

PD Research Report for the 2015 year

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Research Theme Development of electrode fabrication method for new active material
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Research Results (about 2,500 characters in Japanese, about 65 lines times 90 characters in English)

Recently, polyoxometalates and metal–organic frameworks (MOFs) have been found to have potential as the cathode materials for rechargeable batteries. Polyoxometalates are promising multifunctional materials which have numerous applications in catalysis, photoluminescence, as single molecule magnets, and as proton-conductive materials. One of the most important features of POMs is the ability to configure or tailor their redox properties, which allows the development of new functional systems.

We have reported the rechargeable molecular cluster batteries, which were formed by a lithium anode and a cathode active material, polyoxometalate, $[\text{PMo}_{12}]^{3-}$. In operando Mo *K*-edge X-ray absorption fine structure (XAFS) measurements on these cathodes revealed that $[\text{PMo}_{12}]^{3-}$ functioned as an “electron sponge”, cycling reversibly by 24 electrons between $[\text{PMo}_{12}]^{3-}$ and $[\text{PMo}_{12}]^{27-}$ during charging/discharging process. However, the energy density and power density of these cathode materials were limited by the slow rate of charging/discharging: capacities in excess of 200 Ah/kg could be obtained after ten cycles, but only at a low current of 1 mA. Vanadium based polyoxometalates have exhibited high capacities and rapid charging/discharging than the polyoxometalates $[\text{PMo}_{12}]^{3-}$, but their reaction mechanism remained unclear. Herein, in order to investigate the reaction mechanism and fundamental role of $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ molecule in the batteries, I performed in situ XAFS analysis.

The molecular structure of $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ is shown in the inset of Figure 1. The spherical anion $\{\text{V}_{15}\text{O}_{36}\}$ of $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ has a “hollow sphere” structure formed by linkage of 15 tetragonal VO_5 pyramids. The 15 vanadium atoms are arranged on the surface of a sphere from the center of the cluster. $\{\text{V}_{15}\text{O}_{36}\}$ formally contains eight V^{4+} centers and seven V^{5+} centers. $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ shows reversible redox behavior over a wide voltage window 1.9-4.0 V. XAFS analysis is a powerful technique for observing the oxidation state of the absorber atoms and the local structures around them. I carried out in situ vanadium *K*-edge XAFS analyses of the charging/discharging processes of the $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ battery to reveal the microscopic mechanisms of their battery performance. Figure 1 shows the first two charging/discharging cycles of an in situ $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ battery obtained at a constant current of 50mA/g in the voltage range of 1.9-4.0 V. A reversible capacity of around 250 Ah/kg was obtained. This value is similar to that of coin cell battery, which means this electrochemical cell is suitable for in situ XAFS study.

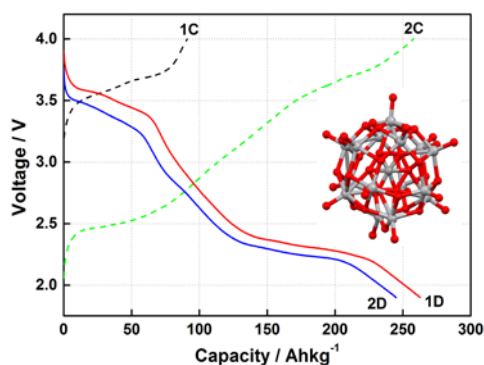


Figure 1. Charging/discharging curves of $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ batteries. (inset: molecular structure of $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$).

By using a linear relationship between the vanadium oxidation state and the X-ray absorption edge energy for the reference materials, the averaged valence of the vanadium ions in $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ was obtained from the normalized vanadium *K*-edge X-ray absorption near edge structure spectra (XANES). The results are shown in Figure 2, where the values of averaged valence are plotted as a function of the battery voltage. The initial value of averaged valence before the first charging is ca. 4.7, which agrees with the neutral annealing $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ sample. This value increase to 4.96 after the first charging. In the first discharging, vanadium averaged valence exhibits a decrease from the initial value to 4.06. The change in averaged valence by 0.9 during the discharging processes agrees with the observed battery capacity of ca. 250 Ah/kg.

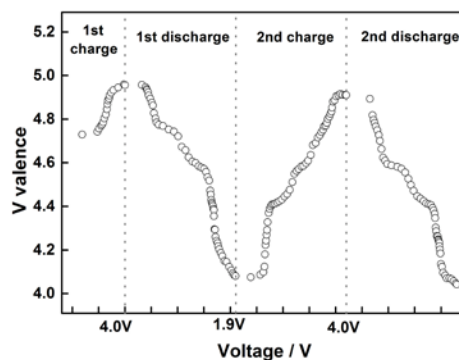


Figure 2. Averaged vanadium valence of $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ in the $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ batteries as a function of the cell voltage.

Extended X-ray absorption fine structure (EXAFS) analyses were performed in order to obtain the structural change of the $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ molecule. Figure 3 shows the Fourier transform spectra of the k^3 -weighted data for the samples denoted by 1C, 1D, 2C, and 2D. After the first charging, sample 1C exhibits three main peaks at 1.2, 1.6 and 2.7 Å. The peaks at 1.2 Å and 1.6 are assigned to short and long V-O distances, whilst the other one is attributed to V-V distance. After the first discharge, 1D exhibits a different curve, the peaks at 1.2, 1.6 and 2.7 Å shift to shorter distance. This suggests that the distances of V-O and V-V decrease after discharging. After the second charging, sample 2C exhibits the initial three peaks compared with those in 1C. After the second discharging, the curve of 2D is nearly the same as that of 1D. This indicates a nearly reversible structural change of the $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ molecule during the charging and discharging processes.

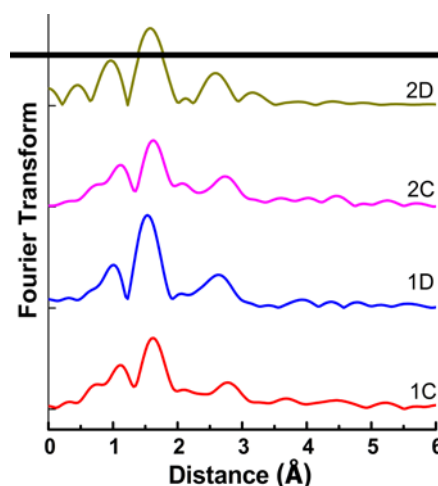


Figure 3. Fourier transforms of the V *K*-edge EXAFS spectra for 1C, 1D, 2C and 2D.

In situ XAFS analyses have revealed the evolution of the oxidation state and the local structure of vanadium ions of in the $\text{Li}_7[\text{V}_{15}\text{O}_{36}(\text{CO}_3)]$ battery. The large capacity can be ascribed to the redox change in the vanadium ions.

Presentations & Papers:

- 1."Reversible oxidation of Pt nanoparticles: In situ hard X-ray photoelectron spectroscopy studies under H_2O and MeOH atmospheres", H. Wang, Y. Takagi, Y. Uemura, O. Sekizawa, T. Uruga, M. Tada, Y. Iwasawa, T. Yokoyama, H. Yoshikawa, The International Chemical Congress of Pacific Basin Societies 2015, Hawaii, Dec. 2015, poster presentation.
- 2."In situ XAFS studies of high performance vanadium oxide cathode materials: a new phase transition behavior of vanadium oxide", H. Wang, J. Isobe, D. Matsumura, H. Yoshikawa, paper in preparation.