Synthesis and characterization of nonstoichiometric $LiCoO_2$

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Abstract

Synthesis, characterization of Li_xCoO_2 ($x > 1.0$) and their electrochemical behaviors are examined. From compositional analysis, the solid solution limit of excess lithium is found around Li/Co = 1.15. These products contain oxygen defects in order to maintain electronic neutrality. To evaluate the effect of oxygen defects, high pressure oxygen treatment was done for these samples. The electrochemical behavior of the treated samples shows much higher efficiency in the first cycle. The reversible capacity shows dependence on the composition and the highest one as much as 140 m Ah g^{-1} was obtained at Li/Co = 1.10. The capacity linearly decreased with Li/Co ratio beyond 1.10 due to decreasing amount of cobalt in the products. This lead to better cycling performance with the reversible capacity of ca. 160 m Ah g^{-1}, when the higher cut off voltage as 4.52 V was set for the charge process. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

$LiCoO_2$ is commercially used as positive electrode of lithium ion battery. The structure of high temperature $LiCoO_2$ has alternately ordered lithium and cobalt layers. This ion arrangement is not easily perturbed under usual synthetic conditions. Thus, $LiCoO_2$ has been believed to always occur in stoichiometric form, on which many papers have been reported [1,2]. This makes a contrast to the identical structural material, $LiNiO_2$ which inevitably contains cubic domains according to the synthetic conditions. There are few studies about $LiCoO_2$ from detailed structural aspects due to much less tendency to show such disordered structure.

Recent studies, however, show preparation of Li_xCoO_2 with $x > 1$, when initial nominal composition is set at Li/Co > 1 [3,4]. Levasseur et al. reported that oxygen defects are generated in a lithium-rich Li_xCoO_2 together with the occurrence of divalent Co^{2+} [5]. In our study the relation between synthetic condition, nonstoichiometry and electrode characteristics of $LiCoO_2$ is discussed. We at first synthesize Li_xCoO_2 ($x > 1$) with wider range of compositions in order to outline the solid solution range. Secondary, the products are characterized in detail by X-ray diffraction, ^{7}Li NMR, iodometry, induced coupled plasma spectroscopy (ICP), etc. Our thermogravimetric measurements indicate

that the sample loses oxygen around 800°C and contain oxygen defects. In order to evaluate effect of oxygen vacancies on structure and electrochemical properties, products are treated under high oxygen pressure to reduce the number of defects.

2. Experimental

LiOH and Co_3O_4 were mixed well in an agate mortar at nominal compositions, Li/Co = 1.02, 1.05, 1.10, 1.15, 1.20, 1.25, 1.30. Cobalt content in Co_3O_4 was determined from thermogravimetric analysis. The 6 h calcination of the mixture was done at 750°C, followed by 24 h annealing at 850°C in air atmosphere.

The stoichiometry of products was determined from ICP and iodometry data. The sample for ICP was dissolved in hydrochloric acid 10 ml, and then diluted to adjust the concentration being within 1–10 ppm range. Fixed amount of yttrium was added to the tested solution as an internal standard. From this data, Li/Co molar ratio was calculated. Cobalt valence or Co/O ratio was decided from iodometry. In this analysis, the reduction of Co^{3+} to Co^{2+} was achieved by adding I^- into the hydrochloric solutions of $LiCoO_2$. Back titration of resulting I^{3-} was carried out by sodium thiosulfate. Oxygen content "y" in Li_xCoO_y was calculated based on the data "x" from ICP result.

Two electrode coin-type cell was used to examine galvanostatic charge–discharge behaviors. Lithium sheet was

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used as negative electrode and placed onto a stainless steel mesh current collector. The sample mixed with acetylene black, and binding agent, PTFE, was used as positive electrode. The positive electrode mixture was pressed at pressure 150 kg cm^{-2}, and then put on the cathode can. The 1 M LiPF$_6$/PC + DMC (volume 1:1) was used as the electrolyte solution. The prepared coin cell was equilibrated for 1 day, then start cycling in the range of 4.3–2.5 V at a constant current 300 μ A cm^{-2}.

3. Results and discussion

The determined stoichiometries of Li/Co and cobalt valences from results of ICP, iodometry are summarized in Table 1. The calculated compositions shown in the fourth column are relative molar ratios and not absolute ones. For convenience, mol number, Li + Co, is fixed at 2 in this table. The cobalt valences are categorized into two groups; in Li/Co < 1.15 they are around 3.0, while in Li/Co > 1.15, they take lower values around 2.9. The discontinuity at Li/Co = 1.15 is interpreted as the solid solution limit. This is consistent with the composition that the lattice constant stops decreasing shown in a separate experiment. When calculating cobalt valences from iodometry results, it is necessary to assume that the samples are in single phase. The inconsecutive valence change at Li/Co = 1.15 suggests that this assumption is not correct and products are in two-phase region beyond Li/Co = 1.15.

As shown in this table, each sample has some oxygen defects of which amounts depend on Li/Co ratio. Thus, in order to evaluate effect of oxygen vacancies on electrochemical properties, Li$_x$CoO$_2$ is treated under high oxygen pressure to reduce the oxygen defects. The treatment is done as follows; the samples were heated at 400°C for 6 h under high oxygen pressure as much as 100 atm.

