Cobalt stabilized layered lithium–nickel oxides, cathodes in lithium rechargeable cells

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Abstract

In the present paper the effect of cobalt, as substituent, on the stabilization of layered lithium–nickel oxides has been shown. Using an original method of synthesis, the series $LiCo_{1-x}Ni_xO_2$ ($0<x<1$), has been obtained and analysed by X-ray powder diffraction. The electrochemical characteristics has been obtained in a three-electrode glass cell using standard electrolyte of 1 M $LiClO_4$ in propylene carbonate:dimethyoxyethene. It has been demonstrated by cyclic voltammetry that the reversibility in the ternary Li–Ni–Co–O system increases with the Co content due to the enhanced stability and structural order of materials.

Keywords: Rechargeable lithium batteries; Cobalt; Nickel oxide; Cathodes

1. Introduction

Lithiated cobalt and nickel oxides are becoming very attractive as active cathode materials for power sources of high energy density. Li_xCoO_2 ($x=0$–0.98) is easily synthesized from lithium and cobalt salts or oxides [1–5] but has a relatively high oxidizing potential on charge (4.2–4.4 V). The nickelate is synthesized by a more complex procedure [2–5] but has a lower charging potential (3.75–4.0 V) which increases the system stability. The $Li_xNi_{2-x}O_2$ is homogeneous in the range $0.6<x<1$, but non-stoichiometric, the lithium content is strongly depending on the way of synthesis [6]. Lithiated cobalt and nickel oxides are iso-structural which makes the preparation of solid solutions of $LiNi_{1-y}Co_yO_2$ for $0<y<1$ possible.

The cathodic materials of a mixed lithiated nickel–cobalt oxide, recently proposed as most perspective [3,4,7], are still little investigated.

The aim of the present paper is to study the electrochemical behaviour, as well as the possibilities for practical application of layered lithiated nickel oxide stabilized by Co^{3+} substitution as active cathode materials in non-aqueous rechargeable cells.

2. Experimental

Zhecheva and Stoyanova [7] kindly supplied us with samples of mixed ternary oxides Li–Ni–Co–O char-acterized chemically, as well as by X-ray and differential thermal analyses for testing their electrochemical parameters.

The electrochemical characteristics are obtained in a three-electrode glass cell with lithium reference electrode (previously described in Ref. [8]) in excess of electrolyte. The used electrolyte is a 1 M solution of $LiClO_4$ in propylene carbonate:dimethoxyethane, 1:1 by volume. The model electrode consists of a mixture of 50% teflonized acetylene black (TAB) and 50% tested active cathode material pressed on a 15 mm expended aluminium net ring. The weight of the test electrode, thus obtained, is 70 mg. The electrochemical performances are carried out by cyclic voltammetry in the potential range from 3.0 to 4.3 V versus Li/Li^+ reference electrode. The scan rate was 0.07 mV/s in all experiments.

3. Results and discussion

The investigated samples with a Co content from 0.2 to 0.8 were pure monophase solid solutions with high crystallinity. Fig. 1 shows the X-ray spectra of the studied compounds. All X-ray patterns indicate that the crystal structure of the tested materials are of the α-$NaFeO_2$ type. The chosen samples have an almost linearly increasing structural order.
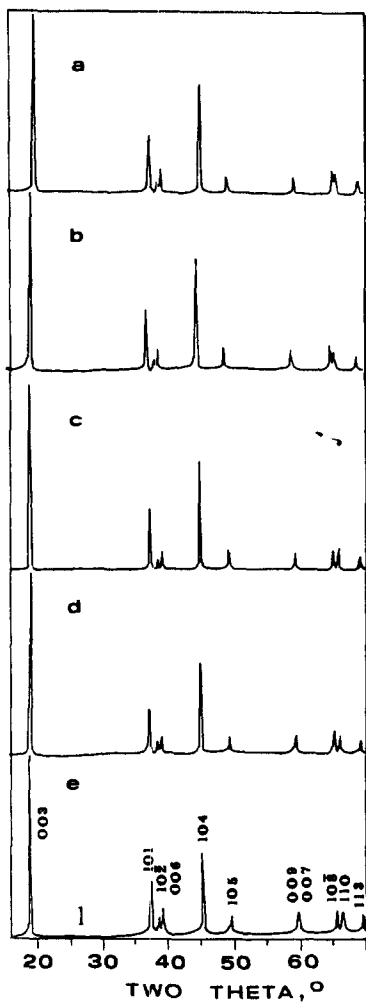
Fig. 1. X-ray diffraction patterns of solid solutions of: (a) LiNi$_{0.8}$Co$_{0.2}$O$_2$;   (b)   LiNi$_{0.6}$Co$_{0.4}$O$_2$;   (c)   LiNi$_{0.4}$Co$_{0.6}$O$_2$;   (d) LiNi$_{0.2}$Co$_{0.8}$O$_2$, and (e) pure LiCoO$_2$ for reference.

