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# Low Temperature Synthesis, Chemical and Electrochemical Characterization of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ( $0 < x < 1$ ) Cathode Materials for Rechargeable Lithium Ion Batteries

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## Abstract

A new method of synthesis for the solid solution cathode materials  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  ( $0 < x < 1$ ) involving enhanced reactions at temperatures  $\leq 700^\circ\text{C}$ , between metal oxy-hydroxide precursors  $\text{MOOH}$  ( $\text{M} = \text{Ni}, \text{Co}$ ) and Li-salts ( $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ , and  $\text{LiNO}_3$ ) has been investigated. The effects of synthesis conditions and sources of Li, on phase purity, microstructure, and theoretical electrochemical capacity (total  $\text{M}^{3+}$  content) are characterized by powder X-ray diffraction analysis, scanning electron microscopy, chemical analysis and room temperature magnetic susceptibility. An attempt has been made to correlate the electrochemical properties with the synthesis conditions and microstructure.

## Introduction

The high voltage (4 V) metal oxide cathode materials  $\text{LiMO}_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ) and  $\text{Li}_{1+x}[\text{Mn}_2]\text{O}_4$  for lithium rechargeable batteries are very well investigated in literature<sup>1-4</sup>. Several other new high voltage cathode materials based on polyanion framework, spinel and olivine related structures have been reported recently<sup>5-7</sup>. However, only  $\text{LiCoO}_2$  has so far proven to be successful commercially, as cathode material for Li-ion batteries that deliver long cycle life.  $\text{LiMO}_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ) crystallize in (2D)  $\alpha\text{-NaFeO}_2$  layered structure<sup>8</sup> at temperatures  $> 400^\circ\text{C}$ , while the low temperature polymorphs have spinel-like (3D) structures. The ordering of Li and transition metal atoms in the structure depends on thermal history. The electrochemical properties such as voltage, capacity and cyclability are very sensitive to the structural disorder.  $\text{LiMn}_2\text{O}_4$  has a spinel (3D) structure and forms a range of defect spinel compositions that show variable stoichiometry,

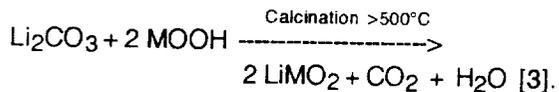
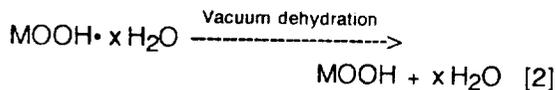
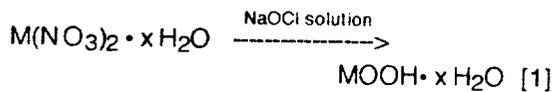
Mn oxidation state and total oxygen content in the phase diagram<sup>9</sup>  $\text{LiMn}_2\text{O}_4 - \text{Li}_2\text{Mn}_4\text{O}_9 - \text{Li}_4\text{Mn}_5\text{O}_{12}$ , making the processing very difficult<sup>10</sup>. In fact a 50% substitution of Mn atom in  $\text{LiMn}_2\text{O}_4$  by Cr results in  $\alpha\text{-NaFeO}_2$  type layered structure in a narrow temperature range of synthesis<sup>11</sup>. Although  $\text{LiNiO}_2$  has marginally higher capacity compared to  $\text{LiCoO}_2$ , the difficulty in processing of  $\text{LiNiO}_2$  stems from the fact that  $\text{Ni}^{3+}$  requires higher oxygen partial pressure. In addition, the increased tetrahedral site stability of nickel intermediates favor the occupation of Li-sites by nickel in  $\alpha\text{-NaFeO}_2$  structure, thereby reducing the capacity and the  $\text{Li}^+$ -ion mobility in  $\text{LiNiO}_2$ <sup>12</sup>. Also,  $\text{LiNiO}_2$  suffers from increased safety concerns due to relatively unstable charged state at higher operating temperatures.

