

# The effects of sintering time on the structure and electrochemical properties of $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$

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## Abstract

We present the findings of a new study on the effects of sintering time on the structure and electrochemical properties of layered  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$ . For this study, we have examined samples prepared with sintering times of 3, 24, 48 and 96 h. The structure was initially examined by powder X-ray diffraction and then more precisely by time of flight powder neutron diffraction, with structural analysis by the Rietveld method being performed. The structural analysis indicated differences in the Li 3a and Ni/Co 3b site occupancies, which appear to be related to the sintering times.

Electrochemical charge/discharge measurements indicated that the initial discharge capacities for the samples prepared at 3, 24, and 48 h were basically invariant. However, a sizeable increase was noted for the sample prepared with a sintering time of 96 h. Also, an increase in the obtained discharge capacity from the first to second cycles was found for the samples prepared with 3–48 h sintering times. The largest increase was noted for the sample prepared for 48 h. No increase was seen for the sample sintered for 96 h. However, for all samples examined in this work, the capacities on first discharge were in excess of 180 mA h/g. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Sintering time; Electrochemical charge/discharge measurements; Structure analysis

## 1. Introduction

The layered phases,  $\text{Li}(\text{Ni}_x\text{Co}_{1-x})\text{O}_2$  have been highlighted as the probable replacement for  $\text{LiCoO}_2$  as the cathode of choice in the next generation of Li ion secondary cells [1]. Particular attention has been paid to the  $x = 0.8$  composition, which has good electrochemical properties and relatively good thermal stability. These phases also have far superior cycling stability compared to  $\text{LiNiO}_2$ . A bibliographic search of the open literature shows that relatively little work has been done on this system when compared to  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$ . Even fewer studies have examined the role of the synthesis conditions required to produce samples with exceptional electrochemical capacities and cycling stability.

In earlier work, we examined the effects of sintering temperature on the electrochemical properties of these materials [2]. These studies show that samples prepared in the region of 700°C had good electrochemical properties. During a more detailed study, we examined samples prepared at various temperatures and the best sample could be prepared in the region of 725°C [3]. All of these samples were prepared with a sintering time of 48 h. This study also highlighted the possibility of 3b site disorder, which appeared to decrease as the sintering temperature was increased. In light of these findings, we have also examined the role of synthesis times (this work), and the effects of different Li contents on the structure of these phases [4].

In this work, we have also examined the role of sample sintering time on a number of samples prepared at 725°C. The structure has been examined by time of flight powder neutron diffraction and any difference in structure has been correlated to changes in the electrochemical charge/discharge properties.

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## 2. Experimental

Samples were prepared in accordance with the methods presented in Ref. [2]. The samples examined for this particular study were prepared with a sintering temperature of 725°C and sintering times of 3, 24, 48 [3] and 96 h, respectively. Powder X-ray data were collected on a Rigaku RAD powder diffraction using Cu K $\alpha$  radiation. Initial phase purity and site occupancies of Ni and Co on the 3b site were determined. Examination of the total occupancy of Ni and Co on the 3b site works on the assumption that the Ni and Co X-ray form factors are practically identical with respect to copper K $\alpha$ . The general model used in the structure refinement is shown in Table 1.

Time of flight powder neutron diffraction was performed on either the Special Environment Powder Diffractometer or the General Purpose Powder Diffractometer, both located at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory, USA [5]. Structural analysis by the Rietveld method [6] was performed using the GSAS software package [7]. The neutron structural model was refined using the basic structural model obtained from X-ray data. An absorption correction due to the incoherent scattering of  $^6\text{Li}$  and Co [8] was also applied.

Two methods are presented relating to the analysis of the 3b site occupancy with respect to Ni and Co. Method 1 assumes that a deviation from 0.8 for the Ni had an equal and opposite effect on the Co occupancy. A different strategy was used for method 2 where the initial occupancy of Ni and Co are determined from the value obtained from powder X-ray diffraction. The Ni and Co are then constrained so that the ratio of the two atoms is always equal to 4:1. This will be discussed at a later stage.

