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Saturated linear dicarboxylic acids as chelating agents for the sol-gel synthesis of LiNi_{0.8}Co_{0.2}O₂

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Abstract

A series of saturated aliphatic dicarboxylic acids have been studied as chelating agents for the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The decomposition temperature of the dicarboxylate precursors was found to increase linearly with the number of $-(\text{CH}_2)$ – groups in the acid. From XRD analysis it was concluded that irrespective of the acid, the optimized heat treatment protocol for the synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was calcination at 800 °C for 12 h. The product obtained from the adipate precursor gave the highest first-cycle capacity (178 mAh/g), while that from the suberic acid complex gave high capacity and cyclability. The effects of the solvent and pH of the precursor solution on the product characteristics are also discussed. Some related work on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ prepared with maleic, oxalic and tartaric acids as complexing agents is also presented.

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1. Introduction

 $LiNi_{1-v}Co_vO_2$ solid solutions, isotypic with the layered α -NaFeO₂ structure, are considered as next-generation cathodes [1,2] in lithium batteries. These solid solutions have end-members LiMO₂, where M is Co or Ni. Both these materials have a theoretical lithium intercalation capacity of 274 mAh/g. In the case of LiCoO₂, only about 130 mAh/g can be reversibly tapped, corresponding to an x value of 0.5 in Li_xCoO_2 . The limitation in the capacity arises from the high charging voltages for x values below 0.5, which lead to an oxidative degradation of the liquid electrolyte [3]. On the other hand, 0.6 Li atom per molecule can be reversibly intercalated in LiNiO₂ (between x values of 0.3 and 0.9 in Li_xNiO_2), corresponding to a practical capacity of 150-160 mAh/g. Additionally, the deintercalation processes in LiNiO₂ occurs at potentials lower than that in LiCoO₂, a factor that gives rise to their higher charge densities. Although Li_xCoO₂ presents advantages such as ease of preparation and a structure robust enough to withstand extended cycling in the limited range (0.0 < x < 0.5), its high cost and toxicity prevent its extensive use, especially for consumer applications. On the other hand, nickel is not only cheap but also environmentally benign. The lower operating voltages of LiNiO₂-based cells (which are about 250 mV less than those based on LiCoO₂) make their electrolytes less prone to oxidation [4]. However, stoichiometric LiNiO₂ is difficult to prepare [5,6], the best sample reported so far being Li_{0.996}Ni_{1.006}O₂ [7]. The non-stoichiometry arises from the fact that Ni²⁺ ions present in the products, acting as local pinning centers, restrict the motion of Li⁺ ions within the layers of the oxide. The non-stoichiometry results in significant degradation in the cyclability of the system [7,8]. In an attempt to derive the maximum benefit from the homologous end-members, several intermediate compositions have been studied.

The cobalt in these nickel-rich phases is believed to reduce cation mixing in the lithium layers and disorder in the $(Ni/Co)O_2$ layers [1,9-11], which are major problems associated with LiNiO₂. LiNi_{1-y}Co_yO₂ solid solutions show lower insertion potentials compared to the pure LiCoO₂ phase [12,13] and are, therefore, expected to be oxidatively less taxing on the electrolyte and possibly to retain good lamellar structure upon repeated cycling [1,9,14-18]. The small size of Co³⁺ ions tends to enhance the crystal field strength, thereby enabling stabilization of the Ni³⁺ ions in the slab [19]. In fact, perfectly layered LiNi_{1-y}Co_yO₂ structures can be obtained for y values greater than 0.3, while for

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y values between 0.3 and 0.1, small departures from stoichiometry could arise [19]. Moreover, capacities as high as 180 mAh/g, corresponding to the cycling of 0.65 Li atom per molecule, have been tapped from LiNi_{0.85}Co_{0.15}O₂ [20]. According to Delmas et al. [1] and Aragane et al. [2], the solid solution of the composition LiNi_{0.8}Co_{0.2}O₂ is a potential next generation cathode material. However, Aragane et al. [2] point out that, given the vast disparity in the electrochemical properties of such solid solutions prepared by different procedures, much care needs to be exercised in the

Several soft chemistry strategies have been adopted for the preparation and processing of such solid oxide materials [20–23]. A popular 'chemie doux' approach involves the sol–gel method in which carboxylic acids serve as chelating agents [22,24–37]. In the sol–gel method, a sol, which is a suspension of small particulates dispersed in a liquid phase, is transformed into a gel, which is a viscous, three-dimensional polymeric network. For this review, the scope of the sol–gel process is extended to such preparative procedures that involve the transformation of a thick viscous liquid medium with no phase segregation into an amorphous glassy mass with no long-range networking.

synthesis and processing of the material.

