

Preparation and characterization of lithium nickel cobalt oxide powders via a wet chemistry processing

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Abstract

Nickel-rich phases of the solid solutions, $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y = 0.1, 0.2, 0.3$), were synthesized by a sol–gel method with citric acid as a chelating agent. Various initial conditions were studied in order to find the optimal conditions for the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The discharge capacity for the compound synthesized under an optimal synthesis condition of 800 °C for 12 h was found to be 187 mAh g^{−1} in the 1st cycle and it was 176 mAh g^{−1} after 10 cycles. The other nickel-rich phases, namely, $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ showed 1st-cycle discharge capacities of 144 and 163 mAh g^{−1}, respectively. The corresponding capacity values were 140 and 159 mAh g^{−1} in the 10th cycle. Excess lithium stoichiometric phases, $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$, where $x = 1.10, 1.15$ and 1.20 , resulted in decreased capacity. Structural and electrochemical properties of the synthesized compounds were compared with those of a commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ sample. The effect of calcination temperature and duration, excess lithium stoichiometry and divalent strontium doping in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ are described. Doping with strontium improved both the capacity and cycling performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

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1. Introduction

Layered lithiated transition metal oxides of the general formula LiMO_2 ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{etc.}$) are being intensively investigated for use as positive electrodes in lithium-ion batteries. Of the various layered cathode materials, LiCoO_2 was the first material to be successfully exploited for commercial applications [1]. Because of the cost and toxicity of cobalt, efforts to replace LiCoO_2 with its nickel analogue have been intensively pursued, but have largely been unsuccessful due to the inherent disadvantages of LiNiO_2 . The main reasons that LiNiO_2 has not been able to reach the commercial stage are the difficulty of synthesizing a stoichiometric compound without any divalent nickel in the lithium sites, irreversible phase transitions during the

topotactic reaction and safety concerns arising from the evolution of flammable gases at an overcharged state at elevated temperatures [2–4]. Research to improve the properties of LiNiO_2 has been extensive [5–7].

The use of solid solutions of lithiated nickel–cobalt oxides, $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($0 \leq y \leq 1$), is one among the successful outcomes of the above investigations [8]. The presence of Co in the lithium nickel oxide matrix greatly stabilizes its structural properties, bestowing improved safety and electrochemical characteristics. The solid solutions formed in the general formula, $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($0 \leq y \leq 1$), crystallize in the $\alpha\text{-NaFeO}_2$ structure similar to their end members. In the entire solid solution region, the nickel-rich phases ($0.1 < y < 0.3$) have been found to be the most promising for longer-cycling, higher-capacity cathode materials [9].

There has always been a strong correlation between the processing and electrochemistry of battery-active oxide materials. Solid-state reaction methods have been widely employed to synthesize these oxide materials. In recent years, interest in aqueous solution-based synthesis of cathode active materials for lithium battery

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applications has greatly increased [10]. The disadvantages of solid-state methods such as larger particle size of the products, inhomogeneous distribution, lack of stoichiometry control etc. can be overcome by wet chemistry, which offers products with a homogeneous distribution of uniform, sub-micron size particles with good stoichiometry control.

Sol–gel processing, one of the promising solution-based methods, has been successfully employed to produce a variety of electrode active materials [11–14]. Nickel-rich phases in $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ have been synthesized via various solution-based routes [15,16]. Various carboxylic acids and polymeric materials have been added as chelating agents to facilitate gel formation and prevent phase segregation, leading to fine polycrystalline powders. In our laboratory, detailed studies of synthesizing $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ using various chelating agents have been performed [17]. Citric acid is one among the widely used chelating agents used for the synthesis of oxide materials [18,19]. However, nickel-rich phases of lithium cobalt oxide, especially $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, have not yet been synthesized with citric acid as a chelating agent to the best of our knowledge.

This paper reports the sol–gel synthesis of nickel-rich phases of the solid solutions $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y = 0.1, 0.2$ and 0.3), especially the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ phase, with citric acid as a chelating agent. Synthesis conditions such as solvents for preparing the solutions of the starting materials, calcination temperature, duration of calcination, and lithium stoichiometry were varied in order to identify the optimal parameters for the best electrochemical performance. A study of strontium doping was also performed and the electrochemical properties are discussed.

2. Experimental

A typical sol–gel synthesis of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ with citric acid as a chelating agent was performed the following way. Stoichiometric amounts of the nitrates of lithium, nickel and cobalt were dissolved in a minimum volume of alcohol. An alcoholic solution of citric acid was added to an intimately mixed solution of the metal nitrates under constant stirring, such that the acid-to-metal ion ratio, R , was 1. After stirring for 24 h the pH of the solution was measured to be around 0.15. Heating the mixture at 80°C for 2 h under constant stirring made the solution dense, leading to the formation of a sol. Further heating at 120°C led to the formation of a gel, which was subsequently dried. The dried powder was calcined in flowing oxygen at various temperatures for different durations. Doping with Sr^{2+} was done as follows. A known quantity of SrCO_3 (99.99%) was dissolved in nitric acid, and diluted with ethanol to make the required stock solutions. Known

volumes of the stock solutions were added to the precursor solution mentioned above such that the $\text{Sr}^{2+}/\text{Li}^+$ molar ratios corresponded to 10^{-6} , 10^{-5} , 10^{-4} , 10^{-3} and 10^{-2} . This mixture was then subjected to the sol–gel process and calcination described above.