Electrochemical studies were performed using Li coin 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 binder. 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  $\text{LiClO}_4$  being used as the electrolyte. The electrochemical properties were examined using instrumentation designed and constructed “in house”, in the range 2.5 to 4.25 V.

Table 1  
Basic model used during Rietveld refinement

	Wyckow	x	y	z	g
Li	3a	0	0	0	1 - X
Ni	3a	0	0	0	X
M (Ni + CO)	3b	0	0	0.5	1
O	6c	0	0	~ 0.24	1

## 3. Structure analysis

Presented in Fig. 1 are the X-ray powder patterns collected for the samples. Visual examination of the powder patterns shows the samples to be of a high quality with no evidence to support the presence of a second phase. It is also noteworthy that the sample prepared with a sintering time of 3 h had apparently fully reacted, with the only real difference being a slight broadening of some of the peaks. The peak broadening was particularly noticeable for the (101), (006), (102), (104) and (105) reflections. This is probably related to a particle size type effect.

Using the Rietveld method, the site occupancy with respect to Ni and Co on the 3b site was examined, with the results obtained presented in Fig. 2. The results suggest that the Ni/Co 3b layer is not fully occupied. However, these values should not be considered as being absolute and should only be used as an indication of a lower than expected site occupancy on the 3b site, with respect to Ni and Co. The basic structural models obtained from analysis of the X-ray patterns were used as the starting models for Rietveld analysis of the neutron patterns.

## 4. Structure analysis by powder neutron diffraction

It is well known that powder X-ray diffraction is not sensitive enough to perform accurate structure analysis of samples containing Li and O, with neutron diffraction being the method of choice for this kind of work.

It was noted that the samples prepared at 3 and 96 h contained a second phase. Several attempts were made to determine the nature of this second phase, however, no satisfactory starting model could be found. Therefore, the peaks relating to the second phase have been excluded from the refinement. The second phase is thought to be  $\text{Li}_2\text{CO}_3$ . The observed, calculated, and difference plots for the samples sintered for 24 and 48 h are presented in Fig. 3. The fits are reasonably good and the errors associated with the refinement are presented in Table 2. Examination of the difference profile shows the fitted patterns are a little noisy at lower d-spacings. This is possibly due to an amorphous component (from unreacted Lithia) or absorbance from  $^6\text{Li}$ .

Fig. 4 shows the lattice parameters and the volume obtained from Rietveld refinement of the neutron patterns. The *a* and *c* unit cell edges show different minima which we have previously interpreted as being due to a lowering of disorder on the 3a site. However, subsequent plotting of the cell volume shows that the difference in cell volume for 24 and 48 h is minimal. Presented in Fig. 5 are the Li 3a site occupancies obtained using model 1 and model 2, respectively. Although the different models do not directly involve the refinement of the Li site, it was noted that

