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Short communication

Synthesis and characterization of LiNi_{0.8}Co_{0.2}O₂ prepared by a combustion solution method for lithium batteries

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Abstract

In the present study, an attempt is made to synthesis $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds by adopting a novel solution combustion route, because this compound is a promising candidate to replace commercial LiCoO_2 in secondary lithium batteries. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is synthesized at 750 °C for 3, 12 and 24 h in an air atmosphere. Its structural and electrochemical properties are characterized by means of X-ray diffraction (XRD), cyclic voltammetry, and charge–discharge studies. The charge–discharge behaviours suggests that the initial discharge capacities are different for different charging cut-off voltages. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ shows high specific discharge capacity and good cycle-life performance.

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1. Introduction

Lithium cobalt oxide has been widely used as a cathode (positive electrode) material for commercial secondary lithium-ion batteries due to its advantages of easy preparation, high voltage, good reversibility, and high theoretical specific capacity. Lithiated cobalt oxide has a layered structure in which the Li^+ and Co^{3+} ions occupy alternating layers of octahedral sites in a rock salt structure [1-3]. The typical reversible limit of de-lithiation for Li_xCoO₂ in commercial lithium batteries is x = 0.5, which corresponds to a charge capacity of 140 mAh g⁻¹. Unfortunately, layered lithium cobalt oxide often suffers from structural instability and safety problems, especially when the lithium content is lower than 0.5 or the charge voltage exceeds 4.3 V [4]. LiNiO₂ has been intensively studied and is considered a promising cathode material for rechargeable lithium batteries due to its low cost and high specific energy. On the other hand, it is difficult to synthesize with consistent quality due to its tendency for non-stoichiometry. Further it has a poor cycling performance, which is attributed to its structural instability upon cycling, as well as and it has greater safety problems.

In order to tackle the problems associated with the high cost and system instability of LiCoO₂, a method for the preparation of a version of the compound which has improved electrochemical characteristics and cationic substitutions on the cobalt sites has been sought extensively. Of these substituted compounds, $LiNi_{x}Co_{1-x}O_{2}$ has been identified as one of the most attractive materials. The layered $\text{LiNi}_x \text{Co}_{1-x} \text{O}_2$ (0 < x < 1) compounds have been studied extensively as cathode materials for lithium batteries [5-8]. Several research groups have investigated the synthesis of $LiNi_xCo_{1-x}O_2$ solid solutions. Julien et al. [9] prepared LiNi_{0.3}Co_{0.7}O₂ using a mixture of citric acid and glycine. Nakai and Nakagome [10] used a precipitation method to produce LiNi_{0.5}Co_{0.5}O₂, Julien et al. [11] employed a series of carboxylic acids as chelating agents to obtain LiNi_{0.5}Co_{0.5}O₂, and synthesized LiNi_{0.6}Co_{0.4}O₂ with citric acid as the complexing agent [12]. Delmas et al. [13] studied the electrochemical behaviours of LiNi_{1-v}Co_vO₂ (0.2 < v < 0.4). There is a minimal change in the unit cell volume during intercalation-de-intercalation. This implies that y = 0.2 and 0.3 phases give good cycling properties and that an ordered two-dimensional structure of

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the material enhances the ease of lithium diffusion in the inter-slab spaces. Cho and Park [14] obtained a spherulitic $Ni_{0.74}Co_{0.26}(OH)_2$ by a co-precipitation method, and reacted it with LiOH·H₂O at 750 °C to produce well-defined spherical particles of LiNi_{0.74}Co_{0.26}O₂. Chang and Kumta [15] developed a spray-drying technique to yield fine particulate LiNi_{0.75}Co_{0.25}O₂ from methanolic solutions. Cho et al. [16] also reported that LiNi_{0.7}Co_{0.3}O₂ exhibits a high current capability as a cathode. Fey et al. [17] reported the sol–gel synthesis of LiNi_{0.8}Co_{0.2}O₂ using maleic acid as a chelating agent and a solution route with malonic acid as the complexing agent [18].

