Synthesis and charge–discharge properties of Li$_{1+x}$Ni$_{1-x-y}$Co$_y$O$_{2-z}$F$_z$

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Abstract

LiNiO$_2$ is one of the best cathode active materials for applying to lithium rechargeable batteries because of large capacity. However, its unsatisfactory cycling properties and difficulties in handling are not yet to be improved. It was found by some groups [M.G.S.R. Thomas, W.I.F. David, J.B. Goodenough, P. Groves, Mater. Res. Bull. 20 (1985) 1137; J.R. Dahn, U. von Sacken, C.A. Michal, Solid State Ionics 44 (1990) 87] that cation substitution reduces the lattice deformation during charging or discharging and improves the cycling properties. On the other hand, we reported [T. Ohzuku, A. Ueda, M. Kouguchi, J. Electrochem. Soc. 12 (1995) 4033] that addition of LiF to the starting materials, causing fluorine substitution for the anion, is also effective to obtain a better cycling life for LiNiO$_2$, though the problem of the lattice deformation is not alleviated. Thus, it was expected that simultaneous substitution of cation- and anion sites might be useful. We synthesized Li$_{1+x}$Ni$_{1-x-y}$Co$_y$O$_{2-z}$F$_z$ by an ordinary solid state reaction and evaluated the charge–discharge properties of this series of samples. The initial discharge capacity of Li$_{1.075}$Ni$_{0.755}$Co$_{0.17}$O$_{1.9}$F$_{0.1}$ was 182 mAh/g. The capacity decrease rate was only 2.8% in the first 100 cycles, and became even smaller as the cycle number increased. The result suggests that each of the Co- and F substitution independently contributes to the improvement of cycling properties of LiNiO$_2$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium nickelate; Cobalt; Cathode active material; Fluorine; Lithium ion battery; Co-substitution

1. Introduction

It has so far been reported that LiNiO$_2$ is one of the most suitable cathode active materials to realize lithium ion batteries with high performance [1–4]. This is one of the few series having the lithium rechargeable structure with not only some ionic but also electronic conductivity. Furthermore, the material can be used to realize a battery possessing high energy density, demonstrating a high charging voltage in the 3.5–4.5 V range. However, its actual cycle life has not reached a satisfactory level. Several efforts have been made to improve the charge–discharge cycling properties. Some groups performed trivalent cation substitution on the nickel site [5,6], to minimize the structural deformation [7,8] during charging or discharging. This method actually gives rise to the improvement of the cycling life. On the other hand, we reported [9] that addition of LiF to the starting materials, causing fluorine substitution for the anion, is also effective to obtain a better cycling life for LiNiO$_2$. Thus, we per-

formed simultaneous substitution of cation- and anion sites to study the mechanism of capacity decrease on cycling and to improve the cycling properties.

2. Experimental

We chose Co as a cation substituent because it is easily introduced into the lattice, and synthesized Li$_{1+x}$Ni$_{1-x-y}$Co$_y$O$_{2-z}$F$_z$ by an ordinary solid state reaction; a mixture of LiOH · H$_2$O, LiF and co-precipitated (Ni, Co)(OH)$_2$ powders with a molar ratio of $1+x-z$: z : $1-x$ ($z = 2x - 0.05$ [7]) was fired at 675°C in an oxygen flow. The synthesized samples were ground to obtain sufficiently fine powders. The crystal structure and phase were identified using an X-ray diffractometer with Cu Kα. The composition and oxidation number of the nickel ion were measured by a combination of ICP analysis, EDTA (ethylene di-amin tetra acetic acid) titration, ion chromatography and redox titration. We found there is almost no significant difference between expected and final compositions [6]. Cathodes were prepared by intimately mixing active materials, acetylene black as a conducting material and a PTFE

