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Characterization of LT-Li$_x$Co$_{1-y}$Ni$_y$O$_2$ Electrodes for Rechargeable Lithium Cells

R. J. Gummow and M. M. Thackeray*

Division of Materials Science and Technology, CSIR, Pretoria 0001, South Africa

ABSTRACT

LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ prepared at 400°C with a structure that is intermediate between an ideal lithiated spinel and a layered structure has been investigated as an electrode in rechargeable lithium cells; it delivers a voltage vs. pure lithium that is significantly lower than the voltage provided by its high-temperature analogue, HT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$, (synthesized at 900°C). The rechargeability of Li/LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ cells can be improved by leaching some lithium and a small amount of cobalt from LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ by acid treatment and loading the cells in a charged state. The improvement in electrochemical performance is attributed to the formation of a defect spinel phase Li$_{0.8}$[Co$_{1.6}$Ni$_{0.2}$]O$_4$ in which the lithium ions adopt the tetrahedral A sites and the cobalt and nickel ions the B sites of an A[B$_2$]O$_4$ spinel.

Lithium-cobalt-nickel-oxides LiCo$_{1-y}$Ni$_y$O$_2$ ($0 \leq y \leq 1$) are of interest as electrodes for rechargeable 4 V lithium cells.[1-6] These electrodes have, in the past, been conventionally synthesized at 800-900°C and are referred to as HT-LiCo$_{1-y}$Ni$_y$O$_2$ electrodes (HT for high temperature); they have layered rock salt structures. Extensive studies[4,6,7] have shown that electrodes with $0 < y < 1.0$ perform better on electrochemical cycling than the end members of the system HT-LiCoO$_2$ ($y = 0$) and HT-LiNiO$_2$ ($y = 1$). A disadvantage of Li/HT-LiCo$_{1-y}$Ni$_y$O$_2$ cells is that it is necessary to charge the cells above 4 V, particularly at low lithium contents, which is outside the electrochemical stability window of many organic-based electrolytes. It has been recently reported, however, that if the synthesis of LiCo$_{1-y}$Ni$_y$O$_2$ materials is carried out at 400°C, hereafter referred to as LT-LiCo$_{1-y}$Ni$_y$O$_2$ (LT for low-temperature), then compounds with a modified structure are produced that have significantly different properties compared to their high-temperature analogues.[8-10] For $0 \leq y \leq 0.2$, LT-LiCo$_{1-y}$Ni$_y$O$_2$ compounds are essentially single-phase and have spinel-like x-ray and neutron-diffraction patterns. In lithium cells, LT-LiCo$_{1-y}$Ni$_y$O$_2$ electrodes discharge most of their capacity at voltages approximately 0.5 V lower than HT-LiCo$_{1-y}$Ni$_y$O$_2$ electrodes. This discovery has raised the possibility of developing lithium-cobalt-nickel-oxide electrodes with an enhanced electrolyte stability. Although preliminary electrochemical data[9] have indicated that nickel-doped LT-LiCo$_{1-y}$Ni$_y$O$_2$ electrodes ($0 \leq y \leq 0.2$) perform better than LT-LiCoO$_2$, these data have unfortunately also shown that LT-LiCo$_{1-y}$Ni$_y$O$_2$ structures are not particularly stable to repeated lithium extraction and insertion reactions. The x-ray data and electrochemical properties of LT-LiCoO$_2$ have been confirmed by Rossen et al.[11,12]

We have attempted to devise methods for improving the cycling properties of LT-LiCo$_{1-y}$Ni$_y$O$_2$ electrodes. In this paper we compare the structural and electrochemical properties of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ ($y = 0.1$) prepared at 400°C with a product of composition Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$, prepared by chemical delithiation of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ at room temperature.

