Relaxation Phase Analysis of Li-Ni-O Cathode for Secondary Lithium-ion Battery

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Introduction

Li-Ni-O cathode, specially $Li(NiCoAl)O_2$, has been attracting much attention as next generation cathode material in secondary Li-ion batteries with great advantages such as low cost and environmental benignity.

Recently, we have conducted the relaxation analysis for various electrode materials such as γ-Fe_2O_3[1-3], $LiMn_2O_4$[4], $LiFePO_4$[5], and $LiCoO_2$[6] after termination of electrochemical Li insertion.

In this study, we extracted Li from $Li(NiCoAl)O_2$ electrochemically and investigated relaxation process by means of the X-ray Rietveld analysis.

Experiment

Commercial $Li(NiCoAl)O_2$ with particle size of 5.2 μm (Sumitomo Metal Mining Co., Ltd., Japan) was used for this study. We extracted Li electrochemically to x = 0.50 or 0.40 in terms of $Li_x(NiCoAl)O_2$ at a rate of 1C. When the respective electrochemical Li extraction conditions were attained, we opened the circuit and immediately removed the working electrode from the cell in a glove box to avoid the local cell action between the electrode material and the current collector or the supplemental conductor.

XRD patterns were measured by using CuKα radiation (Rint-TTR, Rigaku corp., Japan) with various relaxation time. In this range of x, two hexagonal phases coexist in $Li_x(NiCoAl)O_2$. The XRD patterns were analyzed by the Rietveld method using RIEVEC program[1-6]. The crystal structures of two phases were represented by the same space group of $R\bar{3}m$. Parameters such as lattice constants, scale factors and atomic coordinates of the two phases were obtained.

Results and discussion

XRD profiles of the samples for each relaxation time after Li extraction were well fitted with the patterns obtained by the Rietveld calculation. Fig. 1 shows the fitting result of the sample 2.5 h after Li extraction.

Fig. 2 shows relative mole fraction changes calculated from scale factor and unit cell volume obtained by the Rietvelt analysis [7]. The mole fraction of Li-rich phase decreased and that of Li-lean phase increased with the relaxation time. It is considered that Li-rich phase including Li defects preferable for Li diffusion formed during Li extraction process and that the defective Li-rich phase separated to Li-rich phase without defects and Li-lean phase with the relaxation time after the Li extraction.

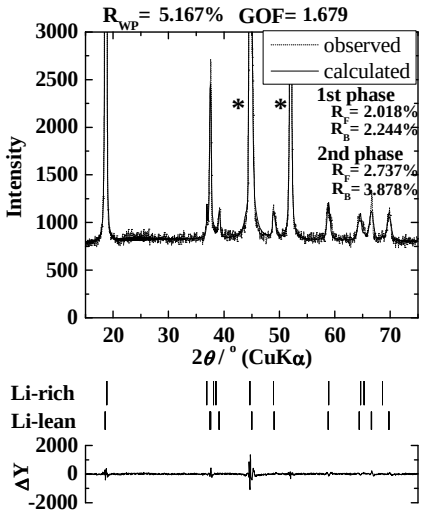

Fig.1 The Rietveld result of the sample 2.5 h after Li extraction. Calculated and observed patterns are shown in the top part by the solid line and the dots, respectively. The vertical marks in the middle part show positions calculated for Bragg reflection. The trace in the bottom part is a plot of the difference between calculated and observed pattern. *'s indicate peaks of Ni mesh collector.

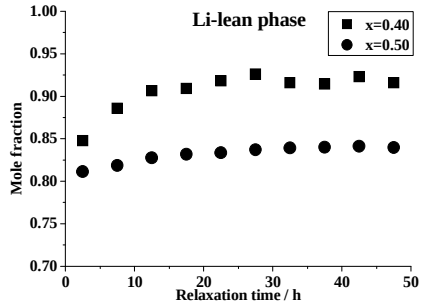

Fig.2 Mole fraction changes of Li-lean phase with relaxation time for Li extracted samples.

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