Electrochemical studies of a new anode material, $Li_{3-x}M_xN$ (M = Co, Ni, Cu)

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Abstract

$Li_{3-x}M_xN$ (M = Co, Ni, Cu) with hexagonal symmetry, $P6/mmm$, was prepared by heating a mixture of Li_3N and metallic powder in a nitrogen gas stream. Solid solutions of $Li_{3-x}M_xN$ are formed in the range of $0 \leq x \leq 0.5$, $0 \leq x \leq 0.6$, and $0 \leq x \leq 0.3$ for M = Co, Ni and Cu, respectively. The cycle performance in an $Li/Li_{3-x}M_xN$ cell was studied in the cell voltage range between 0.01 and 1.5 V. The lithium ion is easily cycled over a wide range of $0.0 \leq z \leq 1.0$ in $Li_{3-x-z}Co_xN$ and is also cycled fairly well $Li_{3-x-z}Cu_xN$ with the cell voltage range between 0 and 1.1 V. It is characteristic that the charge and discharge curves of the second cycle differ from the first one. On the other hand, in the $Li/Li_{3-x}Ni_xN$ cell, the lithium ion is only cycled in a narrow range of $0.0 \leq z \leq 0.5$ between 0.01 and 1.5 V, while the charge and discharge curves of the second cycle are almost similar to the first one. © 1997 Published by Elsevier Science S.A.

Keywords: Lithium secondary batteries; Anode materials; Lithium transition metal nitride; Cobalt nitride; Nickel nitride, Copper nitride

1. Introduction

Recently, we found that lithium transition metal nitrides, $Li_{3-x}M_xN$ which are iso-structural with Li_3N can act as new electrode materials for lithium secondary batteries. The $Li/Li_{3-x}Co_xN$ cell with 1 M $LiClO_4$/propylene carbonate + 1,2-dimethyl carbonate (PC + DME) electrolyte showed good reversibility with high specific capacities of 480 mAh/g in the 0.1 – 1.1 V range, where the lithium ion is cycled from $z = 0$ to about $z = 1$ in $Li_{2.6-z}Co_{0.4}N$ [1]. The charge and discharge curves of the nitride show no remarkable change during many cycles, and their potential in the charge and discharge curves are less than 1.1 V, which is much lower than those of oxide electrodes. This suggests that when combined with a cathode having high electrode potential relative to lithium metal these materials can be used as the anodes for Li secondary batteries. Shyodai et al. [2] studied in detail the electrode properties of these nitride systems and reported that the $Li/Li_{2.6}Co_{0.4}N$ cell with 1 M $LiClO_4$/ethylene carbonate + diethylethoxyethane (EC + DEE) electrolyte exhibited very high specific capacity of 760 mAh/g in the 0.0–1.4 V range, whose value corresponds to the extraction of Li from $Li_{2.6}Co_{0.4}N$ up to $Li_{1.0}Co_{0.4}N$ and is more than twice the theoretical capacity of C_6Li (372 mAh/g). They also pro-

posed the use of this material as the anode for lithium secondary batteries.

Li_3N is composed of $Li_2^+N^{3-}$ layers with Li^+ between them [3]. Metal ions of Co, Ni and Cu can be substituted for Li between the Li_2N layers [4]. In this paper, we prepared a series of compounds in the $Li_{3-x}M_xN$ (M = Co, Ni, Cu) systems and compared their electrode properties for a lithium secondary battery, especially for use as the anode material.

2. Experimental

$Li_{3-x}M_xN$ (M = Co, Ni, Cu) is synthesized from Li_3N (Rare Metallic, 99.5%) and metallic powder using traditional ceramic methods. Mixtures of Li_3N and metallic powder were pressed into tablets, 8 mm in diameter and 5–8 mm in thickness, under a pressure of 3 MPa and then heated in an electrical furnace between 500 and 750 °C under 99.9% N_2 or (1% H_2–99% N_2) stream. The heating rate was 50 °C/min. Before firing, the furnace was evacuated by a rotary pump to remove moisture, oxygen and CO_2.

