

LITHIUM INSERTION INTO Co_3O_4 : A PRELIMINARY INVESTIGATION

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Received 23 May 1985

Lithium has been inserted into the spinel Co_3O_4 both chemically and electrochemically. During lithiation the tetrahedral A-site Co^{2+} cations are displaced into neighbouring empty octahedral sites: the incoming Li^+ ions occupy the remaining interstitial octahedra of the spinel structure to produce the partially ordered rocksalt compound LiCo_3O_4 . The octahedral B-site cations of the $\text{A}[\text{B}_2]\text{X}_4$ spinel are unperturbed by this reaction: the oxide lattice expands by 8.6%. Lithium analyses and powder X-ray diffraction spectra indicate that further lithiation is possible. However, it is demonstrated that a fast lithiation in excess of LiCo_3O_4 is followed by a slow extrusion of B-site cobalt at 50°C until all the Li on the Ba sites has moved to the octahedral vacancies thus created.

1. INTRODUCTION

Lithium insertion/extraction reactions with transition-metal oxides and sulphides at ambient temperature have received considerable interest on account of the recent quest for new electrodes for primary and secondary lithium batteries. These reactions often yield metastable products with unusual ordering and valence states that cannot be obtained by conventional high-temperature synthetic techniques.

In particular it has been reported that certain spinels of general formula $\text{A}[\text{B}_2]\text{X}_4$ can accommodate an appreciable quantity of lithium within their structures. In a cubic spinel, characterized by the space-group $\text{Fd}\bar{3}\text{m}$, the A-site cations occupy one-eighth of the tetrahedral sites (the 8a sites), whereas the B-site cations occupy one-half of the octahedral sites (the 16d sites). The cubic-close-packed anions, X, reside in the 32e positions. The interstitial space of the spinel structure is comprised of 56 tetrahedra (sites 8b and 48f) and 16 octahedra (sites 16c). In cubic close packing the tetrahedra share faces with octahedra.

It has been shown previously that the spinels Fe_3O_4 and Mn_3O_4 with like cations on the A and B sites can accommodate within their structures at least one lithium ion per formula unit

(1,2). The A-cations are displaced into octahedral sites (16c) during lithiation to give a partially ordered rocksalt structure $(\text{Li}_x\text{A})_{16\text{c}}[\text{B}_2]_{16\text{d}}\text{O}_4$ at $x = 1$. Significant volume changes of the anion lattice occur with lithiation, and in $\text{Li}_x\text{Mn}_3\text{O}_4$ the degree of tetragonal distortion ($c/a = 1.16$ at $x = 0$) is reduced to near-cubic symmetry ($c/a = 1.05$ at $x = 1$); nevertheless the $[\text{B}_2]\text{X}_4$ framework of the spinel structure remains intact. Examination of this framework has shown it to provide a three-dimensional interstitial space for Li^+ -ion diffusion through the structure. Since the A-cations reside in the interstitial space of the $[\text{B}_2]\text{X}_4$ framework during all stages of the electrode reaction, those other than Li^+ tend to restrict the mobility of the Li^+ ions; therefore recent attention has been focussed on the lithium spinels $\text{Li}[\text{Mn}_2]\text{O}_4$, $\text{Li}[\text{Ti}_2]\text{O}_4$ and $\text{Li}[\text{V}_2]\text{O}_4$ (2,3,4). These compounds have the advantage that lithium can also be extracted from the spinel framework, which offers the possibility of extending the working range of the spinel electrode (5,6).

In this paper electrochemical data and structural characteristics of lithiated Co_3O_4 samples are presented that provide clues about the nature of the reaction mechanism that occurs during discharge of $\text{Li}/\text{Co}_3\text{O}_4$ cells.

