The role of nickel content on the structure and electrochemical properties of Li$_x$(Ni$_y$Co$_{1-y}$)O$_2$

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Abstract

Samples have been prepared with nominal composition Li$_x$(Ni$_y$Co$_{1-y}$)O$_2$ ($x \approx 1.25$, $y = 0.7$–1.0) with the structures being examined using Rietveld analysis of X-ray diffraction data. Rietveld analysis shows that the samples prepared with $y = 0.70$ and 0.75 have no Ni present on the 3a Li site, with all other samples showing a small degree of nonstoichiometry. Structural analysis of the 3b Ni + Co occupancy also suggests the possibility of 3b site disorder, which is in agreement with the results of previous studies.

Charge/discharge measurements show an increase in discharge capacity with increasing Ni content, which suggests cobalt plays a very small part in the electrochemical capacities of these phases using the current voltage limits. Samples with $y = 0.75$, 0.8 and 0.85 were found to have very high efficiencies over a number of cycles, typically >99% over 15 cycles. Samples prepared with $y = 0.85$ and 0.90 show evidence of a phase change which resembles that seen for LiNiO$_2$. This would suggest that the stabilizing effects of Co in Li$_x$(Ni$_y$Co$_{1-y}$)O$_2$ is lost when $y \geq 0.85$. Therefore, these particular compositions are probably not suitable for use in Li ion cells. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In an attempt to improve the electrochemical properties of LiNiO$_2$ several doping strategies have been attempted (for example [1]), with cobalt doping producing some of the most favorable results. Many possible reasons have been suggested for the improvement in electrochemical properties. A full discussion of the relative merits of each theory lie out-with the scope of the current work. However, it could be argued that there must be a critical Co concentration at which the stabilizing effect is lost.

In terms of electrochemical properties, two main criteria must be satisfied before a decision about the best composition can be made; these are (1) the electrochemical capacity and the (2) cycling efficiency. Delmas and Saadoune [1,2]

and Cho et al. [3] have suggested that a ratio of 0.7:0.3 has the best cycling efficiency, which is thought to be a result of perfect Li 3a site ordering [4]. The effects of Li 3a site ordering was previously examined by Kanno et al. [5] and was shown to be the key factor for controlling the properties of LiNiO$_2$. Other studies have shown a wide variety of differing results, Li and Currie [6] examined Li(Ni$_{0.67}$Co$_{0.23}$)O$_2$ and Li(Ni$_{0.85}$Co$_{0.15}$)O$_2$ and reported that these two compositions have similar capacity fading. Ohzuku et al. [7] reported that the fading behavior is similar to that of LiNiO$_2$ for all members of the Li(Ni$_y$Co$_{1-y}$)O$_2$ solid solution. Therefore, there seems to be a certain degree of conflict between all of these results.

From our own studies on the effects of sintering temperature [8,9], sintering time [10] and Li content [11], it could be said the some of these apparent contradictions can be explained by the choice of sintering conditions. It could also be suggested that the choice of charge/discharge limits, electrolyte, composition of the cells used would also have an effect on the electrochemical properties. As a result of our own studies [8–10], it is felt that the best synthesis temperature is 725°C, with a sintering time of 48 h. The

structures of the materials presented in [8–10] were examined exhaustively using both X-ray and neutron powder diffraction, with the physical properties being examined by electrochemical and magnetic measurements. These studies show clearly correlation between the structure (more specifically the 3a Li site) and the obtained properties.

2. Experimental

The samples were prepared in accordance with the methods presented previously in [8–10], with an excess of Li used in the starting mixture. The excess of Li was used to counteract the possible loss of Li_2O via volatilization, and promote Li site ordering, with the nominal composition prepared being close to $Li_{1.25}(Ni_yCo_{1-y})O_2$. Data sets for Rietveld analysis of X-ray data was collected on a Rigaku Rotaflex 12 kW diffractometer in reflection geometry using copper Kα radiation. Data was collected in the range 10–110° 2θ with a step size of 0.02° with counting time of 2 s per step. As the (0 0 3) reflection is susceptible to preferred orientation, the Rietveld analysis was only performed on the data collected in the region 32–110° 2θ. The Ni content on the 3a site was determined by constraining it to Li present on the Li site [8,12]. It is not possible to determine whether it is Ni and or Co that is present on the 3a site, due to the similarity in there X-ray form factors at the wavelength of copper Kα radiation. However, using the reverse of this idea, the total Ni + Co on the 3b site can be determined. All structural analysis using the Rietveld method was performed with GSAS [13]. For the structural analysis, the space group used was the model being, Li/Ni2 (**3a**) (0, 0, 0), Ni1/Co (**3b**) (0, 0, 0.5) and O (**6c**) (0, 0, ~0.24).

