

LiNi_{0.8}Co_{0.2}O₂ cathode materials synthesized by the maleic acid assisted sol–gel method for lithium batteries

G.T.K. Fey^{*}, R.F. Shiu, V. Subramanian, J.G. Chen, C.L. Chen

Department of Chemical Engineering, National Central University, Chung-Li 32054, Taiwan, ROC

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Abstract

A maleic acid assisted sol–gel method was employed to synthesize LiNi_{0.8}Co_{0.2}O₂ cathode materials, which are of interest for potential use in lithium batteries. Various synthesis conditions such as solvent, calcination time, calcination temperature, acid-to-metal ion ratio (*R*), and lithium stoichiometry were studied to determine the ideal conditions for preparing LiNi_{0.8}Co_{0.2}O₂ with the best electrochemical characteristics. The optimal synthesis conditions were found to be an ethanol solvent with a calcination time of 12 h at 800°C under flowing oxygen. The first discharge capacity of the material synthesized using the above conditions was 190 mAh/g, and the discharge capacity after 10 cycles was 183 mAh/g, at a 0.1 C rate between 3.0 and 4.2 V. Details of how varying initial synthesis conditions affected capacity and cycling performance of LiNi_{0.8}Co_{0.2}O₂ are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: LiNi_{0.8}Co_{0.2}O₂; Sol–gel; Layered; Maleic acid; Cathode materials; Lithium batteries

1. Introduction

Increasing demand for reliable high energy density power sources has greatly intensified the research and development of lithium batteries. The performance characteristics of a lithium battery are very dependent on the insertion–deinsertion properties of the positive electrode material of the battery. The common electrode material of present day commercial lithium batteries is LiCoO₂ [1], but environmental constraints have created pressures to replace toxic lithium cobaltate with either spinel LiMn₂O₄ or layered LiNiO₂. The former suffers from capacity fading with cycling when operated in the 3 V region, because the average Mn valency becomes lower than 3.5, leading to a Jahn–Teller distortion of cubic to tetragonal transition [2]. The latter has irreversible phase transitions associated with topotactic reactions, leading to high irreversible capacity [3]. Also, it is very difficult to synthesize a phase pure compound without any cation mixing [4]. Safety concerns limit LiNiO₂ being used commercially [5]. Solid solutions involving both LiCoO₂ and LiNiO₂, layered cathode materials of the general formula LiNi_{1–y}Co_yO₂ (0 < y < 1) have been scrutinized for possible commercial applications [6]. These solid solutions enjoy the advantages of both the end

members with better cyclability and safety aspects. In the entire solid solution range, y = 0.2–0.3 has the most promising electrochemical characteristics [7].

The synthesis route adopted to prepare battery active materials has a direct impact on their electrochemical performance as an insertion electrode. The LiNi_{1–y}Co_yO₂ solid solutions were initially synthesized by the conventional solid-state method, which involves very high temperatures for a prolonged period of time with intermediate grinding [8], but this led to problems with poor stoichiometry control, larger particle size, and non-homogeneity. In recent years, low temperature wet chemistry methods of synthesizing cathode active materials have gained importance because they do not have the above problems and produce sub micrometer particles with homogeneous distribution and high surface area, which deliver better cell performance. Many cathode materials have been synthesized using the low temperature methods for lithium battery applications and were recently reviewed [9]. In the case of LiNi_{1–y}Co_yO₂ solid solutions, several low temperature methods like sol–gel and combustion methods have been reported [10]. Recently, Chiang et al. reported the synthesis of Mg doped LiNi_{0.75}Co_{0.25}O₂ by a particulate sol–gel method [11]. Julien et al. recently synthesized LiNi_{0.5}Co_{0.5}O₄ using different carboxylic acids at low temperature [12].

In this paper, we report the sol–gel synthesis of LiNi_{0.8}Co_{0.2}O₂ using maleic acid as a chelating agent under different initial conditions in order to optimize the synthesis

^{*} Corresponding author. Tel.: +886-3-422-7151-4206/886-3-425-7325; fax: +886-3-425-7325.
E-mail address: gfey@cc.ncu.edu.tw (G.T.K. Fey).

conditions for the best electrochemical properties. The effect of varying each initial condition has been correlated to electrochemical performance.

