

Operando X-ray Absorption Fine Structure Studies on Rechargeable Batteries using Porous Polyoxometalate Compounds as Cathode Active Materials

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Lithium ion batteries (LIBs), which are used in portable devices and electric vehicles, have attracted much attention at fundamental and practical level. In order to meet the increasing demand for LIBs, among various materials, polyoxometalate compound MoV oxide has been used as cathode active materials. However, the poor reversibility limited its use for LIBs. Here, I studied the performance and reaction mechanism of Li batteries using porous polyoxometalate, Mo-V-Bi oxide ($\text{Mo}_{30.5}\text{V}_{9.5}\text{Bi}_{1.1}\text{O}_{112}$, see Fig. 1), in which Bi ion was incorporated to the previous MoV oxide framework without changing the basic structure.

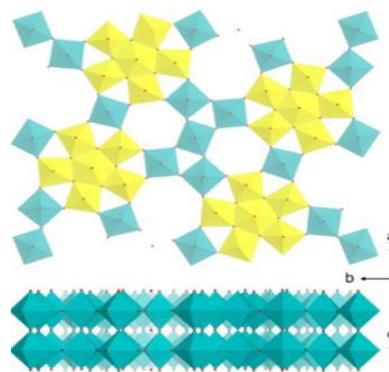


Figure 1. Structure of MoVBi oxide. (Mo or V: blue. O: red).

This battery exhibited a large capacity of ca. 376 mA h/g, which was maintained and decreased only a little after 40 cycles in a voltage range between 4.0 and 1.5 V. They also showed a high rate capability indicating an excellent structural stability, reversibility, long-term property and very high speed Li migration during battery reactions (Fig. 2). To reveal the reason for this high performance, operando Mo *K*-edge, V *K*-edge, and Bi *L*₃-edge X-ray absorption fine structure (XAFS) analyses were carried out. As a result, I obtained the information on the oxidation state of each metal ion and the structural change during battery reactions.

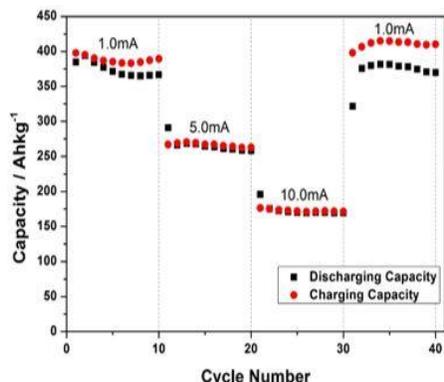


Figure 2. Rate capability of MoVBiOAC400-LBs.

X-ray absorption near edge structure (XANES) spectra exhibited a reversible change during charge/discharge, as shown in Mo *K*-edge XANES spectra (Fig. 3). These XANES spectra indicated that the averaged valences of Mo, V, and Bi changed from Mo^{6+} , V^{4+} to Mo^{4+} , V^{3+} , respectively. Besides that, the valence of Bi was also changed during battery reactions. Totally, more than 70 electrons redox occurred, which can explain the large experimental specific capacity. In addition, extended X-ray absorption fine structure (EXAFS) were analyzed to obtain local structure information. The inserted Li ion in the discharging process lengthened the Mo-O bond along *c*-axis, which returned in the next charging process. The incorporation of third metal Bi ion probably stabilize the structure and improve the battery performance.

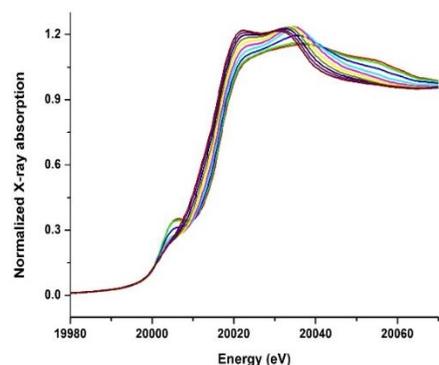


Figure 3. Operando Mo *K*-edge XANES spectra