These materials are considered as strong potential candidates to replace commercially available LiCoO_2 because of the attractive advantages of lower cost and higher reversible capacity than LiCoO_2 , ease of preparation, and better cycling capability than LiNiO_2 . In this paper, an attempt to synthesize $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ compounds by adopting a novel glycine combustion solution method has been made with a view to evaluate their physical and electrochemical properties for lithium-ion batteries.

2. Experimental

A 0.5 M solution of lithium nitrate, cobalt nitrate and nickel nitrate (1:1:1 wt.%) with 30 g of glycine was prepared in water and was heated at 90–100 °C for 1 h to obtain a viscous solution. The resulting solution was dried at 120 °C for 12 h and then heated further at 300, 600 and 750 °C for 3 h. Initially, the sample was prepared at 750 °C and was examined by X-ray diffraction (XRD) and electrochemical techniques. Based on these results, a more precise study was undertaken of the effect of heating time for sample preparation at 750 °C for 12 and 24 h. The phase purity of the products was verified using a Philips X-ray diffractometer. Patterns were recorded using nickel-filtered Cu K α radiation at room temperature in the 2 θ range 10–80 °C at a scan rate of 0.02° s⁻¹.

Charge-discharge studies were conducted with 2016 coin cells. Lithium metal was used as the anode and 1 M LiPF₆ in ethylene carbonate:diethyl carbonate (EC:DEC; 50:50 vol.%) electrolyte. The cathode was prepared by mixing 89 wt.% active material with 4 wt.% super-P carbon and 7 wt.% poly(vinylidene fluoride) (PVdF) binder in N-methyl-2-pyrrolidone (NMP), which was coated on an aluminium foil and dried at 120 °C for 4 h in an oven. The resulting LiNi_{0.8}Co_{0.2}O₂ was roll-pressed and the electrode was punched out with a punching machine. Cells were assembled and cycled at the 0.1 °C rate between 3.0 and 4.2, 4.3 and 4.4 V by means of a multi-channel battery life-cycle tester (Maccor 4000). Cyclic voltammetric studies were performed with using lithium metal foil counter and reference electrodes. Cyclic voltammograms were run on an IM6 electrochemical instrument at a scan rate of 0.1 mV s^{-1} between 2.8 and 4.6 V.



Fig. 1. X-ray diffraction patterns for LiNi $_{0.8}Co_{0.2}O_2$ prepared at (a) 300 °C (3 h), (b) 600 °C (3 h), (c) 750 °C (3 h), (d) 750 °C (12 h) and (e) 750 °C (24 h).

3. Results and discussion

X-ray diffraction patterns for powders heated at 300, 600 and 750 °C for 3, 12 and 24 h, respectively, are shown in Fig. 1. The patterns, show that powders are iso-structural with α -NaFeO₂, space group R3m, in which the O²⁻ ions form a closely-packed, face-centred-cubic structure, in which the Ni³⁺ and Co³⁺ ions occupy the crystallographically equivalent of 3b sites and Li⁺ ion occupy the 3a sites. It can be seen from Fig. 1 that some additional peaks are obtained between the 2θ values of 20° and 40° for the sample heated at 300 °C. These can be attributed to the presence of LiNO₃, Li₂CO₃ and NiO [19,20]. The XRD pattern for the sample heated at 600 °C shows all the peaks, which indicates that the crystallization process has set in at this temperature. For the sample heated at 750 °C for 3 h, the XRD pattern is well-defined and displays the hexagonal doublets (006)/(102) and (108)/(110) with a clear splitting, which indicates that samples have a high degree of crystallinity, good hexagonal ordering, and greater layered characteristics [18]. Based on the above results, it can be concluded that the minimum temperature required for complete hexagonal ordering is 750 °C. After the optimum heating temperature was identified as 750 °C, the influence of the time of heating for 12 and 24 h was studied. As the heating time was increased, the diffraction peaks became sharper and higher, due to an increase in the crystallinity of the product.