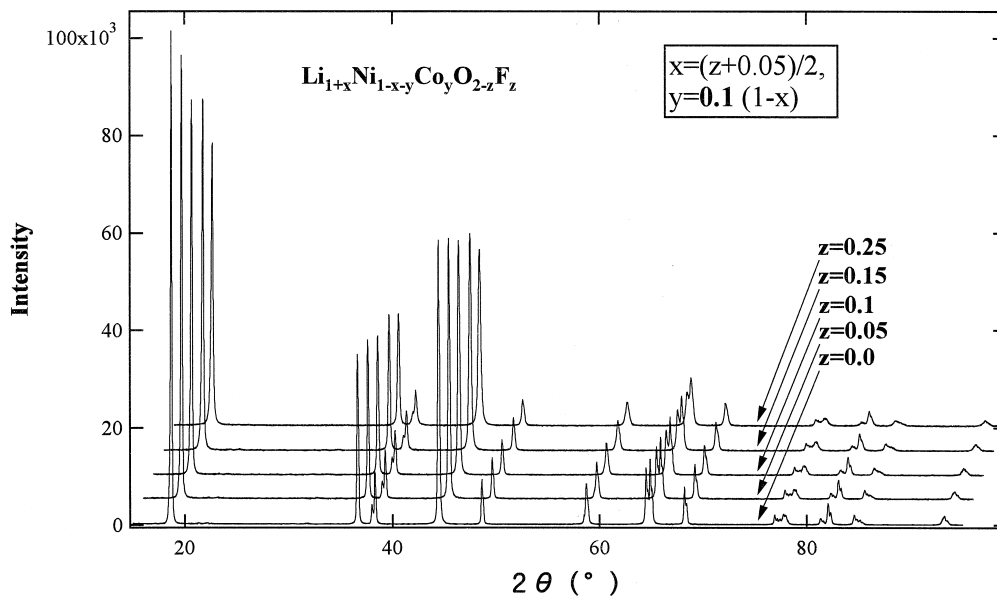* Corresponding author. E-mail: koichi.kubo@toshiba.co.jp

Fig. 1. X-ray diffraction patterns of $Li_{1+x}Ni_{1-x-y}Co_yO_{2-z}F_z$ Co/Ni = 0.18.

(poly-tetra-fluoro-ethylene) binder in the weight ratio of 80:17:3, then cut and pressed into the shape of a 1×1 cm^2 sheet. The 1 M LiClO$_4$ solution in the mixed agent of ethylene carbonate and ethyl–methyl carbonate with the volume ratio of 1 to 1 made by Tomiyama Chemical was used as the electrolyte. for the electrochemical measurements. The reference and the anode material were lithium metal. Cells for the measurements were assembled in a glove box filled with Ar gas. In all the measurements, the charge and discharge current was 1 mA and voltage range was from 3–4.3 V vs. Li$^+$/Li.

3. Results and discussions

We measured X-ray diffraction patterns for the synthesized materials in the range of 2-theta from 15 deg. to 95 deg. to identify the phases. Figs. 1 and 2 show the X-ray
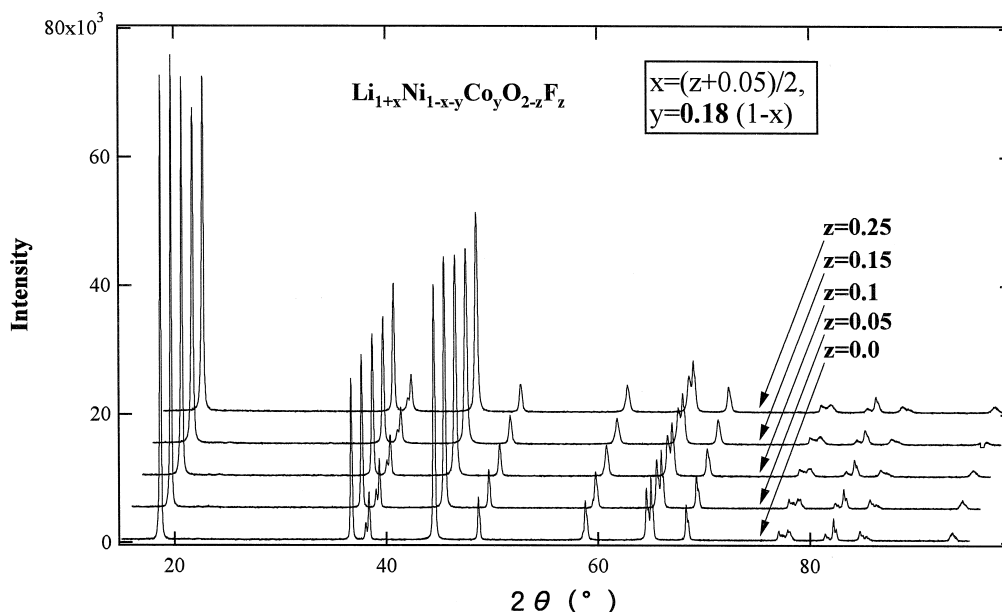

