Technical Report
報　文

Development of Novel $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ System Lithium-Ion Cells

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Abstract

A new positive active material of $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x$ ($0 < x \leqq 1$) has been successfully synthesized by chemical method of lithium-ion doping into the precursor of $Ni_{0.76}Co_{0.24}OOH$ using a reduction function of lithium-naphthalene organic complex solution for the realization of novel lithium-ion cell with the combination of graphite negative active material. The $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system lithium-ion cells have been found out to be a good reversibility with average discharge voltage of 2.85 V. The cell has been also turned out to give a good cycleability with the discharge capacity retention of 92.4% at 20th cycle, though the delivered capacity at 2nd cycle is decreased to the value of 79.8 mAh g^{-1} on the mass basis of positive active material.

1 Introduction

A new battery with high power and good cycle performance has been strongly required as alternatives to existing $LiCoO_2/C$, $LiNiO_2/C$, and $LiMn_2O_4/C$ system lithium-ion cells. A nickel oxyhydroxide, NiOOH, has been a promising candidate as a positive active material for 3-volt-class lithium cells, since this material has a layer structure with the feature of high lithium-ion diffusion coefficient and large theoretical capacity of 292 mAh g^{-1} with one electron change reaction.[1,2] However, NiOOH·Li in the discharged state is required to prepare lithium-ion cells using the nickel oxyhydroxide positive and carbon negative active materials. There are no report on the performance of the NiOOH·Li/C system lithium-ion cell, because the NiOOH·Li is difficult to be synthesized. Recently, we have succeeded in the synthesis of NiOOH·Li by new chemical method using a reduction function of lithium-naphthalene organic complex solution.[3,4] In this report, the appropriate amount of cobalt additive into NiOOH has been investigated, and $Ni_{0.76}Co_{0.24}OOH$ electrode has been found out to show large discharge capacity. The discharged-state material $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x$ ($0 < x \leqq 1$) has been successfully synthesized by the chemical method for the realization of novel lithium-ion cell with the combination of graphite negative active material. The novel $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system cells have been found to be a good reversibility and cycleability. We will discuss the cycle performance of these new cells together with the electrochemical reaction mechanism of charge and discharge process.

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2 Experimental

2. 1 Preparation of $Ni_{1-y}Co_yOOH$ ($0 \leqq y \leqq 0.43$) and lithium contained $Ni_{0.76}Co_{0.24}OOH$ electrode

$Ni_{1-y}Co_yOOH$ ($0 \leqq y \leqq 0.43$) electrode was prepared as follows. First, $Ni_{1-y}Co_yOOH$ ($0 \leqq y \leqq 0.43$) powder was obtained by oxidation of $Ni_{1-y}Co_y(OH)_2$ ($0 \leqq y \leqq 0.43$) by using sodium hypochlorite (NaClO) as an oxidizing agent. The powder, acetylene black (AB) as an electro-conductive additive, and polyvinylidene-fluoride (PVdF) as a binder were mixed in the mass ratios of 80 : 5 : 15 with N-methyl-2-pyrrolidone (NMP) to prepare a paste. $Ni_{1-y}Co_yOOH$ ($0 \leqq y \leqq 0.43$) electrode was prepared by drying at 70 ℃ after coating the paste into foamed nickel substrate.

Lithium contained $Ni_{0.76}Co_{0.24}OOH$ electrode was prepared as follows. The $Ni_{0.76}Co_{0.24}OOH$ electrode was immersed into the complex solution dissolving with 0.25 mol dm^{-3} naphthalene and saturated metallic lithium in 1-methoxybutane solvent. Lithium contained $Ni_{0.76}Co_{0.24}OOH$ electrode was prepared after washing with dimethyl carbonate (DMC) under Ar atmosphere.

Electrochemical behavior of the obtained electrodes were investigated in 3-electrode flooded-type glass cells with a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in the volume ratio of 1 : 1 containing 1 mol dm^{-3} $LiClO_4$ as an electrolyte using metallic lithium foil as counter and reference electrodes. The discharge tests were conducted at 0.25 mA cm^{-2} to 1.5 V vs. Li/Li^+ after charging to 4.2 V vs. Li/Li^+ at the same current density at room temperature under Ar atmosphere.