All the X-ray patterns have sharp peaks, which indicates a high degree of crystallinity, and are identical (Fig. 1 (c–e)). The variation of lattice parameters, i.e. *a*, *c*, *c/a*, *R*-factor, $I_{(003)}/I_{(104)}$ and the unit-cell volume of the LiNi_{0.8}Co_{0.2}O₂ sample with respect to heating time are summarized in Table 1. With increase in heating time, there is no significant change in the parameter values of *a*, *c*, *c/a*. A relatively large increase in the $I_{(003)}/I_{(104)}$ ratio is observed for the

Table 1 Lattice parameters of the LiNi_{0.8}Co_{0.2}O₂ powders

Temperature (°C)	Heating time (h)	a (Å)	c (Å)	c/a Ratio	$I_{(003)}/I_{(104)}$	<i>R</i> -factor $[(I_{(006)} + I_{(102)})/I_{(101)}]$	Unit cell volume (Å)
600	3	2.864	14.171	4.95	0.24	_	100.62
750	3	2.866	14.222	4.96	1.26	0.71	101.12
750	12	2.854	14.192	4.97	1.30	0.54	100.06
750	24	2.862	14.210	4.97	1.43	0.62	100.75

sample heated at 750 °C for 24 h. When the heating time is increased from 12 to 24 h, the intensity ratio $I_{(003)}/I_{(104)}$ increases from 1.30 to 1.43 and the intensities of the (003) reflections are higher than those for the corresponding (104) reflections, which indicates that these samples have good cation ordering [21,22]. According to Reimers et al. [23], the *R*-factor, defined as the ratio of the intensities of the hexagonal characteristic doublet peaks (006) and (102) to the (101) peak, is an indicator of hexagonal ordering. The lower the R-factor, the better is the hexagonal ordering. It was not possible to calculate the intensities of the sample heated at $600 \,^{\circ}$ C. It can be seen, however, that as the heating time is increased at constant temperature, i.e. 750 °C for 3, 12 and 24 h, the *R*-factor decreases. The low *R*-factor for the sample heated at $750 \,^{\circ}$ C for 12 h indicates good hexagonal ordering and hence promises better cycling performance. Furthermore, the unit-cell volume for the LiNi_{0.8}Co_{0.2}O₂ sample heated at 750 °C for 12 h is smaller (0.54) than the sample heated at 750 °C for 3 or 24 h (0.71 and 0.62). Dahn et al. [24] reported that material with more layered characteristics would have a lower cell volume. This would confirm that the LiNi_{0.8}Co_{0.2}O₂ sample heated at 750 °C for 12h has a more layered structure. Hence, it has a lower cell volume other than two samples. Therefore, the lithium intercalation-de-intercalation properties depend mainly on the ordering of the 3a lithium occupancy sites and the 3b transition metal ion sites.

The thermogravimetric analysis (TGA) curve for the dried precursors is shown in Fig. 2. It is evident that water and related impurities are expelled in the temperature range from room temperature to $110 \,^{\circ}$ C with 16% weight loss. The sec-



Fig. 2. TGA curve for LiNi_{0.8}Co_{0.2}O₂ precursor.

ond step of 4% weight loss, which occurs between 110 and 300 °C, is attributed to the presence of LiNO₃, Li₂CO₃ and NiO. Around 600 °C, the active reaction takes place and the precursors start to form the compound. The formation of the compound is completed at around 750°C with an unavoidable further heat loss of 1-2%. A total of approximately 38% weight loss becomes inevitable in the process of synthesizing the final product of the combustion process. This type of thermal behaviour has been observed by Kalaiselvi et al. [25] with respect to all the precursors employed in the present synthesis of LiNi_{0.8}Co_{0.2}O₂. Thus, it may be concluded from the observed TGA pattern that the formation temperature of the LiNi_{0.8}Co_{0.2}O₂ compound is as low as 600 °C and that a good degree of cyrstallinity demands a temperature as high as 750 °C for the final product. The effect of heating time in enhancing the degree of crystallinity is further substantiated from XRD patterns.

