

## Anode performance of a new layered nitride $\text{Li}_{3-x}\text{Co}_x\text{N}$ ( $x = 0.2\text{--}0.6$ )

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### Abstract

The  $\text{Li}_{3-x}\text{Co}_x\text{N}$  ( $x = 0.2\text{--}0.6$ ) system was investigated for use as an anode material for lithium rechargeable cells. The anode performance of this system was evaluated by using Li metal/ $\text{Li}_{3-x}\text{Co}_x\text{N}$  cells.  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  in this system exhibits the highest specific capacity of 760 mAh/g in the 0–1.4 V range, and shows the best cycle performance. The capacity of the first extraction was  $2-x$  Li/mol, and depended on the amount ( $x$ ) of substituted Co. In addition, the structure changed gradually from the crystalline phase with hexagonal symmetry to the amorphous phase as lithium was removed during the first extraction. The cycle performance of a lithium-ion cell was evaluated by using the  $\text{Li}_{1.6}\text{Co}_{0.4}\text{N}/\text{LiNiO}_2$  cell. This cell showed good cycleability of more than 240 cycles. This system is thus very promising for application to lithium-ion cells. © 1997 Elsevier Science S.A.

*Keywords:* Lithium-ion cells; Nitride; Anodes; Cobalt; Insertion; Nickel

### 1. Introduction

A great deal of effort has been put into research on anode materials for lithium secondary batteries, for example, lithium metal, lithium alloys, carbon materials and metal oxides. In particular, lithium-ion batteries with carbon anodes are now commercially available. These batteries, which are based on the lithium-intercalation reaction, perform well in terms of cycleability. However, their shortcoming is their low energy density. Therefore, it is necessary to improve the capacity for practical use. Recently, Nishijima et al. discovered that lithium ternary nitrides of  $\text{Li}_3\text{FeN}_2$  [1],  $\text{Li}_7\text{MnN}_4$  [2] and  $\text{Li}_{3-x}\text{Co}_x\text{N}$  [3] perform well as anode materials for lithium rechargeable cells. These nitrides have a specific capacity of 150–480 mAh/g, which is as large as that of carbon materials. We have subsequently found that the capacity of the  $\text{Li}_{3-x}\text{M}_x\text{N}$  (M: Co or Cu) system can be substantially increased by extracting lithium ions from the matrix [4].

In this paper, we report the anode performance of the  $\text{Li}_{3-x}\text{Co}_x\text{N}$  ( $x = 0.2\text{--}0.6$ ) system and the cycling characteristics of a lithium-ion cell in incorporating this anode material.

### 2. Experimental

The  $\text{Li}_{3-x}\text{Co}_x\text{N}$  ( $x = 0.2\text{--}0.6$ ) system was prepared by firing a mixture of lithium nitride ( $\text{Li}_3\text{N}$ ) and cobalt metal (Co)

as described previously in Refs. [3,5]. The structures of the samples were identified by X-ray powder diffraction (XRD) measurements with monochromated  $\text{Cu K}\alpha$  radiation.

We investigated the anode performance by using Li metal/ $\text{Li}_{3-x}\text{Co}_x\text{N}$  cells. The  $\text{Li}_{3-x}\text{Co}_x\text{N}$  working electrode was fabricated by mixing  $\text{Li}_{3-x}\text{Co}_x\text{N}$  powder, acetylene black powder and Teflon powder (70:25:5 by weight). The electrolyte was 1 M  $\text{LiClO}_4$ -ethylene carbonate (EC)/1,2-diethoxyethane (DEE) (1:1 by volume). The cells were cycled in the 0–1.4 V range at a current density of 0.5 mA/cm<sup>2</sup>. We measured the quasi open-circuit voltage (QOCV) by alternating extraction or insertion (0.1 mA/cm<sup>2</sup>, 2 h) with rest periods (2 h).

We measured the characteristics of the lithium-ion cells by using  $\text{Li}_{1.6}\text{Co}_{0.4}\text{N}/\text{LiNiO}_2$  cells. The  $\text{Li}_{1.6}\text{Co}_{0.4}\text{N}$  electrode was prepared by extracting lithium ions from the  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  electrode electrochemically. The electrolyte used for the lithium-ion cell was 1 M  $\text{LiPF}_6$ -ethylene carbonate (EC)/dime-thyle carbonate (DMC) (1:1 by volume). The cell was cycled in the 2.5–4.2 V range, at a current density of 0.5 mA/cm<sup>2</sup>.

