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Short communication

Hydrothermal synthesis of $LiNi_{0.9}Co_{0.1}O_2$ cathode materials

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Abstract

Ultrafine powders of $LiNi_{0.9}Co_{0.1}O_2$ were prepared under mild hydrothermal conditions. The product was characterized by XRD, TEM and EDS tests, which indicated that the obtained products were pure and well-crystallized $LiNi_{0.9}Co_{0.1}O_2$. The ICP-AES results indicated the products were lithium-deficient compounds. The addition of KOH hardly effected the crystallinity of the product but gave larger crystals.

Keywords: Hydrothermal synthesis; $LiNi_{0.9}Co_{0.1}O_2$; Cathode materials

1. Introduction

Lithium cobalt oxide ($LiCoO_2$) has been used as a cathode material in the majority of commercial lithium batteries due to its excellent electrochemical properties, such as high output voltage, long cycle life, good thermal and structural stability and easy preparation [1]. However, this material suffers from high cost, toxicity and relatively low practical capacity (about 140 mAh/g, around half of its theoretical capacity), which limits its further application. Intensive research for new cathode materials has been devoted in recent years [2,3]. One of the most promising candidates to replace the actually commercialized $LiCoO_2$ is the layered $LiNi_{1-y}Co_yO_2$ ($0 < y < 1$) due to its less toxicity, lower cost and higher reversible capacity [4].

Conventionally, $LiNi_{1-y}Co_yO_2$ is prepared by a solid-state route, which requires high calcining temperature and prolonged calcining time [5,6]. Alternate routes have been explored to overcome these shortcomings, such as acid dissolution method, sol–gel method and co-precipitation method, etc. [7–9]. However, few of them have successfully reduced the calcination time less than 10 h with high performance. Futhermore, they contain multi-step and time-consuming processes to prepare precursors [10].

In this investigation, we report a novel route to synthesis of $LiNi_{0.9}Co_{0.1}O_2$ powders via the mild hydrothermal method which does not need troublesome processes such as preparation of precursors and heat treatments. Hydrothermal synthesis is being successfully utilized for complex coordinate compounds preparations, growth of large monocrystals, as well as nanocrystalline materials and films, etc. [11]. It is a simple and effective route for preparing functional materials.

2. Experimental

2.1. Preparation of the starting solution

The starting materials were analytical reagents: $LiOH{\cdot}H_2O$ (≥90%), $NiCl_2{\cdot}6H_2O$ (≥99.0%), $Co(NO_3)_2{\cdot}6H_2O$ (≥99.0%), KOH (≥82.0%), and NaClO (Cl wt% ≥10% solution). The hydrothermal synthesis process was carried out as follows. Firstly, a desired amount of $LiOH{\cdot}H_2O$ and KOH were added to distilled water to get lithium hydroxide and potassium hydroxide mixed aqueous solution. Ni(II)–Co(II) aqueous solution was prepared by dissolving $NiCl_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ in the molar ratio of Ni(II)/Co(II) = 9.0:1.0. Then Ni(II)–Co(II) aqueous solution was added dropwise under vigorous stirring to the lithium hydroxide and potassium hydroxide aqueous solution. After that, an appropriate amount of sodium hypochlorite was poured into it (Table 1). The molar ratio of Li/(Ni + Co) was varied from 10:1 to 50:1 for 4 M LiOH solution, respectively. The experiment conditions are shown in Table 1.

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Table 1
Hydrothermal experiment conditions in the present work.

	Starting Li/(Ni + Co)	Starting Li^+ (mol/L)	Starting KOH (mol/L)	Starting NaClO (mL)
Group 1	10	4	0	20
Group 2	20	4	0	20
Group 3	30	4	0	15
Group 4	50	4	0	10
Group 5	20	4	12.5	20
Group 6	50	4	12.5	10

2.2. Preparation of samples

The as-prepared starting suspension was rapidly poured into a Teflon-lined autoclave with 0.85 filling factor and sealed, hydrothermally treated at 220 °C for 10 h. After the sample was cooled, the black precipitate was washed with distilled water to remove unreacted lithium and potassium compounds. It was then dried at 80 °C for 3 h.

