Li/Li$_x$NiO$_2$ and Li/Li$_x$CoO$_2$ rechargeable systems: comparative study and performance of practical cells

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Abstract

Lithiated cobalt and nickel oxides have been prepared using an original synthesis process, based on thermal treatment with LiOH. Their properties as reversible cathodic material for lithium rechargeable cell were studied, showing different behavior in electrochemical mechanisms. Excellent energy densities were obtained from the two compounds. At high working potential from 4 to 3 V, up to 300 W h/l and 174 W h/kg were obtained in 'C'-size cells. The kinetics of cathode reactions are fairly rapid, which allows high rate of discharge (>'C'). Cycle life was demonstrated over more than 100 cycles. Storage capability was tested at 45 °C at the charged state. Better results were obtained with Li$_x$NiO$_2$ than with Li$_x$CoO$_2$.
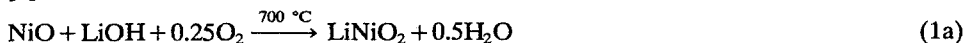
Introduction

Lithiated cobalt and nickel oxides have been known and studied for a long time [1–3]. There is a considerable interest to use them as cathode material for secondary lithium cells and they are the subject of many research studies in recent years [4–7]. Their very high working potential in the range of 4 V makes them presently the best candidates to achieve an outstanding energy density. Furthermore, they are prepared in the 'discharged' state, which provides an additional Li capacity to the cell after the first charge. While the cobalt oxide is being extensively studied, the nickel oxide has been given less attention to, probably because of the absence of commercially-available product up-to-now, and of the apparent difficulty of synthesis.

This paper describes some comparative electrochemical characteristics of this type of materials and performances of actual rechargeable Li cells using them as positive electrodes.

Materials synthesis

Different ways of preparation have been described in the literature. The most usual is the heat treatment of a mixture of Li$_2$CO$_3$ and CoCO$_3$. However, lithiated nickel oxide cannot be prepared this way and more complex techniques were proposed for it. We found that they can be prepared by dry heat treatment of a mixture of

the NiO or Co_2O_3 oxides with Li hydroxide, as described in the patent filed by SAFT [8].

$$NiO + LiOH + 0.25O_2 \xrightarrow{700\ °C} LiNiO_2 + 0.5H_2O \tag{1a}$$

$$Co_2O_3 + 2LiOH \xrightarrow{700\ °C} 2LiCoO_2 + H_2O \tag{1b}$$

A mixture of the two oxides can give a mixed material $LiNi_xCo_{(1-x)}$.

Electrochemical characteristics

In order to compare their electrochemical properties, the materials prepared have been studied as cathode materials in beaker cells.

The electrodes were prepared by pressing a dry mixture of active material (80 wt.%), carbon black (7.5 wt.%) and graphite (7.5 wt.%), and polytetrafluoroethylene (PTFE) slurry (5 wt.% of dry powder) onto an aluminum grid. The thickness of the electrodes was 0.4 mm, and the area 2 cm². The amount of Li is in large excess compared with the cathode capacity. The electrolyte is a solution of $LiAsF_6$ in a proprietary solvent.

The two materials have similar charge and discharge chronopotentiometric curves, as shown in Fig. 1, obtained at a constant low rate of 0.5 mA/cm². Nickel oxides has a more sloping curve at a slightly lower working potential than the cobalt oxide. The voltage profiles are quite 'monotonous', but the electrochemical mechanism of Li insertion is more complicated, as observed by cyclic voltammetry, and quite different between nickel and cobalt oxides.

Figure 2 shows the first cycles obtained with a $LiNiO_2$ electrode at a 5 mV/min scanning rate versus a Li reference electrode. It is observed that the first oxidation is totally different from the following cycles: the material undergoes a structural transformation due to the Li extraction from the lattice. The subsequent reduction step exhibits several peaks. These different steps are more visible at a slower scanning
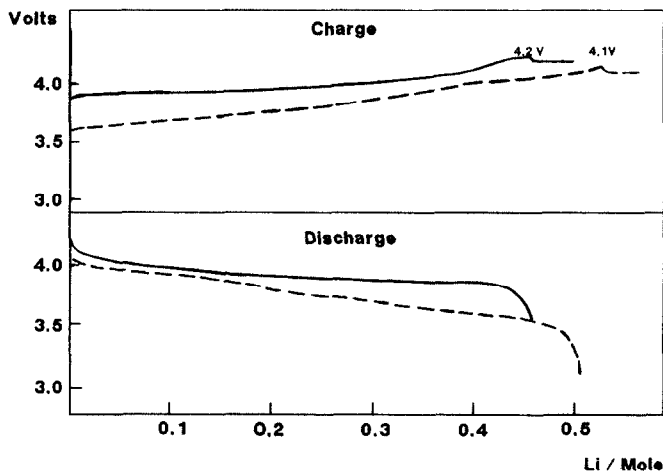