The phase formation and the effect of the temperature and duration of calcination on the structural properties of the synthesized compound were examined by X-ray diffraction studies (Siemens, D-5000 MAC Science MXP18). The capacity and cyclability of the synthesized materials were studied with 2032-type coin cells assembled in an argon-filled glove box. The cells were cycled at a 0.1 C rate between 3.0 and 4.3 V in a multi-channel battery tester (Maccor, Series 4000). The coin cells were assembled with the synthesized material as the cathode, lithium metal (FMC) as the anode and 1 M LiPF_6 in 50:50 v/v EC-DEC (Tomiya Chemicals) as the electrolyte. The composite cathode for the coin cells were prepared by thoroughly mixing 85% active material, 10% carbon black and 5% PVdF as a binder in *N*-methyl-2-pyrrolidone (NMP), and blade-coating the slurry onto an aluminum foil. The coated aluminum foil was allowed to dry in an oven overnight at 120°C . The electrodes for the coin cells were punched as circular discs after the foil was roller-pressed for better adherence of the cathode material to the current collector.

3. Results and discussion

3.1. X-ray diffraction studies

The structures of LiNiO_2 and iso-structural solid solutions such as $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ are based on a nearly perfect cubic close packing of oxygen atoms, with the small lithium and transition metal atoms occupying alternate layers in the octahedral interstices of the oxygen array, forming a face centered cubic structure [20]. Each cation has six oxygen neighbors and each oxygen has three Li neighbors and three Ni/Co neighbors. Thus, this structure assumes a hexagonal symmetry with an $(\cdots\text{O}-\text{Li}-\text{O}-\text{Ni}-\text{O}-\text{Li}-\text{O}-\text{Ni}-\text{O}\cdots)$ basal plane stacking sequence [21]. In this structure, the hexagonal c -axis corresponds to the body diagonal through the cubic unit cells [21]. In this paper, we refer to this lattice arrangement as hexagonal ordering.

The X-ray diffractograms recorded for the solid solutions $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($y = 0.1, 0.2, 0.3$) are shown in Fig. 1. For comparison, the diffractogram of a commercial sample is also shown. All three X-ray diffractograms show a high degree of crystallinity with all the Bragg peaks indexable, assuming a hexagonal system. The layered structure was well evidenced from the splitting of the hexagonal characteristic doublets 006/102 and 108/110, indicating a good ordering of the hexagonal lattice. The lithium ions occupy the planes

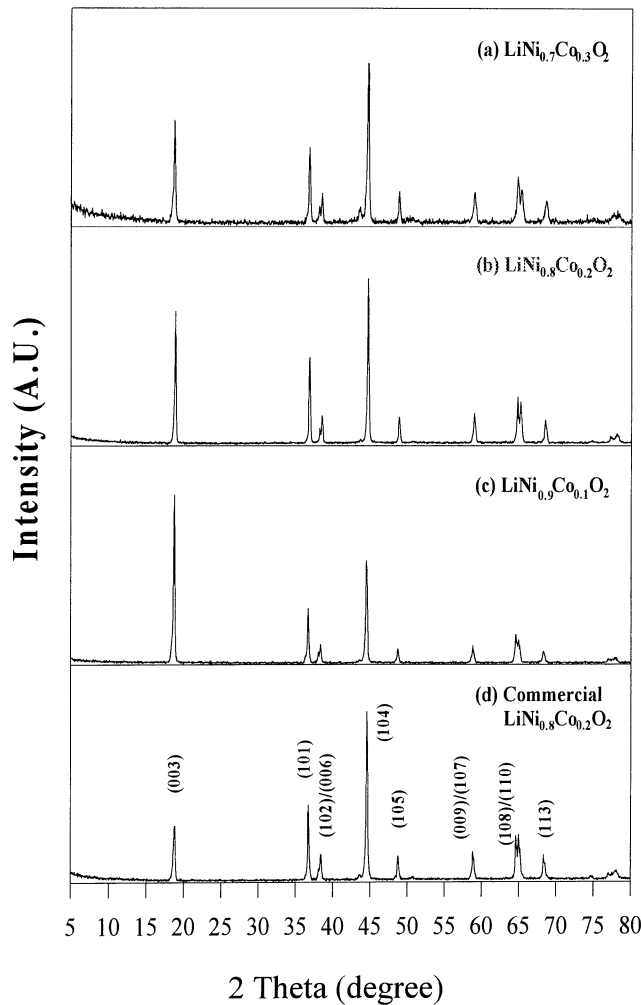


Fig. 1. X-ray diffraction patterns of nickel-rich phases synthesized by 12-h 800 °C calcination. (a) $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$; (b) $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$; (c) $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$; (d) commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

between the $\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ slabs formed by the edge-sharing $(\text{Ni}_{1-y}\text{Co}_y)\text{O}_2$ octahedra [22]. The lattice parameters, calculated assuming a hexagonal lattice in the $R\bar{3}m$ space group for the three systems, are given in

Table 1. The values of the lattice parameters and the c/a ratio agree well with those reported in other literature. The R -factor for the three compositions, obtained by calcination at 800 °C for 12 h, calculated according to the definition of Dahn et al. [21,23], were 0.61, 0.49 and 0.71 for $y = 0.1$, 0.2 and 0.3, respectively. According to Dahn et al. [23], the system with a minimum R -factor will have the best hexagonal ordering. The structural studies indicate that the maximum ordering is achieved for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, which was also well complemented by its electrochemical performance, as explained below. Hence, a detailed structural analysis was performed in order to determine the optimal conditions for the citric acid-assisted synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

The effect of varying the calcination temperature and duration on the structural properties was studied in detail. The X-ray diffractograms of the precursor calcined at various temperatures for a fixed duration of 12 h are shown in Fig. 2. For the product obtained by calcination at 700 °C, the X-ray diffraction pattern showed broad peaks with a splitting of the 104 line. Also, extra peaks unindexable in the $\alpha\text{-NaFeO}_2$ structure were present, indicating an incomplete reaction for the formation of a phase-pure $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. Thus, calcination at 700 °C was not sufficient to form a crystalline single-phase $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, as indicated by the R -factor, which had a high value of 1.15. This clearly shows that calcination at 700 °C was not sufficient to produce a sample with complete hexagonal ordering. When the calcination temperature was increased to 750 °C, the splitting of the 104 peak and the additional phases disappeared. The R -value also decreased to 0.54. There was increased ordering because of the higher calcination temperature. A further increase in the calcination temperature to 800 °C led to a more ordered system, as indicated by the pronounced splitting of the doublets 006/102 and 108/110. An R -factor value of 0.49 for the sample obtained at 800 °C was the lowest noted amongst the samples studied here. Further increasing the calcination temperature to 850 and