2. Experimental

Layered $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders were prepared according to the procedure shown in Fig. 1. A stoichiometric amount of lithium, nickel and cobalt nitrate salts (Merck, Germany) in a cationic ratio $\text{Li}:\text{Ni}:\text{Co} = 1:0.8:0.2$ was dissolved in ethanol and mixed well with maleic acid (Aldrich, USA) dissolved in ethanol. The acid-to-metal ion ratio ' R ' was varied at 1, 2 and 3. The mixture was then stirred for 24 h at room temperature. The pH was measured and it varied from -0.09 for $R = 3$ to 0.13 for $R = 1$. Heating the mixture at 80°C for 2 h under constant stirring resulted in the formation of 'sol'. The sol was heated

at 120°C while being mechanically stirred with a magnetic stirrer. As the ethanol evaporated, the sol turned into a gel and was subsequently dried. The dried mass was collected and subjected to further heat treatment at various times (6–24 h) and temperatures (600 – 800°C). The above procedure was repeated to prepare $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ by varying initial conditions such as other solvents, R values and lithium-rich phases.

Thermal decomposition behavior of the gel precursor was examined by thermogravimetric analysis (TGA) in air using a Seiko, SSC 5500 TGA/DTA analyzer at a heating rate of $10^\circ\text{C}/\text{min}$. The typical weight of the sample was around 10 mg. The powder X-ray diffraction technique (Siemens, D-5000 MAC Science MXP18) was employed to identify the phase purity of the material synthesized under different initial conditions. The electrochemical performance of the materials was studied by assembling 2032 coin cells. The cathodes for electrochemical studies were fabricated by

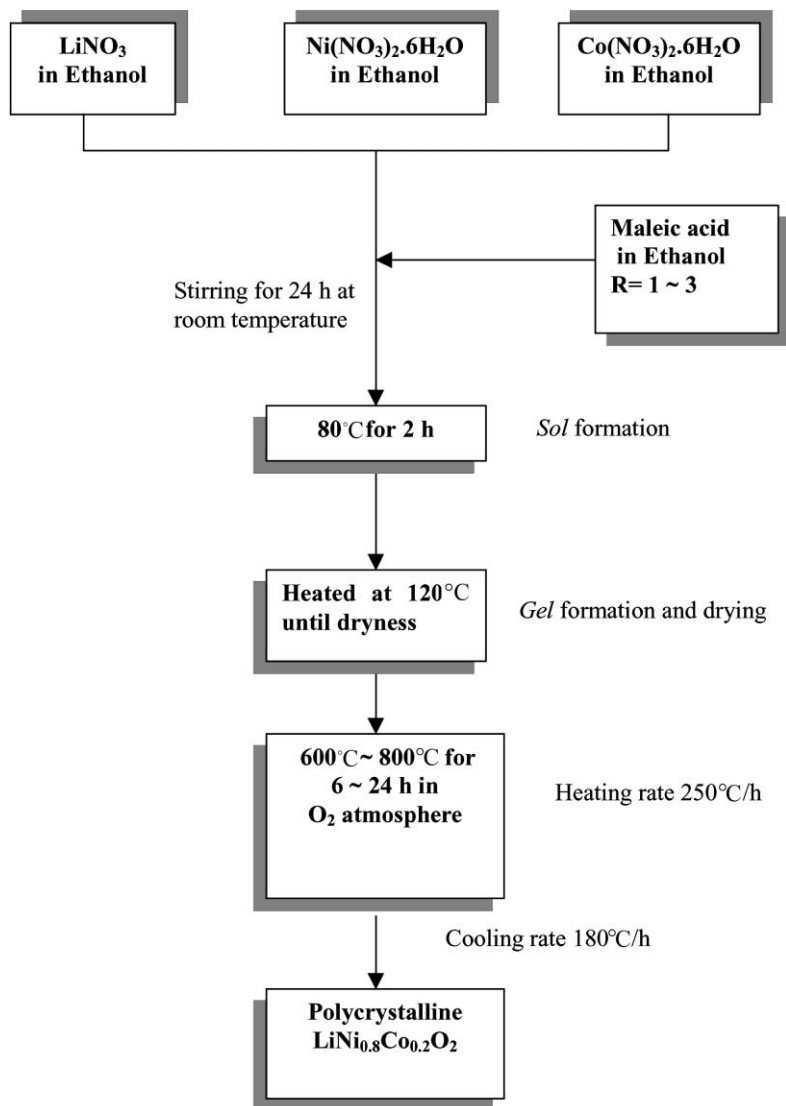


Fig. 1. Flow chart for the sol-gel synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ using maleic acid as a chelating agent.

coating aluminium foils with a slurry mixture of synthesized powder, carbon black and PVdF binder (85:10:5) using NMP as a solvent. The coated aluminum foil was allowed to dry overnight at 120°C in an oven. The cathodes were punched as circular discs from the foil after being roller pressed to better adhere the material to the current collector. The cells were assembled using lithium metal (FMC) as an anode and a 1 M LiPF₆ in 50:50 v/v EC–DEC (Tomiya Chemicals) as an electrolyte in an argon-filled glove box. The intercalation–deintercalation properties were studied by cycling the cells at a 0.1 C rate between 3.0 and 4.2 V in a constant current mode using a multi-channel battery tester (Maccor, Series 4000).