The electrochemical properties of LiNi_{0.8}Co_{0.2}O₂ synthesized at 600 and 750 °C for 3 h were examined. The charge–discharge behaviour of the materials was evaluated galvanostatically at the 0.1 °C rate between 3.0 and 4.2 V for up to 20 cycles, as shown in Fig. 3. The cycling performance of material heated at 600 °C for 3 h shows lower specific capacity. The discharge capacity on the 1st and 20th cycles, as summarised in Table 2, was 55.6 and 46.9 mAh g⁻¹, respectively. The main reason for this low capacity is a lack of hexagonal ordering, i.e. a lack of ordering in lithium-ion and transition metal ion sites and lower crystallinity. When



Fig. 3. Discharge curves obtained galvanostatically at 0.1 $^\circ C$ rate between 3.0 and 4.2 V for LiNi $_{0.8}Co_{0.2}O_2$ heated at 600 and 750 $^\circ C.$

Table 2 Charge–discharge properties obtained for samples heated at 600 and 750 $^{\circ}\mathrm{C}$ for 3 h

Temperature (°C)	1st cycle			20th cycle			
	Charge capacity $(mAh g^{-1})$	Discharge capacity $(mAh g^{-1})$	Irreversible capacity $(mAh g^{-1})$	Charge capacity $(mAh g^{-1})$	Discharge capacity $(mAh g^{-1})$	Irreversible capacity $(mAh g^{-1})$	
600	58.0	55.6	2.4	47.4	46.9	0.5	
750	142.5	134.9	7.6	127.6	126.1	1.5	

the temperature for sample preparation is increased from 600 to 750 °C, the discharge capacity on the 1st and 20th cycles was 134.9 and 126.1 mAh g⁻¹, respectively, with a charge retention of 98.8% on the 20th cycle. These results are in agreement with those of Ohzuku et al. [26], although they used $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ which showed a discharge capacity 130 mAh g⁻¹ in the lower working voltage range of 2.5 to 4.2 V.

The effect of charging cut-off voltage was studied at 4.2, 4.3 and 4.4 V with respect to heating times of 3, 12 and 24 h at 750 °C. The variation in the specific discharge capacity with respect to cut-off voltage for LiNi_{0.8}Co_{0.2}O₂ is shown in Fig. 4 (a)–(c). The electrochemical properties for a sample for LiNi_{0.8}Co_{0.2}O₂ prepared at 750 °C for 3, 12 and 24 h with different charging-discharging cut-off voltages are given in Table 3. The data show that a loss of irreversibility occurs on the first discharge. Lee et al. [27] have undertaken a Rietveld refinement analysis of neutron diffraction data for LiNi_{0.8}Co_{0.2}O₂. The analysis revealed that extra nickel ions occupy in the lithium 3a sites and are the main cause for the capacity loss on the first cycle. The divalent extra nickel ions in the inter Ni_{0.8}Co_{0.2}O₂ slab space are oxidized to the trivalent state at the beginning of the first charge. This lead to a local shrinkage of inter-slab space because of the different ionic radii of the divalent nickel and trivalent nickel ions. Since the oxidized trivalent extra nickel ions cannot be readily reduced to the divalent state during the next discharge, lithium re-intercalation within the collapsed space becomes difficult. Therefore, the lithium sites around the extra nickel ions remain vacant and thereby, cause the initial capacity loss. In addition, once a certain irreversible capacity is obtained on the first cycle, further intercalation-deintercalation of lithium ions occurs only at the lithium sites excluding the vacant sites around the extra nickel ions. Therefore, a good reversibility is maintained after the first cycling. Peres et al. [28] were the first to propose that extra nickel ions are the main cause for the initial capacity fading.

