Lithium Insertion and Extraction Behavior of Vanadium Cobalt Oxide CoV_3O_8 at High Temperature

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Introduction:

Previously, Y. Oka and T. Yao[1] novel cobalt vanadium oxide CoV_3O_8 by a hydrothermal method for the first time, and analyzed the crystal structure. CoV_3O_8 crystallizes in orthorhombic system *Ibam* and has tunnel-like space along c-axis. We have considered that the structure is advantageous for lithium ion insertion and extraction. In the present study, CoV_3O_8 was synthesized by a solid-state reaction, X-ray diffraction pattern was measured and the crystal structure was analyzed by the Rietveld method. The electrochemical lithium insertion and extraction cycle behavior was investigated at 25°C, 45℃, 60℃, and 75℃.

Experimental:

Chemical reagent of CoO, V_2O_5 and V_2O_4 were mixed with the molar ratio of Co:V:O=1:3:8. The mixture was heat-treated in vacuum and CoV_3O_8 was obtained. Powder X-ray diffraction patterns of the products were taken with MoKα radiation and the crystal structure was refined by the Rietveld method using RIEVEC [2,3]. A multicycle discharge-charge experiment was carried out by using a two-electrode cell. The cathode was fabricated by mixing the prepared active material, acetylene black powder and a binder (polyvinyliden difluoride, PVDF) (wt%, 80:15:5) and *N*-methylpyrrolidone (NMP) as the solvent, and coating the mixture onto an Al foil. Lithium metal foil was used as counter electrode. A mixed solvent of 1 $mol \cdot dm^{-3}$ $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (vol%, 2:1) was used as the electrolyte. Discharge-charge cycle test was carried out between 1.5 and 4.5 V vs Li with a constant current density of 80 mA g^{-1} at several kinds of temperatures of 25°C, 45℃, 60℃, and 75℃.

Results and Discussion:

In Figure 1, the Rietveld result for the CoV_3O_8 sample obtained by solid-state reaction is given. The calculated XRD pattern agreed closely with the observed one. Figure 2 shows polyhedral representation of the crystal structure of CoV_3O_8 obtained by the Rietveld analysis. Tunnel-like space along c-axis is clearly observed. The result of discharge-charge cycle test was as follows. During the 1st discharge, three potential plateaus were observed at either 25°C, 45°C, 60°C or 75°C. This indicates that lithium was inserted into CoV_3O_8 by three-step reaction. During the 1st charge, only one plateau was observed at each temperature. This means that the lithium extraction proceeded in one-step reaction. In the 2nd or later charge-discharge cycle, both lithium insertion and extraction proceeded in one-step, and the amount of inserted lithium was almost equal to that of extracted. It was indicated that lithium was inserted into and extracted from CoV_3O_8 reversibly. Figure 3 shows discharge capacity of CoV_3O_8 as a function of cycle number. Excellent discharge cycle performance was obtained. It should be noted that the high temperature does not cause reduce but increase of the capacity. This new cobalt vanadium oxide is promising for electrode material of lithium ion rechargeable battery.

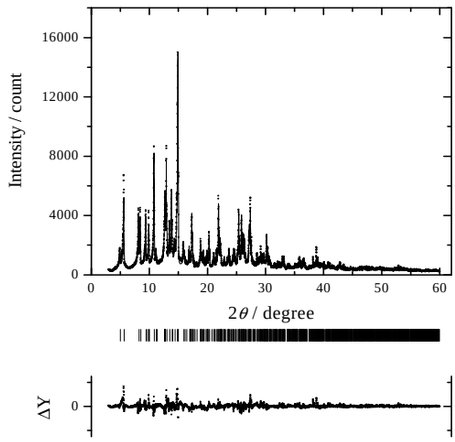

Figure1. Rietveld result of CoV_3O_8. The calculated and observed patterns are shown in the top by the solid line and the dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflection. The trace in the bottom is a plot of the difference: observed minus calculated.

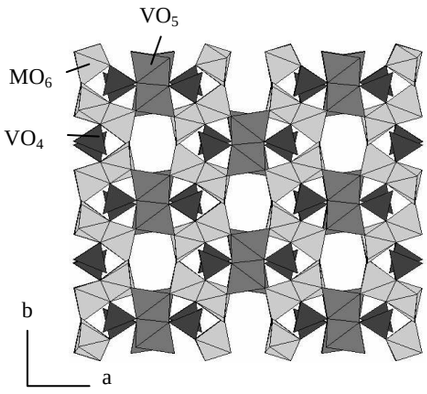

Figure2. Polyhedral representation of the crystal structure of CoV_3O_8 projected onto ab plane.

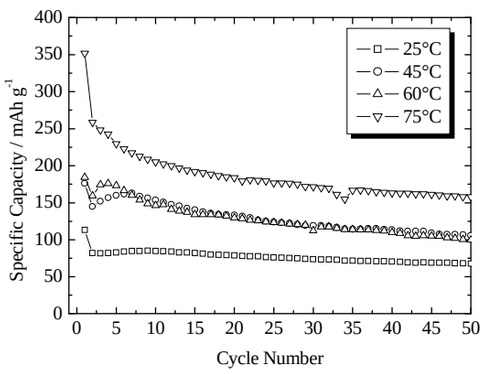

Figure3. Discharge capacity of CoV_3O_8 at 25°C, 45°C, 60°C and 75°C.

Reference:

[1] Y.Oka, T.Yao, N.Yamamoto and Y.Ueda, *J. Solid State Chem.*, **141**, 133-139(1998).
[2] T.Yao, T.Ito and T. Kokubo, *J. Mater. Res.*, **10**, 1079-1082(1995).
[3] T.Yao, Y.Oka and N.Yamamoto, *Mater. Res. Bull.*, **27**, 669-675(1992).