The solid solutions  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  ( $0 < x < 1$ ) achieve a compromise between the complimentary properties of the end members  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$ . These solid solutions have strong potential to replace the commercialized  $\text{LiCoO}_2$  because of their relatively low cost, low volume change<sup>13, 14</sup> during charge/ discharge, as well as higher capacity. The composition with  $x = 0.5$ , has the advantage of slightly lower, sloping voltage plateau compared to other compositions, which is better from electrolyte stability and overcharge protection<sup>15</sup>. However optimizing the synthesis conditions for such solid solutions by commonly used ceramic techniques, that uses  $\text{Ni(II)O}$  or  $\text{Ni(II)-salts}$  as the nickel source is very difficult because of the low reactivity of the  $\text{Ni(II)O}$  and the unstable  $\text{Ni}^{3+}$  that requires higher oxygen pressure at elevated temperatures. A prolonged solid state reaction at high temperatures not only reduces  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$ , but also leads to substantial Li loss resulting in phase

separations of LiCoO<sub>2</sub> and LiNiO<sub>2</sub> and impurity phases such as Li<sub>1-y</sub>Ni<sub>y</sub>O, Co<sub>3</sub>O<sub>4</sub>, etc... We report here the details of a low temperature method<sup>16</sup> that makes use of very reactive metal oxy-hydroxide precursors MOOH (M= Co, Ni), where in the metal atoms are already in trivalent state. Further, the metal atoms in the precursor are mixed homogeneously at the molecular level, helping to reduce the diffusion barriers for the solid state reaction to occur.

### Experimental

The metal oxy-hydroxides precursors MOOH where M is a combination of Co and Ni, were prepared by reacting appropriate amounts of metal nitrates with alkaline NaOCl solution, following the procedure described by Nakagawa et al<sup>17</sup>. The metal oxy-hydroxides were dehydrated in vacuum and further calcined with Li-salts (Li<sub>2</sub>CO<sub>3</sub>, LiOH, and LiNO<sub>3</sub>) at elevated temperatures to get the final compositions LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> (0 ≤ x ≤ 1). The reactions occurring at various stages are represented as follows:



Solid solution compositions (referred to as "samples A", here afterwards) LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> for x = 0.15, 0.40, 0.60, and 0.80 were prepared by direct solid-state reactions in air, starting from stoichiometric amounts of Ni<sub>x</sub>Co<sub>1-x</sub>OOH and Li<sub>2</sub>CO<sub>3</sub> at 500, 700, 900 and 1100°C, with annealing durations of 6, 10 and 14 hours. The samples were cooled to room temperature in about 30 minutes.

Compositions (referred to as "samples B", here afterwards) LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> for x = 0.3 were prepared from calcination of oxy-hydroxide precursor Ni<sub>0.3</sub>Co<sub>0.7</sub>OOH, in air at 700°C with three different sources of lithium, Li<sub>2</sub>CO<sub>3</sub>, LiOH, and LiNO<sub>3</sub>, employing quenching or slow cooling conditions. Quenching from 700°C to room temperature was done in 5 minutes, while slow cooling to room temperature was done in about 61 hours.

The cobalt and nickel contents were analyzed by atomic absorption spectroscopy and Li content was determined by flame photometry. All samples were characterized for total M<sup>3+</sup> content ( M<sup>3+</sup> = Co<sup>3+</sup> + Ni<sup>3+</sup> ) by iodometric titration. X-ray powder diffraction (XRD) and SEM were used for structural and microstructural characterization.

### Results and Discussion

X-ray phase analysis was used to determine the optimum temperature range for ("samples A") solid solutions LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> for x = 0.15, 0.40, 0.60, and 0.80, prepared by direct solid-state reaction in air, from Ni<sub>x</sub>Co<sub>1-x</sub>OOH and Li<sub>2</sub>CO<sub>3</sub>. A reaction temperature of <500°C in air was too low and for the 'x' values mentioned, XRD showed broad peaks due to unidentified phases and Li<sub>2</sub>CO<sub>3</sub>. Reactions at temperature 1100°C resulted in range of impurity phases (Co<sub>3</sub>O<sub>4</sub>, Li<sub>1-y</sub>Ni<sub>y</sub>O) and phase separation of blue colored sample indicating Co<sup>2+</sup> diffusion into the alumina / silicate matrix of the container. Also the chemical analysis showed huge loss of Li (Li contents were as low as 50-60% of the theoretical value, and total transition metal contents were >105% of the theoretical value) at 1100°C. The temperature range between 700-900°C showed much better results in terms of phase purity and chemical analysis. Small amounts (~2-3%) of Li<sub>1-y</sub>Ni<sub>y</sub>O was the only impurity present in the temperature range 700-900°C. The amount of Li present in the samples were close to theoretical values (98-102%) for samples prepared at 700°C, while Li content was reduced to 95-98%, for samples prepared at 900°C.