The specific discharge capacity of the sample prepared at 750 °C for 12 h on the 20th cycles was 144.1, 154.2 and 164.9 mAh g⁻¹ respect to the charge–discharge cut-off voltage of 4.2, 4.3 and 4.4 V, respectively. The decrease of the specific discharge capacity of the samples, that were prepared at 750 °C for 3 and 24 h with respect to the charge–discharge cut-off voltage is attributed mainly to the loss of lithium during the extended heating time. Gover et al. [29] reported that 3a site ordering with respect to Li is time-dependent; a sample prepared with a heating time of



Fig. 4. Specific discharge capacity with cut-off voltage for $LiNi_{0.8}Co_{0.2}O_2$ heated at 750 °C for (a) 3 h, (b) 12 h, (c) 24 h.

Table 3							
Electrochemical properties of LiNi _{0.8} CO _{0.2} O ₂	heated at 75	50°C for 3,	$12 \mbox{ and } 24 \mbox{ h} \mbox{ at}$	different	charge-discharge	cut-off	voltages

Heating Cut-off time (h) voltage (V)	1st cycle			20th cycle			
	Charge capacity $(mAh g^{-1})$	Discharge capacity $(mAh g^{-1})$	Irreversible capacity $(mAh g^{-1})$	Charge capacity $(mAh g^{-1})$	Discharge capacity (mAh g ⁻¹)	Irreversible capacity $(mAh g^{-1})$	
4.2	142.5	134.9	7.6	127.6	126.1	1.5	
4.3	143.8	135.4	8.4	128.1	127.0	1.1	
4.4	150.4	135.8	14.6	134.2	132.3	1.9	
4.2	168.0	154.3	13.7	145	144.1	0.9	
4.3	174.3	160.6	13.7	155.3	154.2	1.1	
4.4	185.5	172.8	12.7	166.5	164.7	1.8	
4.2	162.8	144.9	17.9	140.6	138.0	2.6	
4.3	167.7	151.1	16.6	144.4	142.4	2.0	
4.4	184.3	170.6	13.7	161.4	147.8	13.6	
	Cut-off voltage (V) 4.2 4.3 4.4 4.2 4.3 4.4 4.2 4.3 4.4 4.2 4.3 4.4	$\begin{array}{c} \text{Cut-off} & 1 \text{st cycle} \\ \hline \text{Voltage} \\ (V) & \hline \text{Charge capacity} \\ \hline \text{(mAh g^{-1})} \\ \hline 4.2 & 142.5 \\ 4.3 & 143.8 \\ 4.4 & 150.4 \\ \hline 4.2 & 168.0 \\ 4.3 & 174.3 \\ \hline 4.4 & 185.5 \\ \hline 4.2 & 162.8 \\ \hline 4.3 & 167.7 \\ \hline 4.4 & 184.3 \\ \hline \end{array}$	$\begin{array}{c} \mbox{Cut-off} & 1 \mbox{style} \\ \mbox{(v)} & \hline \mbox{Charge capacity} \\ \mbox{(mAh g^{-1})} & \hline \mbox{Discharge capacity} \\ \mbox{(mAh g^{-1})} & \mbox{(mAh g^{-1})} \\ \mbox{4.2} & 142.5 & 134.9 \\ \mbox{4.3} & 143.8 & 135.4 \\ \mbox{4.4} & 150.4 & 135.8 \\ \mbox{4.2} & 168.0 & 154.3 \\ \mbox{4.3} & 174.3 & 160.6 \\ \mbox{4.4} & 185.5 & 172.8 \\ \mbox{4.2} & 162.8 & 144.9 \\ \mbox{4.3} & 167.7 & 151.1 \\ \mbox{4.4} & 184.3 & 170.6 \\ \end{array}$		$ \begin{array}{c} \mbox{Cut-off}\\ \mbox{voltage}\\ (V) & \hline \mbox{Charge capacity}\\ (W) & \hline \mbox{Charge capacity}\\ \mbox{(mAh g^{-1})} & \hline \mbox{Discharge capacity}\\ \mbox{(mAh g^{-1})} & \hline \mbox{(mAh g^{-1})} & \hline \mbox{(mAh g^{-1})} & \hline \mbox{Charge capacity}\\ \mbox{(mAh g^{-1})} & \hline \mbox{(mAh g^{-1})}$	$ \begin{array}{c} \mbox{Cut-off} \\ \mbox{voltage} \\ (V) \\ \hline \mbox{(mAh g^{-1})} \\ \mbox{(mAh g^{-1})} \\ \hline \mbox{Discharge capacity} \\ \mbox{(mAh g^{-1})} \\ \hline \m$	