Table 1

Lattice and structural parameters for $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ phases ($y = 0.1, 0.2, 0.3$) synthesized under different heat treatment protocols

Composition	Calcination temperature (°C)	Calcination duration (h)	a (Å)	c (Å)	c/a ratio	R -factor	Unit cell volume (Å ³)
$\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$	800	12	2.863	14.018	4.89	0.61	99.51
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	800	12	2.860	14.094	4.92	0.49	99.86
$\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$	800	12	2.861	14.013	4.89	0.60	99.34
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	800	6	2.860	14.119	4.93	0.52	100.03
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	800	12	2.860	14.094	4.92	0.49	99.86
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	800	24	2.861	14.126	4.93	0.53	100.15
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	700	12	2.878	14.197	4.93	1.15	101.85
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	750	12	2.860	14.122	4.93	0.54	100.01
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	800	12	2.860	14.094	4.92	0.49	99.86
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	850	12	2.862	14.082	4.92	0.50	99.87
$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	950	12	2.866	14.172	4.94	0.50	100.82

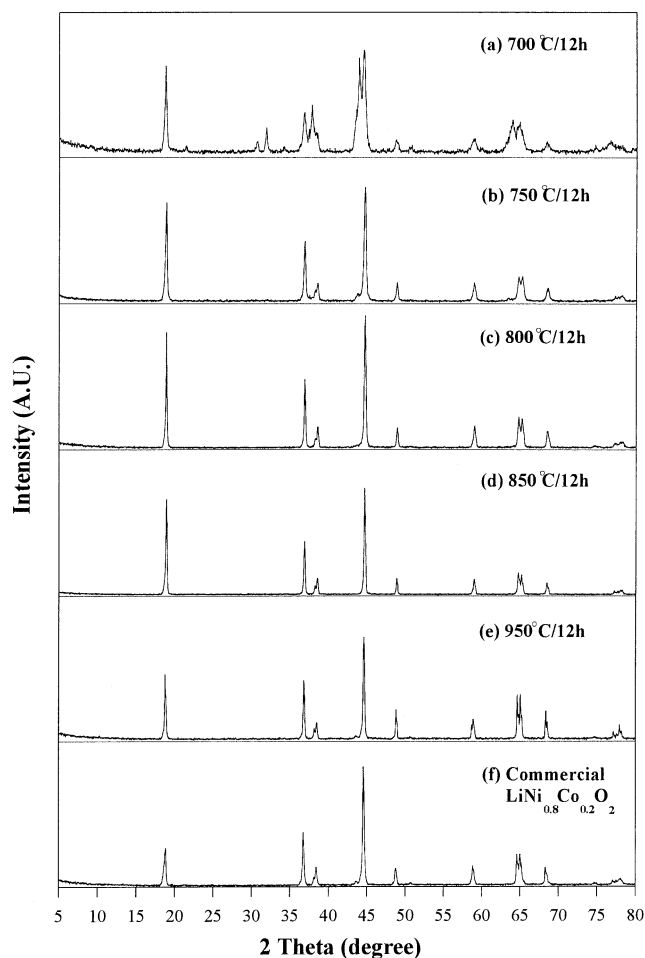


Fig. 2. X-ray diffraction patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized by 12-h calcination at different temperatures. (a) 700; (b) 750; (c) 800; (d) 850; and (e) 950 °C. (f) Commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

950 °C led to a decrease in hexagonal ordering. This dependence of hexagonal ordering on calcination temperature is a common feature of LiNiO_2 and nickel-rich phases of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$. Even small deviations from the ideal synthesis conditions can greatly disrupt the hexagonal ordering in these phases. The R -factor increased to 0.51 and 0.50 for the materials calcined at 850 and 950 °C, respectively. The lattice parameters calculated for the materials obtained by a 12-h calcination at the various temperatures are given in Table 1. The above results indicate that the maximum hexagonal ordering is achieved with 12-h calcination at 800 °C.

In the above study, calcination was performed at various temperatures for 12 h. In order to optimize the duration of calcination, the precursor was calcined at 800 °C for 6 and 24 h. The X-ray diffraction patterns of the products of the 6-, 12- and 24-h calcinations at 800 °C as well as that of a commercial sample are shown in Fig. 3. All three X-ray diffraction patterns show the existence of highly crystalline phases. For the material calcined for 6 h, the R -factor was high, with a

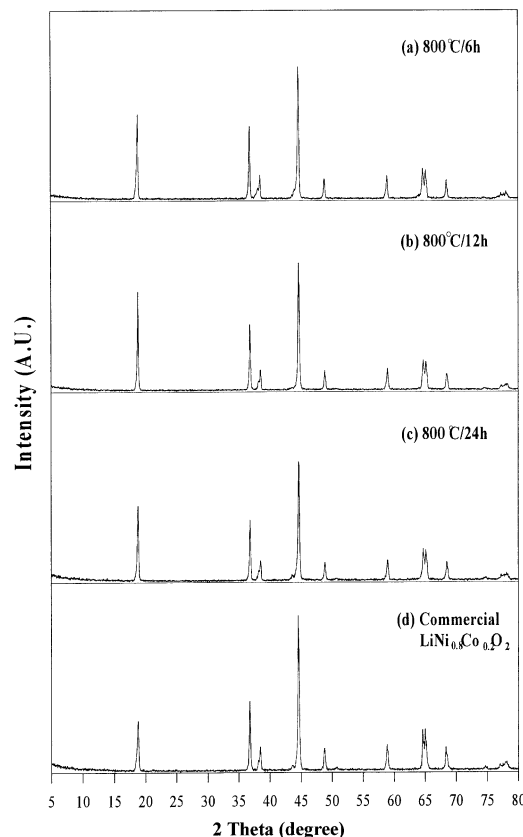


Fig. 3. X-ray diffraction patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ prepared at 800 °C for different durations. (a) 6; (b) 12; and (c) 24 h. (d) Commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$.