3. Results and discussion

3.1. Thermal studies

The TGA and differential thermogram (DTG) curves recorded for the dried precursors with different acid-to-metal ion ratios ‘*R*’ or *R*-values are shown in Fig. 2. There was an observed step-like pattern of weight loss in the thermogravimetric curves for all the precursors studied.

The overall profile of the TGA curve remains the same for all three precursors with different *R*-values. The increase in the acid-to-metal ion ratio has a direct impact on the pH of the solution. The pH of the solution plays an important role in the formation of the chelation complex, which prevents the segregation of the transition metal ions. The pH of the solutions were measured to be 0.13, –0.01 and –0.09 for the system with *R* = 1, 2 and 3, respectively.

In the case of the precursor with an acid-to-metal ion ratio of 1, there were three steps of weight loss. The first step occurred between room temperature and 200°C with a 12% weight loss attributable to the removal of absorbed water. The second major step of weight loss which occurred between 200 and 500°C is attributed to the burning of organic moieties and nitrate components present in the precursor. This was evidenced as a sharp peak in the DTG curve. The final step of weight change is attributed to the initiation of the crystallization reaction. Although, the reaction was complete before 600°C, the complete ordering of the hexagonal lattice occurred only after firing the precursor at higher temperatures.

Increasing the acid-to-metal ion ratio ‘*R*’ influenced the rate of the reaction, well-evident by the increase in the area of the DTG peak corresponding to the major weight loss

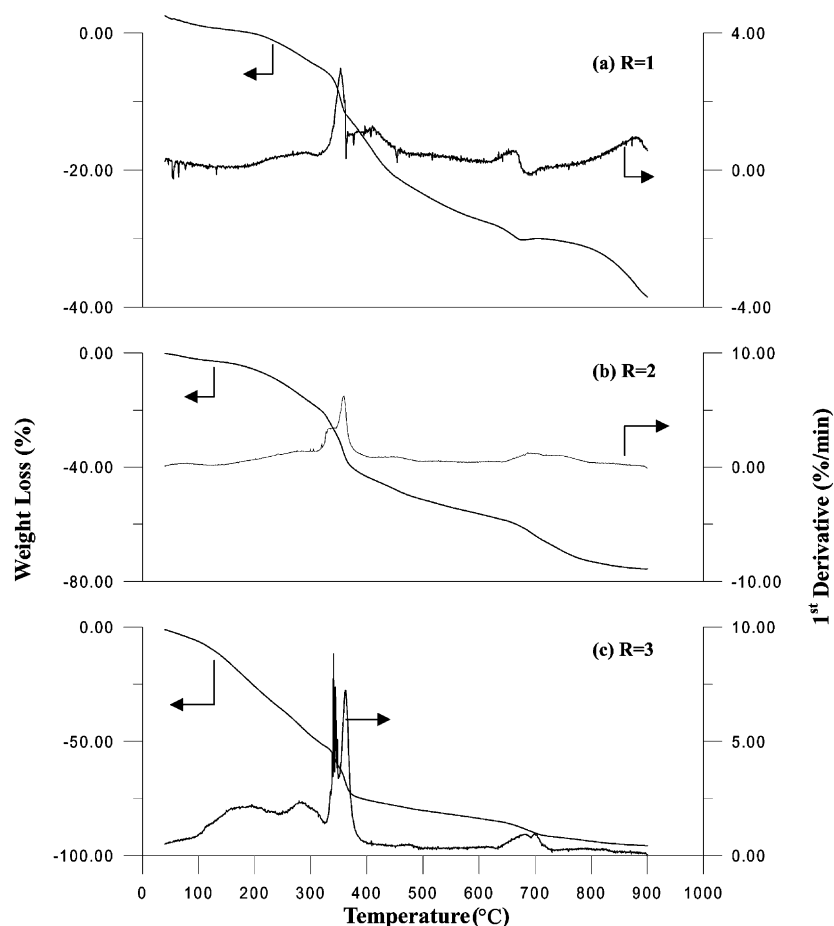


Fig. 2. TGA/DTG curves of the maleic acid–LiNi_{0.8}Co_{0.2}O₂ gel precursors: (a) *R* = 1; (b) *R* = 2; (c) *R* = 3.

occurring between 200 and 500°C. The precursor with $R = 3$ showed a faster completion of the reaction and had a more drastic weight loss. The reason for the faster completion may have been increased local heat because of the presence of more acid content. When carboxylic acids are used as a chelating or complexing agent for the reaction, they have a self-igniting property which provides local heat for the reaction. Although the crystallization reaction started around 500°C, the material attained complete crystallinity only after calcination at 800°C for 12 h, as evident by the X-ray diffraction studies.