Experimental

LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ and a standard LT-LiCoO$_2$ sample were synthesized by reacting stoichiometric quantities of Li$_2$CO$_3$, CoCO$_3$, and Ni(NO$_3$)$_2 \cdot$ 6H$_2$O in air at 400°C for five days. The precursors were ball-milled in hexane prior to

* Electrochemical Society Active Member.

firing to ensure thorough mixing. Two partially delithiated samples were prepared by reacting 1 g of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ with 20 ml 0.625M H$_2$SO$_4$ at 22°C for 3 h. The samples were filtered, washed with distilled water, and dried at 80°C for 24 h. Samples were heated for a further 24 h at 80°C prior to cell assembly to remove as much surface and occluded water as possible. Lithium, cobalt, and nickel contents in the partially delithiated samples were determined by atomic absorption spectroscopy, and the composition was found to be LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$, within experimental error, in both cases.

Two-electrode prismatic lithium cells containing metallic lithium anodes, "LT" cathodes, and an electrolyte of either 1M LiClO$_4$ in propylene carbonate/dimethoxyethane (PC/DME) in a 1:1 volumetric ratio or 1M LiClO$_4$ in propylene carbonate (PC), were assembled as described elsewhere.[9] Cathodes consisted either of an intimate mixture of 20 weight percent (w/o) of a 1:2 Teflon acetylene black mixture (TAB) with 80 w/o active material or alternatively of a mixture of ethylene propylene diene monomer (EPDM), acetylene black, and active material in a ratio 3:7:90 by weight. Cells were charged at a constant current density of 0.1 mA/cm^2 and discharged at 0.2 mA/cm^2 at room temperature (22°C). Powder x-ray diffraction patterns were recorded on an automated Rigaku diffractometer with CuKα radiation, monochromated by a graphite single crystal. Data were recorded using a step width of 0.02 degrees 2θ and a scan rate of 0.53 degrees 2θ per minute. Calculated powder patterns of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ and LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ were generated by means of the program LAZY-PULVERIX.[13]

Results and Discussion

Structural considerations.—The powder x-ray diffraction pattern of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ is shown in Fig. 1a. This pattern can be indexed either to a trigonal unit cell (R$\bar{3}$m) with a = 2.833 Å, and c = 13.881 Å,[8] or, because the c/a ratio = 4.90, to a face-centered cubic unit cell (Fd3m) with a = 8.013 Å. Although an accurate structure refinement of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ has not yet been undertaken, it can be seen from Fig. 1a that the observed pattern of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ strongly resembles the calculated pattern of an ideal layered structure (Li)$_{3a}$[Co$_{0.9}$Ni$_{0.1}$]$_{3b}$O$_2$ that has space group symmetry R$\bar{3}$m (Fig. 1b) and also the calculated pattern of an ideal lithiated spinel (Li$_2$)$_{16c}$ [Co$_{1.8}$Ni$_{0.2}$]O$_4$ that has space group symmetry Fd3m (Fig. 1c). In fact, the calculated powder patterns of the ideal layered and lithiated spinel

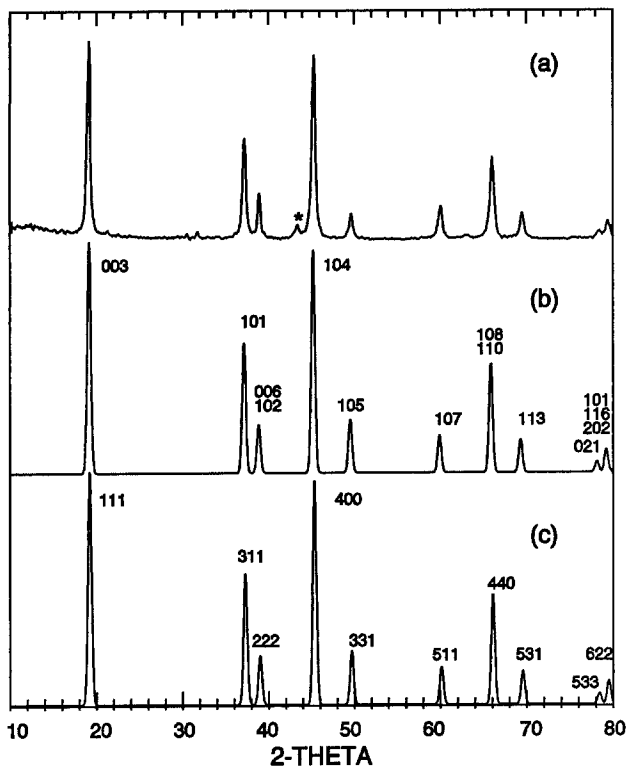Fig. 1. The observed and calculated powder x-ray diffraction patterns of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$. The observed pattern (a) shows a small amount of a second phase, Li$_x$Ni$_{1-x}$O, denoted by an asterisk. Pattern (b) was calculated using R3m symmetry, and pattern (c) using Fd3m symmetry.