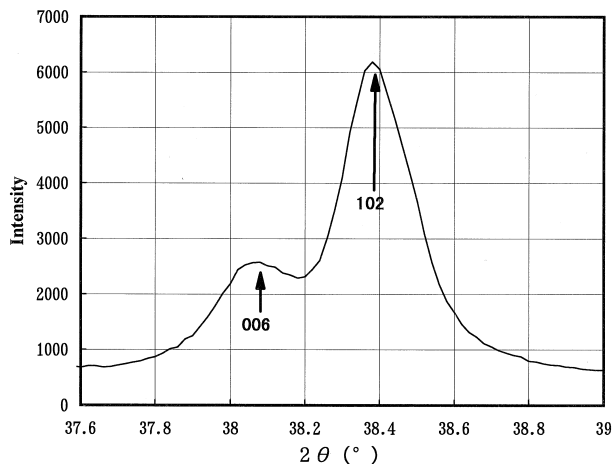Fig. 2. X-ray diffraction patterns of $Li_{1+x}Ni_{1-x-y}Co_yO_{2-z}F_z$ Co/Ni = 0.1.

Fig. 3. X-ray diffraction pattern around 102 peak of $Li_{1.15}Ni_{0.7}Co_{0.15}O_{1.75}F_{0.25}$.

Fig. 5. Cycling properties for $Li_{1+x}Ni_{1-x-y}Co_yO_{2-z}F_z$. Current: 1 mA, voltage: 3.0–4.3 V, electrolyte: 1 M $LiPF_6$ in EC/EMC(1:1).

diffraction patterns of $Li_{1-x}Ni_{1-x-y}Co_yO_{2-z}F_z$, in which atomic ratios of Co/Ni are 0.1 and 0.18, respectively. The diffraction patterns were almost the same as the pattern of pure $LiNiO_2$ and no secondary phases were observed in all samples. In both series, the intensities of diffraction peaks become weaker and broader with the increasing fluorine content.

Fig. 3 shows the fine structures of $Li_{1.15}Ni_{0.7}Co_{0.15}O_{1.75}F_{0.25}$ around the diffraction peak 102. If LiF in the starting materials was not introduced into the $LiNiO_2$ structure, $Li_{1.15}Ni_{0.7}Co_{0.15}O_{1.75}F_{0.25}$ should be separated out as the right side of the following equation shows.