2. EXPERIMENTAL

Samples of Co_3O_4 (Cerac Inc., >99.5%) were lithiated chemically using a 1.6 M solution of n-butyllithium in hexane (Merck) under a nitrogen atmosphere at temperatures between 20°C and 50°C. The lithiated products were washed several times with dry hexane to remove any unreacted n-butyllithium, dried under vacuum and stored under argon. Samples used for X-ray diffraction analysis were coated with a thin film of plastic spray to protect them from air; X-ray diffraction spectra used for structure analysis were obtained within hours of sample preparation. Lithium content of the various samples was determined by atomic-absorption spectroscopy.

X-ray diffraction spectra were obtained from an automated Rigaku diffractometer using $\text{CuK}\alpha$ radiation monochromated by a curved graphite crystal. Interplanar spacings were determined against an internal silicon standard. Structural refinement of $\text{Li}_x\text{Co}_3\text{O}_4$ samples was undertaken by a least-squares refinement of the peak intensities (7).

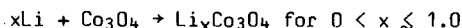
A two-electrode cell consisting of a lithium disc anode and a compacted powdered Co_3O_4 cathode was used for the electrochemical experiments. The electrolyte was a 1 M solution of LiBF_4 (Alfa Products) dissolved in propylene carbonate. A description of the cell design is given elsewhere (1). Cells were discharged galvanostatically at 20 $\mu\text{A}/\text{cm}^2$ at room temperature ($\sim 20^\circ\text{C}$) on a Princeton Applied Research

potentiostat/galvanostat. Discharge was interrupted periodically to obtain open-circuit voltage values: equilibration times of up to five days were allowed between readings.

3. RESULTS AND DISCUSSION

3.1 Electrochemical lithiation of Co_3O_4

The voltage vs composition curve for the slow electrochemical lithiation of Co_3O_4 is given in Fig. 1: both load voltages and open-circuit voltages are recorded. The curves are very similar to those obtained during lithiation of Fe_3O_4 (1). At 20 μA the cell discharges on a voltage plateau of ~ 1.0 V up to reaction with approximately 1.5 lithium ions. The open-circuit voltage initially decreases sharply, indicative of the single-phase reaction



For the range $1.0 \leq x < 1.4$ the gradual drop in voltage suggests that lithiation in excess of $x = 1$ is possible, consistent with the lithium analyses of chemically prepared samples. A multi-phase region exists for the range $1.4 < x < 2.0$.

Surprisingly, X-ray spectra of the reaction products for various values of x were characterized predominantly by Co_3O_4 peaks. For this reason all X-ray data of the reaction products for structure analysis were collected from

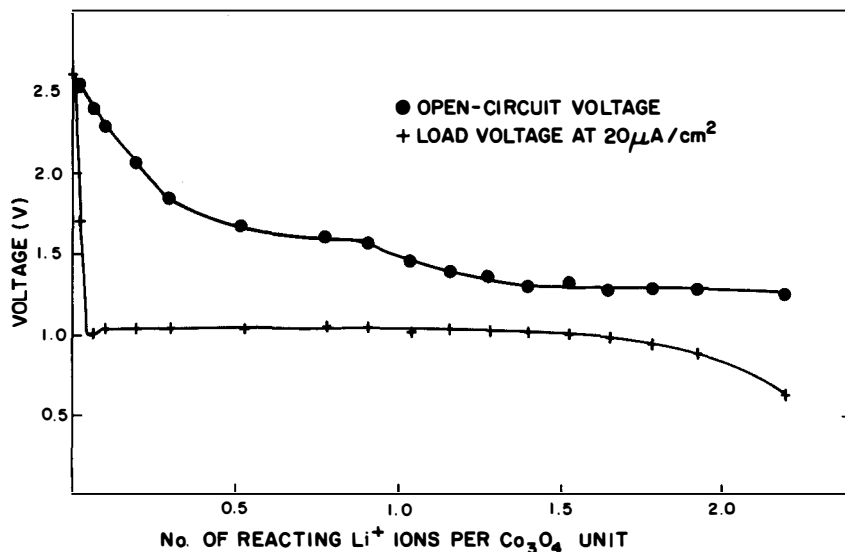


Fig. 1. Discharge curves for the electrochemical lithiation of Co_3O_4 .