Our laboratory has been involved in the synthesis and characterization of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ by the carboxylic acid-assisted sol–gel method as well as by solid-state fusion methods [38–40]. In this paper, we present a review and a comparative study of the sol–gel synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ by saturated linear aliphatic dicarboxylic acids such as oxalic, malonic, succinic, adipic, suberic and sebacic acids. The influence of the acids on the electrochemical characteristics of the final products is compared in terms of the number, *n*, of –(CH₂)– groups between the two carboxylic acid groups in their formulae. Additionally, some related work on $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ prepared with citric, maleic and tartaric acids as chelating agents is also reviewed.

2. Experimental

Layered LiNi_{0.8}Co_{0.2}O₂ products were synthesized by a sol-gel procedure. Stoichiometric amounts of the nitrates of the cations were dissolved separately in a minimum volume of ethanol. A solution of the required dicarboxylic acid in ethanol was gradually added to the solutions with constant stirring such that the acid-to-total cations molar ratio was 1. The initial pH of the mixture was found to be in the 0.05-1.58 range. The pH value was found to vary nearly linearly with the pK_{a1} values of the acids (oxalic: pK_{a1} 1.23, pH 0.05; malonic: pK_{a1} 2.83, pH 0.51; succinic: pK_{a1} 4.16, pH 1.10; adipic: pK_{a1} 4.43, pH 1.29; suberic: pK_{a1} 4.52, pH 1.45). The mixture upon stirring turned into a viscous 'sol', which on heating gently at 80 °C resulted in the formation of a 'gel', with the evaporation of ethanol. The gelly mass was dried at 120 °C to obtain the precursor. The dried mass was then calcined in flowing oxygen at 600, 700 and 800 °C,

for varying durations. In order to compare solvent effect on the electrochemical behavior of the products, the solutions of the reactants were similarly prepared in other solvents. The effect, if any, of the variation of the initial pH on the product characteristics was also examined. For this purpose, the pH of the precursor was adjusted to convenient values with the addition of ammonia.

Thermogravimetric and differential thermal analyses of the gel precursor in static air were carried out on a Seiko SSC-5000 TG/DTA/DSC/TMA analyzer at a heating ramp of 10 °C/min. Structural characteristics of the products were examined by an X-ray diffractometer (Siemens D-5000 MAC Science MXP18) equipped with a nickel-filtered Cu K α radiation source between scattering angles of 20 and 80° in increments of 0.05°. The charge–discharge characteristics of the LiNi_{0.8}Co_{0.2}O₂ products were studied in standard 2032-type stainless steel coin cells, with an electrolyte of 1 M LiPF₆ in 1:1 (v/v) EC–DEC (Tomiyama Chemicals), and lithium metal as the anode. Cell cycling was carried out at a 0.1 C rate between 3.0 and 4.2 V by a 48-channel Maccor Series 4000 battery tester.

3. Results and discussion

3.1. Thermal analysis

The thermograms and the corresponding differential thermograms of the different precursor samples derived from ethanolic solutions are shown in Fig. 1. The weight loss below 150 °C is due to the evaporation of superficial ethanol and moisture in the gel precursors. Major thermal events set in after about 250 °C, with further weight losses up to 500 °C, beyond which there is hardly any discernible change in the profiles. Although the crystal-building processes have been initiated in the temperature region between 350 and 500 °C, calcination at higher temperatures is essential to impart a degree of crystallinity favorable for good battery performance.

In the case of oxalic acid and malonic acid there is a thermal event in the vicinity of $250 \,^{\circ}$ C, attributable to the melting of LiNO₃ [41], accompanied by its decomposition [42]. The exothermic decomposition reactions between about 370 and 420 $\,^{\circ}$ C for the oxalate precursor, and between 260 and 350 $\,^{\circ}$ C for the malonate precursor are accompanied by major weight losses. This is attributable to the highly exothermic combustion reactions between the nitrates and the carboxylate moieties. The exothermicity of the combustion processes triggers the calcination of the oxide product [43–45]. The decomposition reaction can be represented, for example, for the oxalic acid-based precursor as follows:

$$\begin{aligned} \text{LiNO}_{3} + 0.8\text{Ni}(\text{NO}_{3})_{2} + 0.2\text{Co}(\text{NO}_{3})_{2} + 2\text{C}_{2}\text{H}_{2}\text{O}_{4} \\ + \frac{1}{2}\text{O}_{2} \rightarrow \text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_{2} + 4\text{CO}_{2} + 2\text{H}_{2}\text{O} + 3\text{NO}_{2} \end{aligned}$$



Fig. 1. TG and DTG curves of the different precursor samples derived from ethanolic solutions.