$$Li_{1.15}Ni_{0.7}Co_{0.15}O_{1.75}F_{0.25} = 0.88(Li_{0.25}Ni_{0.795}Co_{0.18}O_2 + 0.28LiF) \qquad (1)$$
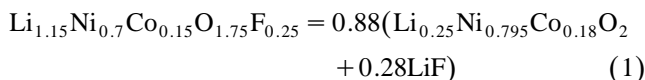
Fig. 4 shows the diffraction pattern of the aforementioned right side mixture in the same angle region as in Fig. 3. The diffraction peak from LiF was clearly observed around the left shoulder of the 102 peak in Fig. 4 while no peak from LiF was seen in Fig. 3. Thus, we conclude that
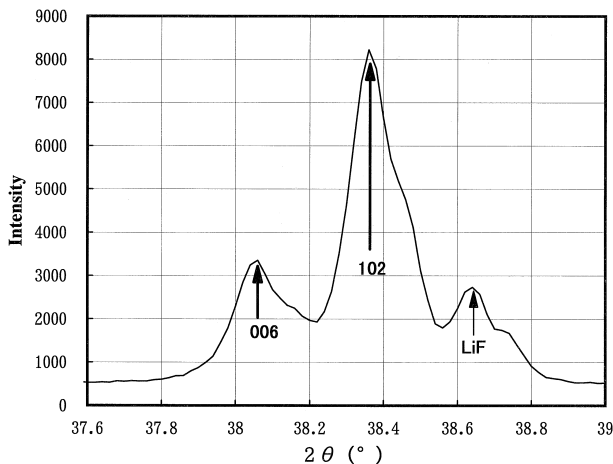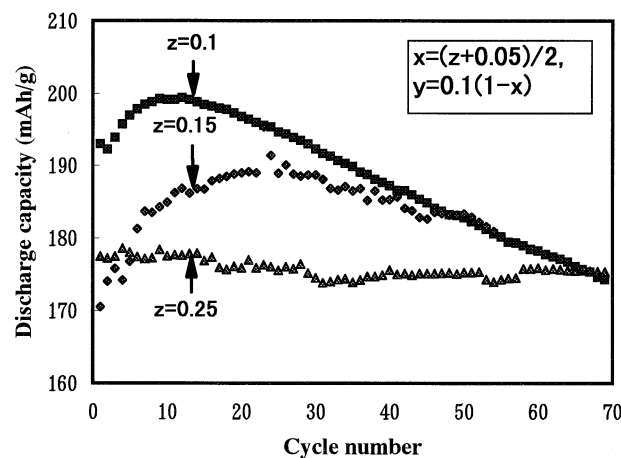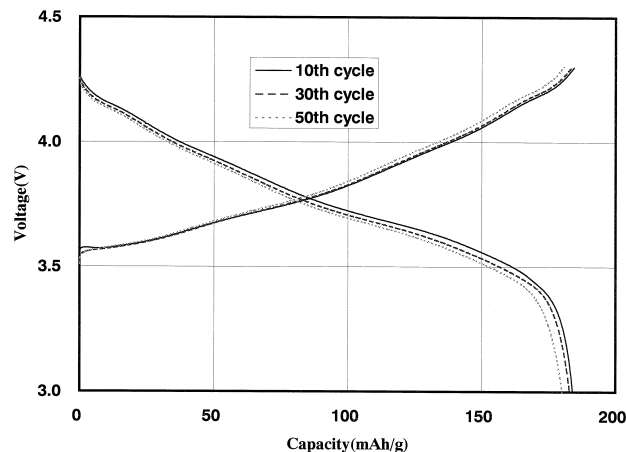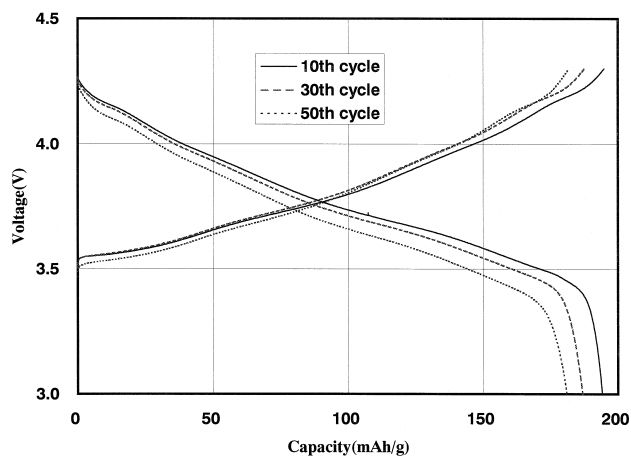

Fig. 6. Cycling properties of $Li_{1+x}Ni_{1-x-y}Co_yO_{2-z}F_z$. Current: 1 mA, voltage: 3.0–4.3 V, electrolyte: 1 M $LiPF_6$ in EC/EMC(1:1).