Table 1
Reaction conditions used for preparing lithiated Co_3O_4 samples

Mass of Co_3O_4	Vol. n-butyllithium (ml)	Reaction temperature ($^{\circ}\text{C}$)	Reaction time (hr)	x in " $\text{Li}_x\text{Co}_3\text{O}_4$ "
0.2	1.3	20	168	0.20
0.5	3.0	40	110	1.97
0.5	1.5	50	48	0.60
0.5	3.0	50	24	0.59
0.5	3.0	50	48	1.07
0.5	3.1	50	111	2.20
0.5	4.5	50	115	1.97

samples prepared by direct chemical reaction of Co_3O_4 with n-butyllithium. A particular advantage of simulating the electrochemical reaction by chemical means is that the chemical lithiation reaction is relatively rapid.

3.2 Structural characterization of lithiated Co_3O_4

The extent of the reaction of Co_3O_4 with n-butyllithium was observed to be dependent on reaction temperature and time as reflected in Table 1. The rate of the reaction at 20°C was slow; it was considerably faster at 50°C . In this discussion the notation " $\text{Li}_x\text{Co}_3\text{O}_4$ " does not necessarily refer to a single-phase compound, but rather to the overall composition of the lithiated product.

The powder X-ray-diffraction profiles of Co_3O_4 and the lithiated products " $\text{Li}_{1.07}\text{Co}_3\text{O}_4$ " and " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ " are shown in Figs 2(a-c). Spectra of " $\text{Li}_{1.07}\text{Co}_3\text{O}_4$ " and " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ " were both characterized by two distinct phases, viz. lithiated particles and "unreacted" particles, the latter showing no significant changes in peak positions or intensities from the parent Co_3O_4 . As would be expected, the X-ray spectra of samples with high lithium content contained a lower concentration of "unreacted" Co_3O_4 particles. In addition, the spectra of the lithiated samples contained two unidentified impurity peaks. The substantial shift in the peak positions of the lithiated particles to lower 2θ values was indicative of an increase in the cubic "a" lattice parameter from $8.084 \text{ \AA}$ to $8.309 \text{ \AA}$, which is equivalent to an 8.6% volume expansion; the change in the relative intensities of the various peaks was indicative of the migration of the cobalt ions in the oxide lattice during lithiation. The large shift of the peaks to lower 2θ , even at small angles, made it possible to determine with reasonable accuracy the relative intensities of the peaks of the lithiated product. The

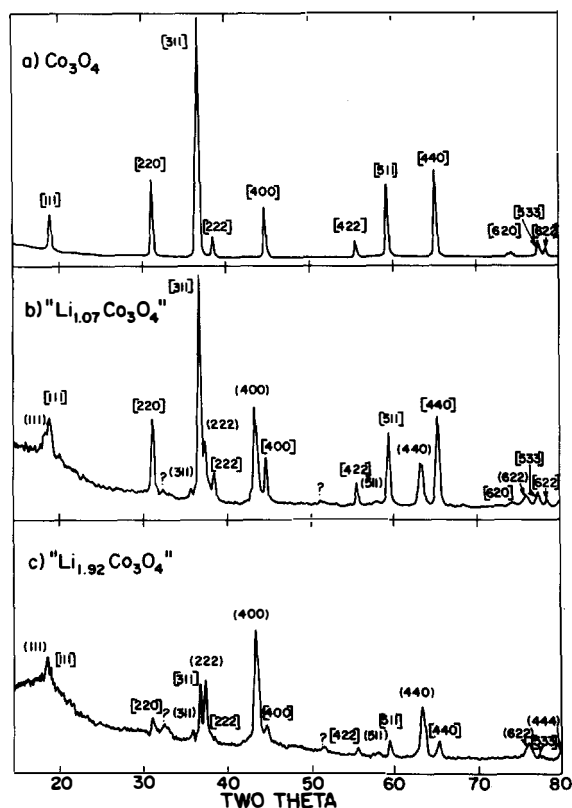


Fig. 2. X-ray powder diffraction profiles of a) Co_3O_4 , b) " $\text{Li}_{1.07}\text{Co}_3\text{O}_4$ " and c) " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ ". The Miller Indices of the reflections of the "unreacted" Co_3O_4 are given in square brackets and those of the lithiated product in curved brackets.

