

The control of nonstoichiometry in lithium nickel–cobalt oxides

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Abstract

The nonstoichiometry of layered $\text{Li}_{1-x}(\text{Ni}_{0.8}\text{Co}_{0.2})_{1+x}\text{O}_2$ has been controlled by varying the starting composition and preparation temperature. X-ray and neutron powder diffraction has been used to determine the composition of the materials prepared, and the electrochemical properties have been examined. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In recent years, one particular area in Li ion battery research that has received a great deal of attention has been the layered phases LiCoO_2 and LiNiO_2 , [1–4]. Both systems have a layered rocksalt structure with the rhombohedral $R\bar{3}m$ space group (number 166). In this structure, alternating layers of Li and M (where M is Ni or Co) occupy the octahedral sites of a cubic close packed oxygen array.

LiCoO_2 is reasonably easy to synthesize and shows no evidence of cation disorder. For LiCoO_2 , reversible deintercalation to $\text{Li}_{0.5}\text{CoO}_2$ is possible, and it is possible to reinsert practically all of the Li removed during the deintercalation process, with intercalation from $\text{Li}_{0.5}\text{CoO}_2$ to $\sim \text{LiCoO}_2$ corresponding to a usable capacity of $\sim 130 \text{ mA h g}^{-1}$. However, Co due to its cost and more importantly its toxicity [5] is probably not an attractive long-term option for Li ion cells.

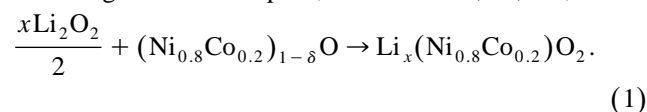
Conversely, stoichiometric LiNiO_2 is extremely difficult to prepare, due to the high temperature preparation conditions. It has been found that this leads to the formation of $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ [6,7] with the best sample reported being $\text{Li}_{0.996}\text{Ni}_{1.006}\text{O}_2$ [4]. Non-stoichiometry is associated with Li deficiency and the presence of Ni^{2+} in the Li 3a layer sites. It is thought that the Ni^{2+} ions act as local pinning centers, which restricts the motion of the Li ions

within the layers. Previous studies [4,8] have shown that the non-stoichiometry leads to a significant degradation in the charge/discharge properties of this system. It has also been shown to significantly change the magnetic properties [9,10]. However, samples with a small degree of nonstoichiometry have been found to exhibit good cycling properties. It is generally accepted that Li_xNiO_2 can be cycled reversibly with a useable capacity of $\sim 150\text{--}160 \text{ mA h g}^{-1}$.

In an attempt to improve the electrochemical properties of LiNiO_2 (as well as taking advantage of the lower cost and toxicity of Ni), we have doped the LiNiO_2 system with 20% Co. This composition has previously been identified by Delmas et al. [11] and Aragane et al. [12] as having significant potential as a cathode material. However, the electrochemical properties of this phase are dependent on the method of manufacture [12], and hence like LiNiO_2 , care must be taken during the sample preparation. The samples prepared during the course of our current study show good electrochemical properties, even when cation disorder is present in the samples.

2. Experimental

The nonstoichiometry of the $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ phases have been controlled by varying the starting composition according to relationship 1 (where $x = 0.9, 1.0, 1.1$):



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Samples were prepared using Li_2O_2 (ALFA, 95.3%) and coprecipitated $(\text{Ni}_{0.8}\text{Co}_{0.2})_{1-\delta}\text{O}$ in an argon filled glovebox. They were then pressed into pellets and carefully heated at 1°C min^{-1} to the desired synthesis temperature and isothermed for 48 h. The samples were then slow cooled to room temperature at 1°C min^{-1} . All experiments were performed under a flowing O_2 atmosphere.