Figures 1-4 give the variations of unit cell parameters a, c, c/a and I<sub>d(003)</sub>/I<sub>d(104)</sub> intensity ratios with amount of Ni present in the compositions, respectively for the "samples A". The solid line is drawn in figures 1 and 2, joining the squares that represent the unit cell constants of the end members with the high temperature layered α-NaFeO<sub>2</sub> structure<sup>8</sup>. The unit cell parameters show relatively larger deviations from this solid line for all the "samples A", that are prepared at ≥900°C. "Samples A", that are prepared ≤700°C show lesser deviations from the the solid line. These variations from the high temperature polymorph could be attributed to the slight deviation from the nominal compositions, relatively broad [hkl] lines due to short thermal annealing, and possible disorder of Li/ M atoms

in the structures, specially in case of low temperature preparations. It is to be noted that low temperature polymorphs (that have structure more like cubic spinels) of  $\text{LiCoO}_2$  show a lower  $c$  and higher  $a$  values, as compared to the high temperature polymorphs<sup>8,18</sup>.

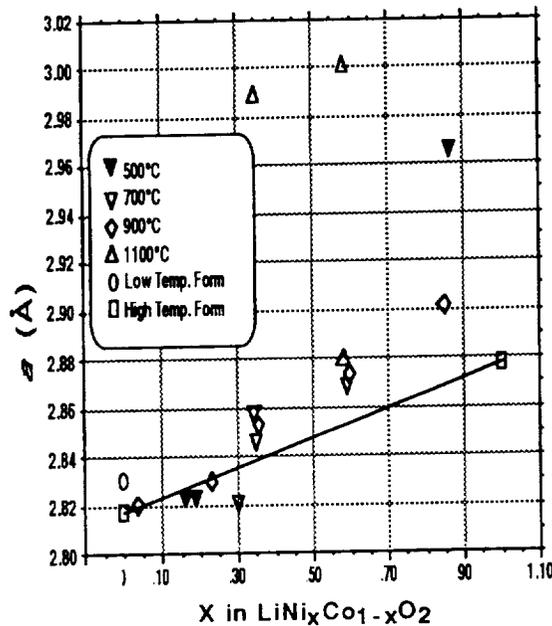


Figure 1. Variation of cell parameter  $a$  with  $x$  for  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  compositions.

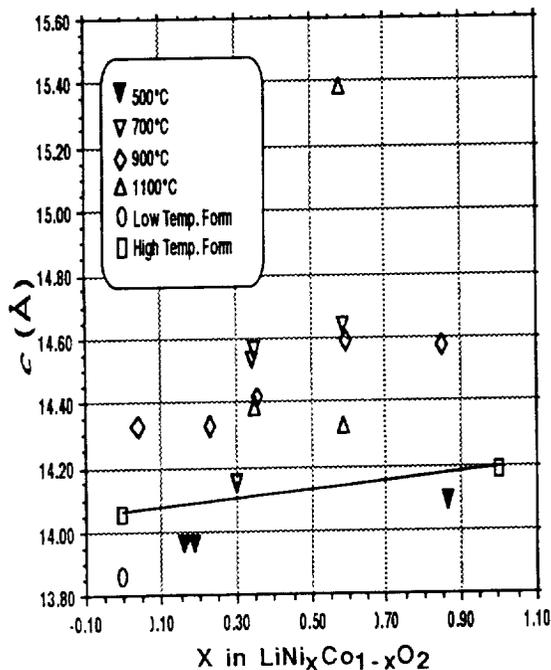


Figure 2. Variation of cell parameter  $c$  with  $x$  for  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  compositions.

We have compared the  $c/a$  ratios in Fig. 3, for all the "samples A" with the literature values reported for high temperature polymorphs<sup>18</sup>. From the plot it is clear that the higher Ni fraction (with  $x \geq 0.6$ ) and higher temperature preparations (1100°C) show larger deviations for the same reasons mentioned above. The  $c/a$  ratios for these samples do not follow a definite trend since the structure can vary considerably with temperature of preparation. In fact low temperature polymorphs can have  $\text{Co}^{3+}$  ( $t_2^6$ ) in low spin state and these are smaller than the  $\text{Ni}^{3+}$  ( $t_2^6 e^1$ ) ion. The  $c/a$  ratio are close to a value of 4.90 for temperatures  $\leq 500^\circ\text{C}$  which is in agreement with the ideal cubic close packed lattice.