3.2. Structural studies

3.2.1. Effect of calcination temperature and time

The X-ray diffractograms recorded for the materials calcined at 600, 700 and 800°C for 12 h are shown in

Fig. 3. For the material calcined at 600°C, it can be clearly seen from Fig. 3(a) that the peaks are broad, indicating low crystallinity of the material. Also, the hexagonal lattice ordering is incomplete at this temperature as further confirmed by the intensity ratio of the 003 and 104 peaks. The lattice parameters calculated are summarized in Table 1. The R -factor, which was defined by Reimers et al. [13] as $[I_{006} + I_{102}]/I_{101}$, should be at a minimum in a system with good hexagonal ordering. Hence, it is clear that the calcination temperature of 600°C was not sufficient to impart the hexagonal ordering required for better electrochemical performance.

As the calcination temperature was increased to 700°C, there was a remarkable improvement in crystallinity of the material as indicated by the sharper peak profile shown in Fig. 3(b). The I_{003}/I_{004} ratio increased to 1.39 and the R -factor attained a value of 0.56.

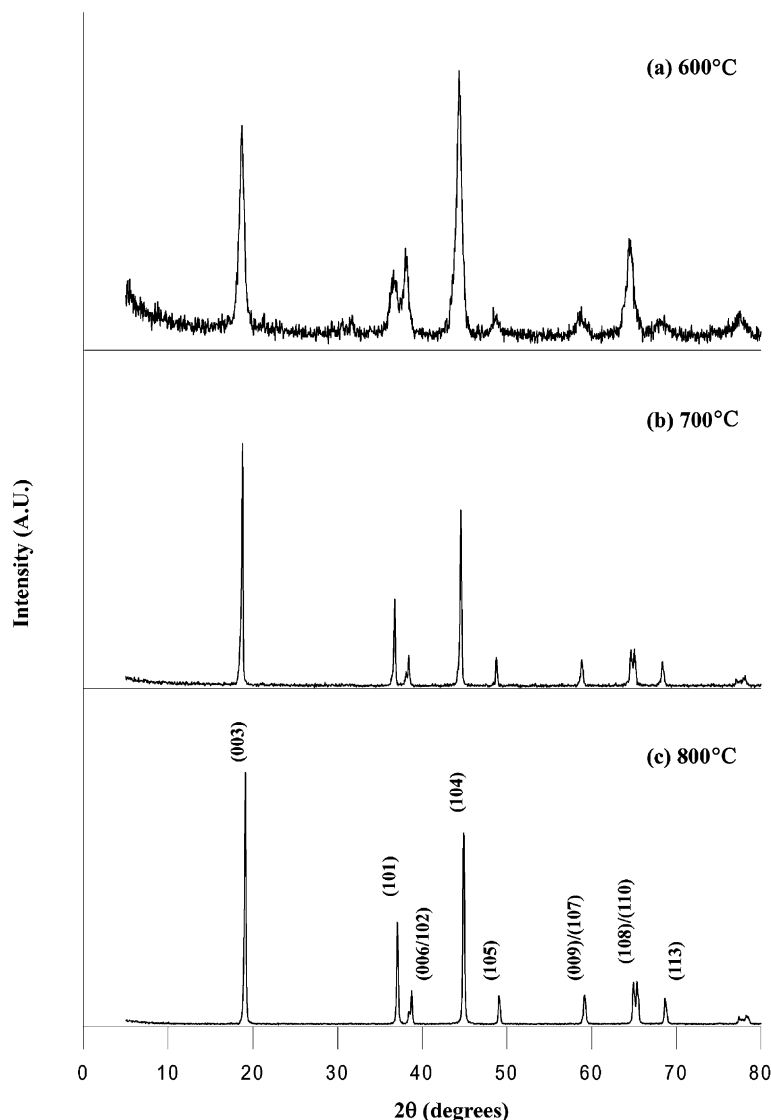


Fig. 3. X-ray diffractograms of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized at different temperatures: (a) 600°C; (b) 700°C; (c) 800°C.

Table 1

Lattice parameters, unit cell volume, structural parameters and discharge capacities for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized at different temperatures for 12 h^a

Temperature (°C)	a (Å)	c (Å)	c/a ratio	R -factor = $(I_{006} + I_{102})/I_{101}$	I_{003}/I_{104}	Unit cell volume (Å ³)	Discharge capacity (mAh/g) ^b	
							Cycle 1	Cycle 10
600	2.8908	14.2280	4.92	1.18	0.80	102.96	142	137
700	2.8652	14.1753	4.94	0.56	1.39	100.77	167	155
800	2.8528	13.9278	4.88	0.47	1.30	98.16	190	183

^a Data for materials synthesized with an acid-to-metal ion ratio, $R = 1$.^b Data at a 0.1 C rate, cycled between 3.0 and 4.2 V.