Determination of phase purity and collection of data for Rietveld analysis [13] was performed on Rigaku RAD 12 kW X-ray diffractometer, using $\text{Cu K}\alpha$ radiation. Data for Rietveld analysis were typically collected from $10\text{--}120^\circ$, 2θ , with a step size of 0.03° , and a counting time of $1.5\text{--}2\text{ s step}^{-1}$. Time of flight powder neutron diffraction was performed on the GPPD diffractometer located at the IPNS facility, ANL, USA. Structural analysis using the Rietveld method was performed with either the *General Structural Analysis Suite* (GSAS) or *Rietan* [14,15]. The space group used was $R\bar{3}m$, with the structural model being Li/Ni_2 **3a** (0, 0, 0), Ni1/Co **3b** (0, 0 0.5) and O **6c** (0, 0, z), where z is approximately 0.25.

Electrochemical intercalation and deintercalation studies were performed using Li cells (2016 type cells) constructed in an argon filled glovebox. The working electrode consisted of 50 mg of $\text{Li}_x(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$, 10 mg of acetylene black and approximately 0.1 mg of Teflon powder. The mixture was mixed thoroughly using an agate mortar and pestle and pressed in thin disks. Lithium metal was used as the counter electrode, and polypropylene used as the separator, with battery grade PC-DMC/1 M LiClO_4 being used as the electrolyte. The electrochemical properties were examined using instrumentation designed and constructed 'in house', in the range 2.5 to 4.3 V.

3. Results and discussions

Examination of the X-ray patterns presented in Fig. 1(a–c) shows that the desired rhombohedral phase can be formed even at the relatively modest temperature of 600°C (single phase samples have also been prepared at 500°C). As would be expected, the samples prepared at the lower temperature show broad peaks (see Fig. 1(a)), which is consistent with the formation of small particles. Presented in Fig. 2(a) and (b) are the unit cell edges obtained as a function of initial composition; presented in Fig. 3(a) and (b) are the unit cell edges presented as a function of the synthesis temperature.

The plots of a unit cell edge vs. composition shown in Fig. 2(a) and a unit cell edge vs. temperature in Fig. 3(a) indicate that the samples prepared at 700°C have the smallest a unit cell dimensions. This is consistent with lower cation disorder on the 3a Li site. The plot of c unit cell edge vs. synthesis temperature indicates that as the synthesis temperature was increased, the unit cell edge also