X-ray diffraction (XRD) measurements were performed on a Rigaku RAD-RC (12 kW) using monochromated Cu Kα radiation. Because the products are very hygroscopic, they were protected against moisture during the XRD measurement by a gas-tight holder filled with argon gas. A 7 µm

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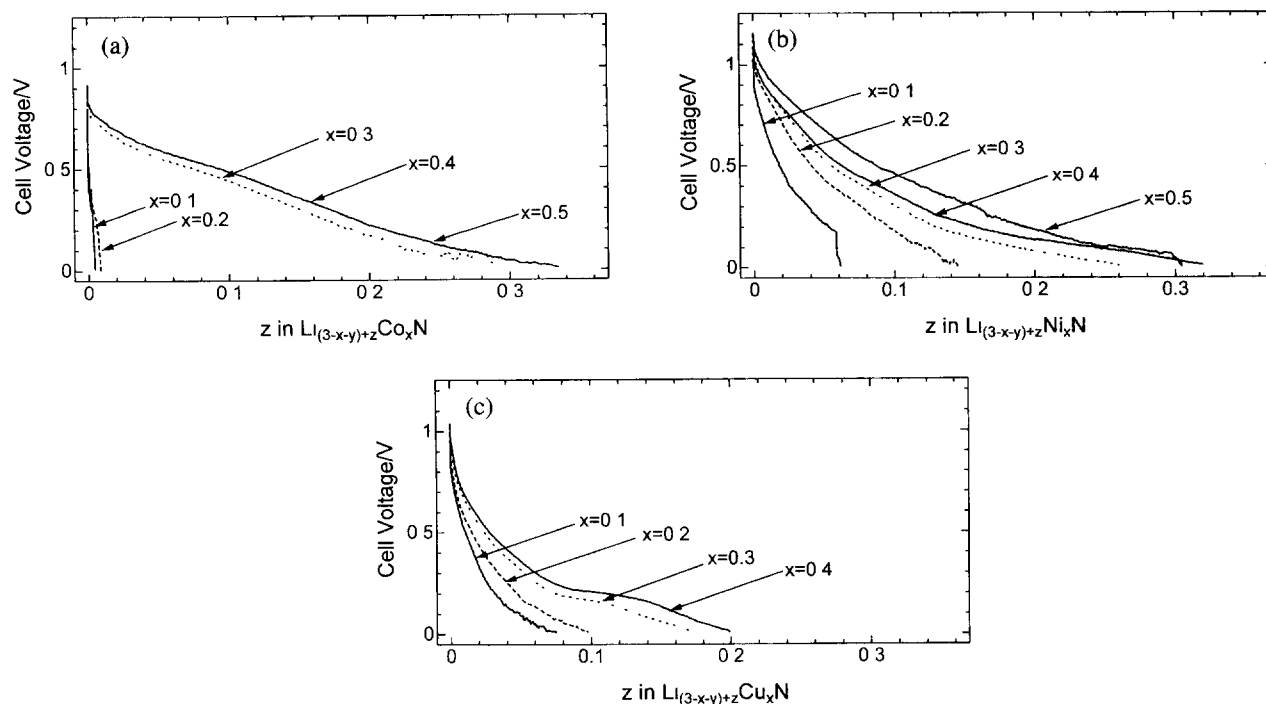
(a) Cell Voltage/V

x=0 3
x=0.4
x=0 1
x=0.2
x=0.5

z in $Li_{(3-x-y)+z}Co_xN$

(b) Cell Voltage/V

x=0 1
x=0.2
x=0 3
x=0 4
x=0.5

z in $Li_{(3-x-y)+z}Ni_xN$

(c) Cell Voltage/V

x=0 1
x=0 2
x=0.3
x=0 4

z in $Li_{(3-x-y)+z}Cu_xN$

Fig. 1. The first discharge curves for the $Li/Li_{3-x-y}M_xN$ cells. The subscript y stands for the lithium vacancy: (a) $Li_{3-x}Co_xN$; (b) $Li_{3-x}Ni_xN$, and (c) $Li_{3-x}Cu_xN$.

thick aluminum window covered the sample holder plate in an arc.