After further increasing the calcination temperature to 800°C, the R -factor attained a value of 0.47, the lowest in the present study which indicated maximum hexagonal ordering. According to Dahn et al. [14], the hexagonal unit cell volume indicates the ordering of a layered structure. If it is low, the structure is more layered. For the system heated at 800°C for 12 h, the unit volume was 98.16 Å³, whereas it was 102.96 and 100.77 Å³, for the systems heated at 600 and 700°C, respectively. Based on the above results, it can be concluded that the minimum temperature required for complete hexagonal ordering is 800°C.

After the optimum calcination temperature was identified as 800°C, the effect of varying calcination time from 12 to 6 and 24 h was studied. All the X-ray diffractograms show sharp peaks, indicating a high degree of crystallinity and are identical to Fig. 3(c). Although the material calcined at 800°C for 6 h showed peaks indexable in the hexagonal lattice, the R -factor calculated according to Reimers et al. [13] was found to be higher with a value of 0.49. Further increasing the calcination time to 12 h decreases the R -factor to 0.47. The decrease in the R -factor indicates the increased ordering of the hexagonal lattice. According to Reimers et al. [13], the lower the R -factor, the greater the hexagonal ordering, and hence, the better the electrochemical properties of the system. When the calcination time was increased to 24 h, the R -factor increased to 0.49, indicating a decrease in hexagonal ordering. From the above study, it is clear that the optimal calcination time for the present system was 12 h.

Any further increase in calcination time led to a decrease in hexagonal ordering. This finding is also well supported by the I_{003}/I_{104} ratio. When the calcination time was increased from 6 to 12 h, the intensity ratio increased from 1.22 to 1.30. Further increasing the calcination time did not increase the I_{003}/I_{104} ratio. The lithium intercalation–

deintercalation properties mainly depend on the ordering of the $3b$ lithium occupancy sites and the $3a$ transition metal ion sites. Especially for LiNiO_2 and the nickel rich phases of the $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ solid solutions, calcination time and temperature are extremely critical in having completely ordered stoichiometric phases. The lattice parameters and structural parameters calculated are summarized in Table 2.

3.2.2. Effect of variation of acid-to-metal ion ratio ‘ R ’

The mole ratio between the chelating agent, maleic acid, and total metal ions is defined as ‘ R ’ or R -value and has a very profound effect on the structure of the final compound formed. Similar to Fig. 3(c), the X-ray diffractograms recorded for materials synthesized at different R -values show that they are highly crystalline. The R -factor ($(I_{006} + I_{102})/I_{101}$) calculated for the compounds synthesized with three different acid-to-metal ion ratios ‘ R ’ was the lowest value for the material synthesized with $R = 1$.

Varying ‘ R ’ has a direct impact on the pH of the mixture, which becomes more acidic as the R -value increases above 1. Also, during heat treatment, greater amounts of acid increases local temperature because of its self-igniting property, leading to a sudden increase in temperature in a short period of time and a reduction in oxygen partial pressure. For all the nickel rich phases of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ solid solutions, the heating in oxygen plays an important role in the structural purity of the system [15]. The I_{003}/I_{104} peak ratio showed a decrease with an increase in R -value as listed in Table 3. Materials with a higher I_{003}/I_{104} ratio are generally expected to show better electrochemical characteristics [15]. Therefore, it can be concluded that for the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, using maleic acid as a chelating agent, the ideal acid-to-metal ion ratio is 1. All the above results are well supported by the electrochemical studies.

Table 2

Lattice parameters, unit cell volume, structural parameters and discharge capacities for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized for different periods of time at 800°C^a

Time (h)	a (Å)	c (Å)	c/a ratio	R -factor = $(I_{006} + I_{102})/I_{101}$	I_{003}/I_{104}	Unit cell volume (Å ³)	Discharge capacity (mAh/g) ^b	
							Cycle 1	Cycle 10
6	2.8577	14.0055	4.90	0.49	1.22	99.04	185	178
12	2.8528	13.9278	4.88	0.47	1.30	98.16	190	183
24	2.8508	13.8518	4.85	0.49	1.30	97.49	161	155

^a Data for materials synthesized with an acid-to-metal ion ratio, $R = 1$.^b Data at a 0.1 C rate, cycled between 3.0 and 4.2 V.

