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Characteristics of LiMO₂ ($M = Co, Ni, Ni_{0.2}Co_{0.8}, Ni_{0.8}Co_{0.2}$) powders prepared from solution of their acetates

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Abstract

Stoichiometric quantities of the acetates of lithium, cobalt and nickel were dissolved in distilled water and stirred with a magnetic stirrer. After complete dissolution was obtained, the solutions were heated at $120 \,^{\circ}$ C under continuous stirring until some dark colored powder materials were formed. These precursor materials were divided into three batches and heated at $250 \,^{\circ}$ C (for 24 h), $370 \,^{\circ}$ C (for 24 h) and $800 \,^{\circ}$ C for 10 h. The precursor and calcined samples were X-rayed. The X-ray diffractograms for the prepared samples were compared to that of commercialized samples and those published in the literature. The Bragg peak with Miller indices (003) in the diffractogram of the LiNi_{0.8}Co_{0.2}O₂ prepared sample showed a lower intensity compared to the (104) peak. The ratio of the (003) to (104) peaks for the LiNi_{0.2}Co_{0.8}O₂ sample is 1.56. Lattice parameters showed that the LiCoO₂ and LiNi_{0.2}Co_{0.8}O₂ samples produced by the method in the present investigation have potential to exhibit good electrochemical performance when used as electrodes in lithium ion batteries.

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1. Introduction

The compounds $\text{LiNi}_x \text{Co}_{1-x} \text{O}_2$ (0<*x*<1) have been suggested as possible alternative cathode active materials to replace LiCoO_2 in lithium ion batteries [1–4]. These compounds have a rhombohedral structure with the *R3m* space group [5]. $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, for example, has shown high discharge capacity and good reversibility [6]. A lot of reports have shown that these compounds can be prepared by the methods of chemical solution [7,8], solid-state reaction [9,10] and solution combustion [11]. Materials produced by the solid-state reaction method have irregular morphology and broader particle size distribution. Compounds prepared through chemical solutions have shown improved solid-state structures and smaller particle size [9].

The present work aims to synthesize $\text{LiNi}_x \text{Co}_{1-x} \text{O}_2$ (*x*=0, 0.2, 0.8 and 1) through a carboxylate precursor in air, without the use of chelating agents and to determine their characteristics at different calcination temperatures and times.

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2. Experimental

The preparation of $\text{LiNi}_x \text{Co}_{1-x} \text{O}_2$ (x=0, 0.2, 0.8 and 1) powder through a carboxylate precursor is schematically shown in Fig. 1. For the formation of LiCoO₂ and LiNiO₂, the mole ratio of lithium acetate dihydrate to cobalt acetate tetrahydrate and that of lithium acetate dehydrate to nickel acetate tetrahydrate is 1:1.

Many publications report obtaining the desired product at a calcination temperature of 700–800 °C and for a calcination time of about 10 h [8,12]. By preparing the materials at several calcination temperatures, the evolutionary stages of the material formation may be understood. X-ray diffraction (XRD) was carried out using the X-ray Phillip Expert System. The X-ray wavelength was 1.5406 Å.

3. Results and discussion

The diffractograms of the uncalcined and calcined precursors for the preparation of LiCoO₂ are presented in Fig. 2. The peaks attributable to the (003), (101) and (104) planes at $2\theta \sim 19^{\circ}$, 37° and 45° , respectively, are present in all diffractograms. The diffractograms show how the intensity of the (003), (101) and (104) peaks varies with calcination temperature. The (006) peak at $2\theta \sim 38^{\circ}$ and (102) peak at $2\theta \sim 39^{\circ}$ are already obvious in the diffractogram of the precursor calcined at 370° C. Peaks at $2\theta \sim 30^{\circ}-32^{\circ}$ may be attributed to Li₂CO₃ The intensity of

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Fig. 1. Flow chart showing sample preparation.

the peaks at (003), (101) and (104) in the diffractogram of the precursor calcined at 800 °C varies in the same way as the peaks in the diffractogram of commercially procured LiCoO₂. Table 1 lists the peaks observed in the diffractograms of the prepared and procured LiCoO₂ materials.

It can be deduced from the table that LiCoO₂ is formed after calcination of the precursor in air at 800 °C for 10 h without the use of a chelating agent. There are some unidentified peaks at $2\theta \sim 44^{\circ}$ and 64° . Table 2 lists the properties of the materials obtained from the analysis of the diffractogram in Fig. 2(d). The values of unit cell dimensions *a* and *c* were calculated using the structural relationship between hexagonal and monoclinic structure.