value of 0.53, which indicates that the lithium ion and transition metal ion sites are not completely ordered, an arrangement that does not favor topotactic reactions. A further increase in the calcination time to 12 h improved the hexagonal ordering to the highest level as discussed above. Further increasing the calcination time led to unfavorable results of a decrease in the ordering of the hexagonal lattice indicated by the R -factor (0.54). From the foregoing, it can be concluded that the optimal calcination temperature and duration are 800 °C and 12 h, respectively. Deviation from this would lead to unfavorable structural characteristics, which would directly affect the electrochemical performance of the product. Thus, the citric acid-based wet chemistry method adopted here does away with the intermittent grinding operations and the extended duration of heat treatment that are necessary for the solid-state fusion method. The lattice parameters calculated for the products obtained by calcination at 800 °C for different durations are given in Table 1.

According to Dahn et al. [23] the unit cell volume of $\text{Li}_x\text{Ni}_{2-x}\text{O}_2$ is the lowest for the ideal layered LiNiO_2 . In the present study, the minimum unit cell volume for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was observed for the product synthesized by a 12-h calcination at 800 °C, as shown in Table

1. Hence it can be concluded that the optimal calcination temperature and duration for the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ are 800 °C, and 12 h, respectively. However, it must be noted that the values of I_{003}/I_{104} intensity ratios are found to be generally less than 1 for our products as well as for the commercial sample. A higher intensity for the (003) reflection compared to the (104) reflection is expected for a two-dimensional structure [23,24]. The lower intensities of the (003) reflections indicate that the crystal lattice of the products have not attained a complete two-dimensional ordering.

3.2. Surface and particle morphology

Scanning electron micrographs of the products obtained by a 12-h calcination at various temperatures are shown in Fig. 4. The 700 °C-calcined product shows loosely agglomerated particles of micrometre size, indicating the low crystallinity of the material as evidenced by X-ray diffraction studies. As the calcination temperature was increased to 750 and 800 °C, the particle size increased and a more uniform distribution was observed. Further increasing the calcination temperature to 850 and 950 °C led to greater increases in particle size. Similarly, an increase in the duration of calcination led to an increase in the size of the grains, as shown in Fig. 5. As the duration of calcination was increased, the loosely distributed fine particles grew in size.

3.3. Charge–discharge studies

3.3.1. $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ systems

The cycling performance of the nickel-rich phases, namely $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, is presented in Fig. 6. The cycling behavior of commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is included for comparison. $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ showed better electrochemical performance than $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$. The 1st and 10th-cycle discharge capacities for $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ were 144 and 140 mAh g^{−1}, respectively. The corresponding values for $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ were 163 and 159 mAh g^{−1}. However, both the systems showed inferior electrochemical characteristics compared to $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The decreased capacity of $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ may be attributed to the insufficient amount of cobalt ions present to impart the necessary structural stability to the system. A further increase in the cobalt content (y) to 0.2 in $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ led to the greatest enhancement in electrochemical characteristics, as explained below. When the cobalt concentration, y , was increased to 0.3, the capacity decreased compared to when $y = 0.2$. However, $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ showed better electrochemical performance than $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ did. Recently, the composition $\text{LiNi}_{0.74}\text{Co}_{0.26}\text{O}_2$ was identified as the one

exhibiting the best capacity and cyclability in the entire solid solution region [9].

Since $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ showed the most promising results among the nickel-rich phases studied here, synthesis of this composition under various conditions such as different solvents for the preparation of precursor, temperatures and durations of calcination, different lithium stoichiometries, and doping with strontium ions was performed in order to optimize the ideal preparative conditions and chemical composition for the best-performing $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$.

3.3.2. Calcination temperature and duration

The cycling performance of the materials synthesized at different temperatures for a constant duration of 12 h is shown in Fig. 7. The material obtained at 700 °C showed poor electrochemical characteristics, complementing the results of our X-ray diffraction studies and SEM analysis. The charge and discharge capacities in the 1st cycle were 102 and 46 mAh g^{−1}, respectively, while those in the 10th cycle were 57 and 56 mAh g^{−1}. The high 1st-cycle irreversible capacity is associated with a lack of ordering of the lithium intercalation and deintercalation sites. Similar results for low-temperature calcined materials have been reported [25]. The low calcination temperature is responsible for the lack of ordering of the lithium sites and the associated reduced capacity. The stabilization of capacity with respect to cycling is a common feature in the case of layered structures. When the calcination temperature was increased to 750 °C the capacity of the oxide increased. The first and the 10th-cycle discharge capacities jumped to 162 and 157 mAh g^{−1}, respectively. This increased capacity is very much related to structural improvements that facilitate the topotactic processes. Calcination at 800 °C for 12 h resulted in a product with the highest capacity, the first and 10th-cycle discharge capacities being 188 and 176 mAh g^{−1}, respectively. A further increase in the calcination temperature to 850 and 950 °C led to decreased discharge capacities. For example, the capacity of the product obtained at 850 °C was 160 mAh g^{−1} in the 1st-cycle but faded to 116 after 10 cycles. Similarly, reduced capacities and high rates of fading were observed for the product obtained at 950 °C. The loss in capacity at the higher temperatures is mainly attributed to the loss of lithium ions because of volatilization.

The cycling performance of the products obtained by calcining at 800 °C for different durations is shown in Fig. 8. The best electrochemical properties were found for the 12-h calcined products, as noted above. When the calcination duration was reduced to 6 h, the capacity decreased because of the incomplete ordering of the hexagonal lattice. The 1st and 10th-cycle discharge capacities were 159 and 160 mAh g^{−1}, respectively.

