

In operando XAFS Studies of Polyoxometalate Molecular Cluster Batteries: Polyoxometalates as Electron Sponges

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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. Among of molecular clusters, polyoxometalates (POMs) have attracted much attention due to their various properties, such as photoluminescence, catalytic activity, and single-molecule magnetism. They are also reported to operate as a cathode-active material of high-capacity lithium batteries, though the valence and structural changes of the POMs in the battery reaction has not yet been investigated. In the present study, we performed in operando Mo K-edge XAFS measurements on the MCBs of a representative Keggin-type POM, (tetrabutyl ammonium)₃[PMo₁₂O₄₀].

2 Experiment

For in 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 Photon Factory Advanced Ring (PF-AR) in KEK, Tsukuba, Japan.

3 Results and Discussion

The XANES analysis indicates that the reduction from Mo⁶⁺ to Mo⁴⁺ takes place at the twelve Mo⁶⁺ sites in one molecule, forming the super-reduced species, [PMo₁₂O₄₀]²⁷⁻, after the twenty-four-electron reduction. In contrast, it is known that the usual solution electrochemistry can produce only two- or three-electron reduction species of [PMo₁₂O₄₀]³⁻ in the typical electrochemical windows of solvents. The [PMo₁₂O₄₀]³⁻ can be regarded as a molecular "electron-sponge" in solid-state electrochemistry.

As shown in Fig. 1(a), the EXAFS analyses exhibited four main peaks at 1.1, 1.6, 2.3, and 3.2 Å in the initial and charged state. They were assigned to an Mo=O double bond (1.7 Å), two kinds of Mo–O single bonds (1.9 and 2.4 Å), and an Mo–Mo distance (3.4 Å) in

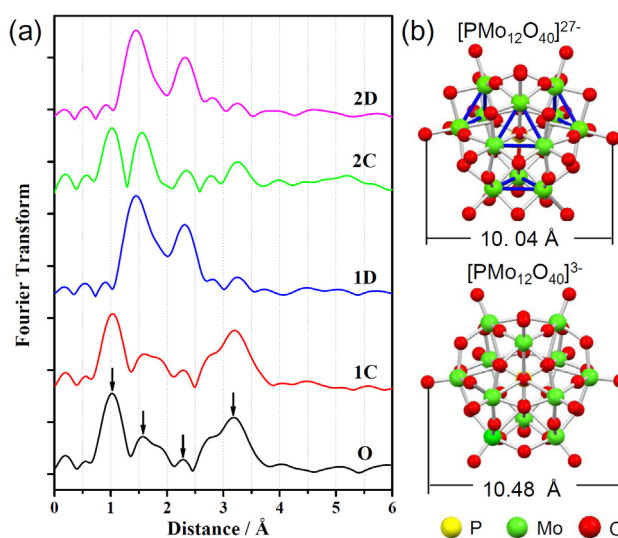


Fig. 1 (a) EXAFS spectra of the initial (O), 1st charge/discharge (1C, 1D), and 2nd charge/discharge (2C, 2D), (b) Structures of [PMo₁₂O₄₀]²⁷⁻ and [PMo₁₂O₄₀]³⁻.

[PMo₁₂O₄₀]³⁻, respectively. However, after the discharging, the peaks at 1.1 and 3.2 Å become very small, and those at 1.6 and 2.3 Å are significantly enhanced (Fig. 1(a)). The curve-fitting for the EXAFS spectra suggested that the distances of Mo–O and Mo–Mo become ca. 2.0 and 2.6 Å, respectively, after discharging. By taking account of these changes from the original [PMo₁₂O₄₀]³⁻ structure, we estimated a molecular structure of the super-reduced species, [PMo₁₂O₄₀]²⁷⁻. This structure is slightly reduced in size from the original one; the maximum dimension of the [PMo₁₂O₄₀]³⁻ decreases from 10.5 to 10.0 Å (Fig. 1(b)). In addition, this structure involves a characteristic triangular structure formed by Mo⁴⁺ metal-metal bonding (blue line in Fig. 1(b)), which stabilizes the structure of the super-reduced one.

This electron sponge behavior is a newly revealed characteristic of POMs, and indicates that they are promising cathode active materials for high-performance rechargeable batteries.

References

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