It can be deduced from the above equation that three extra oxygen molecules are required for the combustion reaction for every additional $-(CH_2)$ - unit in the carboxylic acid chain. Thus, as the value of *n* in the complexing dicarboxylic acid increases, the requirement of the external oxidant (oxygen) becomes higher. This is particularly significant because of the necessity of a highly oxidizing atmosphere to stabilize the Ni³⁺ state in LiNi_{0.8}Co_{0.2}O₂ [46]. A non-oxidizing atmosphere can lead to the formation of Li₂CO₃ and NiO [43]. According to Barboux et al. [43], Li₂CO₃ is stable towards NiO. The resistance to oxidation to the higher valence states as we move from the left to the right in the first row transition metals is manifested in the difficulty in stabilizing the Ni³⁺ state in LiNiO₂. While Co³⁺ is formed as a stable ion in LiCoO₂ during combustion in air, the formation of LiNiO₂ needs the reaction to be performed under flowing oxygen. Thus, as the *n* value is increased, the partial pressure of oxygen needs to be higher in order to burn away the organic moieties as well as to provide a sufficiently oxidizing atmosphere for the formation of Ni³⁺.

Curiously, the differential thermograms of the precursors derived from succinic, adipic, suberic and sebacic acids showed only minor dips corresponding to the melting and subsequent decomposition of LiNO₃. However, all the dicarboxylic acids displayed sharp peaks corresponding to the final decomposition processes. Barring the case with oxalic acid, the temperature at which this peak appeared increased linearly with the *n* value (Fig. 2). This possibly suggests that



Fig. 2. Variation of the temperature of decomposition of the precursor with n.

the nitrate-aided oxidation-decomposition of the dicarboxylate complexes became increasingly difficult as the chain length increased.

According to Tsumura et al. [45], the structure of the lithium-transition metal carboxylate formed by the bidentate acid ligand determines its decomposition pattern. According to the authors [45], the structure of the dicarboxylate complex is possibly determined by the size of the ring, which is formed by the coordinating acid. The authors [45] suggest that the oxalic acid molecule is too short that the formation of a ring-like coordination with the metal ion would involve much strain in its structure. Therefore, oxalic acid may form a linear complex such as

$$Li-O-C(=O)-C(=O)-O-M-O-C(=O)-C(=O)-O-H$$
,

where M is Co or Ni. However, malonic acid may be a suitable configuration for bending to coordinate as a bidentate [45]. The highly stable ring of the anhydrous form of succinic acid suggests that it is possible to bend this molecule to provide a bidentate coordination through a ring structure as shown below.



The strong bonding provided by these carboxylic acids must result in higher decomposition temperatures for their complexes. Going to the higher *n* values, the strain involved in bending the long molecules for a double coordination may reduce. However, because the dissociablity of the acid, as reflected by its pK_a values, decreases as the chain length increases, the ionization of the carboxylic groups, and the subsequent bonding with the cations, may be expected to become progressively weaker.

According to Carewska et al. [47], lithium when present as an acetate goes through the Li₂CO₃ stage before reacting with cobalt oxides to produce LiCoO₂. However, when both lithium and cobalt are present in the form of acetates in the precursor, the mixture decomposes into thermal intermediates that readily react at low temperatures to yield LiCoO2 [47]. In our case, the carboxylate mixtures could decompose into several intermediates, their decomposition aided by the nitrate ions. The several steps in the thermograms and differential thermograms (Fig. 1) indicate the formation of such intermediates. Carewska et al. [47] also report several such steps in their thermal analytical patterns of mixtures of lithium and cobalt acetates. Lundblad and Bergman [48] and Ramesh Babu et al. [49] have discussed the reaction mechanisms in the formation of LiCoO₂ and LiNi_vCo_{1-v}O₂, respectively, from carbonate precursors. In accordance with the general conclusions arrived at by these authors [47–49], the following decomposition scheme is suggested. Succinic acid is chosen as an example, and, for simplicity, the reactions are shown as those for the individual metal carboxylates:

Li–O–C(=O)–(CH₂)–(CH₂)–C(=O)–O–Li +
$$\frac{1}{2}$$
O₂
→ Li₂CO₃ + 3CO₂ + 2H₂O

$$O = C \underbrace{CH_2 - CH_2}_{M} C = O + (3 + \frac{1}{2}x)O_2$$

$$\rightarrow MO_x + 4CO_2 + 2H_2O$$

where the oxide product is Co_3O_4 when M = Co, and NiO when M=Ni. Thus, finely divided Co_3O_4 and NiO in Li_2CO_3 is obtained, which subsequently turn partially into the metal oxides with interstitial Li_2O [48]. The final step of formation of the product involves the reaction between Li_2CO_3 and the transition metal oxides with the interstitial Li_2O [48], which may be represented by the reaction

$$\begin{split} & [0.5\text{Li}_2\text{O}-2.4\text{NiO}-0.2\text{Co}_3\text{O}_4] + \text{Li}_2\text{CO}_3 + 0.65\text{O}_2 \\ & \rightarrow 3\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2 + \text{CO}_2 \end{split}$$

where the composition in the square brackets represents the transition metal oxides with the interstitial lithium oxide.

3.2. X-ray diffraction studies

XRD patterns of the products synthesized at 600, 700 and 800 °C (12 h calcination) from an oxalate precursor are presented in Fig. 3 [50]. The patterns show that the products are iso-structural with α -NaFeO₂ (space group: $R\bar{3}m$) [51] The XRD pattern of the 600 °C-product shows broad peaks, suggesting a low degree of crystallinity as well as small particle size of the products. The XRD pattern is well defined at 800 °C, at which the hexagonal doublets (006)/(102) and (108)/(110) show a clear splitting, indicating a high degree



Fig. 3. Powder X-ray diffraction patterns of $LiNi_{0.8}Co_{0.2}O_2$ synthesized by a 12h calcination at different temperatures from an oxalate precursor: (a) 600 °C; (b) 700 °C; (c) 800 °C.

of crystallinity and good hexagonal ordering. According to Dahn and coworkers [52], the *R* value, 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. According to these authors [52], the lower the *R* value, the better the hexagonal ordering. The *R* values of the products obtained at 600, 700 and 800 °C were 0.87, 0.55 and 0.48, respectively, suggesting that the 600 °C product did not have a completely ordered layered structure, while the 800 °C product had good hexagonal ordering.

Furthermore, the intensities of the (003) reflections were higher than those of the corresponding (104) reflections [50], indicating that these samples had good cation ordering [53]. The good cation ordering is also evident from the well-separated (108) and (110) reflections [53,54]. It was shown [50] that the c/a ratio also generally increased with an increase in temperature. For the product heat-treated at 600 °C, the *c/a* value was 4.81, suggesting that cation mixing was considerable in the two-dimensional lattice [55,56]. However, the samples heat-treated at 700 and 800 °C gave *c/a* values of 4.89 and 4.86, respectively. It must be mentioned here that a *c/a* value of 4.95–4.96 range is expected for a two-dimensional layered structure [20,55,56].

Similarly, an increase in the duration of calcination was shown to improve the ordering of the lattice [50]. The *R* values for the products obtained by an 800 °C-calcination for 6, 12 and 24 h were 0.51, 0.48 and 0.49, respectively. This ordering is crucial in determining the ease with which the topotactic charge–discharge processes occur. Thus, the optimized heat treatment protocol for the synthesis of LiNi_{0.8}Co_{0.2}O₂ from the oxalic acid precursor was determined to be calcination at 800 °C for 12 h. This was the case with the other dicarboxylic acids also.