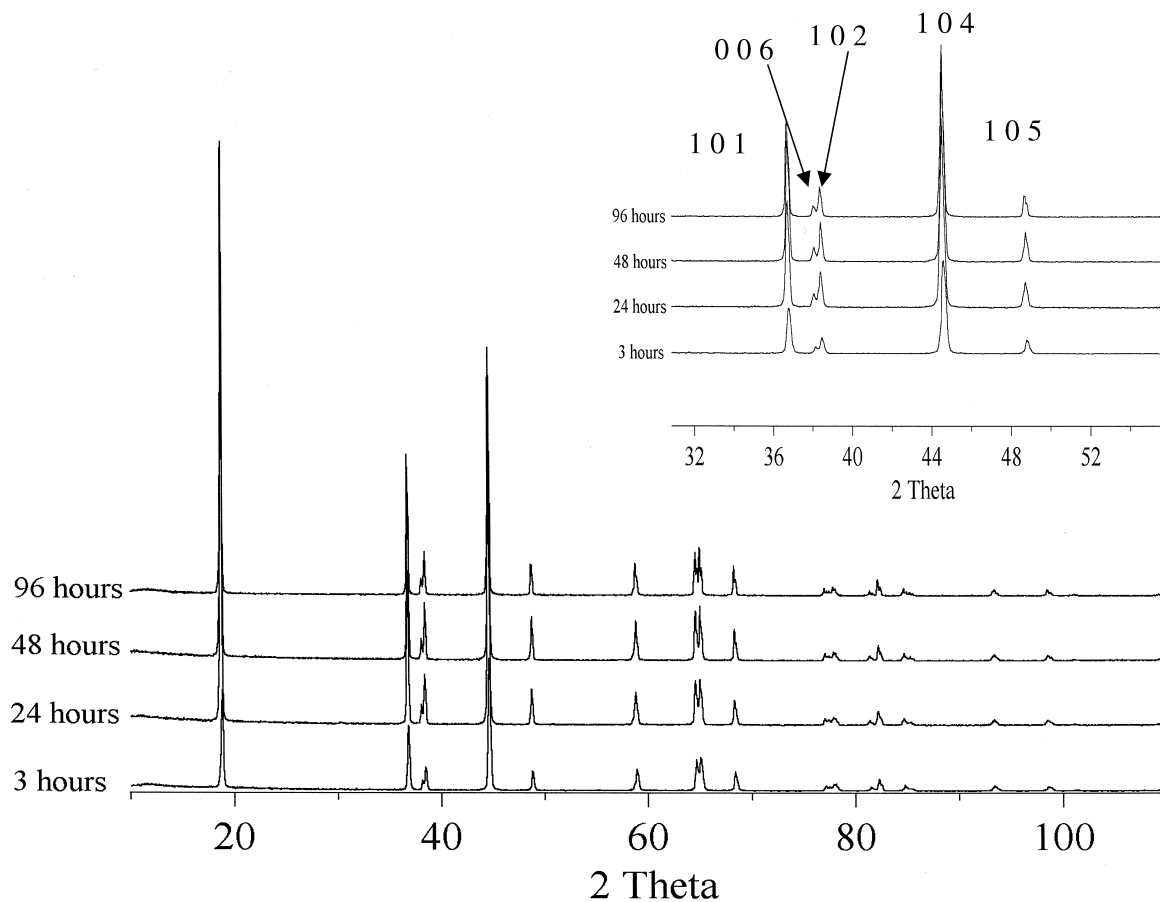


Fig. 1. Collected X-ray patterns for  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$  prepared at 3, 24, 48 and 96 h, respectively.

slight differences were obtained, within errors the difference should not be considered as significant.

It was noted that 3a site ordering with respect to Li is time dependent, with the sample prepared with a sintering time of 3 h having a noticeable amount of disorder. As the time was increased, the Li site order increased with the highest Li order present in the sample prepared with a

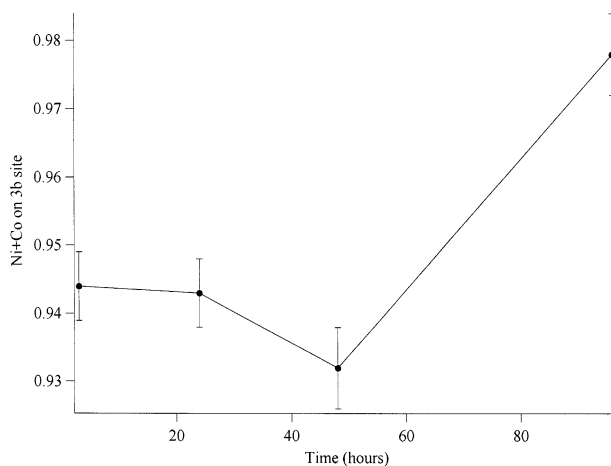


Fig. 2. Total occupancy of Ni and Co on the 3b site determined from Rietveld analysis from powder X-ray data.

sintering time of 48 h. When the sintering time was increased to 96 h, the Li occupancy was seen to decrease, this suggests that Li loss via volatilization of  $\text{Li}_2\text{O}$  may have occurred. This could suggest a minimum sintering time is required to fully order the Li 3a site, however, by increasing the time beyond a certain limit simply leads to  $\text{Li}_2\text{O}$  loss via volatilization.