Fig. 1. Discharge/charge voltage vs. inserted Li/mol of Li_xNiO_2 and Li_xCoO_2 after few cycles. $i_d = i_c = 1$ mA/cm²; (– – –) Li_xNiO_2, $U_{max} = 4.1$ V; (——) Li_xCoO_2, $U_{max} = 4.2$ V.
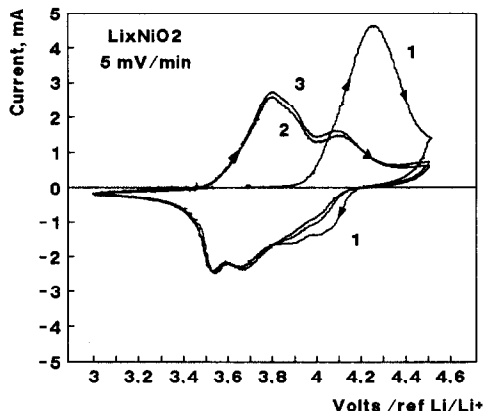
Fig. 2. Cyclic voltammetry of Li$_x$NiO$_2$, cycles 1 to 3; scan rate: 5 mV/min, surface area: 1 cm^2.
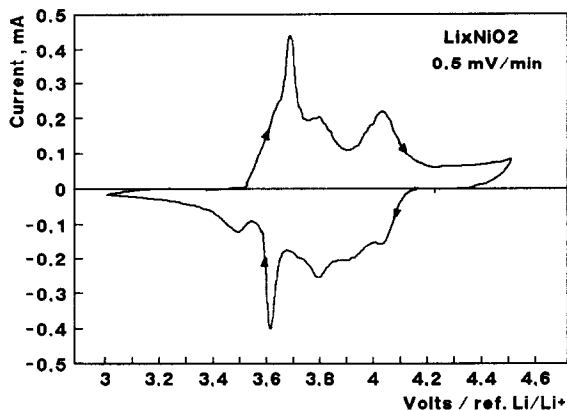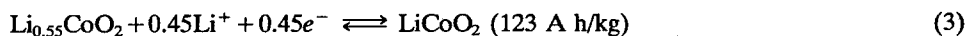

Fig. 3. Cyclic voltammetry of Li$_x$NiO$_2$, cycle 4; scan rate: 0.5 mV/min, surface area: 1 cm^2.

rate, which was obtained at 0.5 mV/min (Fig. 3). The presence of well-defined sharp oxidation and reduction peaks is the indication of reversible phase transformations. No similar modification was noted with the cobalt oxides, as shown in Fig. 4. The first charge and discharge curves are quite similar to the following cycles. The curves obtained at low rate confirmed that the Li insertion is very rapid and reversible. Evidence of several electrochemical steps appears also on those curves (Fig. 5).

Chronopotentiometric experiments confirm the modification of Li$_x$NiO$_2$ during the first cycle (Fig. 6). The extracted Li from LiNiO$_2$ at up to 4.1 V is not fully reinserted during the reduction phase. After a few cycles the material can be reversibly cycled according to the reaction:

$$Li_{0.35}NiO_2 + 0.5Li^+ + 0.5e^- \rightleftharpoons Li_{0.85}NiO_2 \text{ (135 A h/kg)} \qquad (2)$$
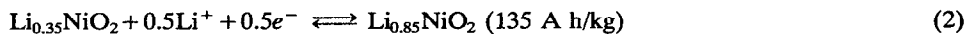
On the contrary, all the Li extracted from the cobalt oxide up to 4.2 V can be reinserted during the following reduction, leading to the general overall reaction:
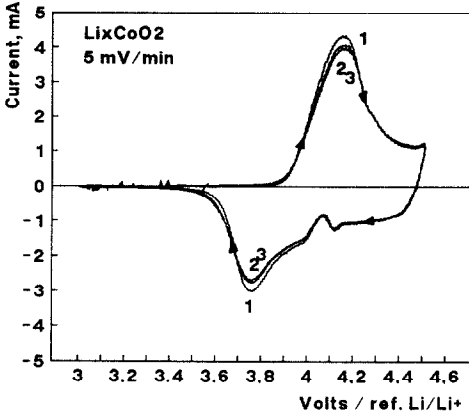
$$Li_{0.55}CoO_2 + 0.45Li^+ + 0.45e^- \rightleftharpoons LiCoO_2 \text{ (123 A h/kg)} \qquad (3)$$