To obtain $Li_{3-x-z}M_xN$ having various z values, a conventional Li coin-type cell was assembled. The sample (50 mg) was ground and mixed with acetylene black (10 mg) as an electron conductor and Teflon (0.5 mg) as a binder; the mixture was pressed into a tablet of 12 mm in diameter under a pressure of 1 MPa. Using this tablet as a cathode, Li sheet as an anode and 1 M $LiClO_4/PC + DME$ as the electrolyte, the cell was assembled. Li ions were de-intercalated by charging the cell at various current densities. The resultant samples having various Li contents were then measured by XRD.

All treatment of the samples, except for the heating in a furnace and the discharge/charge experiments, were carried out in an argon-filled dry box.

3. Results and discussion

The solid solutions in $Li_{3-x}M_xN$ prepared under an nitrogen gas flow are formed in the range of $0 \leq x \leq 0.5$, $0 \leq x \leq 0.5$, $0 \leq x \leq 0.6$, and $0 \leq x \leq 0.3$ for M = Co, Ni, and Cu, respectively. When $1\%H_2-99\%N_2$ gas was used, the solid solution ranges narrowed to $0 \leq x \leq 0.4$, $0 \leq x \leq 0.5$, and $0 \leq x \leq 0.3$, respectively. Our samples prepared by using $1\%H_2-99\%N_2$ gas may contain hydrogen in the structure. In this study, the samples prepared under nitrogen gas were used.

Fig. 1 shows the closed-circuit voltage (CCV) curves of the $Li/Li_{3-x}M_xN$ cells for the first discharge direction at a current density of 300 $\mu A/cm^2$. As shown later, at least in

$Li_{3-x}Co_xN$ and $Li_{3-x}Ni_xN$, the discharge capacity is due to the Li intercalation into the vacant sites of Li caused by the existence of Co^{2+} or Ni^{2+} valence states, that is, the initial composition is represented as $Li_{3-x-y}(M_{x-y}^+M_y^{2+})N$ where y indicates Li vacancy [1]. The first discharge curves of the $Li/Li_{3-x}Cu_xN$ cells show smaller capacity than the other two and changes its slope at around $z \sim -0.08$ in $Li_{3-x-y-z}Cu_xN$ where z represents the discharged amount of Li. As discussed later, only the initial part of the discharge curve seems to correspond to the Li vacancy.

Fig. 2 shows the discharge/charge curves at a current density of 300 $\mu A/cm^2$ for $Li/Li_{3-x}M_xN$ cells with $x = 0.4, 0.5$, and 0.4 for M = Co, Ni and Cu, respectively. The composition of these x values showed the highest capacity, although $Li_{2.6}Cu_{0.4}N$ is a mixture with Cu metal. (The description, $Li_{2.6}Cu_{0.4}N$ means the mixing ratio of the starting materials. The real composition of nitride in this sample may be between $Li_{2.7}Cu_{0.3}N$ and $Li_{2.6}Cu_{0.4}N$.) The charge and discharge depth was limited to $z = 1.0$ and 0.01–1.5 V in $Li_{2.6-z}Co_{0.4}N$ and $Li_{2.6-z}Cu_{0.4}N$, and to $z = 0.5$ and 0.01–1.5 V in $Li_{2.5-z}Ni_{0.5}N$ where z represents the charged (+) or discharged (−) amount of Li.