As mentioned previously, the Ni/Co site was examined using two different models (see Fig. 6). The most noticeable difference between model 1 and model 2 was the higher amount Ni when model 2 was used, and hence, the samples are nearer the intended composition (see Table 3). It was also noted that the error bars were smaller when

Table 2

The obtained residual errors obtained from Rietveld refinements using neutron data for samples examined as a function of sintering time

$x$ in $\text{Li}_x(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$	Sintering time (h)	Rwp (%)	Rp (%)	Chi <sup>2</sup>
1.0	3	4.86	3.40	2.009
1.0	24	7.84	5.36	1.246
1.0 <sup>a</sup>	48	4.59	2.98	2.277
1.0	96	4.96	3.50	1.985

<sup>a</sup>From Ref. [3].

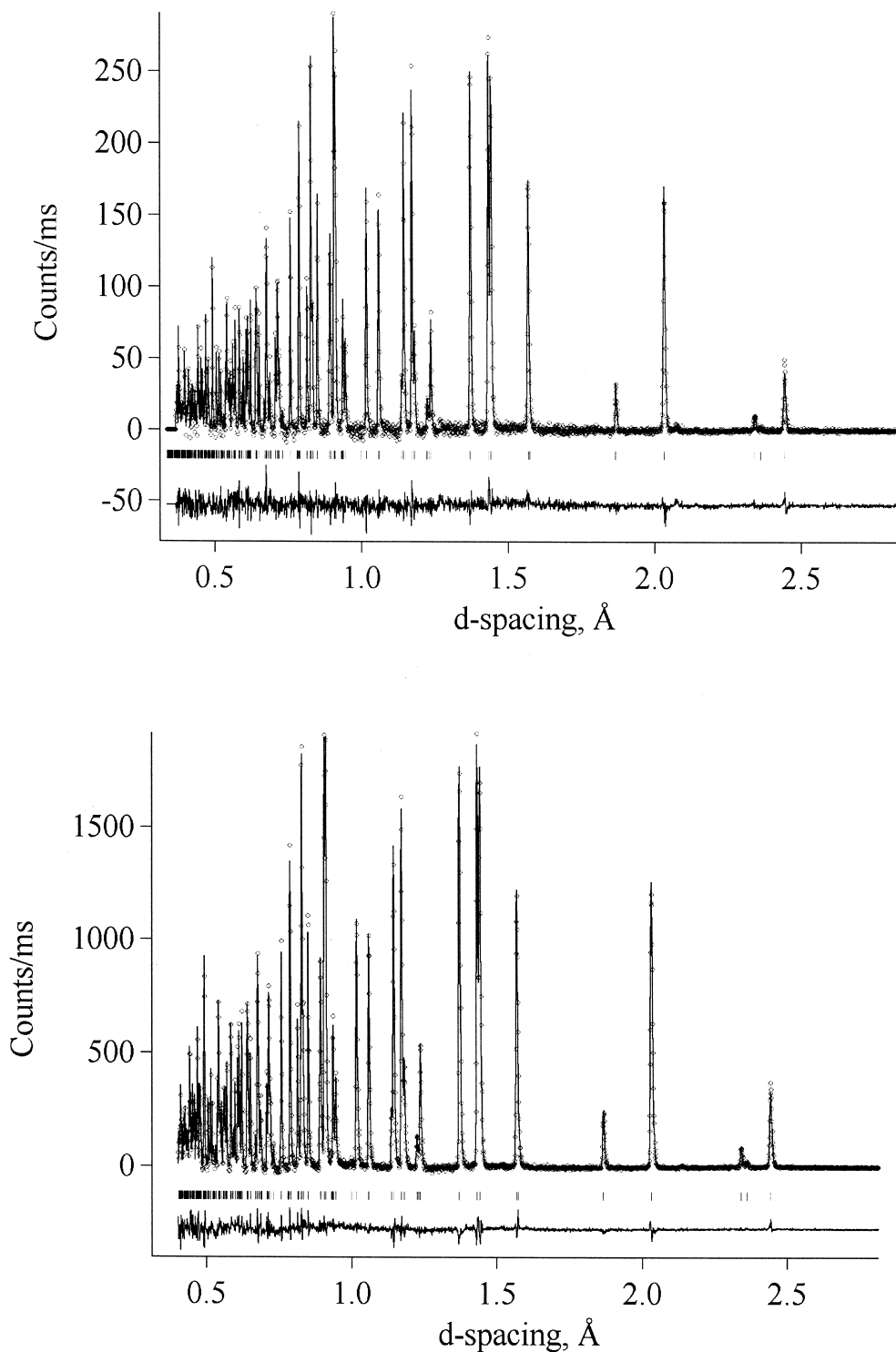


Fig. 3. Observed ( $\cdot$ ), calculated (—) and difference plots for (a)  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$  prepared at  $725^\circ\text{C}$  for 24 h, (b)  $725^\circ\text{C}$  for 48 h. Background has been subtracted from the plot.