Electrochemical studies were performed using Li cells (2016 type cells) constructed in an argon filled glovebox. The working electrode consisted of 50 mg of $Li_x(Ni_y$-$Co_{1-y})O_2$, 15 mg of acetylene black and approximately 0.1 mg of teflon powder. The mixture was mixed using an agate mortar and pestle and pressed into thin disks. Lithium metal was used as the counter electrode, and polypropylene used as the separator, with battery grade EC-DMC/1M $LiPF_6$ being used as the electrolyte. For these studies we have used charge limits of 3–4.2 V.

3. Results

3.1. Structural studies

Rietveld analysis has been used to examine the structure of these materials, the Rietveld method involves full pattern fitting against a structural model. This method has been used extensively for structure analysis of complex oxide materials. A full discussion of the Rietveld method is out with the scope of this paper [14,15]. Previous experiments [9] have shown that some caution should be used when interpreting
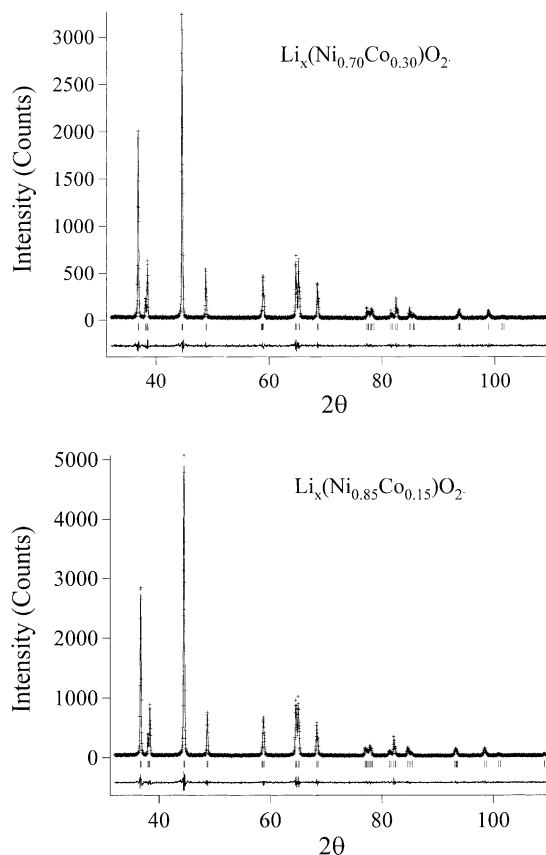

Fig. 1. Observed (+), calculated (−) and difference plots of $Li_x(Ni_{0.70}Co_{0.30})O_2$ and $Li_x(Ni_{0.85}Co_{0.15})O_2$, obtained from Rietveld analysis of powder X-ray data.

the results obtained from powder X-ray data for the systems under examination in this work. The Li is practically invisible using powder X-ray methods as the scattering factor is too low. As the approximate Li content is determined using a constraint to disordered Ni/Co on the site it follows that as the sample ordering improves on the 3a site, the ability to prove this diminishes. A similar argument is also true for oxygen, which is not a strong scatter of X-rays. Previous measurement using powder neutron diffraction (the preferred method of structure determination for Li and O) has shown no evidence of oxygen vacancies.

Problems also arise from the location of Ni and Co in the periodic table. As they are adjacent to each other they have very similar X-ray scattering factors, and hence, the contributions from each cannot be determined accurately or independently. For this reason it is assumed that disordering on the 3a site is related to the presence of Ni and Co. Similarly the presence of Li on the Ni + Co 3b site is suspected.