In the case of cobalt and nickel, the capacity (−z) of the discharge seems to correspond to the amount of lithium vacancy (y) in the nitrides represented as $Li_{3-x-y-z}M_xN$ ($y \sim 0.3$ in $Li_{2.6-y-z}Co_{0.4}N$ and $Li_{2.5-y-z}Ni_{0.5}N$). The cell voltage curves during the following first charge are divided into two parts, that is, at first, they gradually increase up to 1.1 V ($z \sim 0.25$) in $Li_{2.6-y-z}Co_{0.4}N$ and 1.3 V ($z \sim 0.3$) in $Li_{2.5-y-z}Ni_{0.5}N$, and afterwards they remained constant. The capacity of the first part seems to correspond to the de-inter-
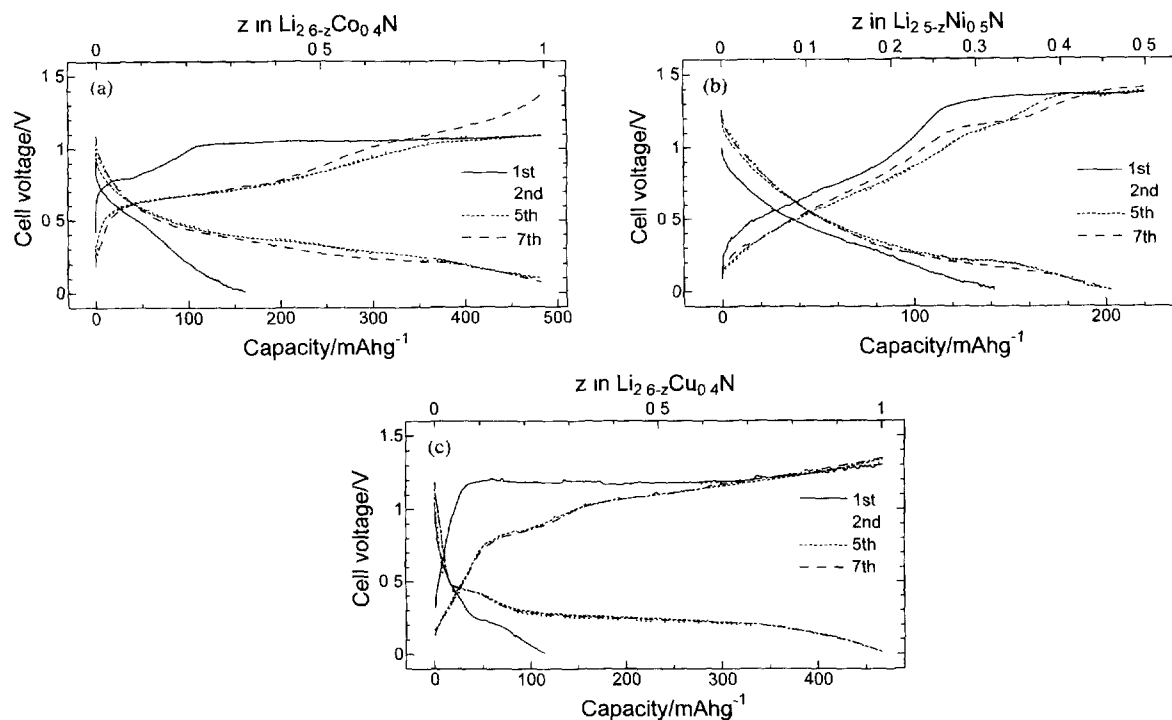
Fig. 2. The discharge and charge closed-circuit voltage curves for the Li/Li$_{3-x}$M$_x$N cells. The current density was 0.3 mA/cm^2: (a) Li$_{3-x}$Co$_x$N; (b) Li$_{3-x}$Ni$_x$N, and (c) Li$_{3-x}$Cu$_x$N.

calation of the same amount of lithium intercalated into Li$_{2.6-y-z}$Co$_{0.4}$N and Li$_{2.5-y-z}$Ni$_{0.5}$N at the first discharge, because the charge transferred is consistent with the first discharged capacity ($z \sim 0.3$ in Fig. 1) and the first part of the first charge ($z \sim 0.3$ in Fig. 2). This is also supported by the variation of lattice parameters with cycling in the Li/Li$_{2.4}$Co$_{0.6}$N cell as mentioned later.