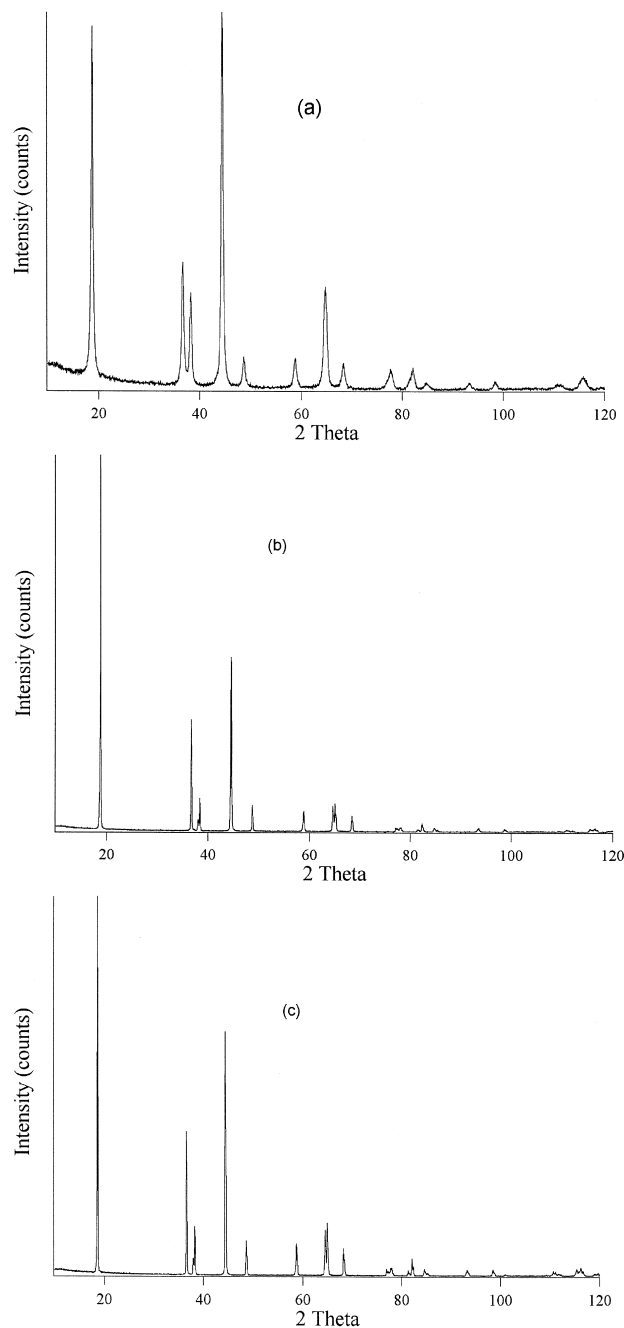


Fig. 1. X-ray powder patterns obtained for $\text{Li}_x(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ at various synthesis temperatures: (a) $\text{Li}_{0.9}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ at 600°C , (b) $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ at 700°C , and (c) $\text{Li}_{1.1}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ at 800°C .

increased. This may indicate that some kind of Ni–Co long-range ordering occurs as the synthesis temperature is increased. In all of the three nominal compositions examined as a function of synthesis temperature, a decrease in unit cell dimensions was noted for samples prepared at 650 or 700°C , after which an increase was seen. The origin of this decrease at 650 and 700°C is yet to be determined.

A sample of nominal starting composition $\text{Li}_{1.1}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ has been examined by powder neutron