Presented in Fig. 1 are the observed, calculated and difference plot for the $Li_x(Ni_{0.70}Co_{0.30})O_2$ and $Li_x(Ni_{0.85}$-$Co_{0.15})O_2$ samples with the residual errors obtained presented in Table 1. From examination of the plot and residual errors (R_{wp}, R_p and χ^2), it was concluded that the model used for Rietveld refinement is good. Presented in Table 2, are the results obtained from the Rietveld analysis. An expansion of

Table 1

Obtained residual errors obtained from Rietveld analysis of powder X-ray data

Y in $Li_x(Ni_yCo_{1-y})O_2$	R_{wp} (%)	R_p (%)	χ^2
0.70	14.52	10.13	1.152
0.75	14.15	9.89	1.282
0.80	11.74	8.31	1.657
0.85	12.65	8.96	1.358
0.90	11.69	8.28	1.566
1.00	11.43	7.83	1.550

the lattice was seen as the Ni content was increased and would be as expected from ionic radii considerations (assuming low spin Co^{3+} $(3d^6) = 0.545$ Å, low spin Ni^{3+} $(3d^7) = 0.56$ Å, [16]).

From Rietveld analysis of X-ray data, it was not impossible to detect the presence of any Ni on the 3a for the samples $Li_x(Ni_{0.70}Co_{0.30})O_2$ and $Li_x(Ni_{0.75}Co_{0.25})O_2$. Therefore, it was concluded that these samples have good lithium 3a site ordering (i.e. very low Ni contents on the 3a site). The other samples were found to have Li site occupancies in the region of 99%. The findings of the experiments are in approximate agreement with the results in [4]. The isotropic temperature factors are presented in Table 2. The Li temperature factors for the $Li(Ni_{0.70}Co_{0.30})O_2$ and $Li(Ni_{0.75-}Co_{0.25})O_2$ should be treated with some reservations as there Li 3a site occupancies could not be determined directly. The other Li temperatures are reasonable. The Ni + Co temperature factors show very little variation with composition. Oxygen Biso show some variations but nothing that can be correlated to the structure. It is well understood that the magnetic properties of these types of layered phases are highly sensitive to the structure [17,18], with good samples having transitions suppressed to lower temperatures (typically <10 K) than poor samples (>10 K). Examination of the samples presented in the current study by SQUID magnetometry [19], show that any transitions occur at low temperature (<9 K). Indeed the samples with the highest Li site occupancies (i.e. $y = 0.70$ and 0.75) have no definite transitions that could be detected at temperature above 4.2 K. Therefore, the samples should be considered as being of a high quality.

Rietveld analysis of the Ni + Co layer shows that the 3b site is not fully ordered. Previous experiments have sug-

Fig. 2. Selected charge/discharge curves for $Li_x(Ni_{0.75}Co_{0.25})O_2$ and $Li_x(Ni_{0.90}Co_{0.10})O_2$. Cycles 1, 5, 10 and 15 shown.

gested the presence of Li on the 3b site [9,11], which appears to be linked to the excess of Li used in the starting mixture. As yet, the presence of 3b Li has not been conclusively proven, nor has effects on the electrochemical properties been determined.

3.2. Electrochemical studies

The electrochemical properties of these materials as prepared were found to be good. The charge/discharge curves obtained for sample $x = 0.75$ and 0.90 are shown in Fig. 2, with only the 1st, 5th, 10th and 15th cycles shown for

Table 2

Atomic parameters obtained from Rietveld analysis of powder X-ray data[a]

Y in $Li(Ni_yCo_{1-y})O_2$	a lattice parameter (Å)	c lattice parameter (Å)	Cell volume (Å³)	O Z position	Li (g) on the 3a site	Ni + Co (g) on the 3b site	Biso Li 3a	Biso (Ni + Co) 3b	Biso O 6c
0.70	2.85901 (8)	14.1461 (4)	100.138 (5)	0.24121 (22)	1[a]	0.940 (10)	1.14 (22)[a]	0.47 (4)	1.21 (6)
0.75	2.86051 (8)	14.1561 (4)	100.314 (5)	0.24076 (20)	1[a]	0.945 (9)	1.10 (21)[a]	0.65 (4)	1.14 (6)
0.80	2.86474 (5)	14.1670 (3)	100.688 (3)	0.24089 (15)	0.994 (1)	0.928 (6)	1.33 (14)	0.63 (3)	1.51 (5)
0.85	2.86719 (8)	14.1735 (4)	100.907 (5)	0.24130 (19)	0.989 (2)	0.923 (8)	0.86 (21)	0.58 (5)	1.55 (8)
0.90	2.87104 (6)	14.1792 (3)	101.219 (4)	0.24134 (17)	0.995 (2)	0.929 (7)	1.14 (17)	0.73 (4)	1.55 (7)
1.00	2.87603 (6)	14.1926 (3)	101.667 (4)	0.24141 (18)	0.988 (2)	0.943 (7)	1.12 (16)	0.65 (3)	1.29 (5)