In the case of the Li/Li$_{2.6-y}$Cu$_{0.4}$N cell, the initial part of the charged curve is very short, whose capacity only corresponds to the first step seen in the first discharge curve (Figs. 1 and 2). As the oxidation state of Cu$^+$ is common in many compounds contrary to the uncommon case of Co$^+$ and Ni$^+$, only a small amount of lithium vacancy is formed in Li$_{3-x}$Cu$_x$N. Therefore, lithium intercalation and de-intercalation occurs only in a small range.

During the second discharge cycle in Li$_{2.6-z}$Co$_{0.4}$N and Li$_{2.6-z}$Cu$_{0.4}$N in Fig. 2, the cell voltage gradually decreases to 0 V, where the capacity is almost similar to that of the next charge and discharge cycles. The charge behavior after the second cycle is different from that of the first one and does not vary with cycle number any more. The cell voltage increases gradually from 0.5 to 1.4 V indicating that topochemical lithium de-intercalation occurs.

Fig. 3 shows the variation of XRD patterns of Li$_{2.6-z}$Co$_{0.4}$N charged up to $z = 1.5$, as an example. The intensity of Li$_{2.6-z}$Co$_{0.4}$N decreases with z and an amorphous pattern becomes dominant at $z = 1.5$, whose phenomenon is also observed in Li$_{3-x}$Cu$_x$N, indicating that the particles of Li$_{3-x}$M$_x$N are crushed with the first charge. The charge/discharge behavior after the second cycle is not due to the

crystalline Li$_{3-x}$M$_x$N but to this amorphous material. On the contrary, the cell voltage in the Li/Li$_{2.5-z}$Ni$_{0.5}$N cell reaches 1.4 V at around $z = 0.5$, whose capacity is half of that of cobalt and copper nitrides. However, as Li$_{3-x-z}$Ni$_x$N retains the structure up to $z = 0.5$, no large difference is seen between the first charge and after the second charge curves.

Fig. 4 shows the variation of lattice parameters of Li$_{2.6-z}$Co$_{0.4}$N, Li$_{2.5-z}$Ni$_{0.5}$N, and Li$_{2.6-z}$Cu$_{0.4}$N at various charge/discharge depths in the range of $0 \leq z \leq 1.0$ after the first discharge. The lattice parameters of Li$_{2.6-z}$Co$_{0.4}$N vary with the first charge until $z \sim 0.3$. The a-axis decreases and
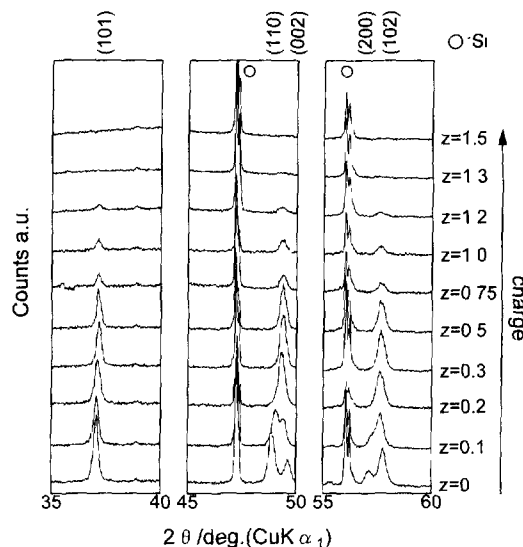

Fig. 3. X-ray diffraction patterns of Li$_{2.6-z}$Co$_{0.4}$N for various charge depths.