### 3. Results and discussion

The  $\text{Li}_{3-x}\text{Co}_x\text{N}$  system is isostructural with  $\text{Li}_3\text{N}$  (hexagonal symmetry, space group:  $P6/mmm$  [5]) as shown in Fig. 1. According to our XRD results, the  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  product

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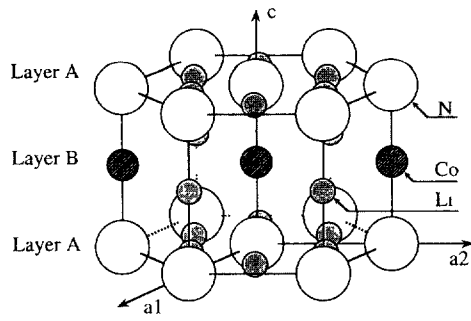


Fig. 1. Structure of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ .

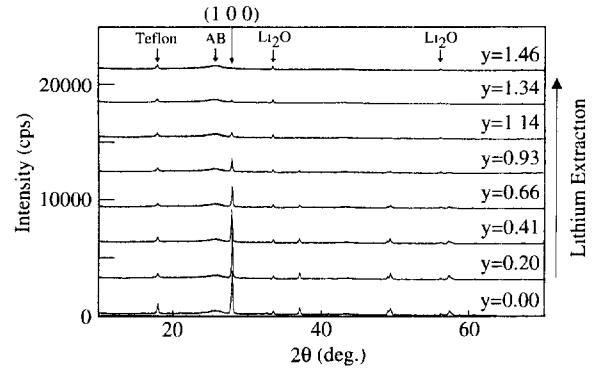


Fig. 4. Structural changes in  $\text{Li}_{2.6-x}\text{Co}_{0.4}\text{N}$  samples during the first extraction for various amounts of lithium.

had this structure [4]. The lattice parameters of the sample were about  $a = 3.68 \text{ \AA}$  and  $c = 3.71 \text{ \AA}$ , and the calculated density was  $2.1 \text{ g/cm}^3$ . This density is the same as that of graphite. Some weak  $\text{Li}_2\text{O}$  phase peaks were also observed as impurity. This was due to the oxide in the  $\text{Li}_3\text{N}$  of the starting material. This system has two kinds of lithium site with  $\text{Li}_2\text{N}^-$  layers and an  $\text{Li}^+$  layer between them. Cobalt can be substituted with lithium in the  $\text{Li}^+$  layer. The substitution limit of cobalt is  $x = 0.5$ . We confirmed by Rietveld analysis that cobalt was substituted for lithium in the  $\text{Li}^+$  layer. Here we define the  $\text{Li}_2\text{N}^-$  layer as layer A and the  $(\text{Li}-\text{Co})^+$  layer as layer B.

The voltage curves and the cycle performance of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  are shown in Figs. 2 and 3, respectively. Cell cycling began with lithium extraction. The voltage of the first lithium extraction was flat at about 1.1 V. After that, the

voltage changed with the amount of lithium ions in the matrix. The discrepancy between the capacity of the first extraction and the following insertion is attributed to some side reaction such as the insertion of lithium into the acetylene black as a conductor and the reduction of the electrolyte. The fading capacity in the early cycles seems to be caused by the growth of a protective film on the surface of the anode material and by a structural change in the sample during the lithium-extraction process. The  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  sample exhibited a high stable capacity of  $760 \text{ mAh/g}$  (about  $1.6 \text{ Li/mol}$ ) at 20 cycles. This rechargeable capacity is more than twice the theoretical capacity ( $372 \text{ mAh/g}$ ) of  $\text{C}_6\text{Li}$ . In addition, the volumetric capacity is about  $1500 \text{ mAh/cm}^3$ .

