Analysis of crystal and electronic structures during charge and discharge process of LiNi$_{0.8}$Co$_{0.2}$O$_2$ as a cathode material for lithium ion battery

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INTRODUCTION

LiCoO$_2$-based materials have been mainly used as a cathode material of the Li ion rechargeable battery, but Co has some problems, such as high cost and high environmental load. As a candidate of the alternative materials, Li(Ni, Co)O$_2$ system has drawn much attention because it shows high capacity comparatively, and has an advantage in respect to environmental problem due to low content of Co. From such background, there are many previous works about the Li(Ni, Co)O$_2$, and the aluminum-substituted material which shows higher heat stability, has been put into practical use. However, detail crystal-structure changes during electrochemical charge and discharge processes, especially Li site and occupancy, distortions of crystal structure, and impurity-phase formation like SEI, are still ambiguous even though these would play important roles on the battery characteristics.

In this research, we synthesized LiNi$_{0.8}$Co$_{0.2}$O$_2$ with the coprecipitation method, and then measured powder neutron diffractions of electrochemically-cycled cathodes, by an ex-situ technique. Crystal structure analysis was conducted using the Rietveld and maximum entropy method (MEM). Based on the results, we tried to reveal the charge and discharge mechanism of this material, and to clarify the influence for the crystal structure on the several depth of charge and discharge.

EXPERIMENTAL

LiNi$_{0.8}$Co$_{0.2}$O$_2$ was obtained by mixing Ni-Co precursor with lithium hydroxide hydrate. The precursor was prepared by co-precipitating the aqueous solution of the two metal nitrate salt (Ni, Co) in a stoichiometric ratio of 8:2, with lithium hydroxide. After suction filtration for a few days, the precipitate was dried at 100°C overnight. The dried material was then mixed with a stoichiometric amount of LiOH-H$_2$O. The mixture was annealed in air at 600 °C for 15 h, and then at 800 °C for 15 h. The product was identified by powder XRD. The composition of lithium and transition metal contents in the active material was determined by ICP-OES. To study change of crystal and electronic structure of this cathode material after charge and discharge, we prepared some samples with various depth of charge at 10th cycle, and measured the synchrotron X-ray diffraction (BL02B2, SPring-8) and the powder neutron diffraction (BL20, J-PARC) of these samples electrode (10mg)[1]. The data was analyzed with the Rietveld technique using Rietan-FP and Z-Rietveld, and by the MEM using the Dysnomia program.

RESULTS AND DISCUSSION

From powder X-ray diffractions, it was found that a product could be attributed to a single phase of the layered structure with space group of R-3m. Moreover, since peak splits of (006) and (102) as well as (108) and (110) diffractions were observed, the structure was interpreted to be the layered structure[2]. The sample with small cation mixing was obtained from the peak intensity ratio of (003) to (104). The ICP-OES analysis indicated the molar ratio of Li and the transition metal ions was Li:Ni:Co = 0.979:0.815:0.206, and thus, in good agreement with the composition of starting reactants. We examined crystal structures of the electrode after 2nd discharge process as well as the pristine electrode by the Rietveld analysis which used neutron diffraction data. As a result, it was demonstrated that the crystal structure analysis by ex-situ measurement could be successfully performed even for the electrode with a weight of 10 mg. Furthermore, the electrodes were prepared about 2.5 V, 3.65 V, 3.85 V, and 4.3 V which corresponded to the plateau portions of a 10th charging curve (Fig. 1). The structural analysis using neutron diffraction and synchrotron X-ray diffraction were conducted in order to clarify a structural change of the cathode material accompanying the charge depth. As a result, values of 3b-6c bond length decreased and σ^2, which expresses the distorted degree of the Li-O$_6$ and M-O$_6$ octahedra, were increased with increasing the charge depth (Fig.2). From the results, the oxidized transition metals at each charging step affected the structureal distortion.
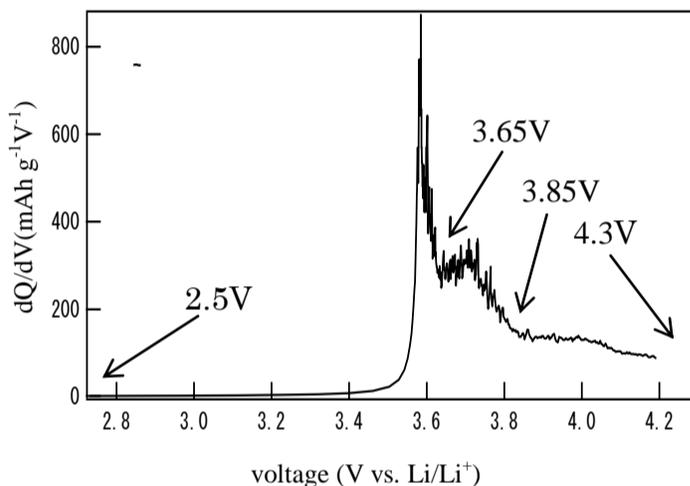

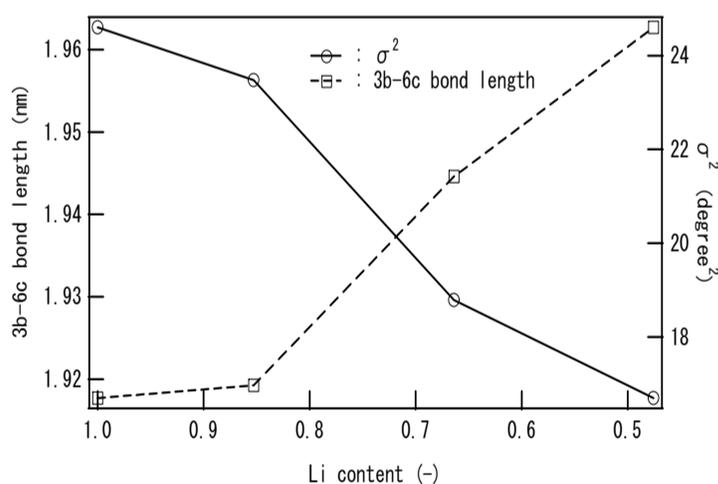Fig.1 Differential capacity vs. voltage of LiNi$_{0.8}$Co$_{0.2}$O$_2$ cell cycled in 2.5-4.3V charge.

Fig. 2 Change of the 3b-6c bond length and the bond angle variance,σ^2 with charge depth by neutron diffraction.

References
1) Y. Idemoto, et al, Chem. Lett., **40**, 165 (2011).
2) C. Delmas, et al, J.Power Sources, **43**, 593 (1993).