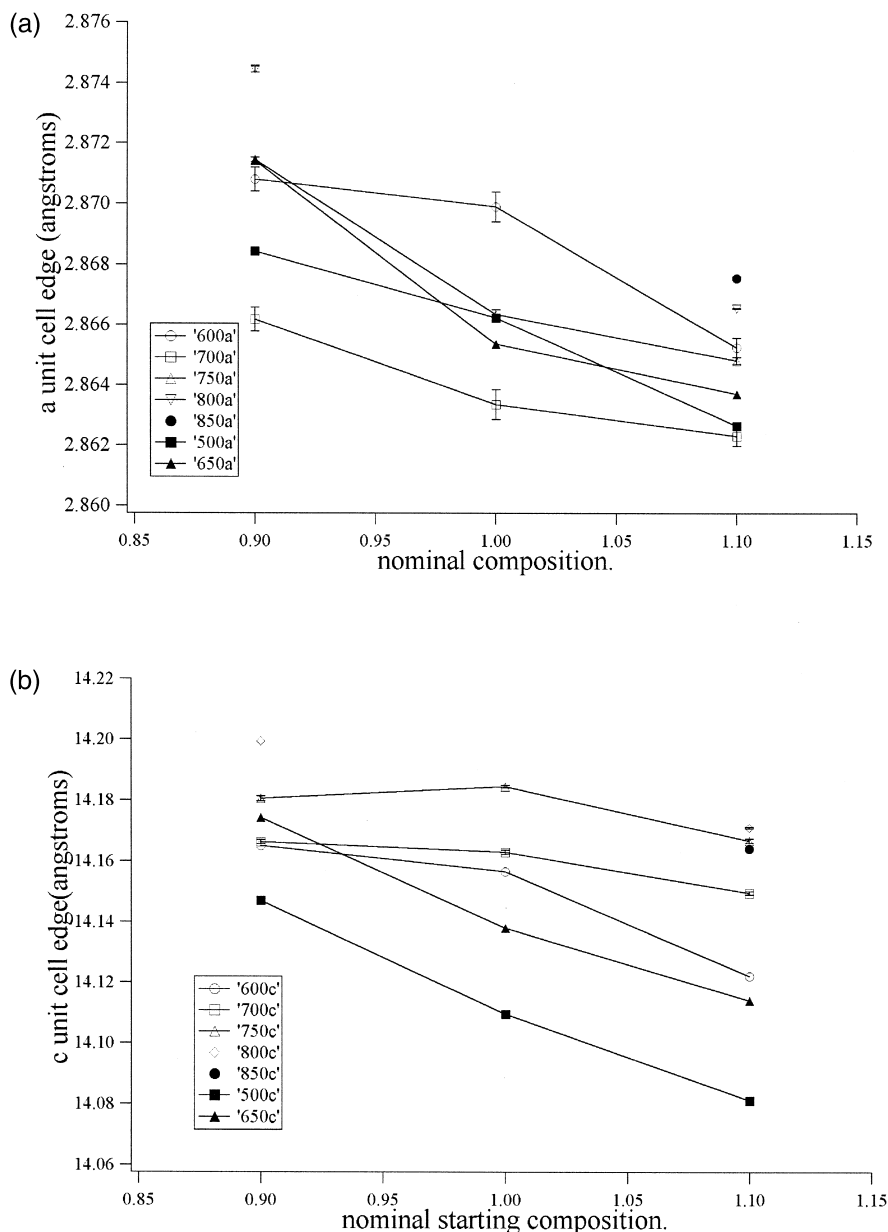


Fig. 2. (a) *a* Unit cell edge vs. nominal composition, (b) *c* unit cell edge vs. nominal composition.

diffraction and found to have the composition $\text{Li}_{0.998(3)}(\text{Ni}_{0.745}\text{Co}_{0.255})_{1.002(3)}\text{O}_2$. Within errors, this phase should be considered as being ordered. It was also noted that the Ni/Co ratio deviated slightly from that expected. This is probably related to a slight degree of nonstoichiometry in the precursor material. Shown in Fig. 4 are the fits obtained for the nominal composition, $\text{Li}_{1.1}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ at 700°C, (a) X-ray, (b) T.O.F neutron diffraction. The obtained R_{wp} and R_{p} for the X-ray and neutron data were 12.19 and 8.89 (X-ray) and 5.60 and 3.79 (neutrons), respectively. The crystallographic data obtained from refinement of the X-ray and neutron data are presented in

Tables 1 and 2, respectively. From examination of the results presented in Tables 1 and 2, it can be seen that there are slight difference between the X-ray and neutron refinements. This is probably related to the inability to directly probe the Li on the 3a site, as well as the associated difficulties of separating the contributions from the Ni and Co, which due to similarities in the atomic number have very similar X-ray scattering factors [16]. It is interesting to note that even with the excess of Li included in the initial starting compositions, there is little evidence to suggest the presence of excess Li as LiOH or Li_2CO_3 .

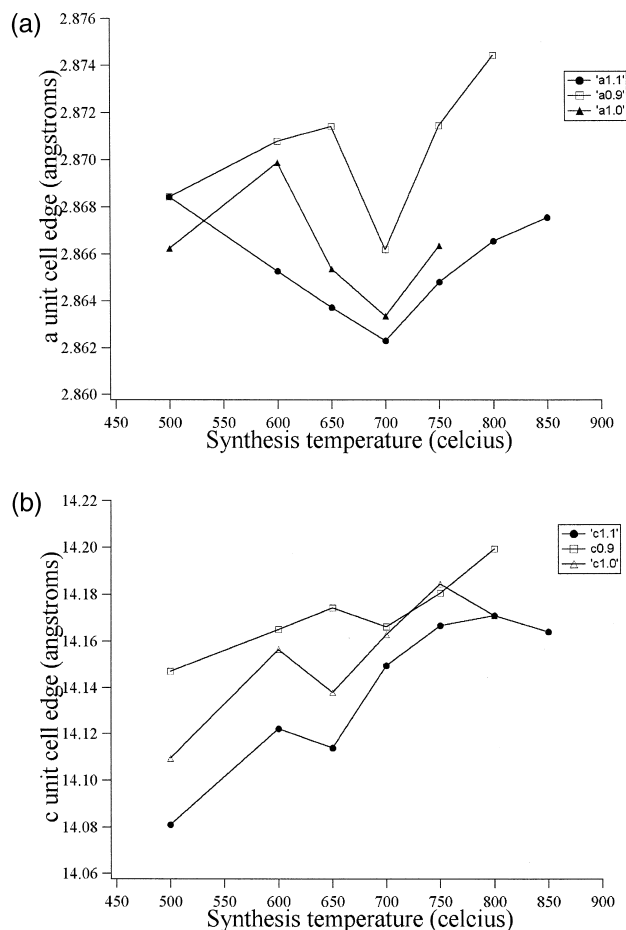


Fig. 3. (a) *a* Unit cell edge vs. synthesis temperature, (b) *c* unit cell edge vs. synthesis temperature.