Fig. 2. The observed and calculated powder x-ray diffraction patterns of LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$. The observed pattern (a) shows a small amount of a second phase, Li$_x$Ni$_{1-x}$O, denoted by an asterisk. Pattern (b) was calculated using R3m symmetry and pattern (c) using Fd3m symmetry.

structures, which are both of the rock salt-type, are identical; this crystallographic anomaly which has already been observed in LT-LiCoO$_2$[8,10] has been explained by Rossen et al.[11] Refinement of the lattice parameters of LT-LiCoO$_2$ with x-ray data has shown an ideally cubic-close-packed oxygen array ($c/a = 4.90$) which supports a spinel model for LT-LiCoO$_2$.[8,10,11] By contrast, refinement of time-of-flight neutron-data gave $c/a = 4.914$ and a cation distribution in LT-LiCoO$_2$ that is intermediate between the distribution found in ideal layered and ideal spinel structures.[8] The structural model of LT-LiCoO$_2$ obtained from neutron data has been termed "quasi-spinel" because of the strong similarity of the diffraction pattern to those of lithium-spinel structures. It is our belief that the neutron data, with information on the peak intensities down to 0.60 Å, has provided the most accurate analysis of the LT-LiCoO$_2$ structure thus far; for this reason the quasi-spinel model for LT-LiCoO$_2$ is preferred, at least for those samples prepared at 400°C by the methods employed at the CSIR.

The atomic absorption analysis of the acid-leached samples gave a composition LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ which, within experimental error for two different samples, suggests that cobalt ions were removed from the structure, in preference to nickel ions, during acid treatment. The reasons for this are not yet understood. It is also possible that during acid treatment some Li$^+$ ions were ion-exchanged by H$^+$ ions, the extent of which was not determined. The mean oxidation state of the cobalt and nickel cations in the defect spinel phase is 4.0, assuming that there are no protons in the structure.

The powder x-ray diffraction pattern of an acid-leached sample LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ is shown in Fig. 2a; it can be indexed, like LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$, to either a trigonal unit cell ($a = 2.826$ Å, $c = 13.845$ Å, $c/a = 4.90$) or to a face-centered-cubic unit cell ($a = 7.993$ Å). Delithiation is accompanied by a 0.5% decrease in unit cell volume. The pattern of the delithiated compound is strikingly similar to that of the parent compound, but can be distinguished from it by a significant difference in the relative intensities of the {101}
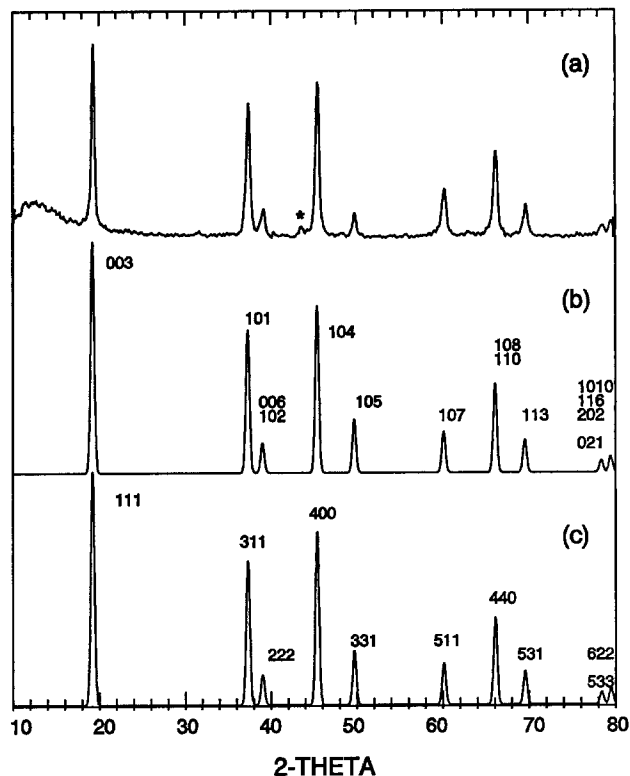
and combined {006}/{102} peaks of the trigonal unit cell, (or alternatively, the {311} and {222} peaks of the face-centered-cubic unit cell). The calculated patterns of a layered structural model (Li$_{0.4}$)$_{6c}$(Co$_{0.8}$Ni$_{0.1}$)$_{3b}$O$_2$ and a spinel model (Li$_{0.8}$)$_{8a}$[Co$_{1.6}$Ni$_{0.2}$]$_{16d}$O$_4$, in which the lithium ions are located in tetrahedral sites and the transition metal ions in octahedral sites, are shown in Fig. 2b and c, respectively. Although the profiles of the two calculated x-ray patterns seem to be identical, there are several weak peaks in the pattern of the spinel model that are not present in the lay-