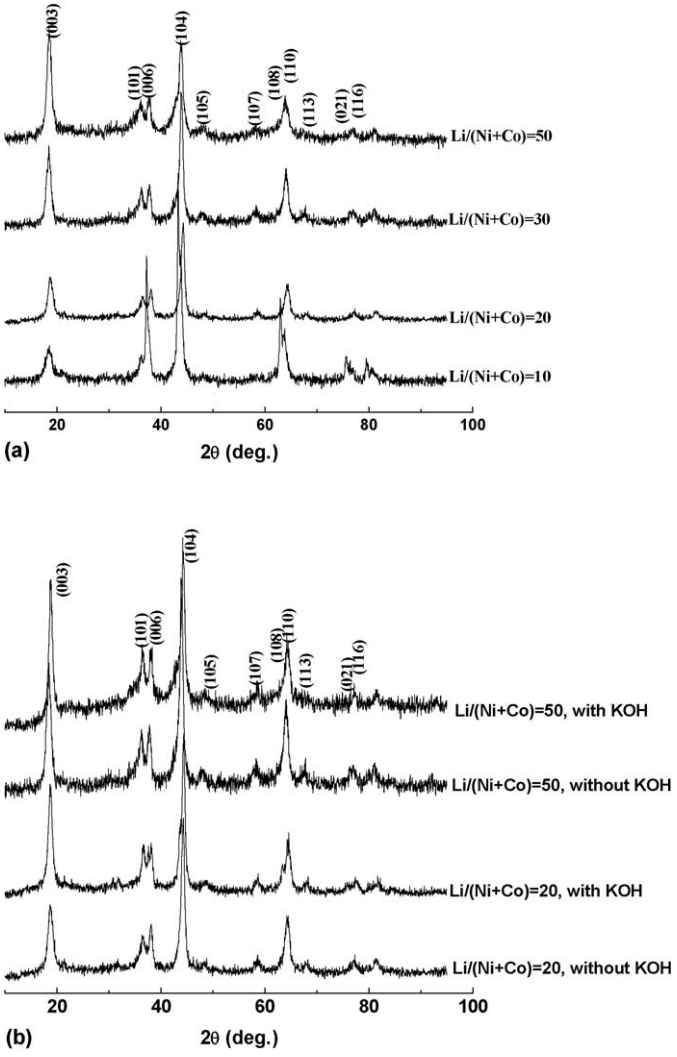


Fig. 1. (a) XRD patterns of $LiNi_{0.9}Co_{0.1}O_2$ powders from different starting Li/(Ni + Co). (b) XRD patterns of $LiNi_{0.9}Co_{0.1}O_2$ powders from different starting Li/(Ni + Co) and different starting KOH (mol/L).

2.3. Characterization

The crystalline phase, chemical composition and morphology were characterized by X-ray powder diffraction (XRD; Model D/max, Rigaku Co., Japan) with Cu Kα radiation (40 kV, 150 mA), energy dispersive X-ray spectroscopy (Oxford Instruments' INCA EDS system), atomic emission spectroscopy (IRIS 1000, Thermo Elemental, America) and transmission electron microscopy (TEM; Model JEM-840, JEOL Co, Japan), respectively.