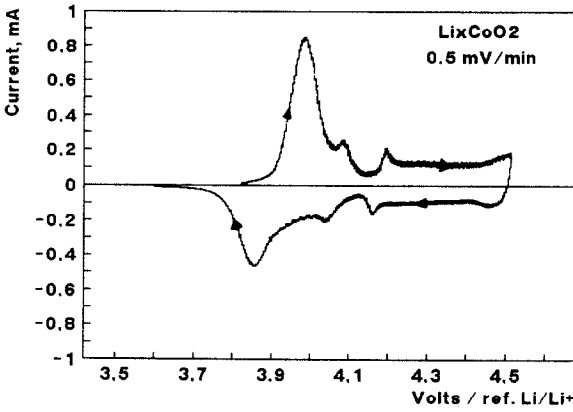Fig. 4. Cyclic voltammetry of Li_xCoO_2, cycles 1 to 3; scan rate: 5 mV/min, surface area: 1 cm^2.

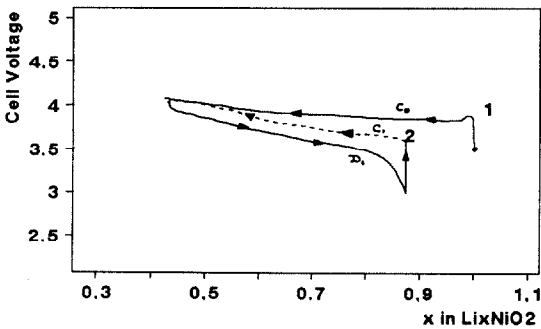Fig. 5. Cyclic voltammetry of Li_xCoO_2, cycle 4; scan rate: 0.5 mV/min, surface area: 1 cm^2.

Fig. 6. Chronopotentiometric curves of Li_xNiO_2, lithium insertion/deinsertion during the first cycle. $I_d = 1$ mA/cm^2, $I_c = 0.25$ mA/cm^2.
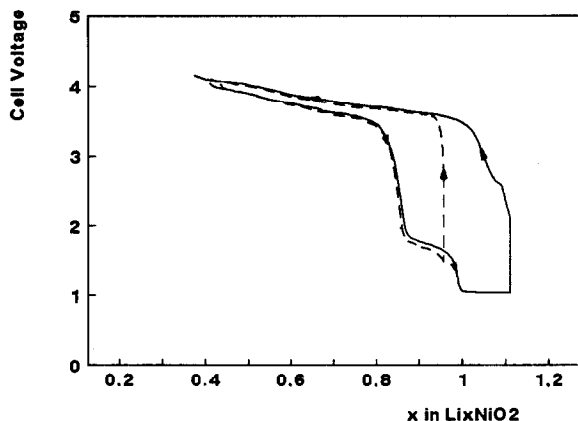
Fig. 7. Charge/discharge curves of Li$_x$NiO$_2$ at different depths-of-discharge, after an initial charge up to 4.1 V, $I_d = 1$ mA/cm^2, $I_c = 0.25$ mA/cm^2. (– – –) $U_{min} = 1.5$ V, (——) $U_{min} = 1$ V.

The corresponding specific capacities are closed to each other, but the nickel material achieves a larger anodic deposit of Li in the first cycle. In complete cells, that results in an extra amount of Li, which leads to a larger number of cycles.

The reduction of the nickel oxide at the lower voltage has also been investigated. A voltage plateau between 1.8 and 1.5 V, as already described [6], appears (Fig. 7). In our experiments this plateau involves about 0.15 Li/mol (1 mA/cm^2), and corresponds to the formation of LiNiO$_2$. Subsequent cycling in the 4.1–3 V range does not show any difference between these cells and those whose first discharge was limited to 3 V. It is also interesting to note that this plateau does not exist if the material is not previously charged (i.e., starting reduction from LiNiO$_2$). This feature does not appear with the cobalt oxide, which is consistent with the fact that it is reduced at 1 Li/mol during the first step down to 3 V.