The structural changes in  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  during the first extraction are shown in Fig. 4. The intensity of the strongest peak ( $1\ 0\ 0$ ) at  $2\theta = 28^\circ$  decreased as lithium ions were extracted. The structure changed gradually from the crystalline to the amorphous state in the plateau region during the first lithium extraction. It remained in the amorphous state during subsequent cycles. Although the short range ordering in the amorphous state is still unclear, we believe that some fundamental rearrangement of elements is caused by the first lithium extraction, which leads to the increase in capacity [4].

The QOCV curves of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  for the second cycle are shown in Fig. 5. Two plateau regions (indicated by arrows)

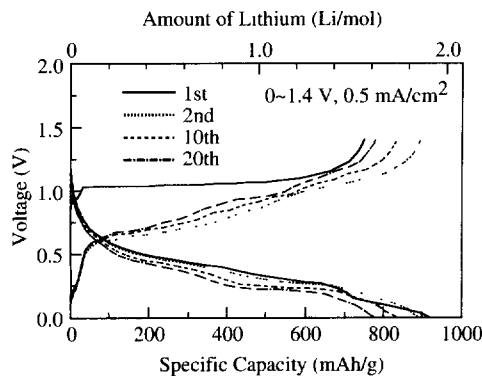


Fig. 2. Voltage curves of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ .

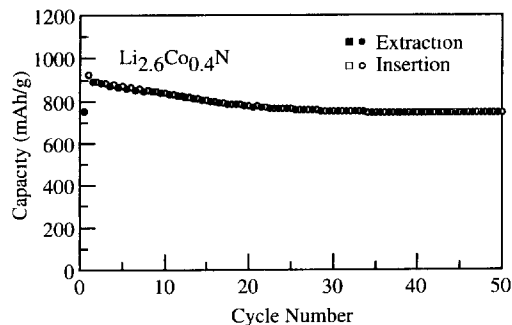


Fig. 3. Cycle performance of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ .

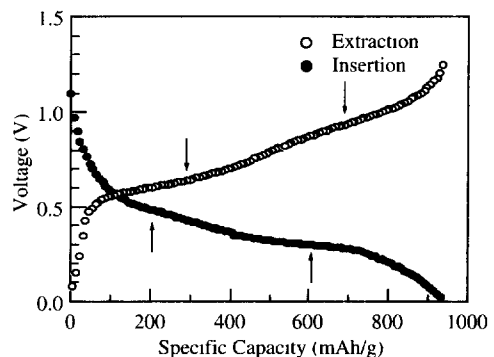


Fig. 5. QOCV curves of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  for the second cycle.

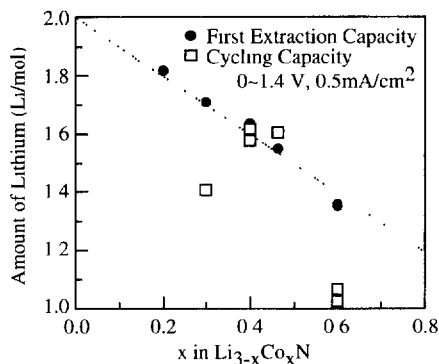


Fig. 6. First extraction capacity and cycling capacity at 20 cycles for various  $\text{Li}_{3-x}\text{Co}_x\text{N}$  compositions

were observed in each of the curves. This shows that two kinds of lithium sites with different potentials are involved in the amorphous state. In addition, we observed a large hysteresis between the extraction and insertion curves in spite of the static measurement. The hysteresis is not a kinetic polarization, and is peculiar to this sample. This result suggests that the electrochemical reaction process of extraction is different from that of insertion.

Fig. 6 shows the composition dependence of the first extraction capacity up to 1.4 V and the specific capacity at 20 cycles as a function of  $x$  in  $\text{Li}_{3-x}\text{Co}_x\text{N}$ . The first extraction capacity decreased linearly as the amount of substituted cobalt increased. The dotted line in Fig. 6 is a theoretical value calculated by assuming that lithium ions can be extracted from  $\text{Li}_{3-x}\text{Co}_x\text{N}$  up to  $\text{Li}_{1.0}\text{Co}_x\text{N}$ , that is  $2-x$  Li per mole of sample. The calculated line is in agreement with the experimental results. We assume that half the lithium ions (1 Li/mol) can be removed from layer A and all the lithium ions ( $1-x$  Li/mol) can be removed from layer B by the first extraction. According to this model, a total of  $2-x$  Li per mol are extracted, and this agrees well with the experimental results.