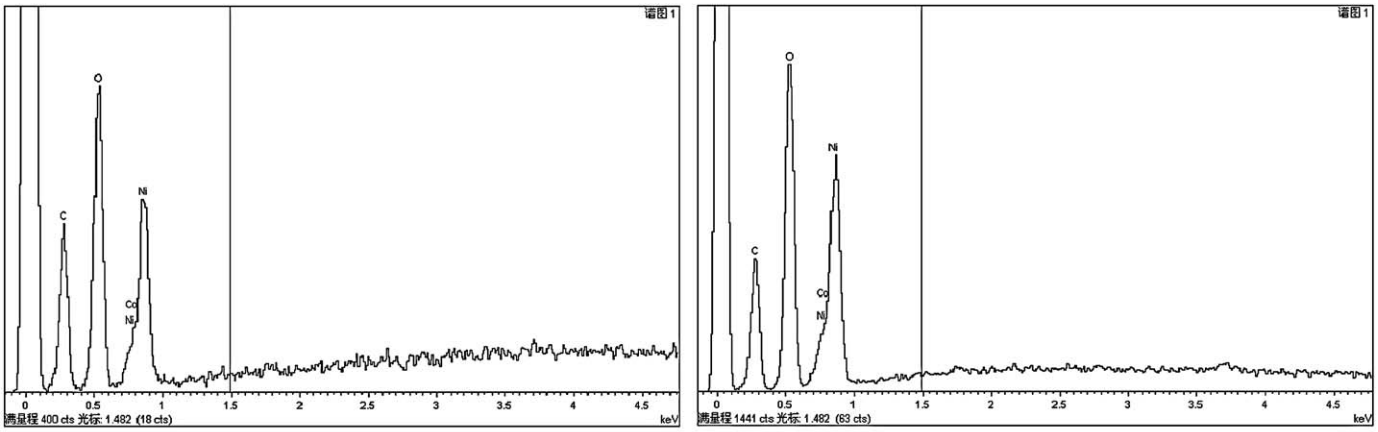
3. Results and discussions

Fig. 1 shows the XRD patterns of the as-prepared products. After 10 h hydrothermal treatment, the final products were all $LiNi_{0.9}Co_{0.1}O_2$ with almost identical XRD patterns. No other impurity phases were found. There was a good agreement with the reported results so far [10,12]. Diffraction peaks were narrow and sharp, index of well-crystallized powders. A relatively large increase in the I (0 0 3)/I (1 0 4) ratio was observed along with the Li/(Ni + Co) ratio rise (Fig. 1a). According to Gao et al. [13], an increase in the I (0 0 3)/I (1 0 4) ratio indicated that the sample had good cation ordering. The good cation ordering was also evident from the well-separated (1 0 8) and (1 1 0) reflections [14,15]. Fig. 1b showed that the addition of KOH hardly effected the crystallinity.

The EDS spectra of the synthesized powders in Fig. 2 show presence in the final products of Ni, Co, and O (Li could not be detected by EDS detector), and there were no other impurity peaks in the spectra except carbon, which derived by the striking of the conductive glue substrate by the electronic beam. The EDS results corresponded to the XRD results, further demonstrating that the final product was $LiNi_{0.9}Co_{0.1}O_2$.

The chemical composition of Li, Ni and Co was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and are listed in Table 2. The molar ratio for Li:Ni:Co of Group 4 and Group 6 is 7:9:1 and 5:9:1, respectively. The results indicated the obtained products were lithium-deficient compounds.

TEM images of the obtained powders (Group 4 and Group 6) are shown in Fig. 3. The obtained $LiNi_{0.9}Co_{0.1}O_2$ powders had a relatively homogeneous size with an average particle size of 10 nm. By comparison, the addition of KOH gave larger crystals.



(a) Ni:Co=25.28:2.96=8.54 (b) Ni:Co=39.23:4.28=9.16

Fig. 2. EDS of $LiNi_{0.9}Co_{0.1}O_2$ powders from different starting KOH (mol/L). (a) KOH (mol/L) = 0; (b) KOH (mol/L) = 12.5.

