Development of Novel $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x/C$ ($0 \leqq x \leqq 1$) System Li-Ion Cells

Miki Yasutomi* Toru Tabuchi*
Hideo Yasuda* Masanori Yamachi**

Abstract

Li-ion has been doped into $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ positive electrode by chemical method using Li-naphthalene organic complex solution. The novel Li-ion system cell has been successfully confirmed to be realized by the evaluation test of laminate-type single cell composed of positive electrode with $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ ($0 \leqq x \leqq 1$) synthesized by the above chemical method and negative electrode with graphite. This $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ / C laminate-type single cell showed a good cycleability of discharge capacity retention of 90% at 20th cycle, though its discharge capacity was 75 mAh g^{-1} on the mass basis of positive active material as the first trial test. This system is regarded as the high theoretical capacity from 591 mAh g^{-1} (y = 1) to 292 mAh g^{-1} (y = 0), when x equals 1 according to the following reaction mechanism : $Ni_{0.8}Co_{0.2}OOH_{1-y}Li_y\cdot Li_x \rightleftarrows Ni_{0.8}Co_{0.2}OOH_{1-y} + (x+y)\,Li^+ + (x+y)\,e^-$.

1 Introduction

A world-wide effort has been made to find alternative positive active materials for $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$ and negative active materials for carbon in existing Li-ion cells to meet the strong demand of higher energy density for portable phones and electric vehicles. The NiOOH with a large theoretical capacity of 292 mAh g^{-1} has been considered to be a promising candidate of positive active material for 3-volt-class lithium cells.[1,2] However, this material was impossible to be used for the positive electrode for Li-ion cells with carbon negative one because of no lithium source in the discharged state. Recently, we have succeeded in the synthesis of NiOOH·Li by new chemical method with Li-naphthalene complex solution.[3,4] Li-ion has been doped into $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ as one of precursors for the derivative positive active materials of NiOOH by the new chemical method. The $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ positive electrode using this synthesized active material doped with lithium has been investigated for its cycleability with the practical cells under the condition of the starved electrolyte, wherein x is $0 \leqq x \leqq 1$. The novel Li-ion cell has been found to be a 3-volt-class high-energy-density cell with good cycleability. In this report, we will discuss the performance of these new cells with $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ positive active materials together with the electrochemical reaction mechanism of charge and discharge process.

*Department-F, Corporate R & D Center
**Corporate R & D Center

2 Experimental

The $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$·$Li_x$ positive electrode showing open-circuit potential of 2.5 V vs. Li / Li^+ was prepared by immersing the electrode with the mixture of $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$: acetylene black (AB) : poly-vinylidene-fluoride (PVDF) in the mass ratios of 80 : 5 : 15 using Al foil as a current collector into the complex solution with 0.25 mol dm^{-3} naphthalene and saturated metallic Li in 1-methoxybutane solvent followed by washing it with dimethyl carbonate (DMC). The negative electrode was prepared with the mixture of graphite, styrene butadiene rubber (SBR), and carboxylic methyl cellulose (CMC) using Cu current collector. The test laminate-type single cells were prepared with both electrodes, polyethylene film separator, and a mixture of 1 mol dm^{-3} $LiClO_4$ containing ethylene carbonate (EC) and diethyl carbonate (DEC) in the volume ratio of 1:1 as an electrolyte. The test cells were discharged to 1.4 V at current density of 0.25 mA cm^{-2} after charging at the same current density to 4.1 V.

3 Results and discussion

The change in open-circuit potential of electrode with $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ synthesized by chemical method with various immersion times is shown in Fig. 1. The open-circuit potential of this electrode is found to shift toward less noble. The electricity charged of this electrode after charging is shown in Fig. 2. The electricity charged is found to be increased with immersion time, and the value is reached to be large capacity of 500 mAh g^{-1} beyond the corresponding to the theoretical capacity of 292 mAh g^{-1} based on one molar Li extraction. These results mean that Li-ion is doped into $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ by chemical method using Li-naphthalene organic complex solution.