Table I. Calculated intensities of the powder x-ray diffraction patterns of a layered structural model of LT-(Li$_{0.4}$)$_{6c}$[Co$_{0.8}$Ni$_{0.1}$]$_{3b}$O$_2$ (R3m) and a defect spinel model LT-(Li$_{0.8}$)$_{8a}$[Co$_{1.6}$Ni$_{0.2}$]$_{16d}$O$_4$ (Fd3m). Intensities were calculated assuming ideal cubic-close-packing of the anion lattice.

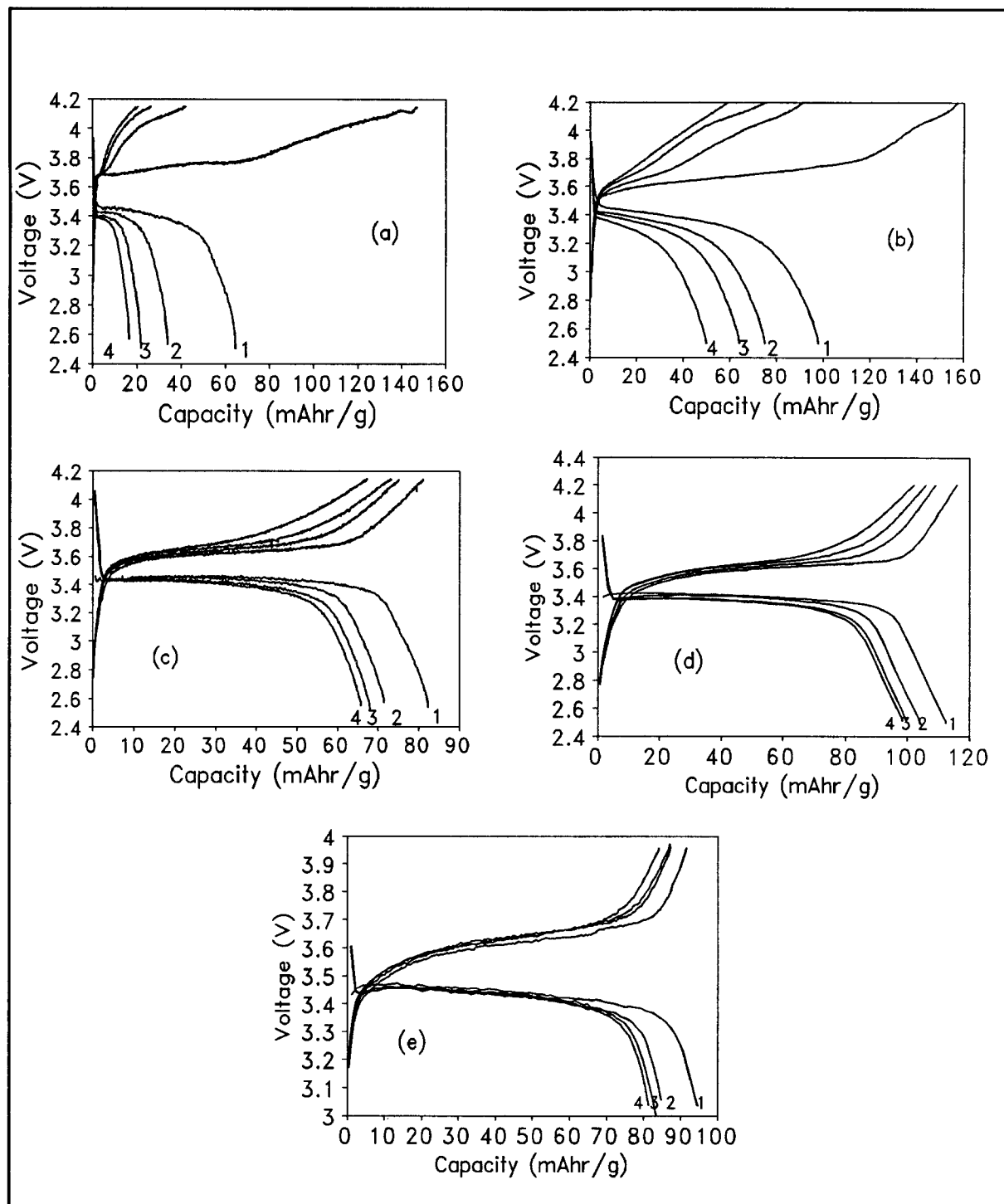| LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ (R3̄m) (Layered structure)			LT-Li$_{0.8}$Co$_{1.6}$Ni$_{0.2}$O$_4$ (Fd3m) (Spinel structure)		
hkl	2-theta	I	hkl	2-theta	I
003	19.22	1000.0	111	19.22	1000.0
			220	31.64	0.7
101	37.29	624.5	311	37.29	624.5
006	39.02	23.5	222	39.02	94.1
012	39.02	70.5			
104	45.36	781.6	400	45.36	800.9
015	49.69	230.7	331	49.69	230.7
			422	56.36	0.2
009	60.12	44.4	511	60.12	133.3
107	60.12	133.3	333	60.12	44.4
018	66.09	206.6	440	66.09	402.8
110	66.09	206.6			
113	69.55	70.9	531	69.55	141.8
11-3	69.55	70.9			
			442	70.67	0.0
			620	75.13	0.1
021	78.42	51.8	533	78.42	51.8
1010	79.50	14.7	622	79.50	58.7
116	79.50	14.7			
11-6	79.50	14.7			
202	79.50	14.7			

Fig. 3. Charge and discharge curves for (a) a Li/LT-LiCoO$_2$ cell, (b) a Li/LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ cell, (c) a Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cell, (d) a Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cell (2.5 to 4.2 V), and (e) Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cell (3 to 4 V). Cells were charged at 0.1 mA/cm^2 and discharged at 0.2 mA/cm^2. Cells a-c contained a 1M LiClO$_4$ in 1:1 propylene carbonate: dimethoxyethane electrolyte, and cells d and e contained a 1M LiClO$_4$ in propylene carbonate electrolyte.

ered model, as shown, for example, by the {220} and {422} reflections in Table I and which can be used to distinguish the two structures from one another. These peaks are not apparent in the calculated x-ray diffraction patterns because of their very low intensity relative to the strong peaks; they have, however, been unambiguously detected in high quality time-of-flight neutron diffraction data of closely related LT-Li$_{0.4}$CoO$_2$ samples prepared by acid treatment of LT-LiCoO$_2$. The structure refinement of LT-Li$_{0.4}$CoO$_2$ has provided unequivocal evidence of a spinel-type structure, not a layered structure.[10]

Therefore, because of the strong analogy between LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ and LT-LiCoO$_2$ samples, and between LT-

Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ and LT-Li$_{0.4}$CoO$_2$ samples in terms of preparation techniques, synthesis temperature, composition, stoichiometry, and x-ray diffraction patterns, it is highly probable that LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ has a structure which is quasi-spinel in character and that LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ is a defect spinel with spinel notation {Li$_{0.8}$□$_{0.2}$}$_{8a}$ [Co$_{1.6}$Ni$_{0.2}$□$_{0.2}$]O$_4$.