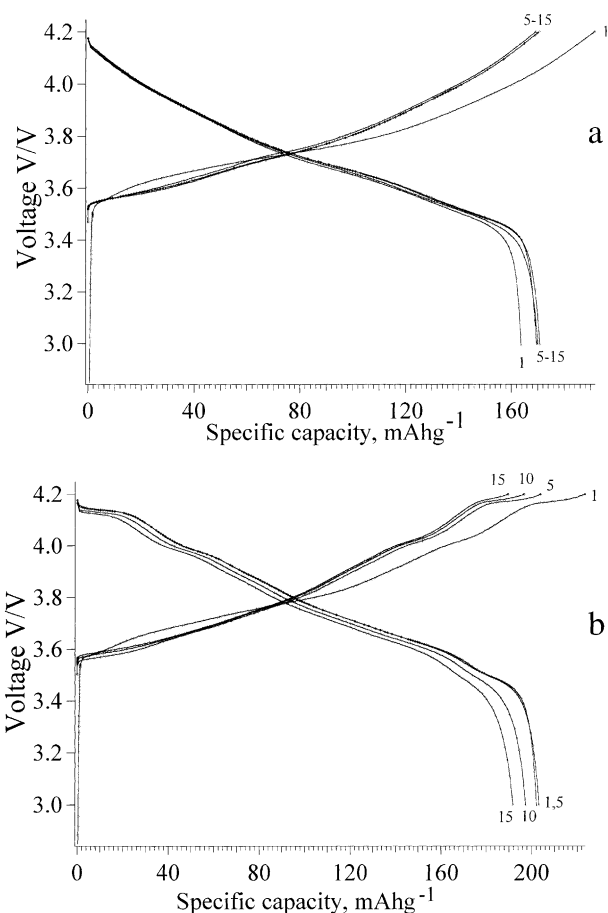[a] It was not possible to determine from powder X-ray data.

Table 3
Charge/discharge capacities obtained for all samples for selected cycles[a]

Y in Li(Ni$_y$Co$_{1-y}$)O$_2$	Charge capacity 1st cycle (mAh/g)	Discharge capacity 1st cycle (mAh/g)	Charge capacity 5th cycle (mAh/g)	Discharge capacity 5th cycle (mAh/g)	Charge capacity 10th cycle (mAh/g)	Discharge capacity 10th cycle (mAh/g)	Charge capacity 15th cycle (mAh/g)	Discharge capacity 15th cycle (mAh/g)	Cycle 1 efficiency (%)	Cycle 5 efficiency (%)	Cycle 10 efficiency (%)	Cycle 15 efficiency (%)	Overall discharge efficiency (%)[b]
0.70	184.3	155.7	138.8	137.6	137.5	136.2	137.4	136.8	84.5	99.1	99.1	99.6	87.9
0.75	191.5	163.7	169.5	169.5	170.8	170.8	170.8	170.1	85.5	100	100	99.6	103.9
0.80	202.2	182.1	186.2	185.6	177.9	176.8	182.3	180.2	90.1	99.7	99.4	98.8	99.0
0.85	211.7	179.8	183.8	183.2	183.2	182.9	183.0	182.6	84.9	99.7	99.8	99.8	101.6
0.90	223.6	202.2	204.1	203.3	196.8	197.3	189.7	191.8	90.4	99.5	100.3	101.1	94.9

[a] Comparison of the obtained efficiencies for the samples examined in this study.
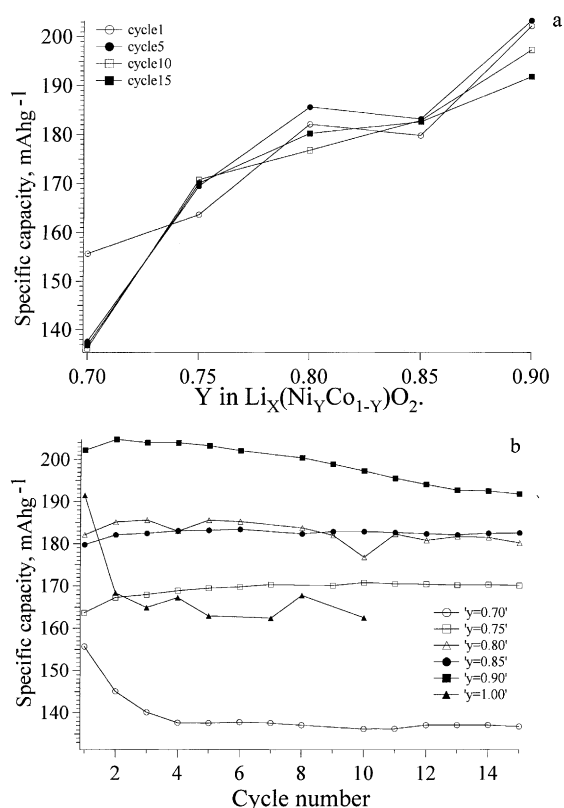
[b] Over 15 cycles.