The initial charge-discharge characteristics of representative $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$·$Li_x$ / C system Li-ion laminate-type cell are shown in Fig. 3. The new Li-ion system cell shows the monotonous discharge curve with the 3-volt-class operation voltage, though the large irreversible capacity is still observed at the present time. The cycle performance of the new laminate-type test cell is shown

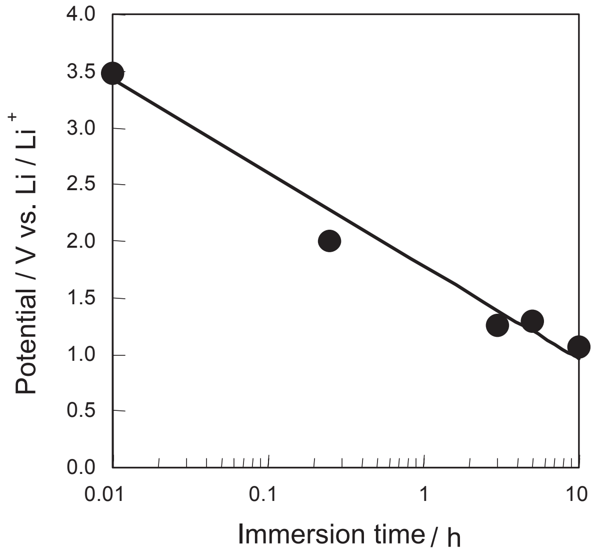

Fig. 1 Change in the open-circuit potential of $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ electrode with immersion time.
Counter and reference electrodes : Metallic Li.
Electrolyte : 1 mol dm^{-3} $LiClO_4$ containing EC and DEC in the volume ratio of 1:1.

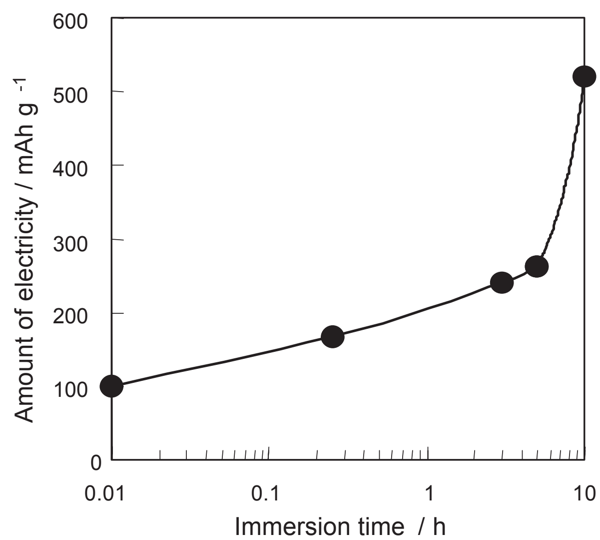

Fig. 2 Change in the amount of charged electricity of $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ electrode with immersion time.
Counter and reference electrodes : Metallic Li.
Electrolyte : 1 mol dm^{-3} $LiClO_4$ containing EC and DEC in the volume ratio of 1:1.
Charge : 0.25 mA cm^{-2} to 4.1 V.

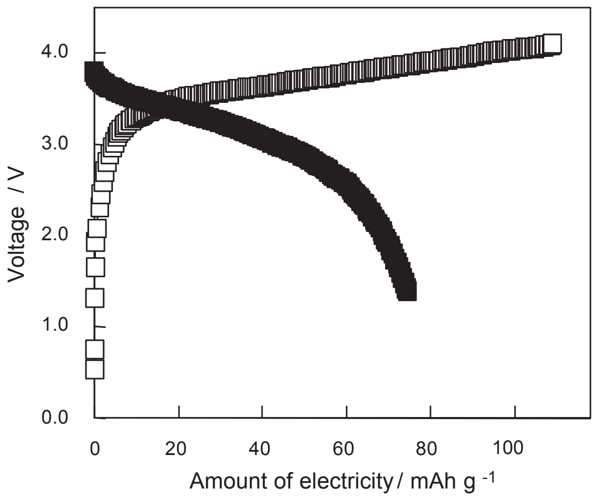

Fig. 3 Charge-discharge characteristics of laminate-type single cell with $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ positive electrode synthesized by chemical method.
Negative active material : graphite.
Electrolyte : 1 mol dm^{-3} $LiClO_4$ containing EC and DEC in the volume ratio of 1:1.
Charge : 0.25 mA cm^{-2} to 4.1 V.
Discharge : 0.25 mA cm^{-2} to 1.4 V.
Amount of electricity : Mass base of positive active material.