Table 2

X-ray diffraction data of Co_3O_4 , CoO and $\text{Li}_x\text{Co}_3\text{O}_4$ ($1 \leq x < 1.92$, from Fig. 1c) for $2\theta < 80^\circ$

	Co_3O_4 (8)	CoO (9)	$\text{Li}_x\text{Co}_3\text{O}_4$
"a"	8.084	8.520*	8.309
h k l			
1 1 1	20	-	17.3
2 2 0	40	-	-
3 1 1	100	-	8.5
2 2 2	12	75	43.0
4 0 0	25	100	100.0
3 3 1	-	-	2.3
4 2 2	12	-	-
3 3 3	-	-	-
5 1 1	35	-	5.2
4 4 0	45	50	45.2
5 3 1	-	-	1.2
6 0 0	-	-	-
4 4 2	-	-	-
6 2 0	6	-	-
5 3 3	12	-	-
6 2 2	8	20	18.8
4 4 4	4	16	14.8

*Although CoO (rocksalt) is normally assigned to space group $\text{Fm}\bar{3}\text{m}$ ($a = 4.26 \text{ \AA}$) the X-ray pattern has been indexed to a supercell with "a" = $2 \times 4.26 \text{ \AA}$ to allow direct comparison with Co_3O_4 and $\text{Li}_x\text{Co}_3\text{O}_4$ both of which have been indexed to the cubic spinel space group $\text{Fd}\bar{3}\text{m}$.

relative intensities of Co_3O_4 , those derived from the lithiated product in " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ " (Fig. 2c) and those of the rocksalt phase CoO have been listed in Table 2.

Comparison of the intensities of the various peaks of the lithiated product in " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ " with those of pure Co_3O_4 (spinel) and CoO (rocksalt) shows that the structure of lithiated Co_3O_4 is predominantly rocksalt-like, as was observed for " $\text{Li}_{1.5}\text{Fe}_3\text{O}_4$ " (1), indicative that the A-site tetrahedral cobalt ions are displaced during lithiation into a neighbouring empty 16c octahedron via a common triangular face.

A structure refinement of lithiated Co_3O_4 was undertaken with the intensities derived from the lithiated product in the spectrum of " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ ". This refinement was carried out with 14 intensities obtained from 15 reflections up to $2\theta = 135^\circ$. Because of the rocksalt-like nature of the X-ray-diffraction profile, an initial refinement was undertaken allowing the occupancy of the cobalt and lithium ions to

vary on the 16c and 16d octahedral sites of the spinel space group $\text{Fd}\bar{3}\text{m}$: the sum of the occupancy of the cations in the 16c and 16d sites was constrained to unity. During this refinement, the positional and isotropic thermal parameters of the oxygen ions were also varied. Final occupancies of the cobalt and lithium ions on the 16d sites, i.e. the B-sites of the spinel structure, refined to 1.00 (11) and 0.00 (11), respectively, whereas the occupancies of the cobalt and lithium ions on the 16c sites refined to 0.51 (6) and 0.49 (6) respectively. This refinement confirms earlier findings that lithium insertion into certain selected spinels at ambient temperature leaves the $[\text{B}_2]\text{X}_4$ framework of the spinel intact. Further refinement of the structure was therefore carried out constraining the occupancy of the cobalt ions in the 16d sites to 1.0, and of the cobalt and lithium ions in the 16c sites to 0.5 and 0.5 respectively. The R factor for this model was 5.60%, where