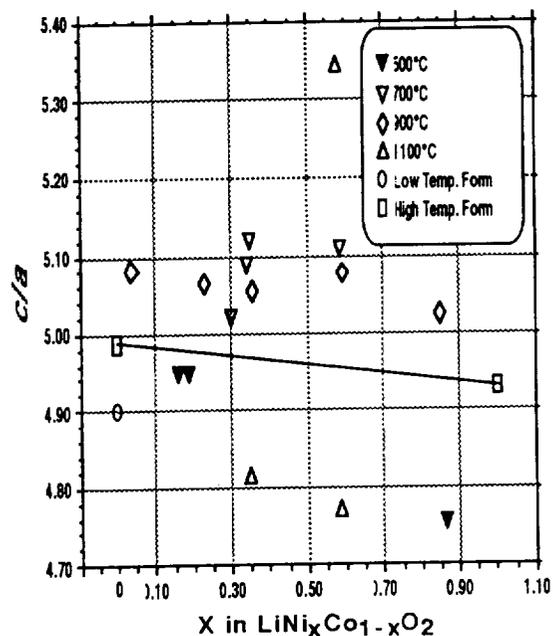


Figure 3. Variation of  $c/a$  with  $x$  for  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  compositions.

The intensity ratios of [003] and [104] reflection lines give an indication regarding the structural arrangement of heavy transition metal atom in the structure. This hypothesis is based on the fact that cobalt and nickel are significantly heavier and therefore considerably stronger scatterer of X-rays. Of the "samples A" in Fig. 4, only the ones prepared at 500°C show larger decrease of intensity ratios with Ni fraction, while the intermediate temperature regions show a smaller trend indicating that the structural disorder is more for low temperature preparations.

From the above results, it is clear that the 700°C in air, is the optimum temperature of preparation for the high temperature polymorph of the solid solutions that are richer

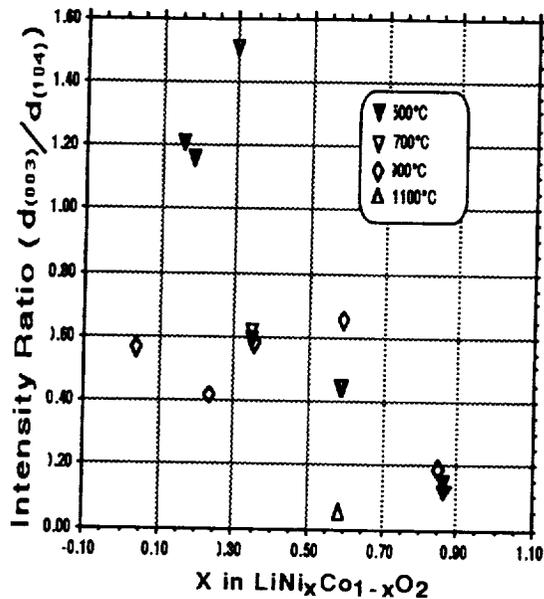


Figure 4. Variation of  $I_{d(003)} / I_{d(104)}$  with  $x$  and temperature for  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ .

in cobalt from precursor method. To determine the effect of Li source on the synthetic conditions, we prepared a set of "samples B" with composition  $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$  starting from carbonate, nitrate and hydroxide salts of Li. Calcining was done at  $700^\circ\text{C}$  for 6 hours, with variations in annealing and quenching conditions.

The "samples B" that are prepared from LiOH showed phase separations to  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ , while the ones from nitrate and carbonate sources were single phase. The XRD lines were more sharp for the samples made from  $\text{LiNO}_3$  with the (006), (102) and (108), (110) lines well separated indicating better crystallization. Figure 5 shows the variations of  $c/a$  and the  $I_{d(003)} / I_{d(104)}$  for six samples of  $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$ . The  $c/a$  ratio is close to the one expected for high temperature polymorph for sample prepared from  $\text{LiNO}_3$  source, while the sample prepared from carbonate source showed slight deviation. Theoretical capacities (total  $\text{M}^{3+}$  content) estimated from iodometric titration are given in Figure 6, and the samples prepared from  $\text{LiNO}_3$  source showed higher theoretical capacities. The lower capacities in all these cases are probably due to the small amounts of impurity phases ( $\sim 2\%$ ) present  $\text{Li}_y\text{Ni}_{1-y}\text{O}$ . The room temperature susceptibility values indicate the presence of more  $\text{Ni}^{2+}$  in samples from carbonate and hydroxide sources of Li, indicating that the partial oxygen pressure to