Table 1									
Lattice and structural	parameters of th	ne various	products	synthesized	by a	12 h	calcination	at	800 °C

Complexing agent		c (Å)	a (Å)	c/a	I_{003}/I_{104}	R parameter	
Oxalic acid	НООС-СООН	14.228	2.928	4.86	1.15	0.49	
Malonic acid	HOOC-CH2-COOH	14.113	2.910	4.85	1.23	0.49	
Succinic acid	HOOC-(CH ₂) ₂ -COOH	14.215	2.925	4.86	1.21	0.47	
Adipic acid	HOOC-(CH ₂) ₄ -COOH	14.363	2.937	4.89	1.28	0.45	
Suberic acid	HOOC-(CH ₂) ₆ -COOH	14.375	2.922	4.92	1.30	0.46	
Sebacic acid	HOOC-(CH ₂) ₈ -COOH	14.313	2.915	4.91	1.33	0.47	

Table 1 shows that the c/a ratio increased with n. This indicates a preferential expansion of the lattice in the *c*-direction as the *n* value is increased. However, beyond n = 6, the value of c/a dropped slightly. The increase in the value of the I_{003}/I_{104} ratio with n suggests that all the products had not only better cation ordering [53], but also that the cation ordering improved with n. It was noted (Fig. 2) that the decomposition temperature generally increased with n. Thus, it is possible that the higher decomposition temperature of the metal-dicarboxylic acid complex triggered an initial crystallization process in the products, conferring on them greater ordering. According to Dahn et al. [57] the unit cell volume of $Li_rNi_{2-r}O_2$ is the lowest for the ideal layered LiNiO₂. In the present study, the unit cell volumes were smaller for the products derived from acids with n > 2 (Table 1). The minimum unit cell volume was obtained for the product derived from the adipic acid complex. The low levels of cation mixing, as indicated by the high integrated intensity ratio I_{003}/I_{104} , and the better layered nature of the products, as revealed by the low unit cell volumes, suggest that the products obtained with dicarboxylic acids with n > 2 would be structurally beneficial for electrochemical applications. All the products had R values below 0.5, indicating good hexagonal ordering of their lattices. However, the lowest R value of 0.45 was obtained for the product derived with adipic acid. Thus, based on the structural parameters, it appears that the product derived from the adipic acid-complexed precursor should display the best electrochemical properties.

3.3. Charge-discharge studies

The charge–discharge curves of the LiNi_{0.8}Co_{0.2}O₂ product obtained from an oxalate precursor (800 °C, 12 h) are shown in Fig. 4. The monotonous nature of the discharge plateau in the 3.4 to 3.6 V region signifies that only the nickel ions undergo redox reactions in the battery cycling range [58] according to

$$\begin{aligned} \text{Li}[\text{Ni}_{0.8}^{3+}\text{Co}_{0.2}^{3+}] \text{ O}_2 \\ \leftrightarrow \Box_{0.6}\text{Li}_{0.4}[\text{Ni}_{0.2}^{3+}\text{Ni}_{0.6}^{4+}\text{Co}_{0.2}^{3+}]\text{ O}_2 + 0.6\text{Li}^+ + 0.6\text{e}^- \end{aligned}$$

The first-cycle discharge capacities of the 12 h-calcined oxalate-derived products were 57, 155 and 163 mAh/g, respectively, for calcination temperatures of 600, 700 and $800 \degree C$ [50]. The improvement in the electrochemical prop-



Fig. 4. A typical charge–discharge curve of the LiNi_{0.8}Co_{0.2}O₂ product obtained from an oxalate precursor. Calcination conditions: 800 °C, 12h.

erties with calcination temperature is attributed to increased hexagonal ordering of the 3b transition metal ion and 3a lithium ion sites, as substantiated by our XRD results.

The variation in the first-cycle capacity of the 800 °C for 12 h calcined products as a function of *n* is shown in Fig. 5. It can be seen that the first-cycle capacity was the highest for the product derived from an adipic acid-based precur-



Fig. 5. Variation in the first-cycle discharge capacity of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as a function of *n*. Calcination conditions: 800 °C, 12 h.

sor. From a value of 163 mAh/g for n = 0, the capacity value increases to 178 mAh/g for the adipic acid-based product (n = 4), and then drops to 163 mAh/g for n = 8. The excellent performance of the adipic acid-based product is in agreement with our structural data, which show the best hexagonal ordering for this product. The cycling behavior of the 800 °C for 12 h calcined products showed that those derived with succinic, adipic and suberic acids yielded the highest capacities. Incidentally, these products had the lowest R values. Although the adipate-derived product gave the highest first-cycle capacity, cycling data indicated a superior performance for the suberic acid-based product. Therefore, in general the suberic acid-based product with low values for the R parameter and unit cell volume, and high values for the c/a and I_{003}/I_{104} ratios gives the best electrochemical performance. This is reflected in its high first-cycle capacity of 174 mAh/g and a charge retention of 98.3% in the 10th cycle.