Electrochemical data.—The charge and discharge profiles for the first four cycles of Li/LT-LiCoO$_2$, Li/LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ and Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cells are shown in Fig. 3a-e, respectively. Doping of LT-LiCoO$_2$ with nickel improves the initial discharge capacity of LT-LiCo$_{1-y}$Ni$_y$O$_2$ electrodes from 63 mAh/g for a sample with $y = 0$ (Fig. 3a)

to 98 mAh/g for a sample with $y = 0.1$ (Fig. 3b) when cells are charged to an upper voltage limit of 4.2 V and discharged to 2.5 V, as reported previously.[9] However, both cells lose capacity quickly, and after four cycles deliver an electrode capacity of 50 mAh/g or less. In these cells the capacity loss can be attributed to a marked increase in polarization during successive charge cycles that probably arises from the instability of the quasi-spinel structures of LT-LiCoO$_2$ and LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ to repeated extraction and insertion of lithium.

By contrast, the data obtained for the charge/discharge profiles of Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cells that had been assembled in a charged state (Fig. 3c-e) (*i.e.*, the cell was discharged on the first cycle), are indicative of a system that is significantly more tolerant to cycling than Li/LT-LiCoO$_2$ and Li/LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ cells. The improved performance of Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cells is evident from the following factors: (*i*) the polarization during both charge and discharge is significantly reduced; the cells deliver approximately 3.4 V for almost the entire length of discharge, and (*ii*) the rate at which capacity is lost on cycling is reduced.

In cells that employed a TAB binder and an electrolyte of $1M$ LiClO$_4$ in PC/DME, an initial capacity of 83 mAh/g was achieved; after four cycles the capacity dropped to only 67 mAh/g. A significantly higher capacity (>98 mAh/g) was obtained from cells in which an EPDM binder and a pure propylene carbonate electrolyte were used and in which the upper voltage limit was set at 4.2 V (Fig. 3d). In this cell the capacity dropped on cycling from 112 mAh/g to 98 mAh/g after four cycles. Cycling of a Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cell of this type between 3 and 4 V (Fig. 3e) resulted in a slight reduction of the capacity but failed to improve the cycling stability; the capacity dropped from 95 mAh/g to 81 mAh/g after four cycles.

Conclusions

The difference in the electrochemical performance of Li/LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ and Li/LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ cells is significant. It demonstrates that electrochemical delithiation of LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ does not result in exactly the same structural framework that is obtained by chemical delithiation, and therefore supports the hypotheses that LT-LiCo$_{0.9}$Ni$_{0.1}$O$_2$ is quasi-spinel in character with a structure which is intermediate between an ideal layered and an ideal spinel structure, and that LT-Li$_{0.4}$Co$_{0.8}$Ni$_{0.1}$O$_2$ is a defect spinel in which all the cobalt and nickel ions reside on the B sites of an A[B$_2$]O$_4$ spinel structure. The spinel phase

is significantly more stable to lithium insertion/extraction reactions than the quasi-spinel phase. It is believed that by optimizing the processing conditions it may be possible to increase further the rechargeable capacity and stability of LT-Li[Co$_{2-z}$Ni$_z$]O$_4$ ($0 < z < 2$) spinel electrodes that operate at 3.4 V *vs.* pure lithium. A challenge also remains to synthesize a lithiated spinel phase with a cation distribution, LT-Li$_2$[Co$_{2-z}$Ni$_z$]O$_4$, in which the transition metal cations fully occupy the octahedral B-sites, to allow the fabrication of carbon/LT-Li$_2$[Co$_{2-z}$Ni$_z$]O$_4$ cells in an inherently safe, discharged state.

Acknowledgments

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