Charge-Discharge Curve of $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$

Fig. 7. Charge–discharge curves for 10th, 30th and 50th cycles of $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$. Current: 1 mA, voltage: 3.0–4.3 V, electrolyte: 1 M $LiPF_6$ in EC/EMC(1:1).

Fig. 4. X-ray diffraction pattern around 102 peak for mixture of $LiNi_{0.82}Co_{0.18}O_2$ and 0.28LiF.

Fig. 8. Charge–discharge curves for 10th, 30th and 50th cycles of $LiNi_{0.82}Co_{0.18}O_2$. Current: 1 mA, voltage: 3.0–4.3 V, electrolyte: 1 M $LiPF_6$ in EC/EMC(1:1).

and the cycling life is improved. As the Co content increases, more fluorine content is necessary to suppress the capacity decrease. Above all, $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$ exhibited the best performance. While the initial discharge capacity of $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$ was 182 mAh/g, the capacity decrease rate was only 2.8% in the first 100 cycles and became even smaller as the cycle number increased. Therefore, in order to clarify the influence of the fluorine introduction, we compared the difference of the charge–discharge properties between the materials with or without fluorine. The charge–discharge curves at 10th, 30th and 50th cycles for $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$ and $LiNi_{0.82}Co_{0.18}O_2$ are shown in Figs. 7 and 8, respectively. The curves for $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$ maintained almost the same shape up to a large cycle number. However, the curve for $LiNi_{0.82}Co_{0.18}O_2$ slightly changed in the shape as the cycling proceeds. In order to compare the change in the shapes of the charge–discharge curves for $LiNi_{0.82}Co_{0.18}O_2$ and $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$ more clearly, the differential chronopotentiograms calculated from the curves at the 10th, 30th and 50th cycles are shown in Fig. 9. Using this kind of analysis, the characteristic change of the shapes of the charge–discharge curves is emphasized. In each figure, the upper parts of the curves show some structures during charging, lower parts during discharging. The most distinguishable difference between the curves for $Li_{1.075}Ni_{0.755}$-