From examination of the results presented in Figs. 2, 3 and 5 and Table 2, it has been shown that the samples with least disorder can be prepared at 700°C, when $x = 1.1$.

4. Charge–discharge experiments

Fig. 6 shows the results obtained for samples prepared at 600–700°C, with a nominal Li/NiCo ratio of 1.1:1. It can be seen from the results presented in Fig. 6 that all of the compositions examined so far have the following characteristics.

(1) High initial capacities were seen for all of the compositions presented in Fig. 6. The samples show initial capacities on charging of approximately 220 to 230 mA h g^{-1} .

(2) Capacity fade after the first charge/discharge cycle. Without exception, the samples examined show a decrease in capacity from first charge to first discharge. The origins of the capacity fade are not known and further studies are required.

(3) As the synthesis temperature was increased from 600 to 700°C, an increase was seen in the useable capacity.

This was unexpected, as it would be expected that the increasing particle size would cause the useable cell capacity to decrease. The approximate capacities for the 600,

Table 1

Atomic positions and temperature factors obtained from X-ray refinements for nominal starting composition, $Li_{1.1}(Ni_{0.8}Co_{0.2})O_2$

Name	Site	<i>x</i>	<i>y</i>	<i>z</i>	$(U_1/U_c)^a$ × 100	Fraction ^a
Li	3a	0.00	0.00	0.00	3.09	0.986(2)
Ni2	3a	0.00	0.00	0.00	3.09	0.014(2)
Ni1	3b	0.00	0.00	0.50	2.16	0.80
Co	3b	0.00	0.00	0.50	2.16	0.20
O	6c	0.00	0.00	0.2422(2)	1.79	1

Name	U11	U22	U33	U12	U13	U23
Li/Ni2	3.2(4)	3.2(4)	2.7(6)	1.62(18)	0.00	0.00
Ni1/Co	2.30(6)	2.30(6)	1.82(8)	1.15(3)	0.00	0.00
O	1.83(10)	1.83(10)	1.67(18)	0.92(5)	0.00	0.00

Note: $a = 2.86219(12)$, $c = 14.1489(5)$, $\alpha, \beta = 90$, $\gamma = 120$, cell volume = 100.381(7).

^aTotal occupancy constrained to unity. The contribution from Ni and Co cannot be easily distinguished by X-ray diffraction, hence no effort was made to determine the Ni/Co ratio.