2. 2 Fabrication of $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system lithium-ion cells

$Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system lithium-ion cells were fabricated as follows. First, $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x$ positive electrode with open-circuit potential of 1.26 V vs. Li/Li^+ was prepared by immersing the $Ni_{0.76}Co_{0.24}OOH$ electrode using Al foil as a current collector into the complex solution. The value of potential means that average valence of nickel and cobalt is almost divalent corresponding to x=1. The graphite negative electrode was then prepared by drying at 150 ℃ after coating on Cu foil current collector with the paste obtained by using the mixture of graphite, styrene butadiene rubber (SBR) as a binder, and carboxylic methyl cellulose (CMC) as a rheology control agent with water. The 2-electrode flooded-type $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system lithium-ion cells were fabricated using the positive and negative electrodes, and a mixture of EC and DEC in the volume ratio of 1 : 1 containing 1 mol dm^{-3} $LiClO_4$ as an electrolyte. The area of both electrodes were 3.0 cm^2. The design of discharge capacity was 4.0 mAh. The discharge tests were conducted to 1.4 V at 0.25 mA cm^{-2} after charging at the same current density to 4.1 V at room temperature.

3 Results and discussion

The initial discharge capacities of the electrodes using $Ni_{1-y}Co_yOOH$ positive active material with different y value of 0, 0.17, 0.21, 0.24, and 0.43 are summarized in Table 1. Discharge capacity tends to be increased with the amount of additive cobalt. The $Ni_{1-y}Co_yOOH$ electrode with the y value of 0.24 shows 146.7 mAh g^{-1} of the largest discharge capacity. This fact means that the addition of cobalt leads to the formation of β-phase NiOOH. However, the decrease of its discharge capacity, in the case of the y value of 0.43, is considered to be the formation of inactive phase $Co(OH)_2$. For the confirmation of this tendency, the crystalline structures of $Ni_{1-y}Co_yOOH$ powder with the y value of 0, 0.24, and 0.43 were investigated by X-ray diffraction (XRD). The XRD patterns of these materials are shown in Fig. 1. The peaks at around 2θ = 19, 38 and 67° are attributed to the indices of (001), (002), and (110) of crystalline structure of β-NiOOH, respectively.

Table 1 Effect of addition $Co(OH)_2$ on initial discharge capacity of $Ni_{1-y}Co_yOOH$ positive electrode.

y	Discharge capacity / mAh g^{-1}
0	102.1
0.17	90.0
0.21	143.5
0.24	146.7
0.43	124.2

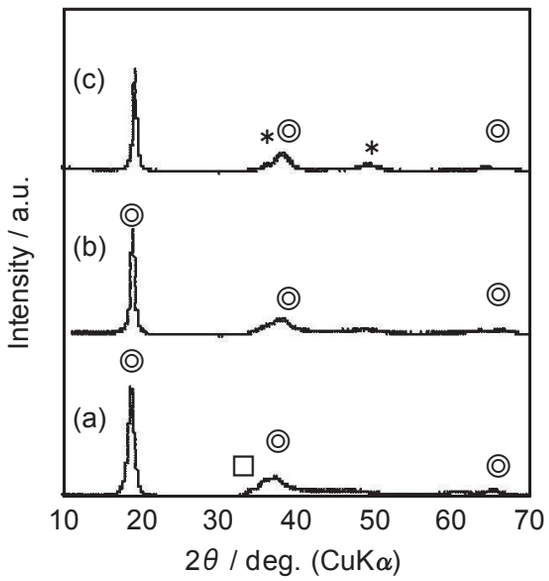

Fig. 1　XRD patterns of powder samples for NiOOH (a), $Ni_{0.76}Co_{0.24}OOH$ (b), and $Ni_{0.57}Co_{0.43}OOH$ (c).
◎: NiOOH , □: $Ni(OH)_2$, ∗: $Co(OH)_2$