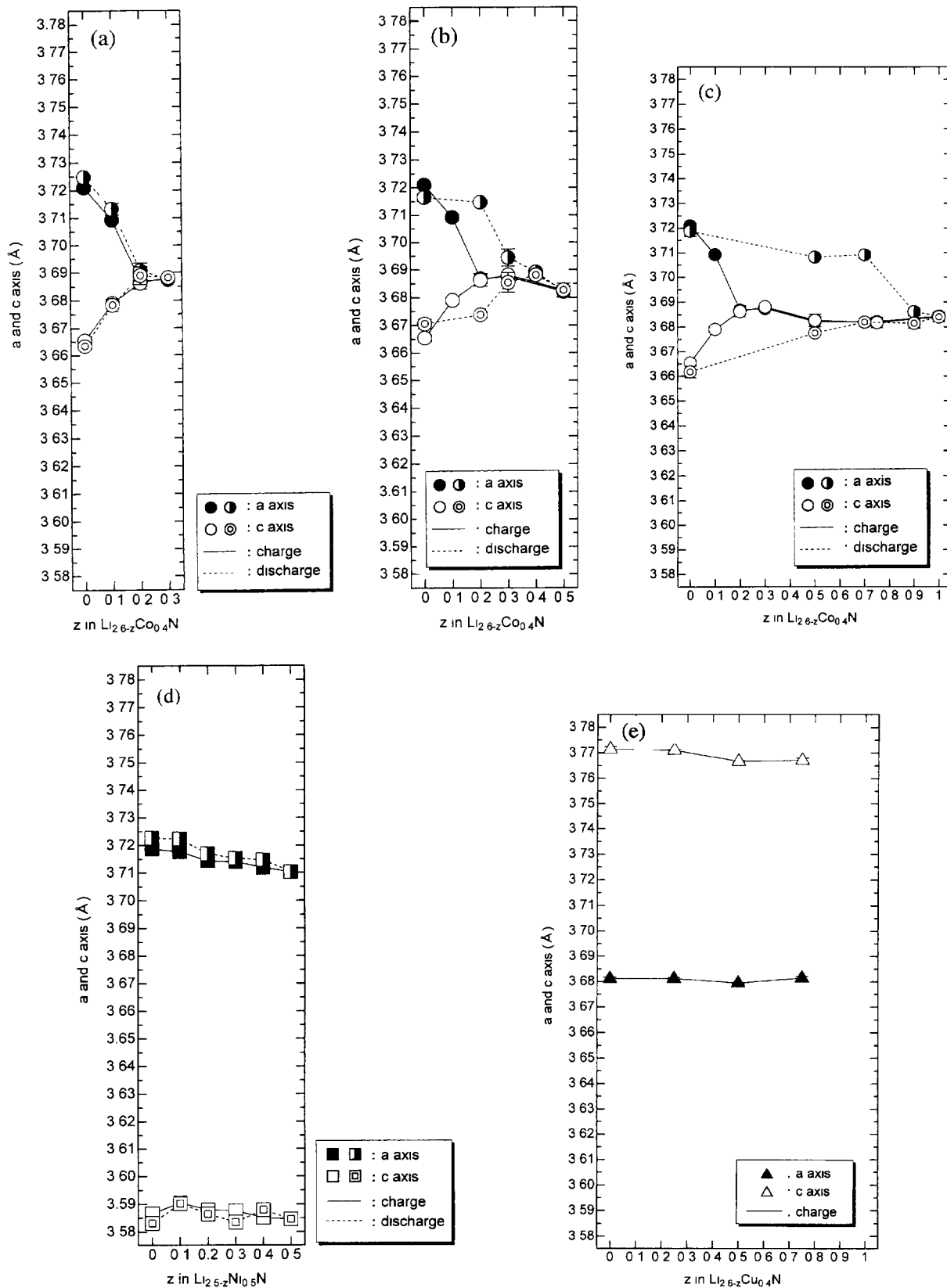Fig. 4. Variation of lattice parameters of $Li_{3-x-z}M_xN$ with various charge/discharge depths (z): (a) $Li_{2.6-z}Co_{0.4}N$ cycled in the range of $0 \leq z \leq 0.3$, (b) $Li_{2.6-z}Co_{0.4}N$ cycled in the range of $0 \leq z \leq 0.5$, (c) $Li_{2.6-z}Co_{0.4}N$ cycled in the range of $0 \leq z \leq 1.0$; (d) $Li_{2.5-z}Ni_{0.5}N$ cycled in the range of $0 \leq z \leq 0.5$, and (e) $Li_{2.6-z}Cu_{0.4}N$ cycles in the range of $0 \leq z \leq 0.8$.