The lattice parameter, R is a measure of the degree of lattice disorder. R is given by

$$R = \frac{I_{(1\,0\,2)} + I_{(0\,0\,6)}}{I_{(1\,0\,1)}} \tag{1}$$

and the lattice ordering from

$$y = 1.073 - 0.228R + 0.039R^2 \tag{2}$$

The integrated intensity ratio of the (003) to (104) peaks, I_{003}/I_{104} , indicates that the prepared LiCoO₂ sample have good electrochemical potential and hexagonal ordering.



Fig. 2. X-ray diffraction of precursor for LiCoO₂ preparation (a) after drying by heating at 120 °C and after calcination at (b) 250 °C for 24 h, (c) 370 °C for 24 h and (d) 800 °C for 10 h.

Fig. 3 depicts diffractograms for LiNiO₂ preparation. At 250 °C, peaks due to Li₂CO₃ and NiO [8] are observed. Li₂CO₃ is represented by peaks at $2\theta \sim 21^{\circ}$, 23.5°, 30°, 32°, 34°, 40° and 52°. The NiO peaks are marked on the diffractogram, Fig. 3(b). NiO and Li₂CO₃ peaks are also observed in Fig. 3(c). Fig. 3(d) shows peaks that can be assigned to LiNiO₂, but the intensity of the peaks do not follow the trend as shown in the diffractogram reported in [8]. Bragg peaks with Miller indices (105), (107), (113) and the doublets (201)/(116) were not observed.

Table 1	
2θ peaks from samples in the present	work and that procured commercially

Sample	2θ peak al	2θ peak along the (<i>h k l</i>) planes										
	(003)	(101)	(006)	(102)	(104)	(105)	(009)	(108)	(110)	(113)		
LiCoO2 ^a	19.00 18.90	37.48 37.44	38.44 38.40	39.16 39.05	45.28 45.10	49.52 49.50	59.68 59.50	64.58 65.20	66.40 66.24	69.76 69.60		

^a Commercial grade LiCoO₂.

^b Prepared LiCoO₂.

c/a

5.20

LiCoO ₂ ^b	2.71	14.07	5.19	103.27
^a Commercial ^b Present worl	samples. k.			
	1 i .			In soluti
MMM	Mull Munh home	Manundalin	with many the	LiOAc ·
(a) ¹⁵ 20	25 30 35 40	45 50 55 60	65 70 75	$\Rightarrow xI$
	NiO NiO			+ $\left(\frac{1}{2}\right)$
ł		Ni	O NiO	On heati
(b) 15 20	25 30 35 40	45 50 55 60	65 70 75	xLiOH -
(6)				\times Ni(OA
(c) ¹⁵ 20	A 25 30 35 40	45 50 55 60	AA 65 70 75	These different of to 800 °C LiNiO ₂ . 7 (104) and
	(006) (102 I	(104))8) (110) I	disorderin to the ele ilar diffra reported i

с

14.00

Lattice parameters of the $\ensuremath{\text{LiCoO}_2}$

Axis length (Å)

а

2.69



Fig. 3. X-ray diffraction of precursor for LiNiO₂ preparation (a) after drying by heating at 120 °C and after calcination at (b) 250 °C for 24 h, (c) 370 °C for 24 h and (d) 800 °C for 10 h.

The existence of the Li₂CO₃ and NiO peaks indicates the decomposition of lithium acetate dehydrate and nickel acetate tetrahydrate. In solution form, a portion of these chemicals could have reacted to form LiOH and Ni(OH)₂ as shown below:

olution form,

 $V(Å^3)$

101.66

LiOAc · 2H₂O + Ni(OAc)₂ · 4H₂O

$$\Rightarrow x \text{LiOH} + (1 - x) \text{LiOAc} + \left(\frac{1 - x}{2}\right) \text{Ni(OH)}_2$$

$$+ \left(\frac{1 + x}{2}\right) \text{Ni(OAc)} + 5\text{H}_2\text{O(g)}$$

R

0.499

0.423

v

0.969

0.983

 I_{003}/I_{104}

(113)68.89

69.50

2.34

1.43

heating at 120°C,

$$x\text{LiOH} + (1 - x)\text{LiOAc} + \left(\frac{1 - x}{2}\right)\text{Ni(OH)}_2 + \left(\frac{1 + x}{2}\right)$$
$$\times \text{Ni(OAc)} \Rightarrow \frac{1}{2}\text{Li}_2\text{CO}_3 + \text{NiO} + \text{gases}$$