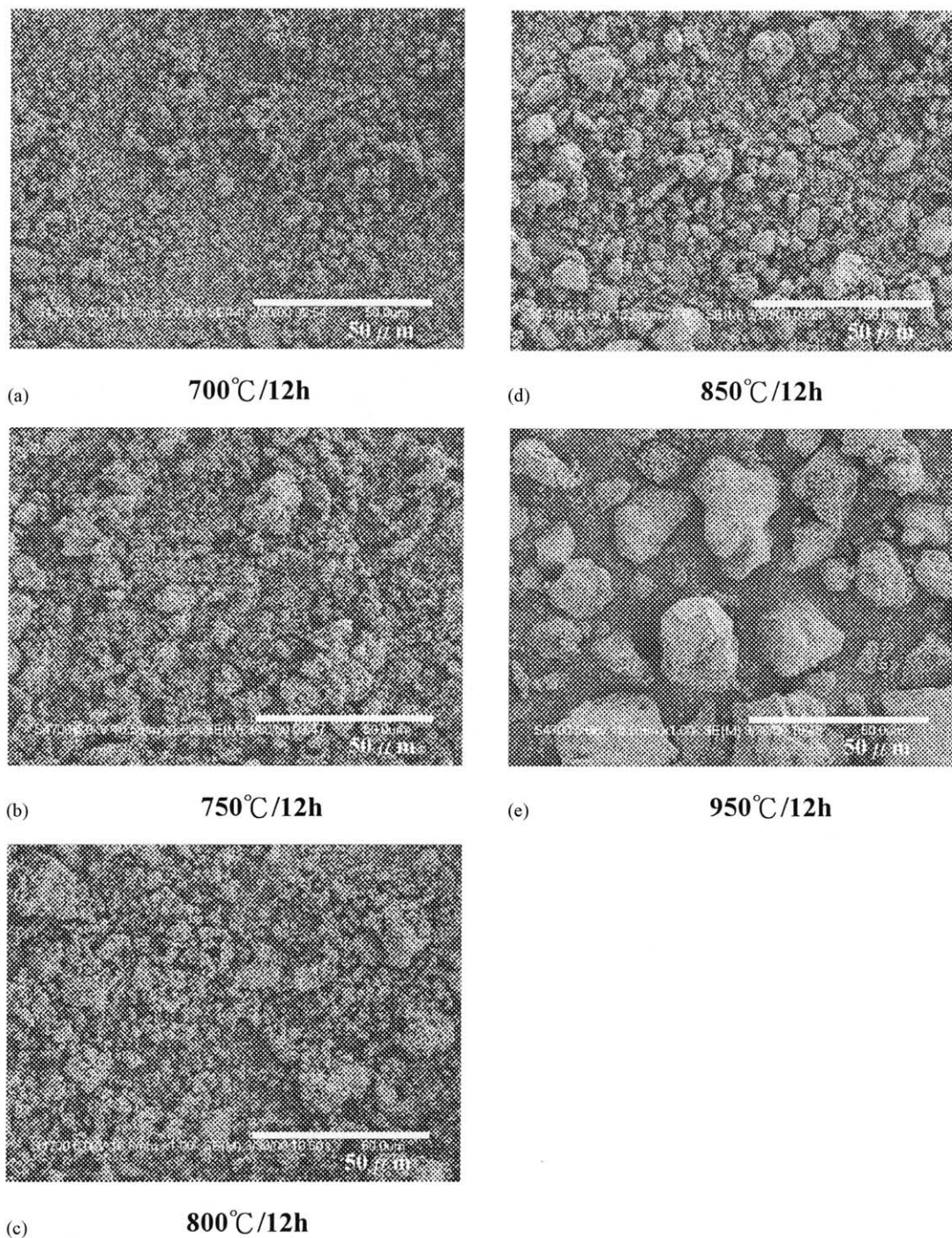


Fig. 4. Scanning electron micrographs of 12-h calcined $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ phases. Calcination temperatures: (a) 700; (b) 750; (c) 800; (d) 850; (e) 950 °C.

Similarly, when the duration of calcination was raised to 24 h, the performance deteriorated, the 1st and 10th-cycle capacities being 158 and 153 mAh g^{-1} , respectively. As mentioned above, both high calcination temperatures and prolonged heating can lead to a volatilization of lithium, resulting in products with inferior electrochemical performance.

3.3.3. Effect of solvents

The electrochemical performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized from precursors prepared in solvents such as alcohol, water, 1-propanol and 1-butanol is depicted in Fig. 9. All the samples were prepared by calcination at 800 °C for 12 h. The best capacity values were obtained for the compound synthesized from an ethanol-based