the c-axis increases, which corresponds to the composition range where the voltage increases gradually up to 1.1 V. The lithium de-intercalation reaction goes on as a single-phase reaction. Above $z \sim 0.3$, no remarkable change in the cell parameters is observed until $z = 1.0$, but the decrease in peak intensity becomes remarkable. In Fig. 4(a)–(c), the variation of cell parameters with the second discharge in the Li/ $Li_{2.6-z}Co_{0.4}N$ cell from $z = 0.3$, 0.5 and 1.0 are shown. From $z = 0.3$, the variation of both the a- and c-axes trace exactly those of the first charge, but shift to the left in 0.2 and 0.7 in the case of the second discharge from $z = 0.5$ and 1.0, respectively. This means that only 0.3 Li can be extracted from the crystalline $Li_{2.6}Co_{0.4}N$ and the amorphous phase formed with the first charge affects the charge/discharge behavior after the second discharge.

In $Li_{2.5-z}Ni_{0.5}N$, however, the lattice parameters continue to vary until $z = 0.5$, both the a- and c-axes decrease with the charge but the degree of change is smaller than that in $Li_{2.6}Co_{0.4}N$. In the case of $Li_{2.5-z}Ni_{0.5}N$, lithium de-intercalation and intercalation occurs at least between $z = 0.0$ and 0.5, which is reflected with no large difference between the first charge and the second charge curves in the Li/$Li_{2.5}Ni_{0.5}N$ cell.

$Li_{2.6-x}Cu_{0.4}N$ shows no change in the lattice parameters with change in x, but only a decrease of the peak intensities. This shows that the lithium de-intercalation hardly occurs and the formation of an amorphous phase appears in the very early charged region. The very short part in the first charged curve before the second plateau (Fig. 1(c)) may correspond to the lithium de-intercalation region.

Shyodai et al. [2] reported a higher capacity than ours in these systems; for example, in $Li_{2.6}Co_{0.4}N$, the capacity reported is 760 mAh/g in the 0.0–1.4 V range (in our case, 480 mAh/g). This may be explained by the difference in electrolyte used. Our electrolyte was 1 M $LiClO_4$/ PC + DME, but 1 M $LiClO_4$/EC + DEE. We also tried the latter electrolyte system and got a similar capacity as Shyodai et al. The amorphous phase may be a sort of compound involving the reaction with the electrolyte, which plays an important role in the capacity and cycle performance of Li/ $Li_{3-x}M_xN$ cells.

4. Conclusions

It was shown that lithium transition metal nitrides, $Li_{3-x}M_xN$ (M = Co, Ni, Cu) can be easily synthesized from Li_3N and metallic powder under a nitrogen gas stream. Metal ions are substituted for the lithium site in the range of $0 \le x \le 0.5$, $0 \le x \le 0.6$, and $0 \le x \le 0.3$ for M = Co, Ni and Cu, respectively. Li/$Li_{3-x-z}M_xN$ cells were cycled in the range of $0 \le z \le 1.0$ and showed a high capacity of 480 mAh/ g in $Li_{2.6-z}Co_{0.4}N$, and 460 mAh/g in $Li_{2.6-z}Cu_{0.4}N$, but only 200 mAh/g in $Li_{2.5-z}Ni_{0.5}N$. The high capacity in M = Co and Cu was due to the amorphous phase formed during the first charge, which shows good reversibility and low potential to the lithium metal (0.5 V in average). The crystalline $Li_{3-x-z}M_xN$ (M = Co and Cu) can de-intercalate and intercalate lithium ions only in the limited z range. On the crystalline $Li_{3-x-z}M_xN$ (M = Co and Cu) can de-intercalate and intercalate lithium ions only in the limited z range. On the contrary, lithium ions are de-intercalated and intercalated in $Li_{3-x-z}Ni_xN$ more widely (at least $z \sim 0.5$) showing small change of the cell volume. $Li_{3-x}M_xN$ (M = Co and Cu) is thus suggested to be a good candidate for the anode in a lithium secondary battery because of their good reversibility and low voltage in Li/$Li_{3-x}M_xN$ cells.

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