model 2 was used. In both cases, it was noted that the Ni occupancy changed as a function of sintering time. The Ni occupancy reaching a maximum when the sintering time used was 48 h. When the sintering time was increased to 96 h, no increase in Ni occupancy was apparent. Examination of the results obtained by Kanno et al. [9] shows that

no structural disorder exists on the 3b site of  $\text{LiNiO}_2$ , similarly for the results obtained by Rougier et al. [10] for the composition  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$  which showed no 3b site disorder. However, the work of Gummow et al. [11] and Orman and Wiseman [12] on  $\text{LiCoO}_2$  and the work of Armstrong and Bruce [13] on the layered monoclinic struc-

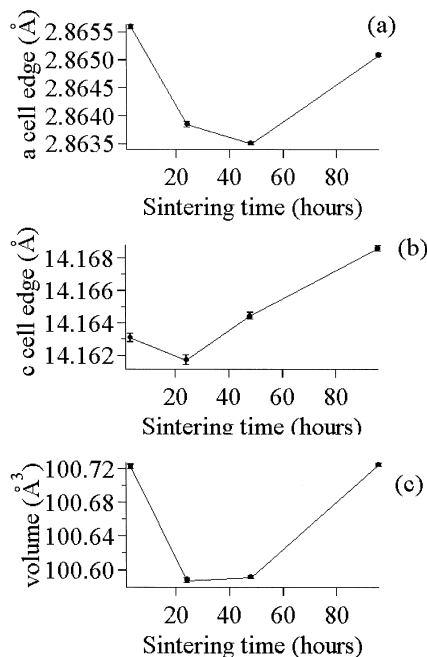


Fig. 4. Lattice parameters and volumes obtained from Rietveld refinement of neutron patterns.

ture of  $\text{LiMnO}_2$  highlighted the presence of Li in the transition metal layer.

It is worth noting that the refinement of our phase using model 2 generally gave compositions that are closer to the intended composition (see Table 3). Unpublished results suggest that this third atom is most probably Li [4]. Further experiments are currently in progress to prove these ideas.

Examination of the isotropic temperature factors, Fig. 7, show that increasing sintering time leads to an increase in the Li temperature factors, which suggests that the Li mobility increased. Presented in Table 4 are the anisotropic temperature factors obtained for the Li. For the nickel and cobalt present on the 3b site, at first glance, it would

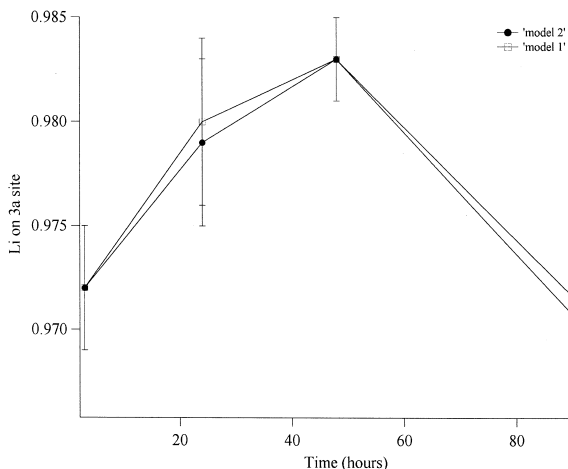


Fig. 5. Obtained Li occupancies on 3a site from neutron diffraction.