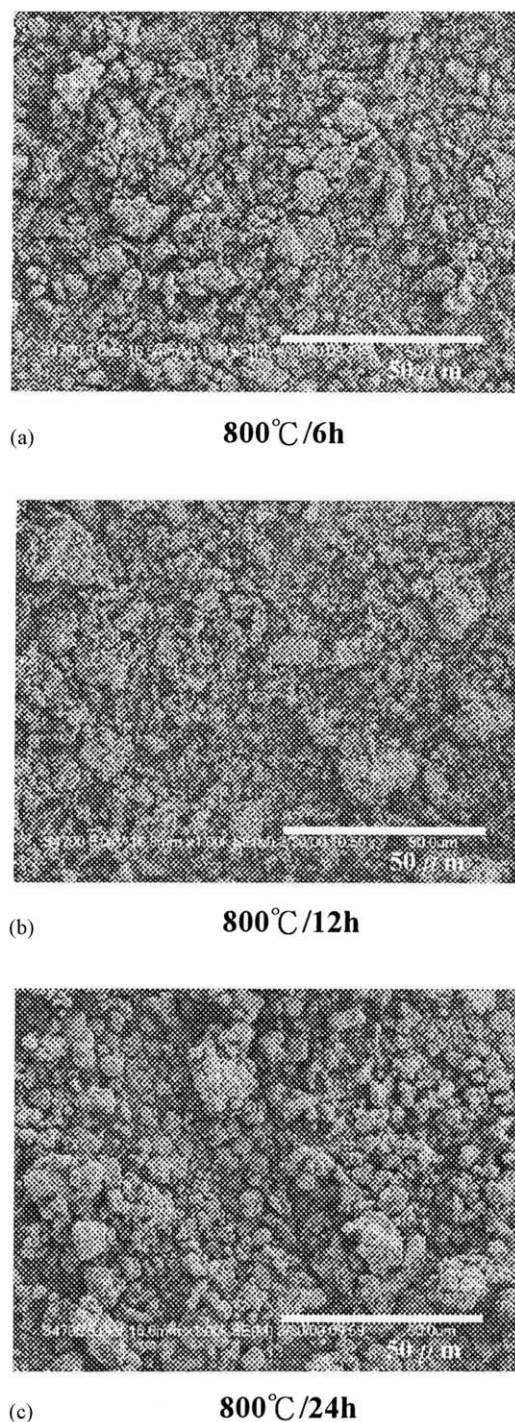


Fig. 5. Scanning electron micrographs of 800 °C-calcined $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ phases. Duration of calcination: (a) 6; (b) 12; (c) 24 h.

precursor, with the material synthesized from an aqueous solution a close second. The 1st and 10th-cycle discharge capacities of the material synthesized from an ethanolic precursor were 188 and 176 mAh g^{-1} , respectively. The corresponding values for the aqueous solution-based product were 185 and 167 mAh g^{-1} . For the other two solvents, 1-propanol and 1-butanol, the

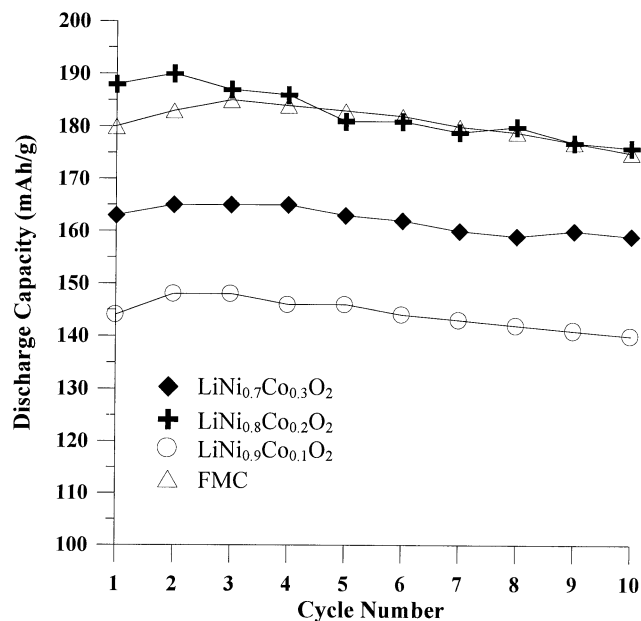


Fig. 6. Cycling performance of nickel-rich phases prepared in flowing oxygen. Heat treatment conditions: 800 °C, 12 h. Charge–discharge: 0.1 C rate; 3.0–4.3 V.

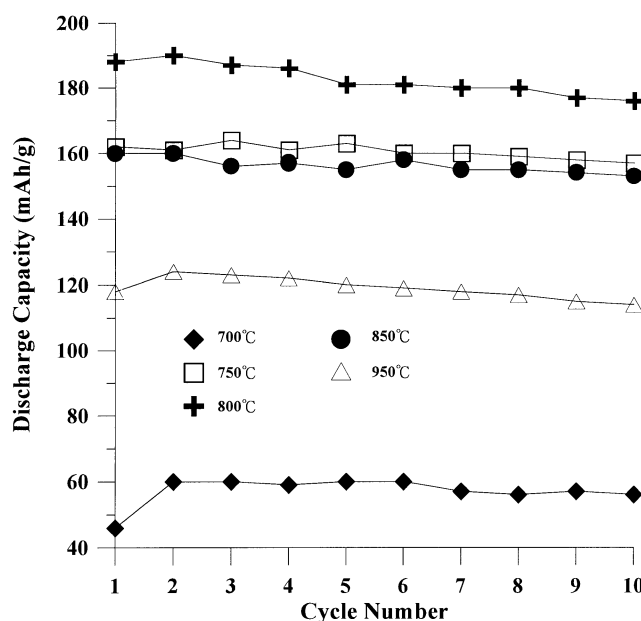


Fig. 7. Cycling performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ phases calcined at different temperatures. Duration of calcination: 12 h. Charge–discharge: 0.1 C rate; 3.0–4.3 V.

performance was not that promising. Their capacity and cycling performance were lower than those of materials synthesized from ethanol or water-based precursors. Of the compounds synthesized with alcohol and water, the one prepared with alcohol had better cycling stability, with an overall cycling efficiency of 94% for 10 cycles, whereas it was only 90% for the one based on the aqueous precursor. The reason the electrochemical

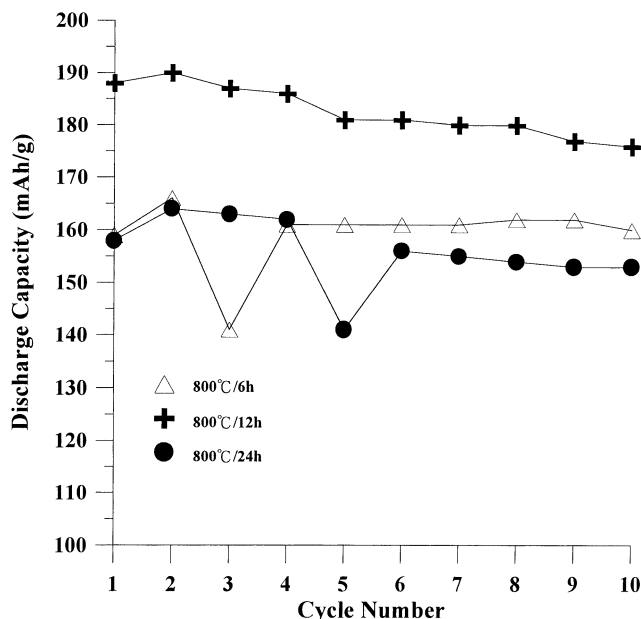


Fig. 8. Cycling performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ phases prepared by calcination at $800\text{ }^\circ\text{C}$ for different durations. Charge–discharge: 0.1 C rate; $3.0\text{--}4.3\text{ V}$.