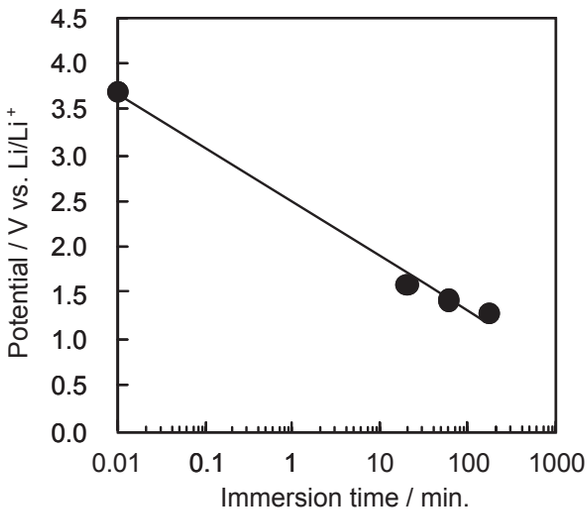

Fig. 2　Change in open-circuit potential of $Ni_{0.76}Co_{0.24}OOH$ electrode with immersion time.
Counter and reference electrodes : Metallic Li.
Electrolyte: EC and DEC mixture in the volume ratio of 1:1 containing 1.0 mol dm^{-3} $LiClO_4$.

In the case of y value of 0.43, the peaks are also detected at around 2θ = 36° and 51° attributed to the indices (101) and (102) of $Co(OH)_2$, respectively. This means that $Co(OH)_2$ isolated from the solid solution of cobalt with nickel is formed in the case of large y value of 0.43. The discharge capacity retention of these test electrodes at 20th cycle is shown in Table 2. The electrode with y value of 0.24 shows 92.2% of the highest discharge capacity retention. This fact is based on the formation of β-NiOOH in $Ni_{0.76}Co_{0.24}OOH$ resulting in large capacity and good cycleability. The change in open-circuit potential of electrode with $Ni_{0.76}Co_{0.24}OOH$ is shown in Fig. 2 as a function of immersion time in the lithium-naphthalene organic complex solution. The open-circuit potential of this electrode is found to shift toward less noble value, since the reduction reaction of $Ni_{0.76}Co_{0.24}OOH$ is proceeded with the immersion time. The change in amount of electricity charged of this

Table 2　Effect of addition $Co(OH)_2$ on 20th discharge capacity retention of $Ni_{1-y}Co_yOOH$ positive electrode.

y	Discharge capacity retention / %
0	18.6
0.17	85.1
0.21	73.7
0.24	92.2
0.43	24.8

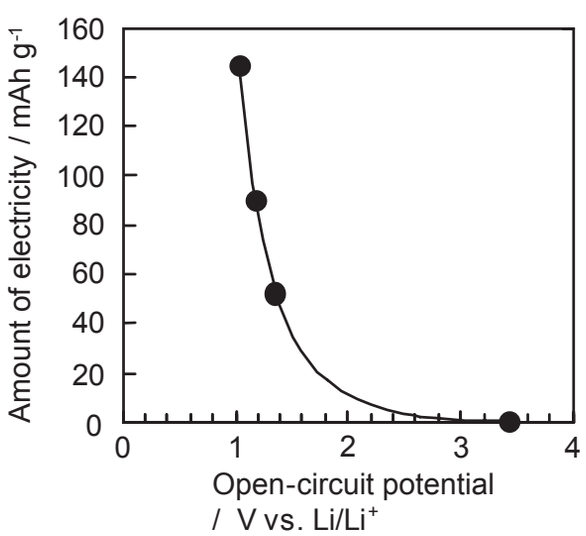

Fig. 3　Change in amount of electricity charged for $Ni_{0.76}Co_{0.24}OOH$ positive electrode with function of open-circuit potential.
Electrolyte: EC and DEC mixture in volume ratio of 1:1 containing 1.0 mol dm^{-3} $LiClO_4$.
Charge: 0.25 mA cm^{-2} to 4.2 V.