This property of the nickel oxide is specially attractive to avoid overdischarge of the cells in series connected configuration.

If the discharge is continued further, another plateau appears at about 1 V (Fig. 7), which is difficult to separate from the solvent reduction. This reaction does not seem to irreversibly destroy the material, but induces a continuous degradation of the specific capacity during subsequent cycling in the 'normal' conditions between 4.1 and 3 V.

Cell performances

Cell design

The cells are designed in the spirally-wound configuration. The size varies from 'C' (diameter: 26 mm, height: 50 mm) to 'D' (diameter: 33 mm, height: 60 mm). They are hermetically sealed, using a glass-to-metal feed-through positive terminal. The cell cover includes a vent which operates at 25 to 30 bars. An appropriate cell filling makes it working at a temperature comprised between 100 and 150 °C. The positive electrode is connected to the pin and the negative to the stainless-steel or nickel-

plated steel can. The positive electrode is a mixture of the cathodic material, graphite and/or acetylene black, and PTFE-based binder, coated onto a perforated aluminium sheet.

The negative electrode is a pure Li foil, whose thickness is chosen to have an excess of capacity, from 3 to 5 times that of the cathode, depending on the number of cycle expected. A microporous polypropylene film is used as separator. The electrolyte is a solution of $LiAsF_6$, similar to the previous experiments.

Cell characteristics

Typical charge/discharge curves of Li_xNiO_2 and Li_xCoO_2 cells are reported in the Figs. 8 and 9.

Figures 10 and 11 describe the specific capacity of Li_xNiO_2 and Li_xCoO_2 in 'C' cells during cycling at maximum charge voltage of 4.1 and 4.2 V, respectively. The performances obtained are summarized in the Table 1. A very important characteristic of this type of cell is its shelf life, specially with these highly oxidizing materials.
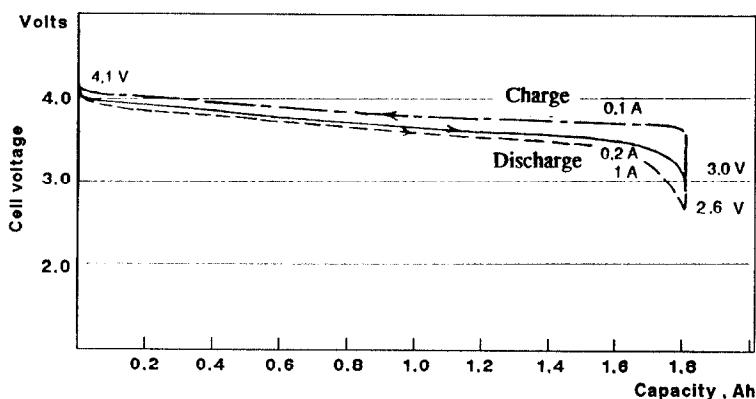

Fig. 8. Charge/discharge curves of a Li_xNiO_2 C-size cell (cycle no. 10); charge at 0.1 A to 4.1 V; discharge (– – –) at 1 A to 2.6 V and (——) 0.2 A to 3.0 V.
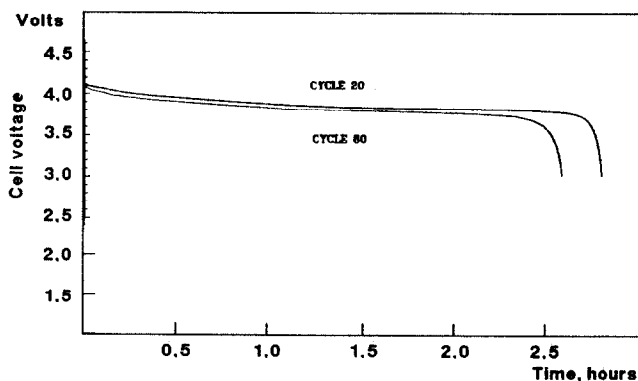

