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Enhanced Capacitor Effects in Polyoxometalate/graphene Nanohybrid Materials Revealed by Operando XAFS

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1 Introduction

Recently, we have proposed a novel rechargeable battery, "molecular cluster battery (MCB)", in which the cathode comprises polynuclear metal complexes (molecular clusters), and the anode is lithium metal. It is expected that MCBs would show a high capacity and a rapid charging/discharging due to multi-electron redox reactions of the molecular clusters and quick lithium-ion diffusion, respectively. So far we have reported that the MCBs of a representative Keggin-type POM, (tetrabutyl ammonium)$_3$[$PMo_{12}O_{40}$], exhibited a higher battery capacity of ca. 260 Ah/kg, compared with those of the usual lithium ion batteries (LIBs) (150 Ah/kg). Operando XAFS studies on this POM-MCB demonstrated a twenty-four-electron reduction from $[PMo(VI)_{12}O_{40}]^{3-}$ to $[PMo(IV)_{12}O_{40}]^{27-}$ during discharge, which can explain the observed high battery capacity [1]. However, since the cathode was a mixture of the microcrystals of POMs and carbon black (CB) combined by a binder in the initial experiments, the battery performance was considered to suffer from frictional penetration/removal of Li^+ into/from the microcrystals and from non-smooth electron transfer between POMs and electrodes. In this work, to improve these drawbacks, we prepared nanohybrid materials between POM and graphene (RGO) (see the inset of Fig. 1), and examined their performance as cathode active materials for MCBs. Finally, operando Mo K-edge XAFS measurements on these nanohybrid MCBs revealed the cooperative enhancement of the capacitor effects in the POM/RGO hybrid materials.

2 Experiment

The 1:2 POM/RGO hybrid materials were prepared by simply mixing an acetonitrile solution of the POM and a toluene suspension of the as-prepared RGO under vigorous stirring at room temperature. Then, the cathode was made by mixing this hybrid material, CB, and polyvinylidenefluoride (PVDF) at a weight ratio of 30:50:20. After fabricating the coin cell battery by using this cathode and a lithium foil as an anode, the charge/discharge measurements were carried out in the voltage range of 1.5 - 4.2 V at 1.0 mA.

For operando XAFS measurements, the battery was fabricated in a similar way using a special battery cell with an X-ray window in the center, which we developed previously [1]. During the charging/discharging tests at a constant current of 1.0 mA, in operando Mo K-edge XAFS spectra were recorded in the energy range from 19498.9 to 20003.9 eV with a transmission mode at room temperature, using the beam line BL-NW10A of the PF-AR in KEK, Tsukuba, Japan..

3 Results and Discussion

The charge/discharge tests demonstrated that the POM/RGO-MCBs exhibited a higher battery capacity than the microcrystal POM-MCB by ca. 200 Ah/kg.

To understand the enhanced capacity of the POM/RGO MCB, operando Mo K-edge XAFS measurements were carried out during the charge/discharge processes of the POM/RGO-MCB. The open circles in Fig. 1 show the averaged valence N_v of the Mo ions in this MCB during discharge, which were estimated from the edge energies of the Mo K-edge XANES spectra. Figure 1 also shows the data for the microcrystal POM-MCB (closed circles), which were obtained previously [1]. The values of N_v for this MCB show a decrease from 6.0 to 4.0 in the voltage range of 3.5-1.5 V. This change in N_v by 2.0 means that all the $12Mo^{6+}$ ions in POM are reduced to Mo^{4+}; namely, one POM molecule can store 24 electrons, which agrees with the observed battery capacity for the microcrystal POM-MCB (260Ah/kg). In contrast, the POM/RGO-MCB exhibits a much smaller change in N_v; the initial value of 6.0 decreases to 5.2 at 1.5 V, indicating that the POM molecules are not fully reduced at this voltage. These results indicated that the enhanced capacity for the POM/RGO-MCB is caused by a significant increase in the capacitor effects, which overcomes the decrease in the redox capacity, which suggests that a synergetic approach to combine a chemical battery and supercapacitor is useful toward high-performance energy storage devices.

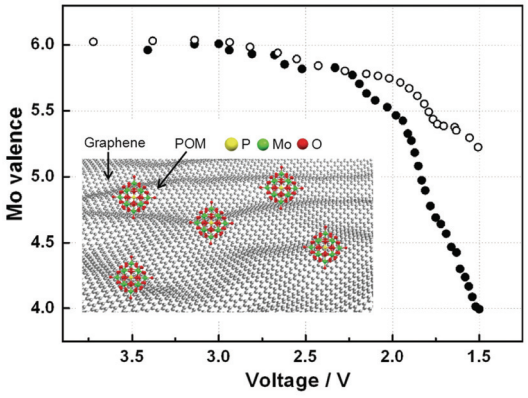

Fig. 1: Averaged Mo valence of the POM as a function of the cell voltage. (the inset: a structure of the POM/RGO)

Reference

[1] H. Yoshikawa, *J. Am. Chem. Soc.,* **134**, 4918 (2012)

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