3.4. Effect of solvent

Solvents other than water have been employed for solution synthesis of inorganic oxides [59–61]. In our studies we investigated the effect of different solvents in the solution synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The effect of solvents on the discharge behavior of the products obtained from an adipate precursor is shown in Fig. 6. Ethanol gave a product with the best performance, while water gave one with the worst performance: the first and tenth-cycle discharge capacities of the former were 178 and 166 mAh/g, respectively, those for the latter were 142 and 86 mAh/g. The capacity fade of the aqueous precursor-based product were also steeper: the capacity fade over 10 cycles being 39.5% as compared to just 6.7% for the ethanol-based product. Products with



Fig. 6. Effect of solvent on the cycling behavior of $LiNi_{0.8}Co_{0.2}O_2$ derived from an adipate precursor. Calcination conditions: 800 °C, 12 h.

intermediate performance were obtained with methanol and 2-propanol.

Recently, we demonstrated the inferior performance of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ derived from an aqueous maleic acid-complexed precursor as compared to products derived from solutions made in ethanol, 1-propanol and 1-butanol [32]. A similar trend was noted with precursors with other dicarboxylic acids too. For example, the initial discharge capacities of the products derived from ethanolic and aqueous solutions of malonate precursors [35] were 173 and 168 mAh/g, respectively. The corresponding values in the 10th cycle were 169 and 158 mAh/g [35].

Although a major participation of the solvent in the combustion process is ruled out, its role in coordinating with the cations cannot be discounted. The coordinated solvent molecules can be expected to participate in the combustion process and to provide local heat for the formation of the product. Solvents generally tend to donate electrons to cationic species (which act as Lewis acids). This tendency of solvents to donate electrons, called donicity, is expressed in terms of donor numbers [62]. The donor numbers of the solvents used in our study (Fig. 6) are: 2-propanol: 21.1; ethanol: 19.2; methanol: 19.1; water: 18.0. Thus, it appears that the tendency of the solvent molecules to bond with the cations is the highest for 2-propanol, and the least for water. However, the steric hindrance arising from the two flanking methyl groups in 2-propanol should result in diminished coordination/solvation. Thus, 2-propanol may only contribute less towards the combustion process. On the other hand, the presence of water molecules in the coordination sheath would, instead of fueling the decomposition reaction, impede the combustion process. Given the closeness of their donor numbers, both ethanol and methanol should produce similar coordinations with the cations. However, the higher fuel calorific value of ethanol as compared to that of methanol should ensure a product with improved structural and electrochemical properties for the ethanol-based precursor. Thus, the organic solvents, participating in the form of an additional coordination species, would yield precursors more amenable to combustion. Hence, it would appear that the use of a combustible solvent with high donicity and coordinating ability would facilitate a definitive design of the final product.

3.5. Effect of pH

It is known that the complexing ability of any acid-type ligand depends on the pH of the medium, which determines the dissociability of the ligand-laden molecule. The effect of the pH of the precursor solution on the product characteristics is illustrated for malonic acid in Fig. 7. The pH values of the aqueous precursor were fixed at 4, 7 and 9. Malonic acid is a dicarboxylic acid with dissociation constants of $pK_{a1} = 2.83$ and $pK_{a2} = 5.69$. Thus, at pH value of 4 with only one carboxylic acid group dissociated, the complexation process is just about half accomplished. On the other



Fig. 7. Effect of the pH of the precursor solution on the cycling behavior of $LiNi_{0.8}Co_{0.2}O_2$ derived from a malonate precursor. Calcination conditions: 800 °C, 12 h.

hand, at a pH value of 7 both the carboxylic acid groups have dissociated, enabling their availability for co-ordination with the metal ions. At pH 9, the dissociation equilibrium is shifted so far that no undissociated malonic acid should be available. However, the additional competition for coordination from the strong OH⁻ nucleophile renders coordination by the carboxylate ligands incomplete.

According to Kim et al. [63] LiCoO₂ prepared at pH 7 with malonic acid as the complexing agent showed excellent electrochemical behavior. Our results are in agreement with the results of Kim et al. [63]. As the pH was increased from 4 to 7, the first-cycle capacity slightly decreased from 157 to 153 mAh/g [35]. However, the corresponding 10th cycle capacities were 143 and 145 mAh/g. Thus, as the pH was increased, the charge retention in the 10th cycle was found to increase from 91.1 to 94.8%, in accordance with the fact that at a pH of 7 a more complete coordination with the carboxylic acid ensues. However, there was a drop in the capacity to 122 and 115 mAh/g, respectively, for the first and tenth cycles when the pH was raised to 9.