$$R = \frac{\sum |I_{\text{obs}} - I_{\text{calc}}|}{\sum I_{\text{obs}}}$$

Lithium in excess of $x = 1$ in $\text{Li}_x\text{Co}_3\text{O}_4$ necessarily requires occupation of tetrahedral sites. In $(\text{LiCo})_{16c}[\text{Co}_2]_{16d}\text{O}_2$, each 8b tetrahedron shares all four faces with cobalt-filled octahedra; with a random occupation of the 16c sites by Li and Co ions, each 48f tetrahedron shares faces with at least three cobalt-filled octahedra: each 8a tetrahedron has on average two cobalt- and two lithium-filled octahedra as neighbours; the 8a tetrahedra would therefore be most energetically favoured for further lithium occupation. A further refinement of the structure of the lithiated product was thus undertaken in which the Li occupancy of the 8a-tetrahedral sites was varied. This refinement yielded an occupancy of 0.47 (25) and an R-factor of 5.71. However, as lithium is such a light scatterer of X-rays, this finding will have to be confirmed conclusively by other techniques, for example neutron diffraction. Nevertheless, this result, like the electrochemical data and previous data for $\text{Li}_x\text{Fe}_3\text{O}_4$ (1), does suggest the possibility of introducing more than one lithium ion into the spinel lattice at ambient temperatures.

Atomic parameters for $\text{Li}_{1.47}\text{Co}_3\text{O}_4$ are given in Table 3a; observed and calculated intensities are listed in Table 3b.

The discrepancy between the lithium content of " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ " obtained chemically (1.92) and that of the lithiated phase in " $\text{Li}_{1.92}\text{Co}_3\text{O}_4$ " obtained from the structure analysis (1.47) can be attributed to an instability to oxidation of

Table 3a
Atomic parameters for Li_{1.47}Co₃O₄

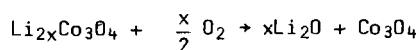
Space Group Fd3m (O_h^7) $a = 8.309$ (1) Å						
Atom	Position	x	y	z	B _{iso} (Å ²)	Occupancy
Li	8a	0.125	0.125	0.125	1.0	0.47 (25)
Li	16c	0.0	0.0	0.0	1.0	0.5
Co	16c	0.0	0.0	0.0	0.4 (4)	0.5
Co	16d	0.5	0.5	0.5	0.9 (3)	1.0
O	32e	0.254 (2)	0.254 (2)	0.254 (2)	3.4 (7)	1.0

Table 3b
Observed and calculated intensities for
Li_{1.47}Co₃O₄, R = 5.71

h k l	I _{obs}	I _{calc}	h k l	I _{obs}	I _{calc}
1 1 1	173	164	5 3 1	12	19
3 1 1	85	86	6 2 2	188	196
2 2 2	430	423	4 4 4	148	127
4 0 0	1 000	981	8 0 0	64	56
3 3 1	23	21	6 6 2	99	100
5 1 1	52	29	8 4 0	152	168
3 3 3			8 4 4	191	180
4 4 0	452	496			

the lithiated spinel particles.

In the presence of air, the room temperature mobility of Li⁺ ions and electrons in Li_xCo₃O₄ allows the reaction



in which the mobile species move out of the solid into O₂ adsorbed on the particle surface to form an Li₂O surface layer. X-ray-diffraction spectra of lithiated samples exposed to air often showed a predominance of "unreacted" Co₃O₄, and we assume that the amount of this unreacted Co₃O₄ would increase with time of exposure to the air.