Fig. 2. Variation of the hexagonal cell parameters a, c, and of c/a ratio vs. Co^{3+} content, y.
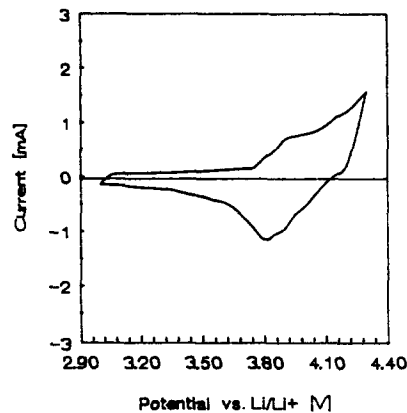
Fig. 3. Cyclic voltammogram of LiNi$_{0.8}$Co$_{0.2}$O$_2$ electrode during the first cycle.

In Fig. 2 are given the a, c and c/a crystal lattice parameters of LiNi$_{1-y}$Co$_y$O$_2$ as a function of the cobalt content. The interlayer metal–metal distance a and the c related to the interslab distance, both decrease smoothly with increase of y. The c/a ratio, characteristic of the trigonal distortion of the crystal lattice increases almost linearly with y. These data show that upon an increase of the Co content the non-stoichiometry diminishes while the order of the structure becomes higher.

Figs. 3 to 6 show the cyclic voltammograms of the tested materials. It can be seen that all compounds investigated have a reversible structure. The delivered capacity also increases with the Co content.

In Fig. 3 is given the voltammogram of LiNi$_{0.8}$Co$_{0.2}$O$_2$. A small initial peak of de-intercalation of Li$^+$ is observed at 3.9 V for Co content of 0.2, after that the potential steeply rises to the upper limit. The relatively small amount of the lithium extracted shows that the latter
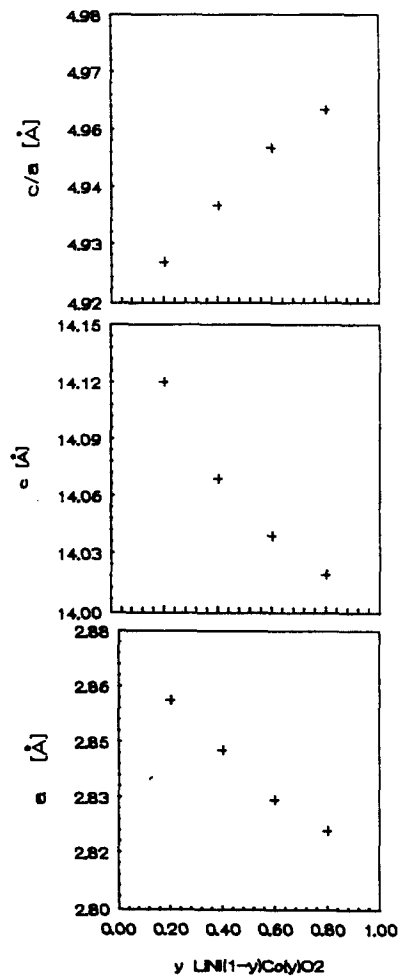
is firmly implanted in the initial structure in the synthesis process.