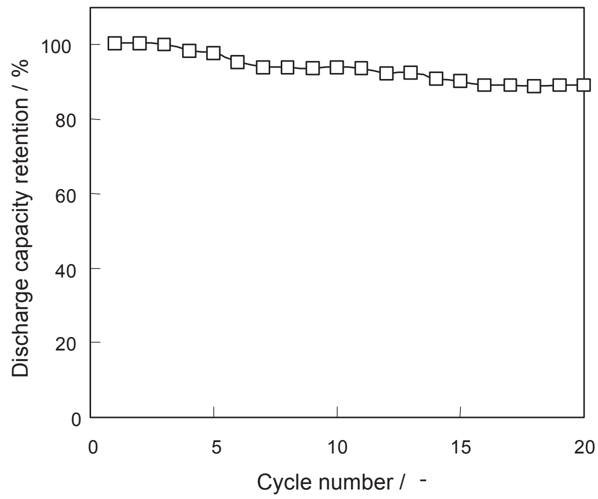

Fig. 4 Cycle performance of laminate-type single cell with $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ positive electrode synthesized by chemical method.
Negative active material : graphite.
Electrolyte : 1 mol dm^{-3} $LiClO_4$ containing EC and DEC in the volume ratio of 1:1.
Charge : 0.25 mA cm^{-2} to 4.1 V.
Discharge : 0.25 mA cm^{-2} to 1.4 V.

in Fig. 4. This cell shows good cycleability with the discharge capacity retention of 90% at 20th cycle. The cycleability of this system is considered to be based on the starved electrolyte condition of laminate-type single cell judging from the fact that the cycleability of NiOOH positive electrode derivative of $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ active material was very poor in flooded condition of electrolyte.[2] The electrochemical charge-discharge reaction mechanism of novel Li-ion system seems to be described by the following equation (1).

This system is regarded as the high theoretical capacity from 591 mAh g^{-1} (y = 1) to 292 mAh g^{-1} (y = 0), when x equals 1.

$$Ni_{0.8}Co_{0.2}OOH_{1-y}Li_y\cdot Li_x \rightleftarrows Ni_{0.8}Co_{0.2}OOH_{1-y} + (x+y)\,Li^+ + (x+y)\,e^- \quad \cdots\cdots (1)$$

4 Conclusions

Li-ion has been doped into $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}$ by the new chemical method using Li-naphthalene organic complex solution. The novel Li-ion cell with this obtained positive active material and graphite negative active material has been evaluated using the practical cell in the condition of starved electrolyte. The results were summarized as follows.

(1) The novel Li-ion system cell has been successfully confirmed by the experimental cells composed of positive electrode with $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ synthesized by chemical method and negative electrode with graphite.

(2) The $Ni_{0.8}Co_{0.2}OOH_{0.43}Li_{0.57}\cdot Li_x$ / C laminate-type single cell showed a good cycleability with discharge capacity retention of 90% at 20th cycle, though its initial discharge capacity was 75 mAh g^{-1} on the mass basis of positive active material as the first trial experiment.

(3) The $Ni_{0.8}Co_{0.2}OOH_{1-y}Li_y\cdot Li_x$ electrode is regarded as the high theoretical capacity from 591 mAh g^{-1} (x=1) to 292 mAh g^{-1} (x=0).

References

1) J. Maruta, H. Yasuda, Y. Fujita, and M. Yamachi, *Electrochem. Soc. Proc.,* Vol. 97-18, 151 (1997).
2) H. Sasaki, H. Yasuda, and M. Yamachi, *GS News Technical Report*, 60, 12 (2001).
3) M. Kitano, T. Tabuchi, H. Yasuda, M. Yamachi, Y. Matsuda, and Y. Imai, *The 44th Battery Symposium in Japan*, p.292 (2003).
4) M. Yasutomi, T. Tabuchi, H. Yasuda, M. Yamachi, Y. Matsuda, and Y. Imai, *GS News Technical Report*, 63, 13 (2003).