Although the particles were coated with a plastic spray in order to protect them from the air, some surface reaction with the spray cannot be discounted: the unidentified X-ray peaks in Figs 2b and 2c are probably due to a lithium-containing compound. More significant is the fact that any particles having only a partial coating of the plastic would, on exposure to air, revert to Co₃O₄ and Li₂O. The "Li_{1.92}Co₃O₄" sample was prepared at 50°C, at which temperature lithium uptake is significantly more rapid than at 20°C (Table 1), which

is the temperature at which the X-ray spectra were obtained. Nevertheless, as Co²⁺ has a slight tetrahedral-site preference, migration of a 16c octahedral Co²⁺ ion back to an 8a tetrahedral site with simultaneous extrusion of lithium from the structure in the presence of an oxidant would account for the regeneration of "unreacted" Co₃O₄ observed in the X-ray spectra of Figs 2b and 2c. This instability explains the two-phase nature of the X-ray spectra in Figs 2b and 2c. It follows that there should then be a discrepancy between the lithium content of "Li_{1.92}Co₃O₄" obtained from chemical and structural analysis.

The X-ray spectrum of a sample that had been extensively lithiated with a large excess of n-butyllithium at 50°C for a week is shown in Fig. 3. Only a small concentration of "unreacted Co₃O₄" is evident. A noteworthy feature of this spectrum is that the even [hkl] peaks of the lithiated product, particularly the [400] peak, show distinct asymmetric broadening towards higher 2θ values, suggesting that cobalt is extruded from the 16d sites to yield a phase (LiCo)_{16c}[Li_yCo_{2-y}]_{16d}O₄ for 0 < y < 1, with a continuously contracting "a" lattice parameter. At y = 1, the product formed would be a novel rocksalt phase Li₂Co₂O₄(LiCoO₂) in which the Li⁺ and Co³⁺ ions are randomly distributed: LiCoO₂ is normally ordered as a layered structure. Moreover, the relative intensities of the [222], [400] and [440] Co₃O₄ spinel peaks are significantly altered towards a rocksalt distribution when compared to the 100% [311] peak (see Table 2), suggesting the overlap of the spinel Co₃O₄ peaks with the rocksalt end-member Li₂Co₂O₄. Peaks in the X-ray diffraction profiles of extensively lithiated samples heat-treated at 400°C in air corresponded to Co₃O₄ and the layered LiCoO₂ structure. No crystalline metallic cobalt was detected by X-ray analysis in any sample (whether heat-treated in air or not): it would be expected that the extruded cobalt metal would be in extremely finely divided form, pos-

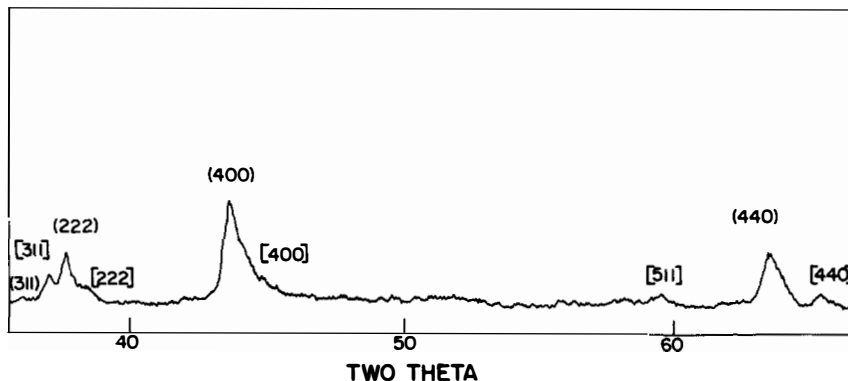


Fig. 3. The X-ray powder diffraction profile of an extensively lithiated Co_3O_4 sample. Square brackets denote the peaks of "unreacted" Co_3O_4 and curved brackets those of $\text{Li}_x\text{Co}_3\text{O}_4$ ($0 < x < 2$).

sibly adhered to the particle surface, and easily oxidized.

The apparent contraction of the cubic lattice in heavily lithiated samples as cobalt is extruded from the 16d sites of the $(\text{LiCo})_{16c}[\text{Co}_2]_{16d}\text{O}_4$ structure and replaced by lithium is consistent with Vegard's Law. Fig. 4 gives a plot of the variation of the "a" lattice parameter vs the concentration of cobalt in the octahedral sites for the rocksalt phases CoO , LiCo_3O_4 , and $\text{Li}_2\text{Co}_2\text{O}_4$ (predicted).