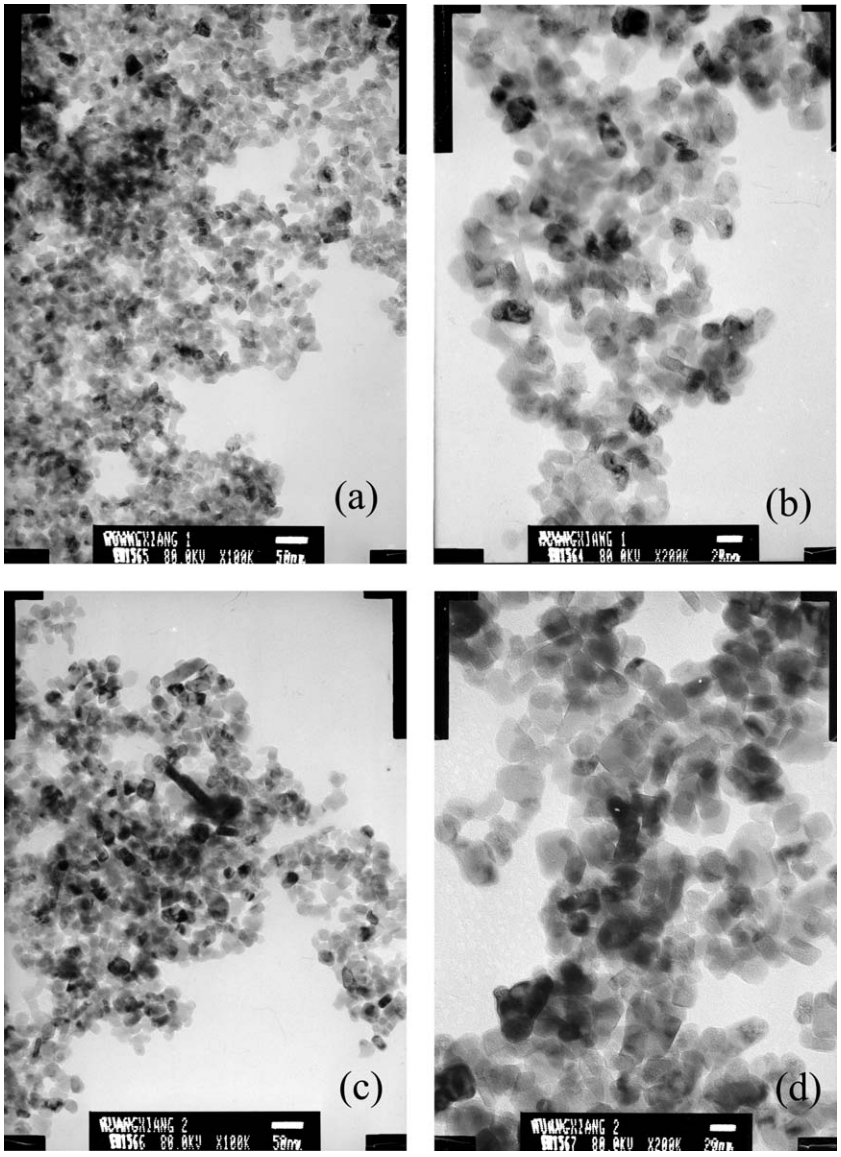


Fig. 3. TEM of $LiNi_{0.9}Co_{0.1}O_2$ powders from different starting KOH (mol/L). (a and b) KOH (mol/L) = 0; (c and d) KOH (mol/L) = 12.5.

Table 2
Elemental composition of the materials (expressed in mg/L).

Sample	Li (mg/L)	Ni (mg/L)	Co (mg/L)
Group 4	23	270	31
Group 6	27	450	49

4. Conclusions

Ultrafine powders of $LiNi_{0.9}Co_{0.1}O_2$ were successfully synthesized by hydrothermal method at 220 °C with the holding time 10 h. The XRD, EDS and TEM results indicated the product was pure and well-crystallized $LiNi_{0.9}Co_{0.1}O_2$ which had a relatively homogeneous size. The ICP-AES results suggested the product was lithium-deficient compounds. The I (0 0 3)/I (1 0 4) ratio increased with the Li/(Ni + Co) ratio indicated that the cation ordering of the sample $LiNi_{0.9}Co_{0.1}O_2$ got better and better. The addition of KOH hardly effected the crystallinity of the product but gave larger crystals.

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