Fig. 4 shows the behaviour of LiNi$_{0.6}$Co$_{0.4}$O$_2$ upon substitution of 0.4 Ni^{3+} with an equivalent amount of Co^{3+}. A well-expressed maximum of the de-intercalation of Li$^+$ from the initial structure is observed in a narrow potential range. More than half of the Li$^+$ is extracted
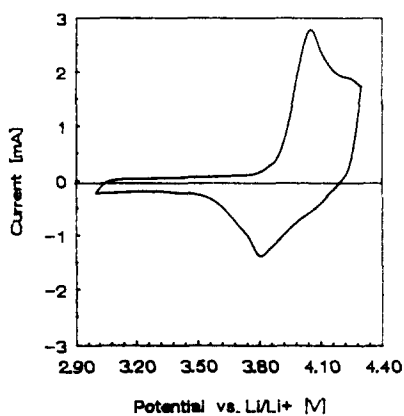
Fig. 4. Cyclic voltammogram of LiNi$_{0.6}$Co$_{0.4}$O$_2$ electrode during the first cycle.

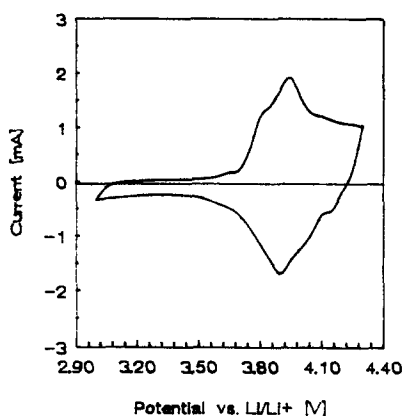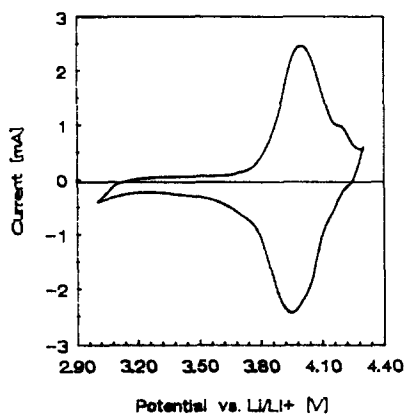Fig. 5. Cyclic voltammogram of LiNi$_{0.4}$Co$_{0.6}$O$_2$ electrode during the first cycle.

Fig. 6. Cyclic voltammogram of LiNi$_{0.2}$Co$_{0.8}$O$_2$ electrode during the first cycle.

at a potential of about 4.0 V. The observed well-defined peak indicates that the implanted, during the synthesis, Li$^+$ is situated at an easily for de-intercalation place, which in its turn shows the greater probability for reversible intercalation of Li$^+$ during the discharge period with a well-expressed plateau at 3.8 V.

The curve in Fig. 5 is quite similar to that in Fig. 3. However, the former has a wide peak with an Li$^+$ de-intercalation maximum at a potential lower than in the case of 0.4 Co^{3+}. It should be noted that the delivered capacity is higher than represented in Fig. 4.

In Fig. 6 is shown the voltammetric curve in the case when 80% of Ni^{3+} is substituted with Co^{3+}. The well-defined peak indicates that the extraction of Li$^+$ occurs easily from an ordered and stabilized layer structure. The curve begins to resemble the pure LiCoO$_2$ one with a difference between the cathode and anode peak of less than 200 mV. The same curve points out the increased capacity of the material.

4. Conclusions

It is shown by cyclic voltammetry, that the reversibility in ternary Li–Ni–Co–O systems increases with the Co content due to the enhanced stability and structural order, and these materials can be employed as cathodes in rechargeable lithium cells.

References

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