electrode at 1st cycle is shown in Fig. 3 as a function of open-circuit potential. The amount of electricity is found to be drastically increased with shifting the open-circuit potential toward less noble beyond 2.0 V vs. Li/Li^+. In other words, the amount of inserted lithium-ion is increased with its tendency, since the amount of electricity is corresponding with the content of lithium-ion inserted into $Ni_{0.76}Co_{0.24}OOH$ by chemical method. The charge-discharge curves of $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system cell at 2nd cycle are shown in Fig. 4. The cell is found out to show the average discharge voltage of 2.85 V and a good reversibility with high value of coulombic efficiency of 99.8% to the discharge capacity of 79.8 mAh g^{-1} on the mass basis of positive active material. The cycle performance of this cell is also shown in Fig. 5. The cell is turned out to be a good cycleability with the discharge capacity retention of 92.4% at 20th cycle. Therefore, $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system lithium-ion cells will be a very promising candidate for a novel battery.

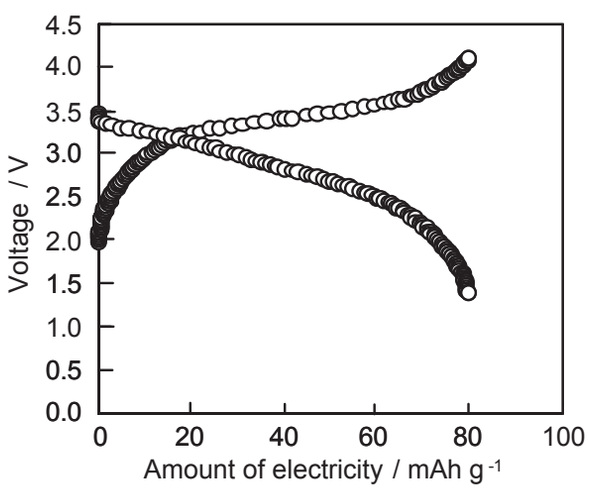

Fig. 4 Charge-discharge characteristics of $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system lithium-ion cell at 2nd cycle under flooded condition.
Electrolyte: EC and DEC mixture in volume ratio of 1:1 containing 1.0 mol dm^{-3} $LiClO_4$.
Charge: 0.25 mA cm^{-2} to 4.1 V.
Discharge: 0.25 mA cm^{-2} to 1.4 V.
Amount of electricity: Mass base of positive active material.

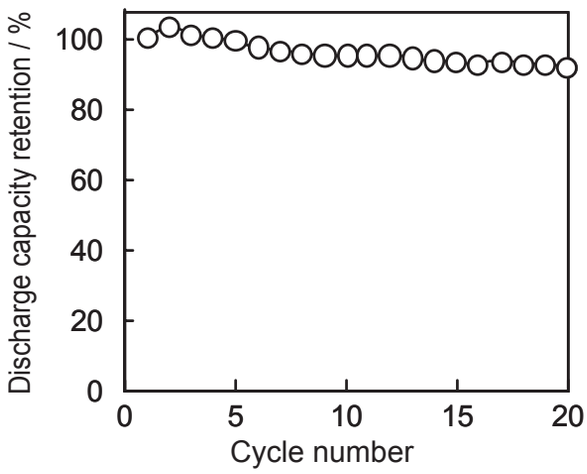

Fig. 5 Cycle performance of $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system lithium-ion cell under flooded condition.
Electrolyte: EC and DEC mixture in volume ratio of 1:1 containing 1.0 mol dm^{-3} $LiClO_4$.
Charge: 0.25 mA cm^{-2} to 4.1 V.
Discharge: 0.25 mA cm^{-2} to 1.4 V.

4 Conclusions

$Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x$ ($0 < x \leqq 1$) positive active material has been successfully synthesized by chemical method using a reducing function of lithium-naphthalene organic complex solution. The novel lithium-ion system cell using the positive active material and graphite negative active material has been found out to be the average discharge voltage of 2.85 V. Furthermore, the $Ni_{0.76}Co_{0.24}OOH{\cdot}Li_x/C$ system cell has been also found out to be good reversibility and cycleability, resulting from the coulombic efficiency of 99.8% at 2nd cycle and the discharge capacity retention of 92.4% at 20th cycle.

References

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