

Charge-discharge Mechanism of Lithium Cobalt Vanadium Oxide as a High Reversible Capacity Anode Material for Lithium-ion Cells

J. Shirakawa, Y. Uchimoto and M. Wakihara

Department of Applied Chemistry, Tokyo Institute of Technology, 2-12-1, Okayama, Meguro-ku, Tokyo, 152-8552, Japan

The great demand of improvement for anode materials in lithium ion cells is increasing due to development of various portable electronic products. Several oxide anode materials with their high chemical stability and large capacity have been studied. Especially, vanadium oxides are more attractive because vanadium ion shows various oxidation states that directly relate to large capacity. However, these anodes suffer from large irreversible capacity during the first cycle. In order to overcome such a problem, it is necessary to clarify the first lithium insertion and removal mechanism. From our previous report¹, it was revealed that the inverse spinel-type LiCoVO_4 showed a much higher reversible capacity compared with a commercially available graphite anode. In this study, we focus on the behavior of reversible and irreversible capacities of LiCoVO_4 . From a viewpoint of fundamental study, the variation of long-range-order structure, local environmental structure and oxidation states of each metal were investigated by XRD and XAS, respectively.

The inverse spinel, LiCoVO_4 was prepared by solid-state reaction from the stoichiometric mixture of Li_2CO_3 , $\text{Co}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and V_2O_5 at 750°C for 2 days. The result of XRD measurement for phase identification was consistent with inverse spinel structure, $(\text{V})_{8a}[\text{LiCo}]_{16d}\text{O}_4$ (subscripts 8a and 16d indicated the cation sites in space group, $Fd\bar{3}m$).

The charge-discharge measurement of LiCoVO_4 was performed by a conventional coin-type cell under galvanostatic condition with current density, 70 mA g^{-1} . Cut-off voltage was set at 0.01 V and 3.0 V. Fig. 1 shows the result of the first charge-discharge measurement with the derivation curves of the capacity with cell voltage. In this study, the Li insertion process is defined as charge, while the Li removal one is referred as discharge. In the lithium insertion process, except for the plateau at ca. 0.8 V due to side reaction of acetylene black and SEI formation, two potential plateaus (around 0.5 V and 0.2 V) were observed. From XAS analysis, the first plateau region is attributed to the reduction of vanadium ion from V^{5+} to V^{4+} , and the environmental coordination of vanadium also transformed from tetrahedral symmetry to octahedral one. In view of long-range-order structure, XRD analysis showed that the phase transition from inverse spinel into atacamite-type with cation distribution $[\text{LiV}]_{16c}[\text{LiCo}]_{16d}\text{O}_4$ occurred. In the second plateau, both the vanadium and cobalt ion were reduced its oxidation state ($\text{V}^{4+} \rightarrow \text{V}^{2+}$, $\text{Co}^{2+} \rightarrow \text{metallic Co}$) and the structure of LiCoVO_4 irreversibly transformed into amorphous structure during the first lithium insertion. Following lithium removal process up to 1.9 V, the oxidation state and coordination environment of vanadium completely returned to the initial state which means a tetrahedral environment of V^{5+} despite the structure deformation to an amorphous phase, and it was closely related to the large reversible capacity. On the other hand, it was

difficult to return the deposited cobalt metal to initial state, Co^{2+} , after lithium removal process up to 2.5 V due to kinetically unfavorable for charge-discharge reaction. It would be directly connected with irreversible capacity, especially in the case of following cycles.

Cyclability and coulomb efficiency of LiCoVO_4 with difference in cut-off voltage during first charge process is shown in Fig.2. Charge-discharge cycles between 0.35 V and 3.0 V did not accompany metal deposition reaction of cobalt, and revealed higher coulomb efficiency than that in the cycle between 0.01 V and 3.0 V. The capacity fading occurred due to kinetic restriction for reoxidation of cobalt deposition upon several cycle.

In conclusion, during the first lithium insertion and removal process, vanadium ion shows good reversibility in view of oxidation state and local environmental structure, directly connected to large reversible capacity, while the oxidation state of cobalt does not revert due to poor kinetic property which is unfavorable for cycle performance.

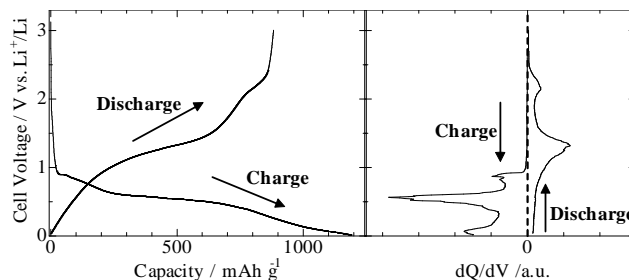


Fig.1 (a) First charge-discharge curves, and (b) derivation curves of the capacity with cell voltage for LiCoVO_4 .

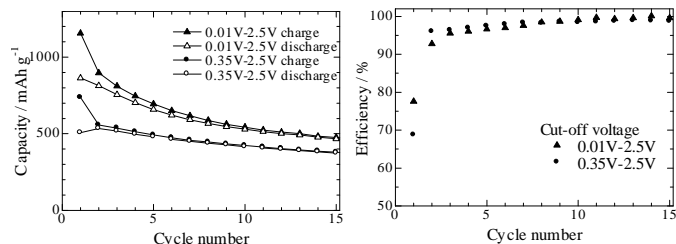


Fig.2 Variation of (a) charge and discharge capacities, and (b) coulomb efficiencies of LiCoVO_4 with cycle number, respectively.

References

1. J. Shirakawa, M. Nakayama, H. Ikuta, Y. Uchimoto and M. Wakihara, *Electrochem. Solid-State Lett.*, **7**, A27 (2004)