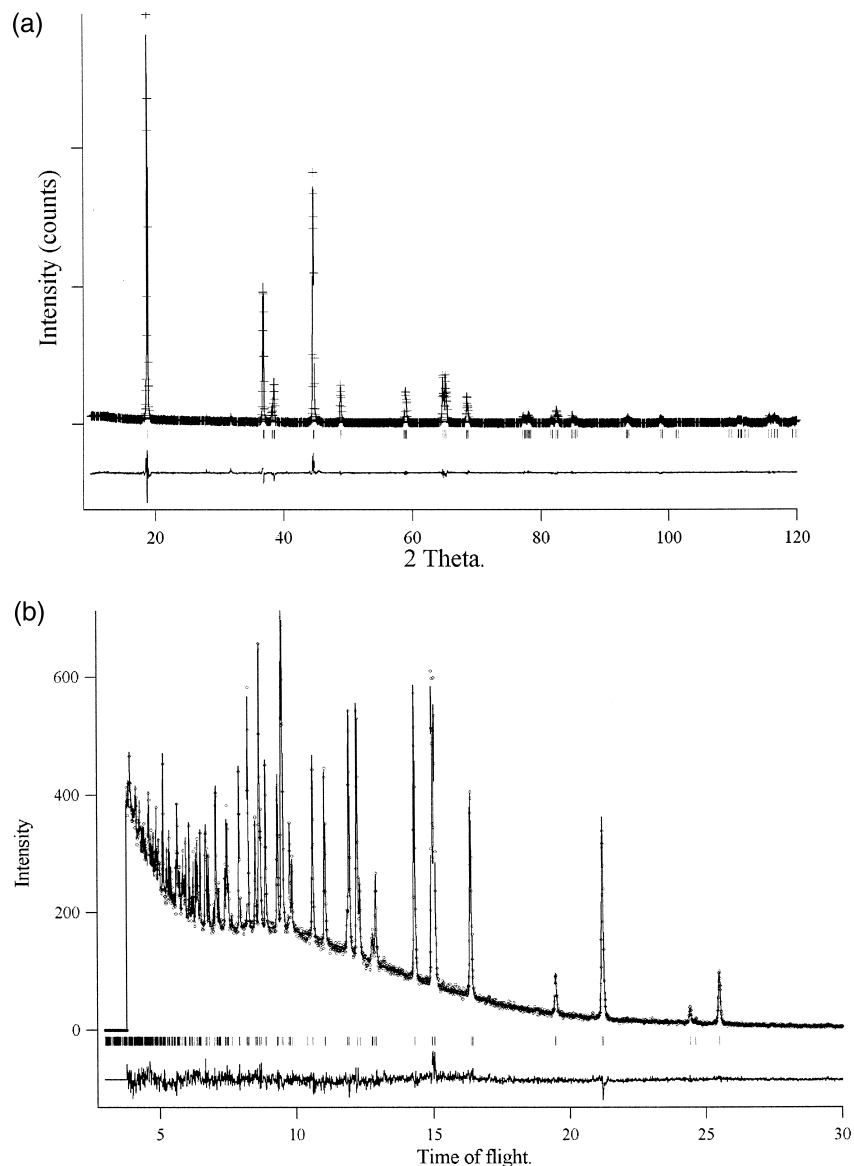


Fig. 4. Observed, calculated and difference plots for nominal starting composition $\text{Li}_{1.1}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ (a) X-ray (b) neutrons.

650 and 700°C sample were 150, 165 and 185 mA h g^{-1} , respectively.

(4) Good cycling characteristics for cycles 2–6 were seen for all samples. Considering the effects of nonstoichiometry on the parent LiNiO_2 phase, this result was not expected. This indicates that in some way the addition of Co helps to stabilize the system on cycling.

(5) No change of gradient is seen in the charge/discharge curves, this is a probable indication that no phase change occurred on Li deintercalation. This observation is in agreement with the recent findings of Saadoun and Delmas [17] and our own X-ray diffraction results [18]. These X-ray experiments provided no evidence to indicate any of the phase changes associated with LiCoO_2 and LiNiO_2 on lithium intercalation/deintercalation.

(6) Samples with $x = 0.9$ and 1.0 (not shown) show slightly lower capacities but very good cycling characteristics.

5. Conclusions

The initial results obtained during this study for $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ show a significant improvement in properties over the those reported previously for the LiNiO_2 system [4]. The best samples prepared so far have useable capacities of the order of $\sim 190 \text{ mA h g}^{-1}$ ($\text{Li}_{1.1}$ prepared at 700°C). The sample examined by neutron diffraction has been shown to be highly stoichiometric in nature. More interestingly, samples that have disorder on the 3a Li site

Table 2

Atomic positions and temperature factors obtained from neutrons refinements for nominal starting composition, $\text{Li}_{1.1}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$

Name	Site	x	y	z	$(U_i/U_e)^b$ $\times 100$	Fraction ^b
Li	3a	0.00	0.00	0.00	2.16	0.998(3)
Ni2	3a	0.00	0.00	0.00	2.16	0.002
Ni1	3b	0.00	0.00	0.50	0.46	0.745(6)
Co	3b	0.00	0.00	0.50	0.46	0.255
O	6c	0.00	0.00	0.24016(6)	1.00	1