Table 3

Lattice parameters, unit cell volume, structural parameters and discharge capacities for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized at different R -values at $800^\circ\text{C}/12\text{ h}$

R -value	a (Å)	c (Å)	c/a ratio	R -factor = ($I_{0\ 0\ 6} + I_{1\ 0\ 2}$)/ $I_{1\ 0\ 1}$	$I_{0\ 0\ 3}/I_{1\ 0\ 4}$	Unit cell volume (Å ³)	Discharge capacity (mAh/g) ^a	
							Cycle 1	Cycle 10
1	2.8528	13.9278	4.88	0.47	1.30	98.16	190	183
2	2.8481	13.8644	4.86	0.48	1.24	97.39	177	173
3	2.8620	14.1064	4.92	0.49	1.08	100.06	179	168

^a Data at a 0.1 C rate, cycled between 3.0 and 4.2 V.

3.2.3. Effect of variation of lithium stoichiometry 'x'

Similar to Fig. 3(c), the X-ray diffractograms recorded for materials synthesized with different lithium stoichiometries show that they are highly crystalline. However, an increase in x from the ideal stoichiometry 1 results in a corresponding increase in unit cell volumes. Also, the $I_{0\ 0\ 3}/I_{1\ 0\ 4}$ peak intensity ratio decreases with the increase in x value. The increases in unit cell volume and the decreases in the $I_{0\ 0\ 3}/I_{1\ 0\ 4}$ peak intensity ratio indicate that increasing x in $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ from 1 leads to a deviation from hexagonal ordering, which obviously has adverse effects on capacity and cyclability of the material. Hence, the ideal lithium stoichiometry for maleic acid assisted $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ is 1 and any deviation from that results in a system with a lower hexagonal order. The lattice parameters and other structural data for the compounds with various lithium stoichiometry 'x' in $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ are summarized in Table 4.

3.2.4. Effect of various solvents used for synthesis

Different solvents such as ethanol, 1-propanol, 1-butanol and water were used to prepare the precursor for the maleic acid assisted sol-gel synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The X-ray

diffractograms of materials prepared using different solvents at 800°C for 12 h showed identical profiles. However, the R -factor calculated from the XRD data revealed that $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized using ethanol as a solvent showed the lowest R -factor, indicating maximum hexagonal ordering of the system. The lattice parameters and other structural data for the compounds synthesized using different solvents are summarized in Table 5. The reason for the lowest R -factor for the compound synthesized with ethanol as a solvent may be attributed to the complex formation reaction between the maleic acid and transition metal ions, which was more facilitated in an ethanol medium than other solvents. Formation of a stable chelation complex will lead to the formation of homogeneous and uniform oxide particles.

3.3. Electrochemical studies

3.3.1. Effect of calcination temperature

The cycling performance of the synthesized material at 600, 700 and 800°C are shown in Fig. 4. Charge-discharge studies were performed galvanostatically at a 0.1 C rate between 3.0 and 4.2 V. The cycling performance of the

Table 4

Lattice parameters, unit cell volume, structural parameters and discharge capacities for $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized at different lithium stoichiometries 'x' at $800^\circ\text{C}/12\text{ h}$ ^a

'x' in $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$	a (Å)	c (Å)	c/a ratio	R -factor = ($I_{0\ 0\ 6} + I_{1\ 0\ 2}$)/ $I_{1\ 0\ 1}$	$I_{0\ 0\ 3}/I_{1\ 0\ 4}$	Unit cell volume (Å ³)	Discharge capacity (mAh/g) ^b	
							Cycle 1	Cycle 10
1.00	2.8528	13.9278	4.88	0.47	1.30	98.16	190	183
1.05	2.8536	13.9299	4.88	0.46	1.29	98.23	175	171
1.10	2.8598	14.0784	4.92	0.47	1.02	99.71	170	162
1.20	2.8588	14.1897	4.92	0.45	1.10	99.73	161	158

^a Data for materials synthesized with an acid-to-metal ion ratio, $R = 1$.^b Data at a 0.1 C rate, cycled between 3.0 and 4.2 V.

Table 5

Lattice parameters, unit cell volume, structural parameters and discharge capacities for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized using different solvents at $800^\circ\text{C}/12\text{ h}$ ^a

Solvent	a (Å)	c (Å)	c/a ratio	R -factor = ($I_{0\ 0\ 6} + I_{1\ 0\ 2}$)/ $I_{1\ 0\ 1}$	$I_{0\ 0\ 3}/I_{1\ 0\ 4}$	Unit cell volume (Å ³)	Discharge capacity (mAh/g) ^b	
							Cycle 1	Cycle 10
Ethanol	2.8528	13.9278	4.88	0.47	1.30	98.16	190	183
Water	2.8557	13.9335	4.88	0.51	1.34	98.40	154	153
1-propanol	2.8551	13.9532	4.89	0.51	1.41	98.50	180	170
1-butanol	2.8525	13.8995	4.87	0.50	1.17	97.94	177	172

^a Data for materials synthesized with an acid-to-metal ion ratio, $R = 1$.^b Data at a 0.1 C rate, cycled between 3.0 and 4.2 V.