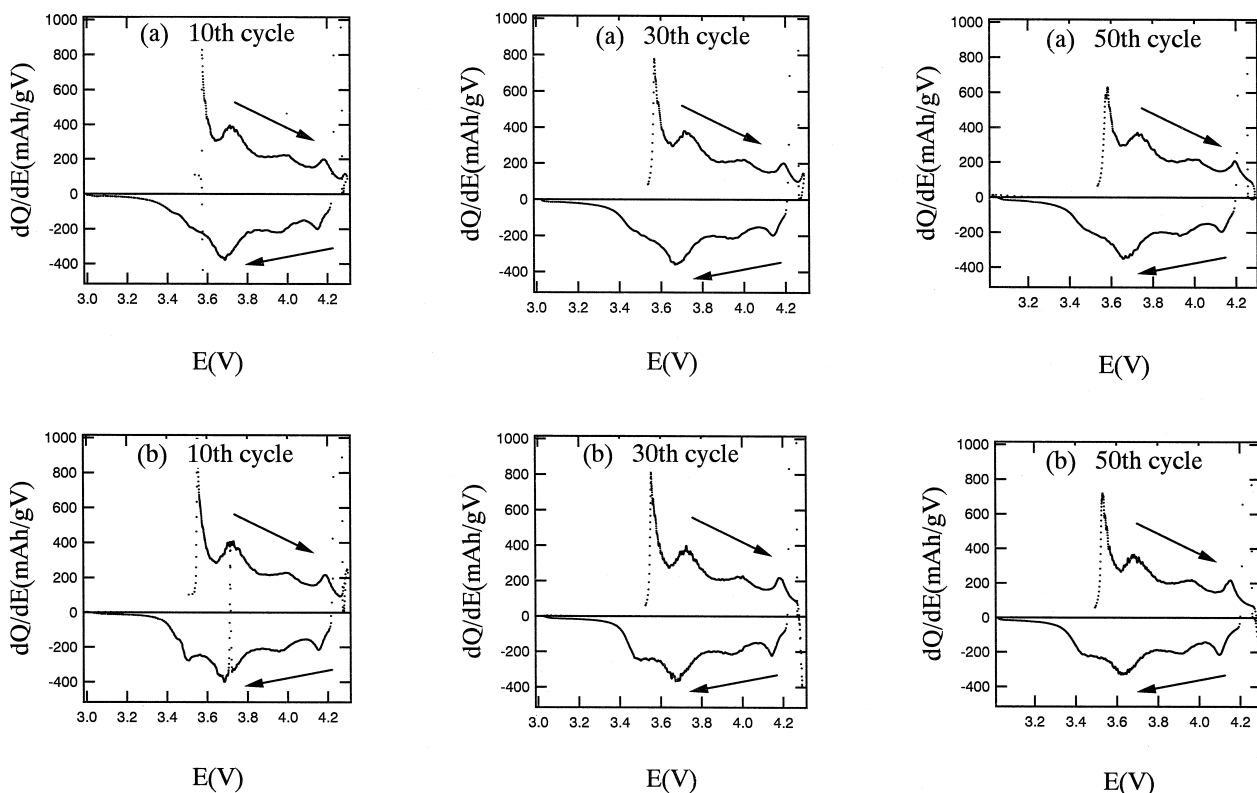$Li_{1.15}Ni_{0.7}Co_{0.15}O_{1.75}F_{0.25}$ showing the pattern in Fig. 3 is essentially a single phase material. The cycling properties of $Li_{1+x}Ni_{1-x-y}Co_yO_{2-z}F_z$ in which Co/Ni atomic ratio is 0.1 and 0.18 for various fluorine contents are shown in Figs. 5 and 6, respectively. The results indicate that, as the fluorine content increases, the initial capacity decreases

Fig. 9. Differential chronopotentiogram for $Li_{1+x}Ni_{1-x-y}Co_yO_{2-z}F_z$: (a) $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$ and (b) $LiNi_{0.82}Co_{0.12}O_2$.

$Co_{0.17}O_{1.9}F_{0.1}$ and $LiNi_{0.82}Co_{0.18}O_2$ is the shape of the peaks near the end of discharging (around 3.45 V in the lower curves). The former material, containing fluorine, shows almost no differences of the shape among the various cycle numbers. However, in the latter material, the shape of the peak is initially sharp, and as the cycling proceeds, the shape of the peak becomes dull and rather closer to the shape of the former material. The results indicate that the material containing fluorine has a more stable structure against the charging and discharging than the material without fluorine. Furthermore, even in the material without fluorine, the shape of the charge–discharge curve approaches the shape of the material containing fluorine as the cycling proceeds.

4. Conclusion

We found each of the Co- and F substitution independently contributes to the suppression of capacity fading in the cycling properties of $LiNiO_2$. We confirmed the initial discharge capacity of $Li_{1.075}Ni_{0.755}Co_{0.17}O_{1.9}F_{0.1}$ is 182 mAh/g, the capacity decrease rate is only 2.8% in the first 100 cycles and becomes smaller as the cycle number increases. The fluorine introduction makes the shape of the charge–discharge curve remain almost constant even after the a large number of cycling. In particular, the shape around the end of discharge curves is influenced by the fluorine introduction. In order to elucidate the real reason for the improvement of the cycling properties, however, further efforts will be needed.

Acknowledgements

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