3 h had an amount of disorder. As the time was increased, the Li site order increased with the greatest effect being shown by the sample prepared with a heating time of 12 h. When the heating time was increased to 24 h, the Li occupancy decreased. This suggests that Li loss via the volatilization of Li_2O might have occurred. This suggests that a minimum heating time is required to order fully the Li 3a sites.

The electrochemical performance was studied using cyclic voltammetry in a potential range from 2.8 to 4.6 V versus Li/Li^+ with Li metal as the reference and counter electrodes. The scan rate was 0.1 mV s^{-1} . The cyclic voltammogram for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (synthesized at 750 °C for 12 h), in 1 M LiPF_6 in EC:DMC (50:50 vol.%) is given in Fig. 5. An anodic peak for de-intercalation of Li^+ is observed at 4.3 V in a broad potential range and an amount of lithium is extracted on the negative-going scan over a broad potential range at about 3.3 V. The behaviour on the first cycle differs from that on the second and subsequent cycles. This is due to the large irreversible loss of capacity on the first cycle [30].

The large de-intercalation currents in the cyclic voltammogram agree with the first cycling capacities [31]. From the second cycle onwards, the curves overlap excellently.



Fig. 5. Cyclic voltammogram of $LiNi_{0.8}Co_{0.2}O_2$ synthesized at 750 °C for 12 h.

This indicates the quantitative reversibility of the electrode reactions. Lee et al. [27] investigated and analysed the phase transition during cycling using cyclic voltammetry. For LiNiO₂, three sharp peaks were observed at potentials



Fig. 6. Variation of specific capacity with charge-discharge cycling for Li|LiNi_{0.8}Co_{0.2}O₂ cell heated at 750 °C for 3 and 12 h.

of 3.66, 4.03 and 4.20 V versus Li/Li⁺ on the positive-going scan. The peaks were identified as hexagonal to monoclinic, monoclinic to hexagonal, and hexagonal to hexagonal phase transitions, respectively. Similarly, on the negative-going scan, three peaks were observed at 3.62, 3.98 and 4.13 V, respectively, which correspond to the inverse phase transitions. The sharp peaks were gradually diminished by cobalt substitution in LiNiO₂ and were not observe for LiNi_{0.8}Co_{0.2}O₂ compounds. These reports are in agreement with the cyclic voltammetric. Observation reported here. A broad maximum at 3.9-4.3 V in the oxidation region and a broad minimum at 3.2-3.6 V in the reduction region is observed for LiNi_{0.8}Co_{0.2}O₂ synthesized at 750 °C for 12 h. This indicates that a single-phase reaction may occur for a lithium nickelate with 20% cobalt substitution. The phase transitions that occur during the charge-discharge studies of LiNi_{0.8}Co_{0.2}O₂ were confirmed by XRD.

The variation of the charge and discharge specific capacity on cycling a Li|Li Ni_{0.8}Co_{0.2}O₂ cell for the samples heated at 750 °C for 3 and 12 h is shown in Fig. 6(a) and (b), respectively. The corresponding reversible capacity after 30 cycles was 120.4 and 149.7 mAh g⁻¹ with capacity losses 11.1 and 6.8%.

4. Conclusions

LiNi_{0.8}Co_{0.2}O₂ can be synthesized using a combustion method with glycine as the fuel agent at various temperatures. All the samples heated at 750 °C for 3, 12 and 24 h have a two-dimensional layered structure, as confirmed by X-ray diffraction. The optimum synthesis temperature and heating time are 750 °C and 12 h, respectively. Electrochemical performance studies indicate that charging–discharging at different voltage ranges such as 4.2, 4.3 and 4.4 V result in a significant capacity loss only at the first discharge. With further cycling, good reversibility is maintained.

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