Fig. 3. (a) Capacity as a function of y in Li$_x$(Ni$_y$Co$_{1-y}$)O$_2$ for selected cycles. (b) Capacity vs. cycle number for all compositions.

reasons of clarity. The results shown in Fig. 3a show the obtained capacities for these samples as a function of nickel content. In general, that obtained cell capacities increase as the nickel content was increased. This suggests that cobalt plays a very small part in the electrochemical properties, although this is dependent on the voltage limits used. The sample prepared with $x = 0.85$ has a slightly lower capacity than would have been expected, and this is thought to be related to the lower than expected Li 3a site occupancy. The best sample in terms of discharge capacity was the Li$_x$(Ni$_{0.9}$Co$_{0.1}$)O$_2$ sample, with values of approximate 205 mAh/g being obtained for the initial discharge capacity. The LiNiO$_2$ sample was found to have lower capacity than should be expected, this is probably related to the detectable

degree of disorder seen for the sample. This is also in addition to the phase changes seen on charge and discharge. An unexpected result (compared to the properties seen in [1–3]) was the poor properties of Li$_x$(Ni$_{0.7}$Co$_{0.3}$)O$_2$. The initial discharge capacity was found to be about 155 mAh/g. However, from cycles 2–4, this rapidly dropped to ∼137 mAh/g, during subsequent cycles (cycle 5–15) very good efficiency was seen (>99%).[3] Examination of the results shown in Fig. 3b and Table 3 show that the overall cycling properties of these materials were actually good, with very little capacity fade seen for $y = 0.75$, 0.8 and 0.85 samples. Significant capacity fade was seen for the sample prepared with $y = 0.9$. Examination of the charge/discharge curves presented in Fig. 2b show that this composition clearly undergoes numerous gradient changes as a function of cell voltage. These changes are reminiscent of those seen for LiNiO$_2$ and in agreement with the recently published cyclic voltametry experiments of Cho et al. [3]. Closer examination of the results obtained for the Li$_x$(Ni$_{0.85}$Co$_{0.15}$)O$_2$ sample suggests that this sample may also be susceptible to phase changes, however, it does not seem to overly affect the results obtained. Further studies should be performed using cyclic voltametry to determine whether a phase transition really occurs in this composition.

4. Conclusions

Initial structure analysis using powder X-ray diffraction has shown the samples are of a good quality and this is reflected in the electrochemical properties. During our previous studies [9,10] on these materials we have examined the structure using both X-ray and neutron data. From the studies, we have learned that structural analysis from X-ray data usually underestimates the degree of lithium site disorder. Neutron diffraction has been performed on these samples and will be presented in a future work [19,20], however, disorder was detected in these compositions.

The results obtained for the Li$_x$(Ni$_{0.7}$Co$_{0.3}$)O$_2$ sample are disappointing, compared to [1,2], and as yet we cannot

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[3] Cycling efficiency defined as (capacity of nth cycle/capacity of 1st cycle) × 100.

explain why this is so. For samples prepared with $y = 0.75$, 0.80 and 0.85, it has been found that the capacities and efficiencies are acceptable, this is not in agreement with previous results, which have suggested $y = 0.7$ is a better composition [2,3]. Although the $y = 0.85$ and 0.90 sample shows very good initial properties, the appearance of a phase change at higher voltage probably means these compositions should not be considered as viable cathode materials. The results presented also suggested that the variety of properties seen in literature for these materials is probably related to the method of sample preparation. Care must be taken to prepare samples with low disorder if good electrochemical properties are desired.

In a subsequent work, we will present the results obtained from various other techniques, which we hope will explain the properties of these phases more fully [19].

Acknowledgements

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