nese reactions have already been suggested in [13] under ent conditions. As the calcination temperature is increased 0°C, lithium carbonate and nickel oxide reacts to form O_2 . The peaks with the highest intensity are the (003),) and (101) peaks and are in that order [8,9,13] otherwise dering due to cationic mixing occurs, which is detrimental e electrochemical performance of the electrode. A simliffraction pattern to that of the present work has been ted in [12]. In that report, LiNO₃ and Ni(NO₃)₂·6H₂O were the active compounds used with glycol as the chelating agent. They have also performed flame atomic absorption spectroscopy and obtained the formula for lithium nickelate as Li_{0.86}NiO₂.

The attempt to produce good LiNi_{0.8}Co_{0.2}O₂ was not quite successful. After calcination at 800 °C for 10 h in air only Bragg peaks with Miller indices (003), (101) and (104) were observed. The I_{003}/I_{104} ratio signals poor electrochemical performance if used as an electrode material. The diffractogram of the precursor calcined at 250 and 370 °C for the preparation of LiNi_{0.2}Co_{0.8}O₂ show peaks attributable to Li₂CO₃ and NiO. After heating at 800 °C for 10 h in air, peaks attributable to LiNi_{0.2}Co_{0.8}O₂ can be observed, Fig. 4.

$\frac{2\theta}{\text{Sample}}$ peaks from diffra	$\frac{1}{2\theta \text{ along the } (h k l) \text{ planes}}$										
	(003)	(101)	(006)	(102)	(104)	(105)	(009)	(108)	(110		
LiNio 2Coo 8O2 ^a	18.89	36.67	_	38.89	45.56	48.89	60.00	64.44	65.56		

38.82

45.00

49.12

59.38

65.03

66.12

^a 2θ angles estimated from ref. [14]. For (006) plane, could not determine.

37.06

38.24

18.82

^b Present work.

LiNi_{0.2}Co_{0.8}O₂^b

Table 3

Sample

LiCoO2^a

Table 4	
Lattice parameters for LiNi0.2Co0.8O2	

Sample	Axis length	Axis length (Å)		$V(Å^3)$	R	у	I ₀₀₃ /I ₁₀₄
	a	С					
LiNi _{0.2} Co _{0.8} O ₂ ^a	2.835	14.098	4.973	113.309	_	_	1.51
LiNi _{0.2} Co _{0.8} O ₂ ^b	2.72	14.13	5.2	104.58	0.448	0.979	1.56

^a Taken from ref. [14].

^b Present work.



Fig. 4. X-ray diffraction of precursor for preparation of $LiN_{10.2}Co_{0.8}O_2$ (a) after drying by heating at $120 \degree C$ and after calcination at (b) $250 \degree C$ for 24 h, (c) $370 \degree C$ for 24 h and (d) $800 \degree C$ for 10 h.

Table 3 lists the peaks obtained from the X-ray diffractograms of the prepared samples and from the literature [14].

It is obvious that the X-ray diffractograms of the prepared samples match that of [14]. From the table it can be deduced that the sample produced after calcinations at 800 °C for 10 h in air is $LiNi_{0.2}Co_{0.8}O_2$. Table 4 lists the lattice parameters for $LiNi_{0.2}Co_{0.8}O_2$.

The I_{003}/I_{104} ratio is greater than 1.2 and the (006)/(102) and (008)/(110) reflections are well separated. Thus the LiNi_{0.2}Co_{0.8}O₂ sample produced has good cation ordering.

Hence topotactic charge–discharge processes can occur with ease and the material should exhibit good electrochemical performance as an electrode material.

4. Conclusions

The method used to prepare the samples in the present work bypasses the gel stage by not using any chelating agent. The LiCoO₂ and LiNi_{0.2}Co_{0.8}O₂ compounds prepared have good cation ordering that is also evident from the (006)/(102) and (008)/(110) separations. Hence, these materials should allow intercalation and de-intercalation of lithium ions to occur with ease during the charge–discharge processes and exhibit high discharge capacity and good reversibility when used as the cathode active material in lithium ion batteries.

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