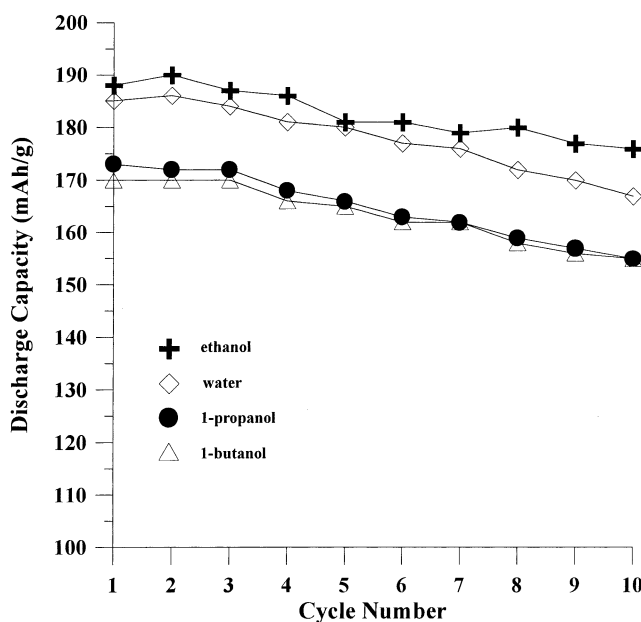


Fig. 9. Effect of the solvent used for the precursor solution on the cycling performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ products. Charge–discharge: 0.1 C rate; $3.0\text{--}4.3\text{ V}$.

characteristics of the final product are dependent on the solvent used to prepare the precursor is related to the formation of a chelation complex and the pH of the solution. The formation of the chelation complex affects the homogeneous distribution of sub-micron sized particles. This use of alcohol must have favored the above criteria, leading to the most promising results.

In order to compare the electrochemical performance of the ethanol-based $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ product with a commercially available $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ sample, coin cells with the latter material were cycled between 3.0 and 4.3 V at a 0.1 C rate. The results were inferior to those obtained with our product ($800\text{ }^\circ\text{C}$ for 12-h calcination, ethanol-based precursor), the 1st- and 10th-cycle capacities of the commercial sample being 180 and 175 mAh g^{-1} , respectively. The capacity values are listed in Table 2.

3.3.4. Effect of excess lithium stoichiometry

Non-stoichiometric phases of lithium nickel oxides produce unfavorable results because of the occupancy of divalent nickel ions in the lithium sites. The best stoichiometry reported in literature is $\text{Li}_{0.996}\text{Ni}_{1.006}\text{O}_2$ [26]. The cycling performances of stoichiometric and lithium-excess phases of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ are shown in Fig. 10. It can be seen that as the lithium stoichiometry is increased, the capacity decreases. For example, when the lithium stoichiometry was $x = 1.05$, the 1st and 10th-cycle capacities fell to 183 and 169 mAh g^{-1} , respectively. The trend continued, with the corresponding values for the composition with $x = 1.10$ deteriorating further to 158 and 150 mAh g^{-1} , respectively. The biggest drop was observed for the composition with the highest lithium stoichiometry studied here, $x = 1.20$. The discharge capacity for this compound was 149 mAh g^{-1} in the 1st cycle, which deteriorated to 142 mAh g^{-1} after 10 cycles.

The decrease in capacity values may be attributed to the presence of excess lithium in the transition metal sites, disenabling their availability for the topotactic

Table 2

Comparison of charge and discharge capacities of commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ synthesized by $12\text{-h } 800\text{ }^\circ\text{C}$ calcination

Cycle number	Specific capacity (mAh g^{-1})			
	Synthesized $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$		Commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$	
	C.C.	D.C.	C.C.	D.C.
1	247	188	223	180
2	191	190	181	183
3	191	187	184	185
4	187	186	191	184
5	186	181	184	183
6	181	181	183	182
7	182	179	182	180
8	179	180	180	179
9	180	177	178	177
10	177	176	177	175

C.C.: charge capacity; D.C.: discharge capacity. Galvanostatically cycled at a 0.1 C rate between 3.0 and 4.3 V .

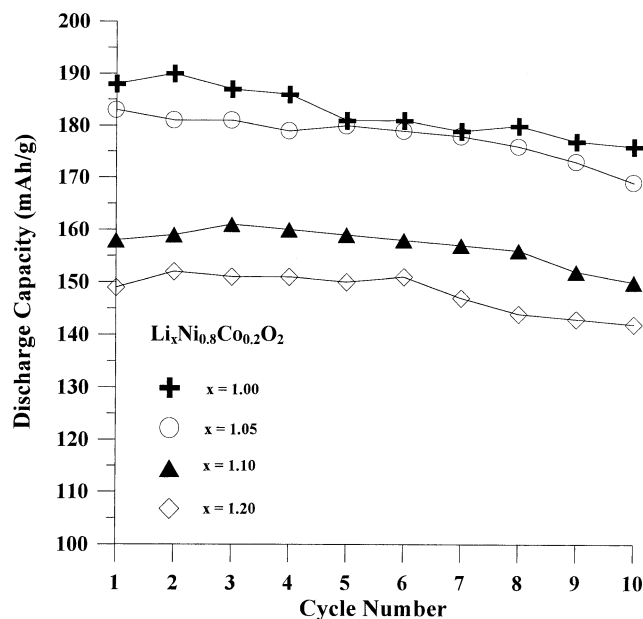


Fig. 10. Variation in discharge capacity as a function of cycle number for various lithium stoichiometries. Charge–discharge: 0.1 C rate; 3.0–4.3 V.

reactions. However, the electrochemical performance of the non-stoichiometric phases depends also on the synthesis method adopted. In the case of sol–gel synthesis, the chelating agent has an influence on the electrochemical performance of the products. For instance, in our earlier study, where oxalic acid was used as the chelating agent, we were able to achieve excellent capacity and cyclability for the compound with a lithium stoichiometry of $x = 1.10$ [27].