As shown in Fig. 6, the cycling capacity depends on the cobalt content ( $x$ ) in  $\text{Li}_{3-x}\text{Co}_x\text{N}$ . The lack of cobalt causes the structure to break during cycling. We think that cobalt acts as a kind of brace maintaining the interlayer spacing of layer A. On the other hand, the excess of cobalt causes the formation of another cobalt-rich phase, which disturbs the diffusion of the lithium ions. In conclusion,  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  is the best composition in terms of cycling capacity and cycle life.

The charge balance mechanism during insertion/extraction is interesting. With  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ , 1.6 Li/mol is involved in the first extraction. If cobalt compensates for all the charge balance of 1.6 Li/mol, the oxidation state of cobalt can be changed from  $\text{Co}^+$  to  $\text{Co}^{5+}$ . However, it is impossible for cobalt to exist in the  $\text{Co}^{5+}$  state. If lithium forms an alloy with cobalt, the capacity should increase as the amount of substituted cobalt increases. However, the capacity of  $\text{Li}_{2.4}\text{Co}_{0.6}\text{N}$  decreased more than that of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ . We think

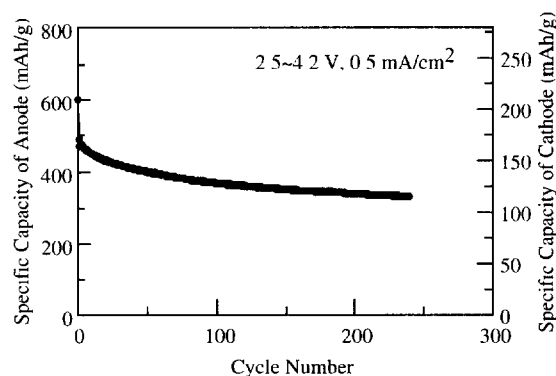


Fig. 7. Cycle performance of the  $\text{Li}_{1.6}\text{Co}_{0.4}\text{N}/\text{LiNiO}_2$  cell.

that there is little possibility of the formation of an Li-Co alloy. Therefore, we propose following models:

1. An oxidation reaction of nitrogen occurs in the extraction process. Part of  $\text{N}^{3-}$  changes to  $\text{N}^+$  according to the amount of lithium removed. For example, the oxidation state of both  $\text{N}^{3-}$  and  $\text{N}^+$  coexist in some azides such as  $\text{LiN}_3$ .
2. Some of the  $\text{N}^{3-}$  electrons are localized in the lithium site. Both the  $\text{Li}^{\sim 0+}$  (metallic) state and  $\text{Li}^+$  state coexist in the matrix. In the extraction process, oxidation reactions of  $\text{Li}^{\sim 0+}$  and  $\text{Co}^+$  occur in serial order.
3. We think that there is also a possibility of the existense of cluster-like lithium [6] in a metallic state. These models will be checked by measuring the charge balance of lithium, cobalt and nitrogen in the near future.

The cycle performance of an  $\text{Li}_{1.6}\text{Co}_{0.4}\text{N}/\text{LiNiO}_2$  lithium-ion cell is shown in Fig. 7. This cell was designed so that the  $\text{Li}_{1.6}\text{Co}_{0.4}\text{N}$  anode operated between 0–1.0 V (Li versus  $\text{Li}^+$ ) and the  $\text{LiNiO}_2$  cathode operated between 4.2–3.5 V (Li versus  $\text{Li}^+$ ). This cell showed a good cycleability of more than 240 cycles. It is now being cycle-tested. This result suggests that this system may be the most promising to date for fabricating lithium-ion cells with high capacity and good cycleability. The  $\text{Li}_{1.6}\text{Co}_{0.4}\text{N}$  anode has a specific capacity of about 500 mAh/g in the 0–1.0 V range [4]. About 100% of the anode material in this cell was utilized in the early cycles. However, the capacity decreased gradually as cycling continued. If the cell design of the voltage window and the capacity balance of the anode/cathode is optimized, this capacity decline should be improved. In addition, if this cell can be designed so that the anode operates in the 0–1.4 V range, the capacity will be substantially improved.

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