Fig. 9. Discharge curve of a Li_xCoO_2 D-size cell, at constant power of 5 W, after charge at 0.36 A to 4.2 V. Cycles nos. 20 and 80.
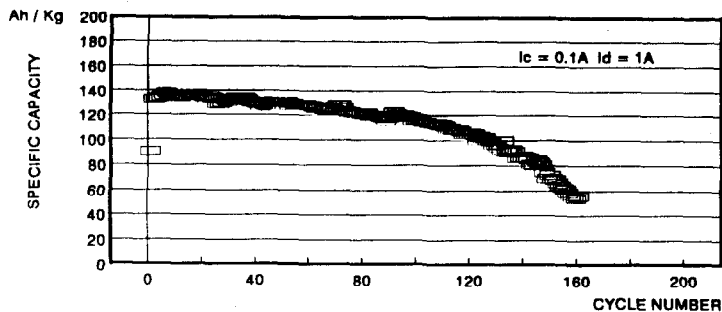
Fig. 10. Evolution of specific capacity of Li_xNiO_2 during cycling of a 1.8 A h C-size cell: $I_c = 0.1$ A, $I_d = 1$ A; $U_{max} = 4.1$ V, $U_{min} = 2.6$ V.
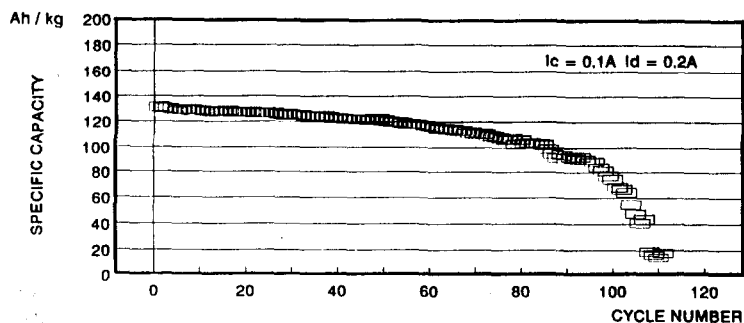

Fig. 11. Evolution of specific capacity of Li_xCoO_2 during cycling of a 2 A h C-size cell: $I_c = 0.1$ A, $I_d = 0.2$ A; $U_{max} = 4.2$ V, $U_{min} = 3$ V.

TABLE 1

General characteristics of Li_xNiO_2 and Li_xCoO_2 spirally-wound cells[a]

System	Li_xNiO_2	Li_xCoO_2	Li_xCoO_2
Cell type	C[b]	C[b]	D[c]
Cycling voltage limits (V)	4.1–3	4.2–3.5	4.2–3
Charge current (A)	0.1 (C/20)	0.1 (C/20)	0.36 (C/10)
Discharge rate	1 A	0.2 A	5 W
Capacity (A h)	1.8	2	3.6
Discharge average voltage (V)	3.6	3.92	3.85
Cycle life (100% DOD)	150	100	110
Energy density (W h/l)	246	300	260
Specific energy (W h/kg)	145	174	145

[a]Results in column 3 are obtained at constant power 5 W.
[b]C cell: diameter 26 mm, height 50 mm.
[c]D cell: diameter 33 mm, height 60 mm.

TABLE 2

Self-discharge of Li_xNiO_2 and Li_xCoCo_2 C-size cells during repeated storages for 1 month, at 45 °C

Self-discharge at 45 °C	1st month	2nd month	3rd month
Li_xNiO_2	1–3%	3–6%	3–10%
Li_xCoO_2	10–12%	20–25%	short circuit

Table 2 reports results obtained during repeated storages of cells in the fully charged state, during one month at 45 °C.

Conclusions

High energy densities are obtained with $LiNiO_2$ and $LiCoCo_2$, associated to a still reasonable cycle life. Depending on the type of application, the best compromise between these two properties, can be found by choosing the right cell balance.

The electrolyte stability towards high oxidizing materials was one of the biggest concerns for this cell development. The excellent good shelf life at 45 °C demonstrates this electrolyte stability. This was achieved by using $LiAsF_6$ solutions in the proper choice of solvent mixture, which cannot be disclosed at this moment. Capacity retention is significantly worse with Li_xCoO_2 than with Li_xNiO_2, probably due to the higher oxidizing power of the former material.

The kinetics of cathode reactions are fairly rapid, and high rate discharge, e.g., greater than the C-rate, can be easily obtained.

These results demonstrate the usefulness of these compounds as cathode materials in rechargeable Li cells. Very high energy densities can be achieved in these cells, which can satisfy the most demanding high-technology applications.

Acknowledgements

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