3.6. Other carboxylic acids as complexing agents

We also investigated the use of other carboxylic acids such as citric, maleic and tartaric acids as complexants in the sol-gel synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. We found that the temperature protocol for producing $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ with desirable performance characteristics was a 12 h calcination at 800 °C, the same as the optimal conditions for the dicarboxylic acids discussed above. Under these conditions, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ derived with maleic acid as the complexing agent delivered a first-cycle capacity of 190 mAh/g between 3.0 and 4.2 V at a 0.1 C rate [32]. This is the highest capacity reported so far for this material. However, the first-cycle capacities obtained with LiNi_{0.8}Co_{0.2}O₂ obtained from complexes of citric [34] and tartaric acids [64] were 176 and 174 mAh/g, respectively. In all the cases, the LiNi_{0.8}Co_{0.2}O₂ phases obtained under a 12h calcination at 800°C had the lowest R parameter values, suggesting the superior hexagonal ordering of their lattices. The charge-discharge behavior of the maleic acid-derived LiNi_{0.8}Co_{0.2}O₂ in electrolytes of 1 M LiPF₆ in mixtures of carbonate electrolytes—50:50 (v/v) EC:DEC, 50:50 (v/v) DEC:DMC, 50:50 (v/v) PC:DMC, and 35:15:50 (v/v) EC:DEC:DMC-showed that the best performance was obtained in the electrolyte based on EC-DEC [65]. Although the electrochemical impedance response of the cell was independent of the electrolyte, it was suggested that the variation in the performance had to do with ester exchange reactions between the carbonate esters [66,67], which would dictate the characteristics of the passive film formed on the cathode surface.

Other LiNi_yCo_{1-y}O₂ phases (y = 0.1 and 0.3) were also investigated. Here again, the capacities were commensurate with the values of the *R* parameter. For example, the values of the *R* parameter for LiNi_yCo_{1-y}O₂ phases obtained by a citric acid-assisted sol-gel process were 0.60, 0.49 and 0.61 for y = 0.3, 0.2 and 0.1, respectively [34]. The first-cycle capacities of the respective phases were 159, 176 and 140 mAh/g [34]. It is pertinent to note that according to Cho [68], in the entire solid solution range LiNi_yCo_{1-y}O₂ the phase with y = 0.26 was identified as the best-performing composition.

The effect of doping $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ was also studied. The best results were obtained with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ doped with Sr^{2+} [34]. At a dopant level of $\text{Sr}^{2+}/\text{Li}^+ = 10^{-3}$, the first-cycle capacity was 187 mAh/g for a material obtained with citric acid as the complexing acid. The capacity faded to 183 mAh/g in the 10th cycle, registering a capacity fade of only 2% in 10 cycles. This is a definite improvement over the undoped material, which gave 176 mAh/g in the first cycle but faded by as much as 6% by the 10th cycle. The beneficial effect of the dopant was explained by a defect model proposed by Van der Ven and Ceder [69,70].

4. Conclusions

The dicarboxylic acid-aided sol-gel process provides a simple soft chemistry route for the elaboration of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$. The decomposition temperature of the dicarboxylate precursors was found to increase linearly with the number, *n*, of -(CH₂)- groups in the dicarboxylic acid. A possible mechanism involving an intermediate of the transition metal oxides with interstitial Li₂O is presented. XRD results suggested that the 800 °C for 12 h calcined samples from dicarboxylic acid complexes with *n* > 2 would be structurally beneficial for electrochemical applications. Charge–discharge studies showed that the adipate-derived product gave the highest first-cycle capacity (178 mAh/g), although cycling data indicate a superior performance for the product derived from the suberic acid complex. We also conclude that organic solvents, participating in the form of an additional coordination species, would yield precursors more amenable to combustion. Products with well-defined characteristics are obtained at such pH values at which both the carboxylic acid moieties are free to coordinate with the cations, free from other competing nucleophiles. Studies with the various carboxylic acid as a complexing agent gave a first-cycle capacity of 190 mAh/g between 3.0 and 4.2 V at a 0.1 C rate, which is the highest capacity reported so far for LiNi_{0.8}Co_{0.2}O₂.

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