3.3.5. Influence of divalent strontium doping

Plots of discharge capacity vs. cycle number for $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ doped with Sr^{2+} are shown in Fig. 11. The Sr^{2+} ions were doped with an intention to improve the capacity and cyclability of the host material. Of the various dopant ratios, $\text{Sr}^{2+}/\text{Li}^+$, studied (10^{-6} – 10^{-2}), the compound with a molar dopant ratio of 10^{-3} , showed improved capacity and cyclability, both with respect to the undoped and the other doped compositions. The discharge capacity for the compound with a dopant ratio of 10^{-3} was 187 mAh g^{-1} in the 1st cycle, diminishing to 183 mAh g^{-1} in the 10th cycle. Any further increase in the dopant concentration decreased the capacity. For the compound with $\text{Sr}^{2+}/\text{Li}^+ = 10^{-2}$, the 1st and 10th cycle discharge capacities were 169 and 158 mAh g^{-1} , respectively.

Sr^{2+} doping in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ has not been reported so far, to the best of our knowledge. However, a study to improve the safety characteristics of $\text{LiSr}_{0.002}\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_2$ by coating with MgO was reported [28]. The superior electrochemical performance was explained based on a defect model proposed by Van der Ven

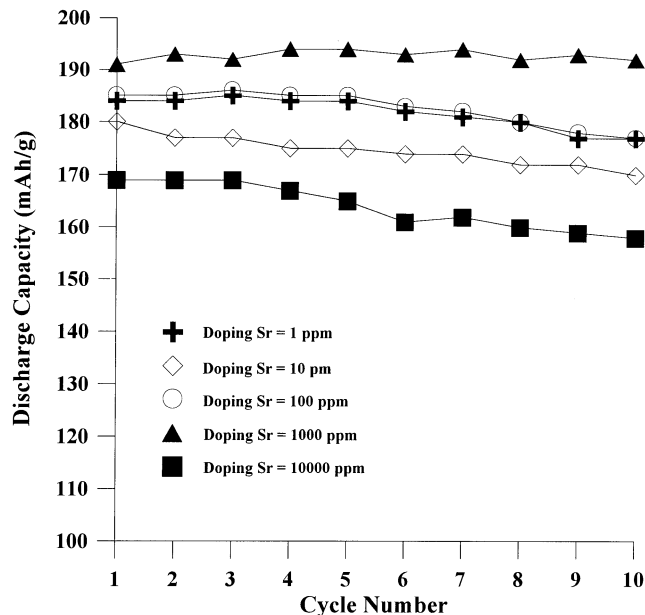


Fig. 11. Effect of the strontium dopant ratio on the cyclability of doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ phases. Charge–discharge: 0.1 C rate; 3.0–4.3 V.

and Ceder [29,30]. The occupancy of the divalent strontium ions in the lithium sites led to the formation of positive defects with a corresponding reduction of M^{3+} ions to the M^{2+} state. Similar observations were made by Petrov et al. [31] for Sr^{2+} -doped LaCoO_3 perovskites, which show a defect-induced improvement in conductivity. According to Van der Ven and Ceder [29], electrochemical properties are greatly influenced by the diffusion of lithium ions in transition metal oxides of the O3-type structure. The diffusion of lithium ions occurs by two hopping mechanisms, oxygen dumbbell hopping (ODH) and tetrahedral site hopping (TSH) [29]. If a lithium ion hops to a destination site that has a nearby vacancy, then it is said to follow the TSH mechanism. If there are no vacant sites available for hopping near the destination site, then the mechanism followed is the ODH mechanism. By pseudo-potential calculations, Van der Ven and Ceder [29] have calculated the activation energy required for the above two processes as 300–600 and 800 meV, respectively. The presence of vacancies near the destination site in the lithium plane favors the TSH mechanism, leading to better lithium diffusion [29]. Hence, the presence of strontium ions in the lithium sites would lead to the formation of vacancies, favoring a TSH process, improving the diffusion and electrochemical characteristics of the Sr^{2+} -doped $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ($\text{Sr}^{2+}/\text{Li}^+ = 10^{-3}$). The reason for a decrease in capacity at a dopant ratio of 10^{-2} may be an increased defect concentration leading to an agglomeration of the defects, which hinders lithium ion mobility. Hence, the optimal $\text{Sr}^{2+}/\text{Li}^+$ doping ratio for the present composition is 10^{-3} .

4. Conclusions

A citric acid-assisted wet chemistry method was employed to synthesize nickel-rich phases of lithium nickel cobalt oxides. Of the three systems studied, viz. $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ showed promising results in terms of capacity and cyclability. The 1st and 10th-cycle discharge capacities for this composition were 187 and 176 mAh g^{-1} , respectively. Of the different solvents studied, ethanol was the most successful. $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ phases with excess lithium stoichiometries were found to be electrochemically inferior. Their capacities fell with an increase in the value of x . Strontium ions were doped in order to improve the capacity and cyclability of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. Improved cycling and capacities were obtained at a $\text{Sr}^{2+}/\text{Li}^{+}$ ratio of 10^{-3} . The dopant effect is explained by a defect model.

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