimagnetic transition. In this voltage range, there is no change in temperature dependence of the magnetization. This is consistent with the results of XANES, no electrochemical reaction above 2.5 V. As the voltage decreases from 2.5 V, the transition temperature appears to increase up to 2.2 V and to decrease significantly below that. The observed electrochemical magnetic change in the range of 2.5-1.7 V can be explained by the reduction of Cr ions in the PBA: the valence reduction of Cr ions resulted in changes of both spin numbers and magnetic interactions between Cr ions bridged by CN ligand in the PBA. This phenomenon is consistent with the fact that the valence of Cr ions changes only in the voltage of 2.5-1.7 V.

We succeeded in controlling the redox state of the PBA by solid-state electrochemistry (battery reaction), and observed its seamless magnetic variation.

References

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