Name	U11	U22	U33	U12	U13	U23
Li/Ni2	1.94(13)	1.94(13)	2.6(3)	0.97(7)	0.00	0.00
Ni1/Co	0.46(2)	0.46(2)	0.44(5)	0.23(1)	0.00	0.00
O	1.20(4)	1.20(4)	0.58(6)	0.60(2)	0.00	0.00

Note: $a = 2.86154(7)$, $c = 14.1467(4)$, $\alpha, \beta = 90$, $\gamma = 120$, cell volume = 100.320(4).

^bTotal occupancy constrained to unity.

still show a useable capacity of $\sim 150 \text{ mA h g}^{-1}$, which is comparable with the best results obtained for LiNiO_2 [4]. It should also be noted that all of the compositions examined so far have shown very good reversibility, including the samples with cation disorder. Results obtained from neutron diffraction show that the Ni/Co ratio is slightly different from that expected. For the samples prepared with excess Li, we have found no evidence of an impurity phase. It may be possible that we have Li rich grain boundaries, which have 'locked in' the excess Li. It was also noted that the capacity of the cells increased as the synthesis temperature was increased. It is possible that this could be related to grain boundary formation at lower temperatures, which have the effect of blocking the Li migration pathways. Further study using AC impedance spectroscopy and transmission electron microscopy is planned to determine whether this is the case.

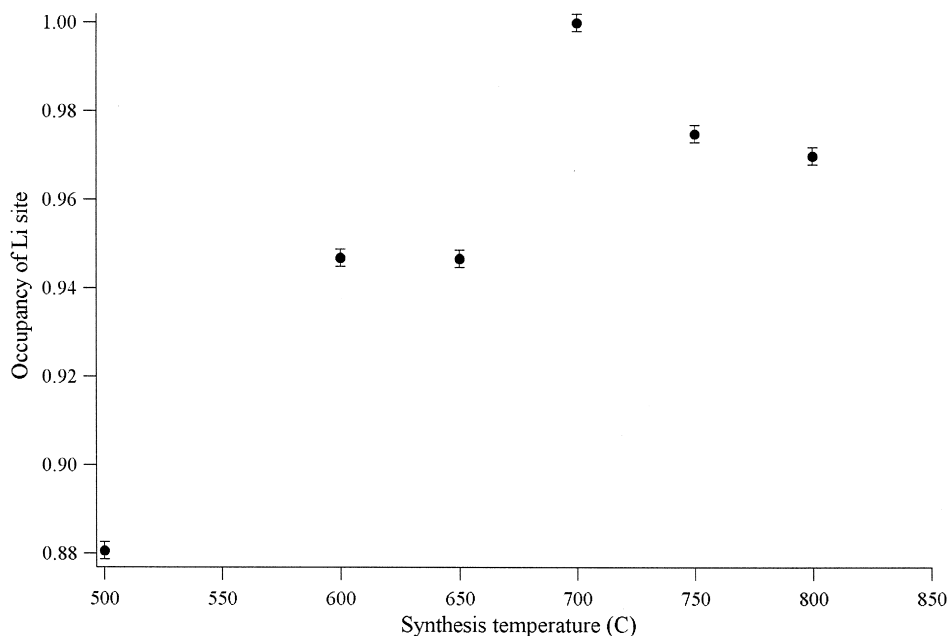


Fig. 5. Lithium 3a site occupancy vs. synthesis temperature, for composition $\text{Li}_{1.1}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$.