If the refined "a" lattice parameter of

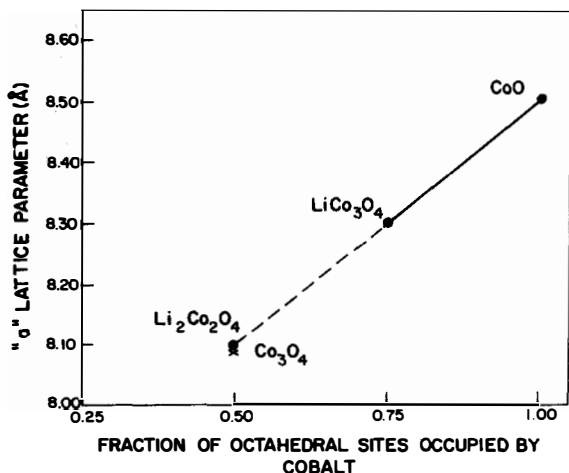
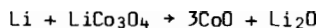


Fig. 4. A plot of the variation of the cubic "a" lattice parameter vs. the fraction of octahedral sites occupied by cobalt for the rocksalt phases CoO , LiCo_3O_4 , and $\text{Li}_2\text{Co}_2\text{O}_4$ (predicted) and the spinel phase Co_3O_4 .

8.309(1) Å obtained from the spectrum in Fig. 2b corresponds to LiCo_3O_4 , the extrapolated "a" value for a rocksalt phase of composition $\text{Li}_2\text{Co}_2\text{O}_4$ would be 8.10 Å, which is close to the "a" lattice parameter of Co_3O_4 (8.084 Å). Thus lithiation of Co_3O_4 initially induces an increase in the "a" lattice parameter as the cobalt concentration in the octahedral sites increases from 50 to 75%. Further lithiation ultimately extrudes cobalt from the oxide lattice with a resulting contraction of the "a" parameter. A displacement reaction of the type



would have shifted the peaks to lower 2θ values.

It was also noted that the dry lithiated Co_3O_4 particles interacted with the magnetic stirrer in the reaction vessel. This reaction manifests either extruded cobalt or a room-temperature ferrimagnetism of the lithiated particles. With a dominant Co-O-Co interaction, ferromagnetic (111) planes aligned antiferromagnetically to one another on progressing along the [111] axis would give rise to ferrimagnetism as a result of inequivalent Co concentrations on sites 16c and 16d. Alternate (111) planes contain one 16c to three 16d and one 16d to three 16c sites, respectively.

CONCLUSION

Lithium insertion into the spinel structure of Co_3O_4 has been demonstrated. At 50°C the tetrahedral site Co^{2+} ions are cooperatively displaced into neighbouring octahedral sites: the lithium ions in LiCo_3O_4 occupy the remaining octahedral sites to yield the rocksalt

phase $(\text{LiCo})_{16c}[\text{Co}_2]_{16d}\text{O}_4$ in which the B cations of the spinel structure are unperturbed. At 20°C, and in the presence of an oxidizing agent, $\text{Li}_x\text{Co}_3\text{O}_4$ is unstable and lithium ions are extruded from the lattice. Further lithiation of Co_3O_4 at 50°C appears to be possible with the Li^+ ions in excess of 1.0 residing in tetrahedral 8a sites. However, this fast reaction appears to be followed by a much slower extrusion of cobalt. Extensive lithiation of Co_3O_4 at 50°C results in extrusion of metallic cobalt from the lattice to generate a novel rocksalt phase LiCoO_2 with random occupation of lithium and cobalt ions on the octahedral sites.

ACKNOWLEDGEMENT

Mr H H Lachmann of the National Chemical Research Laboratory is thanked for performing the lithium analyses.

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