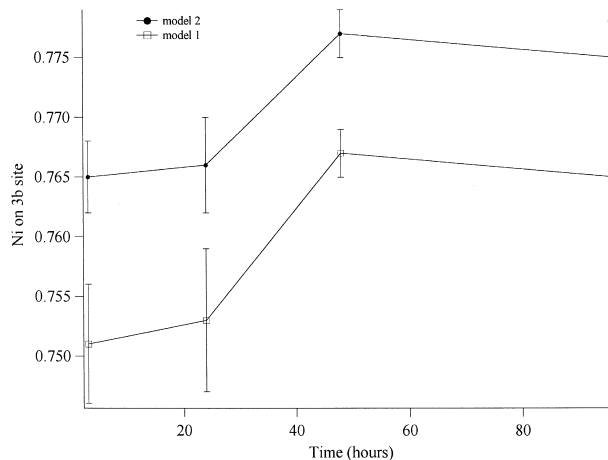


Fig. 6. Obtained Ni occupancies on 3b site from neutron diffraction.

appear that the temperature factors are quite small. This could be interpreted in two possible ways. The first obvious interpretation would be that these values are correct. Alternatively, this could indicate the presence of a third atom on the 3b site. This would have the effect of changing the scattered intensity from the site, which would manifest as a lower than expected temperatures factors. Overall, examination of the Ni/Co temperature factors is basically unchanged as the sintering time is increased. No notable behaviour was noted for the O temperature factors.

Presented in Table 5 are the selected bond angles and bond lengths obtained from structural refinements from neutron data. Shown for a comparison are the bond angles and lengths determined by Kanno et al. [9] for  $\text{LiNiO}_2$ , and Hirano et al. [14] for  $\text{Li}(\text{Mn}_{0.2}\text{Ni}_{0.8})\text{O}_2$ . The Li(3a)–O and Li interlayer distance for the four samples showed very little difference, this is perhaps not surprising considering the basic similarities in the structure. However, a comparison of these bond lengths with  $\text{LiNiO}_2$  and  $\text{Li}(\text{Mn}_{0.2}\text{Ni}_{0.8})\text{O}_2$  shows that these bond lengths are practically invariant with composition. This is surprising considering the differences in lattice parameters. Examination of these bond lengths for  $\text{LiCoO}_2$  showed similar values to those highlighted above. Examination of the Ni–O and Ni interlayer distance shows that these do change with sintering

Table 3

Composition as determined from powder neutron diffraction using model 1 and model 2. Model 1 and 2 assume that Ni and Co on 3a site is total multiplied by 0.8 and 0.2, respectively. As Li could not be determined on the 3b site, we have not included this in the total final composition

Sintering time (h)	Model 1	Model 2
3	$\text{Li}_{0.972}(\text{Ni}_{0.773}\text{Co}_{0.255})\text{O}_2$	$\text{Li}_{0.972}(\text{Ni}_{0.787}\text{Co}_{0.197})\text{O}_2$
24	$\text{Li}_{0.980}(\text{Ni}_{0.769}\text{Co}_{0.251})\text{O}_2$	$\text{Li}_{0.979}(\text{Ni}_{0.783}\text{Co}_{0.195})\text{O}_2$
48	$\text{Li}_{0.983}(\text{Ni}_{0.781}\text{Co}_{0.236})\text{O}_2$	$\text{Li}_{0.983}(\text{Ni}_{0.791}\text{Co}_{0.201})\text{O}_2$
96	$\text{Li}_{0.969}(\text{Ni}_{0.789}\text{Co}_{0.241})\text{O}_2$	$\text{Li}_{0.970}(\text{Ni}_{0.799}\text{Co}_{0.200})\text{O}_2$

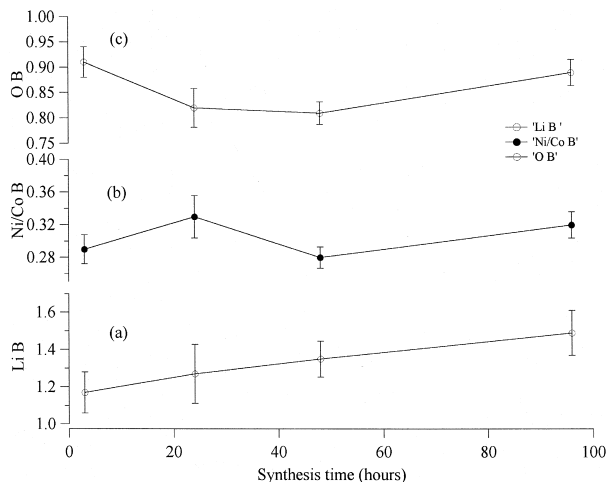


Fig. 7. Isotropic temperature factors obtained for Li, Ni/Co, and O from neutron diffraction.