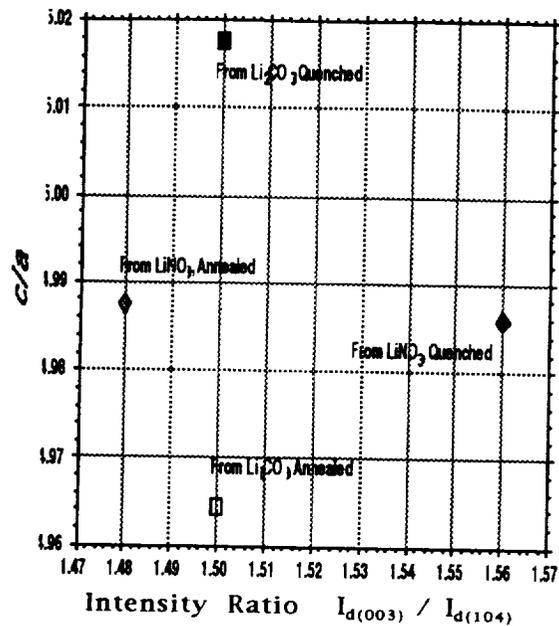


Figure 5. Effect of Li source on  $c/a$  and  $I_{d(003)} / I_{d(104)}$  for  $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$

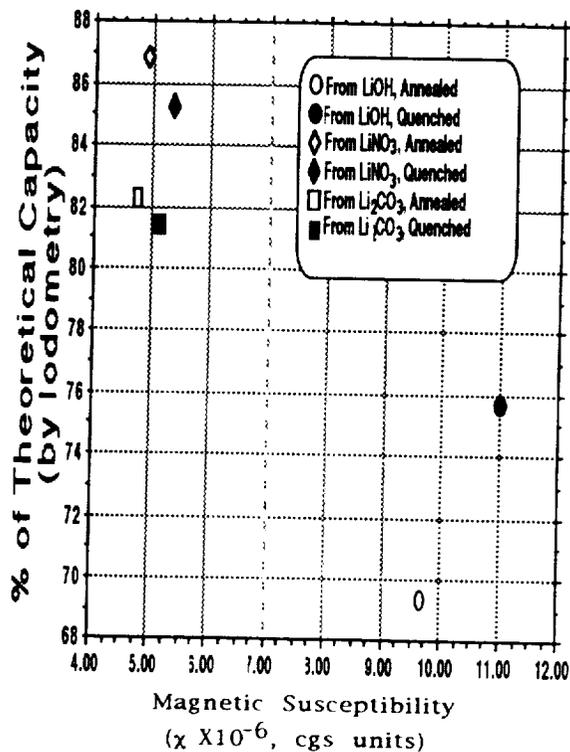


Figure 6. Effect of Li source on theoretical capacity and magnetic susceptibility for  $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$

keep all the nickel in  $\text{Ni}^{3+}$  state is not high enough.

The scanning electron micrographs were taken for "samples B" that are prepared from the carbonate and nitrate salts of lithium. The particle sizes showed a mean distribution around 1  $\mu\text{m}$ .

Soft chemistry methods employ low temperatures and involve decomposition reactions that evolve gases, resulting in fine particles. If, controlled properly they could give uniform particle size distributions for the end product. Fine particles of the cathode materials are important for rate capability, and homogeneous distribution of particle size contributes to better density. On the other hand, larger cathode particles reduce the interface contact with electrolyte solution, resulting in increased cycle life for the battery. There are different approaches to increase the particle sizes such as prolonged annealing, flux induced crystallization and anion substitution. The precursor method reported here could be tuned to get the desired microstructure for the cathode material and such an effort is underway. Also, measurements of cell characteristics for cathode samples  $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$  made from  $\text{LiNO}_3$  source is under progress, against carbon.

### Conclusions

We have shown that the oxy-hydroxide precursor MOOH that has the transition metals (M = Co, Ni) homogeneously mixed at the molecular level, in  $\text{M}^{3+}$  state could be effectively used for fine particles synthesis of solid solution  $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$  ( $0 \leq x \leq 1$ ) in air. The method is cheap, fast and better compared to the conventional ceramic route that is constrained by solid state diffusion barrier. Further, a temperature of 700°C, 6-14 hours of annealing time, in ambient oxygen pressure and  $\text{LiNO}_3$  as lithium source, are better for cobalt-rich compositions, while nickel-rich compositions need a higher partial pressure of oxygen. The method could be conveniently modified to get desirable microstructural changes and suitable anion substitution for fine tuning the electrochemical properties. We also have shown that iodometric titration and XRD phase analysis could be effectively used to pre-characterize the electrochemical properties.

### Acknowledgments

The contributions from Ms. T.M. Nguyen and Ms. Ruth K Long of Pacific University and Dr. Mike Shaw and Mr. Mark Dudley of the

Specialty Materials Division of Eagle-Picher, Miami, OK are gratefully acknowledged.

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