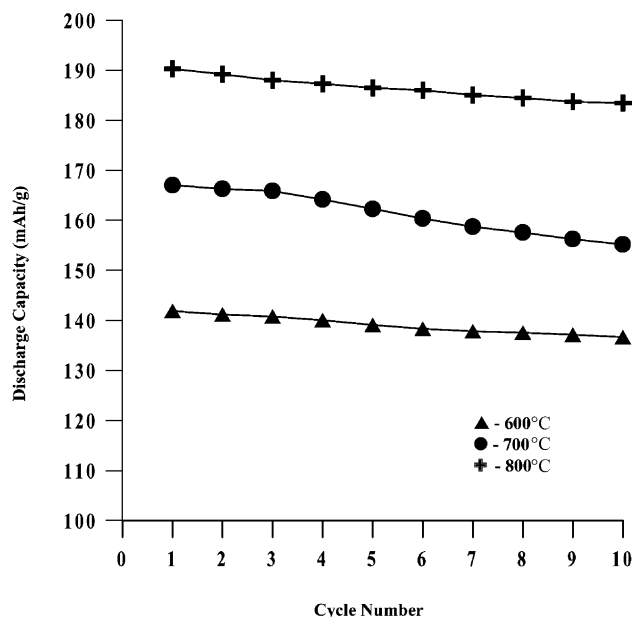


Fig. 4. Variation of discharge capacity with respect to cycle number for $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized at different temperatures.

material calcined at 600°C for 12 h shows inferior capacity because of its lower crystallinity and lack of hexagonal ordering, as supported by X-ray diffraction results. The first discharge capacity was 142 mAh/g and tenth cycle discharge capacity was 137 mAh/g. The main reason for this lower capacity value is the lack of ordering in lithium ion and transition metal ions sites. As the calcination temperature was increased to 700°C , discharge capacity increased to 167 mAh/g for the first cycle and 155 mAh/g after 10 cycles. As indicated by X-ray diffraction results, the system became more layered at 700°C and the $3b$ lithium and $3a$ transition metal ion sites became ordered, facilitating the intercalation–deintercalation process. Further increasing the calcination temperature to 800°C , remarkably improves the electrochemical characteristics of the system. The discharge capacity was 190 mAh/g after the first cycle and 183 mAh/g after the tenth cycle. Hence, calcination at 800°C is an optimal condition for preparing $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ using maleic acid as a chelating agent.

3.3.2. Effect of calcination time

Using the optimal calcination temperature of 800°C , time was varied from 12 h, because it also plays an important role. The variation in discharge capacity with respect to cycling for the compounds calcined at different times at 800°C is shown in Fig. 5. The material calcined for 6 h showed a first cycle discharge capacity of 185 mAh/g and that of cycle 10 was 178 mAh/g. As indicated by the X-ray diffraction studies, the ordering of the lithium ion occupancy site and the transition metal ion site was not complete. Hence, when calcination time was increased to 12 h, the capacity increased appreciably to 190 mAh/g for the first cycle discharge and 183 mAh/g for the cycle 10. Further increasing

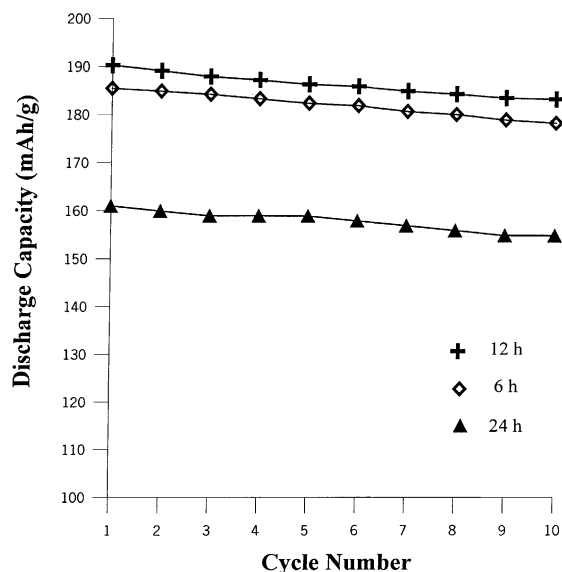


Fig. 5. Variation of discharge capacity with respect to cycle number for $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized at different times.

calcination time to 24 h led to a decrease in capacity with first and tenth cycle discharge capacities of 161 and 155 mAh/g, respectively. The decrease in the electrochemical performance of the system calcined at 800°C for 24 h, is mainly attributed to the loss of lithium by volatilization due to prolonged heating [16]. The structural studies indicate a decrease in hexagonal ordering when the calcination time was increased from 12 to 24 h. Hence, from the structural and the electrochemical studies, it is clear that the optimal calcination time for better performance was 12 h.