Table 4  
Anisotropic temperature factors for Li on 3a site  
Temperature factors of the form  $T = e - [2\pi^2(u_{11}h^2a^{*2} + \dots 2u_{12}hka^*b^* + \dots)]$ .

Sintering time (h)	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$
3	2.00(1)	= $u_{11}$	0.6(2)	0.98(6)
24	1.73(14)	= $u_{11}$	1.2(3)	0.86(7)
48	1.89(9)	= $u_{11}$	1.2(2)	0.94(4)
96	2.2(1)	= $u_{11}$	1.2(2)	1.08(5)

time and are different to those obtained in Refs. [9] and [14].

### 5. Electrochemical studies

Presented in Fig. 8 are selected charge/discharge curves for the samples examined previously by neutron diffraction. A number of interesting observations can be made about electrochemical results.

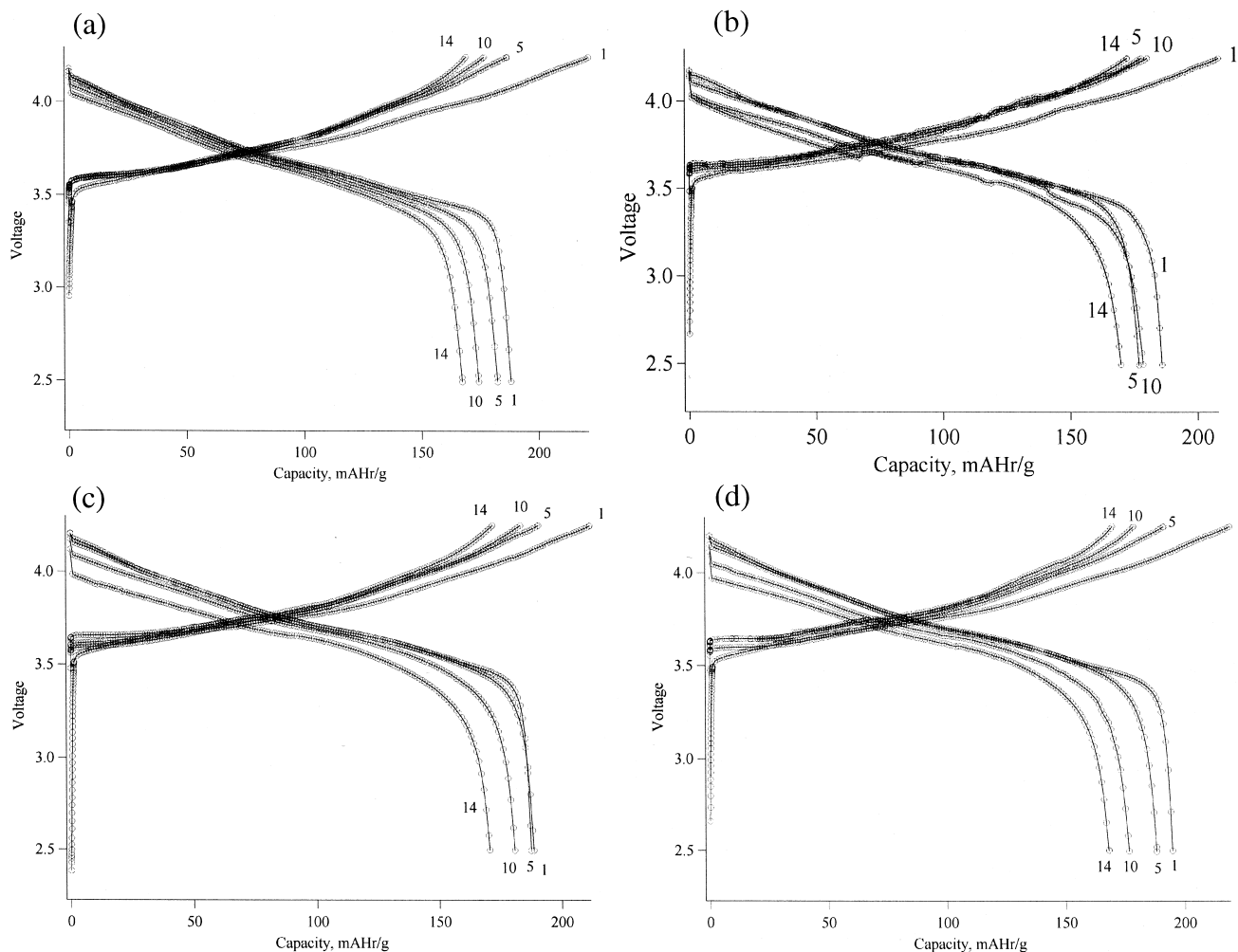


Fig. 8. Selected charge/discharge curves for the samples sintered for (a) 3 h, (b) 24 h, (c) 48 h and (d) 96 h.

Table 5  
Selected bond angles and bond lengths obtained from Rietveld analysis of neutron data

Time/structure	Li(3a)–O (Å)	Ni(3b)–O (Å)	O–Li(3a)–O (°)	O–Ni(3b)–O (°)	O–Li–O (Å)	O–Ni–O (Å)
3	2.1129(6)	1.9576(5)	85.40(3)	94.10(3)	2.450	2.271
24	2.1145(8)	1.9545(6)	85.25(4)	94.21(4)	2.452	2.268
48	2.1125(4)	1.9562(4)	85.34(2)	94.09(2)	2.451	2.271
96	2.1135(5)	1.9571(4)	85.35(3)	94.11(3)	2.451	2.272
LiNiO <sub>2</sub> [9]	2.1154(14)	1.9692(12)	85.24(15)	94.77(19)	2.450	2.292
Li(Ni <sub>0.8</sub> Mn <sub>0.2</sub> )O <sub>2</sub> [14]	2.1125(5)	1.9761(4)	85.93(2)	93.54(2)	2.450	2.282

In terms of capacity, the samples should be considered as being good, with discharge capacities of the order of 185 mA h/g being obtained for the samples as prepared. The initial capacities of the 3, 24, and 48 h samples all had similar discharge capacities, whereas the sample sintered for 96 h had an initial capacity of approximately 195 mA h/g. For the samples prepared for 3–48 h, an increase was noted in discharge capacity from first to second discharge, with the highest increase seen for the sample sintered for 48 h. As yet, we do not understand the origins of this increase, however, samples prepared with slightly higher Li contents have shown this type of behaviour over a larger number of cycles.