The summary of charge–discharge properties of the samples before and after the treatment is shown in Fig. 1. There are several different points in electrode properties by the treatment. The slight but distinct increase in reversible capacities as much as 5–20 m Ah g^{-1} is observed in all compositions. The irreversible capacity between the first charge and discharge process is much smaller and the
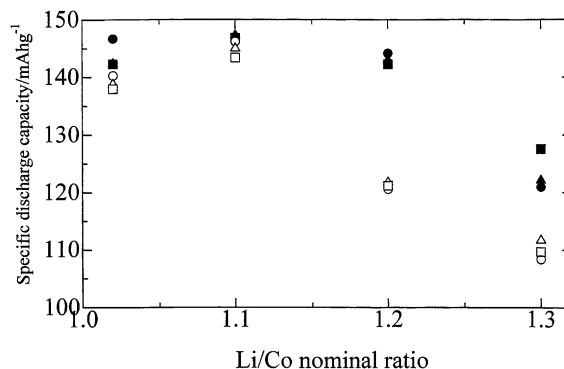

Fig. 1. Charge–discharge capacities in the first three cycles of samples before and after high pO_2 treatment. (●), (▲), (■): 1st, 2nd, and 3rd discharge capacity of treated sample, respectively. (○), (△), (□): 1st, 2nd, and 3rd discharge capacity of untreated sample, respectively.

efficiency becomes near 100%. The reversibility of the following cycles is also quite good. Whereas, a common feature before and after the treatment is that the highest capacity is shown at Li/Co = 1.10 and hereafter gradual decrease of capacity is observed. This is rationally explained by the decrease of the cobalt content in the products. Small amount of excess lithium can improve the electrode behavior regardless of the oxygen treatment.

Fig. 2 shows the effect of cut off voltages in the charge process. The upper figure shows the first charge curves of Li/Co = 1.02 and 1.10 samples. The inset shows enlarged

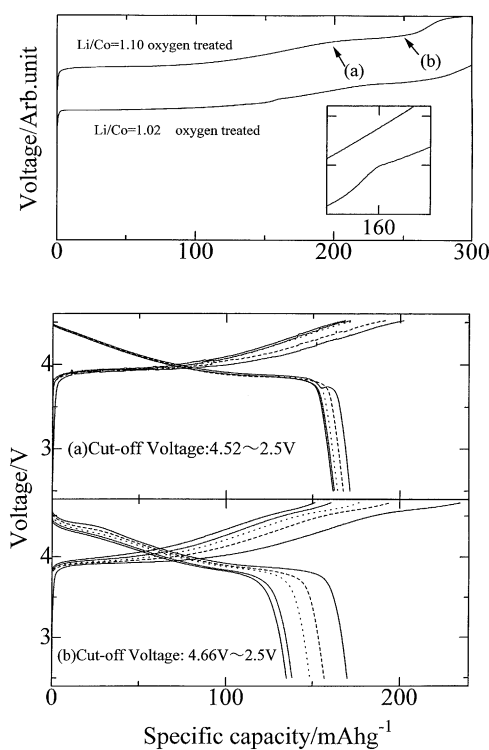Fig. 2. The first charge profiles of Li/Co = 1.02 and 1.10 (upper figure). For the inset, see the text. The lower figure shows cycling behaviors of Li/Co = 1.10 with different cut off voltages of 4.52 and 4.66 V.

Table 1
Composition analysis of Li$_x$CoO$_2$ by ICP and iodometry

Starting ratio Li/Co	ICP value Li/Co	Cobalt valence	Composition
1.02	1.02	2.96	Li$_{1.01}$Co$_{0.99}$O$_{1.97}$
1.05	1.09	2.97	Li$_{1.04}$Co$_{0.96}$O$_{1.95}$
1.10	1.11	2.97	Li$_{1.05}$Co$_{0.95}$O$_{1.94}$
1.15	1.14	2.96	Li$_{1.07}$Co$_{0.93}$O$_{1.91}$
1.20	1.20	2.88	Li$_{1.09}$Co$_{0.91}$O$_{1.86}$
1.25	1.22	2.88	Li$_{1.10}$Co$_{0.90}$O$_{1.85}$
1.30	1.26	2.86	Li$_{1.13}$Co$_{0.87}$O$_{1.81}$

region near $160 \, \text{m Ah g}^{-1}$. A step is observed in case of $\text{Li/Co} = 1.02$ which corresponds to the phase transformation at $\text{Li}_{0.5}\text{CoO}_2$ from rhombohedral to monoclinic. This does not appear in $\text{Li/Co} = 1.10$ due to the deviation from ideal structure. The phase change accompanied by the structural rearrangement is thought disadvantage for long cycle life. The lower figure shows the charge–discharge curves of the sample of $\text{Li/Co} = 1.10$ with cut off voltage being set higher at 4.52 and 4.66 V. These voltages are shown by (a) and (b) in the upper figure. Obviously 4.66 V is too high to obtain good cycling efficiencies, while 4.52 V cut off provides a reasonable cyclability and high reversible capacity as much as $170 \, \text{m Ah g}^{-1}$. From the results in this study, the capacity improvement of LiCoO_2 is observed by increasing Li/Co ratio, as well as high oxygen pressure treatment.

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