3.3.3. Effect of varying of acid-to-metal ion ratio 'R'

The compound synthesized with an acid-to-metal ion ratio of 1 showed a first cycle discharge capacity of 190 mAh/g and a cycle 10 discharge capacity of 183 mAh/g. When the acid-to-metal ion ratio was increased to 2, there was a decrease in capacity, with a first cycle value of 177 mAh/g and tenth cycle value of 173 mAh/g. Further increasing the acid-to-metal ion ratio to 3 led to a decrease in capacity and cyclability. The first discharge capacity was 179 mAh/g and the cycle 10 discharge capacity was 168 mAh/g. There was increased capacity fading with respect to cycling when the acid-to-metal ion ratio was increased to 3. The main reason for capacity and cyclability decrease with an increase in acid-to-metal ion ratio may be attributed to the burning of the organic moieties used as a chelating agent which influences the formation of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as explained in Section 3.1.2 of this paper. Hence, the optimal acid-to-metal ion ratio for the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ using maleic acid as a chelating agent is 1.

3.3.4. Effect of lithium stoichiometry 'x'

This study was performed in order to understand the effect of excess lithium stoichiometry on the electrochemical properties of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. When lithium stoichiometry

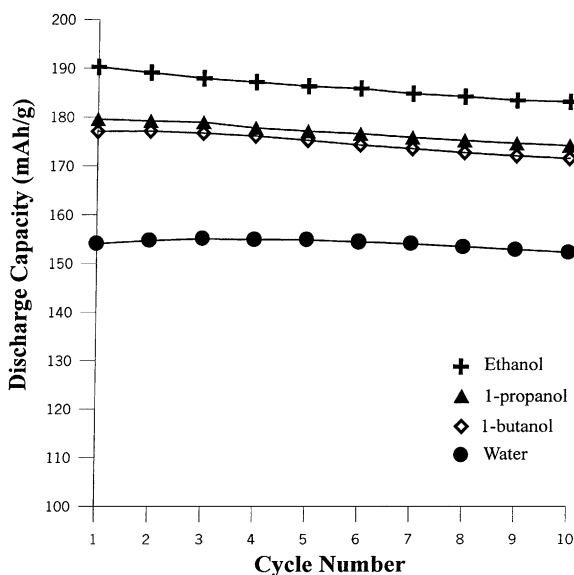


Fig. 6. Cycling performance of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ systems synthesized using different solvents.

' x ' was increased from the ideal value of $x = 1.00$ to 1.05, the first discharge capacity decreased from 190 to 175 mAh/g, and after 10 cycles, the discharge capacity decreased from 183 to 171 mAh/g. Further increasing lithium stoichiometry led to a decrease in the capacity. The main reason for this capacity fading is that lithium sites available for intercalation of lithium ions during discharge are saturated. Capacity further decreases as the x value increases. Another possible explanation is that the presence of excess lithium in the transition metal ion sites leads to a decrease in the capacity.

3.3.5. Effect of various solvents used for synthesis

Since the cycling performance and capacity of a material is directly affected by the synthesis procedure adopted, a study was performed using various solvents such as ethanol, water, 1-propanol and 1-butanol. These solvents were used to prepare the precursor and the heating process was performed uniformly at 800°C for 12 h.

The cycling performance of the materials synthesized using different solvents is shown in Fig. 6. Of all the solvents, the compound synthesized using ethanol showed better capacity and cyclability than the material synthesized using other solvents. The first discharge capacity of the compound synthesized using ethanol was 190 mAh/g and the cycle 10 discharge capacity was 183 mAh/g. The electrochemical performance of the material prepared using 1-propanol as a solvent was second with a first discharge capacity of 180 mAh/g and cycle 10 of 170 mAh/g. When 1-butanol was used as a solvent, the first and 10th discharge capacities were found to be 177 and 172 mAh/g, respectively. However, using water produced even lower capacity and cyclability. The main reason for solvent dependent

capacity and cycling performance may be the initial formation of a chelation complex, which decides the homogeneity of the final compound. Ethanol assisted synthesis leads to the formation of a material with good homogeneity and better electrochemical characteristics.

4. Conclusions

Polycrystalline $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was synthesized by a sol-gel method with maleic acid as a chelating agent under various conditions. The optimal synthesis temperature and time were 800°C and 12 h, respectively. Increasing the maleic acid-to-metal ion ratio ' R ' above 1 led to a lack of hexagonal ordering and a corresponding decrease in the capacity. Of the various solvents used, ethanol assisted synthesized materials yielded the best capacity and cycling performance.

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