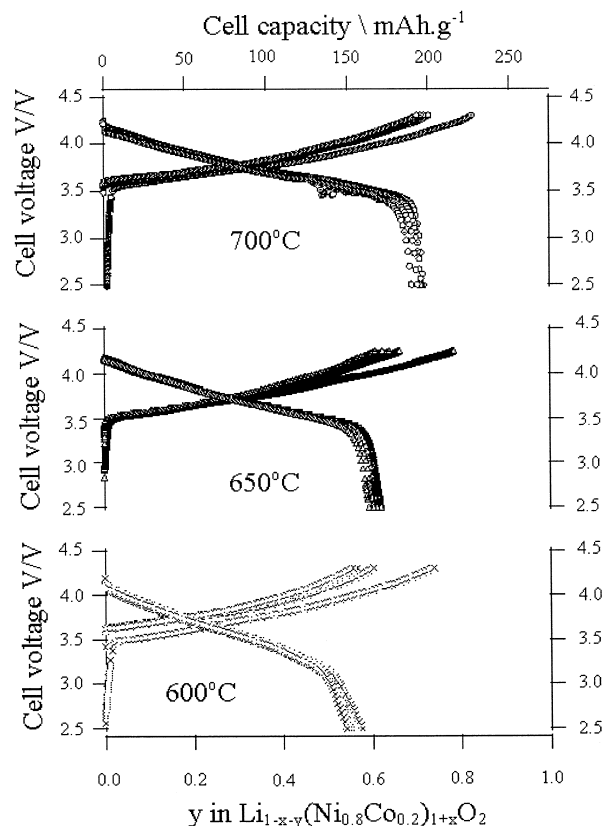


Fig. 6. Discharge/charge data obtained for $\text{Li}_{1.1}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ prepared at 600, 650 and 700°C.

Although this system still has to be fully optimized, it shows potential as a cathode in the next generation of rechargeable Li ion cells.

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References

- [1] See for examples, P.G. Bruce, Chem. Comm. (1997) 1817.
- [2] M.S.G.R. Thomas, W.I.F. David, J.B. Goodenough, P. Groves, Mat. Res. Bull. 20 (1985) 1137.
- [3] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, Mat. Res. Bull. 15 (1980) 783.
- [4] R. Kanno, H. Kubo, Y. Kawamoto, T. Kamiyama, F. Izumi, Y. Takeda, M. Takano, J. Solid State Chem. 110 (1994) 216.
- [5] C.R. Hammond, in: D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics, 72nd edn., Vols. 4–8, CRC Press, 1991.
- [6] J. Morales, C. Perez, J.L. Tirado, Mat. Res. Bull. 25 (1990) 623.
- [7] W. Li, J.N. Reimers, J.R. Dahn, Phys. Rev. B 46 (1992) 3236.
- [8] H. Arai, S. Okada, Y. Sakurai, J. Yamaki, Solid State Ionics 95 (1997) 275.
- [9] J.N. Reimers, J.R. Dahn, J.E. Greedan, C.V. Stager, G. Liu, I. Davidson, U. von Sacken, J. Solid State Chem. 102 (1993) 542.
- [10] A. Hirano, R. Kanno, Y. Kawamoto, Y. Takeda, K. Yamaura, M. Takano, K. Ohyama, M. Ohasi, Y. Yamaguchi, Solid State Ionics 78 (1995) 123.
- [11] C. Delmas, I. Saadoune, A. Rougier, J. Power Sources 43–44 (1993) 595.
- [12] J. Aragane, K. Matsui, H. Andoh, S. Sukuzi, F. Fukuda, H. Ikeya, K. Kitaba, R. Ishikawa, J. Power Sources 68 (1997) 13–18.
- [13] H.M. Rietveld, J. Appl. Cryst. 2 (1969) 65.
- [14] A.C. Larsen, R.B. Von Dreele, Los Alamos Laboratory report, NO-LA-U-86-746, 1987.
- [15] F. Izumi, in: R.A. Young (Ed.), The Rietveld Method, Chap. 13, Oxford Univ. Press, 1993.
- [16] B.L. Henke, E.M. Gullikson, J.C. Davis, Atomic Data and Nuclear Data Tables 54 (1993) 2.
- [17] I. Saadoune, C. Delmas, J. Solid State Chem. 136 (1998) 8–15.
- [18] M. Yonemura, R. Kanno, unpublished results.