For all of the samples prepared, the capacity retention was found to be between 84% and 86%. It is felt that the capacity fade is in part related to the samples, cell design, the ratio of sample to acetylene black and the voltage limits used during this study. The discharge curves do show a noticeable voltage drop at the start of discharge, which could be evidence to suggest that the charge voltage is a little too high.

The samples show a deviation from a flat charging in the region of 3.9 V. Saadoune and Delmas [15] have also noted this type of behaviour in this composition, and attributed it as being characteristic of two adjacent solid solution domains.

## 6. Conclusions

This study has shown that sintering time has an effect on the structure and hence, electrochemical properties of these phases. From the results presented, relating to the structure, it can be said that the best samples should be prepared in the region of 24 and 48 h. The neutron diffraction clearly showed ordering of the 3a and 3b layer sites probably occurs at slightly different temperatures, for the Li on the 3a site, it was found that 24–48 h had comparable Li occupancy. The Ni/Co apparently required at least 48 h sintering to attain optimal ordering. However, to our knowledge, we are the first to report the possibility of 3b site disorder, with clear deviation from the expected

stoichiometry occurring. These results coming from both X-ray and neutron powder studies.

An unexpected result was obtained for the electrochemical properties of the sample, with the best initial capacities being obtained for the sample prepared with a sintering time of 96 h. This was unexpected as the structure analysis showed that this sample probably had the highest degree of disorder on the 3a site.

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