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Short communication

Hydrothermal synthesis of $LiNi_xCo_{1-x}O_2$ cathode materials

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Abstract

Ultrafine powders of $LiCoO_2$, nonstoichiometric $LiNiO_2$ and $LiNi_{0.9}Co_{0.1}O_2$ were prepared under mild hydrothermal conditions. The influence of the molar ratio of Li/Co, Li/Ni and Li/(Ni + Co) was studied. The final products were investigated by XRD, TEM and EDS. To synthesize a stoichiometric $LiNiO_2$ under mild hydrothermal conditions was found to be a big challenge. Transmission electron microscopies (TEM) revealed the formation of well-crystallized $LiCoO_2$ and $LiNi_{0.9}Co_{0.1}O_2$ with average size of 100 nm and 10 nm, respectively.

Keywords: Hydrothermal synthesis; $LiNi_xCo_{1-x}O_2$; Cathode materials

1. Introduction

Recent achievements in the development of miniature portable electronic devices such as cellular phones, computers and camcorders require a new high-energy compact batteries. As compared with conventional systems, lithium rechargeable batteries exhibit higher energy density, higher voltage and longer shelf life [1].

$LiCoO_2$ remains one of the most attractive positive electrode materials for secondary lithium batteries due to its excellent electrochemical properties, such as high output voltage, long cycle life and easy preparation [2]. However, this material suffers from high cost, toxicity and relatively low practical capacity, which limits its further application [3,4]. $LiNiO_2$ appears to be one candidate as a cathode material because of the high-specific capacity and low cost. However, this material has poor cycle life and thermal instability and it is very difficult to synthesize a stoichiometric $LiNiO_2$ [5]. In an attempt to overcome the problems associated with $LiCoO_2$ and $LiNiO_2$, iso-structural solid solutions of $LiNi_xCo_{1-x}O_2$ have been studied for their excellent performances, such as lower cost, less toxicity and higher reversible capacity [6–12].

In this investigation, we report a novel route to synthesize $LiNi_xCo_{1-x}O_2$ via the mild hydrothermal method. It does not need troublesome processes such as preparation of precursors and subsequent heat treatments.

2. Experimental

2.1. Materials and process

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%), and NaClO (Cl wt% ≥10% solution). The hydrothermal synthesis process was carried out as follows. Firstly, a desired amount of $LiOH{\cdot}H_2O$ was added to distilled water to get lithium hydroxide aqueous solution. Co(II) aqueous solution was prepared by dissolving an appropriate amount of $Co(NO_3)_2{\cdot}6H_2O$. Then Co(II) aqueous solution was added dropwise under vigorous stirring to the lithium hydroxide aqueous solution. The molar ratio of Li/Co was varied from 10:1 to 50:1 for 4 M LiOH solution, respectively. Similarly, in order to synthesize $LiNiO_2$ and $LiNi_{0.9}Co_{0.1}O_2$, equal molar $LiOH{\cdot}H_2O$ and $NiCl_2{\cdot}6H_2O$ or mixture of $NiCl_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ (the molar ratio of Ni(II)/Co(II) = 9.0:1.0) were added to distilled water and went through the same process as described above. The experiment conditions were shown in the Table 1.

Reactant mixtures with different Li/Co, Li/Ni and Li/(Ni + Co) ratios were hydrothermally treated at 220 °C for 10 h in a Teflon-lined autoclave with 0.85 filling factor and presence of moderate sodium hypochlorite. After the sample was cooled, the precipitate was washed with distilled water

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Table 1
Hydrothermal experiment conditions of $LiNi_xCo_{1-x}O_2$.

	Li/Co	Li/Ni	Li/(Ni + Co)	NaClO (ml)	Li^+ (mol/L)
Group 1	10	10	10	20	4
Group 2	20	20	20	20	4
Group 3	30	30	30	15	4
Group 4	50	50	50	10	4

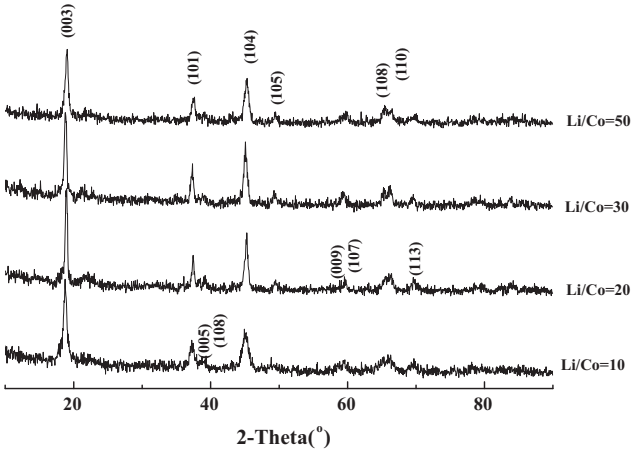


Fig. 1. XRD patterns of $LiCoO_2$ powders from different starting Li/Co.

to remove unreacted lithium. It was then dried at 80 °C for 3 h.

2.2. Test method

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), and transmission electron microscopy (TEM; Model JEM-840,JEOL Co, Japan), respectively.

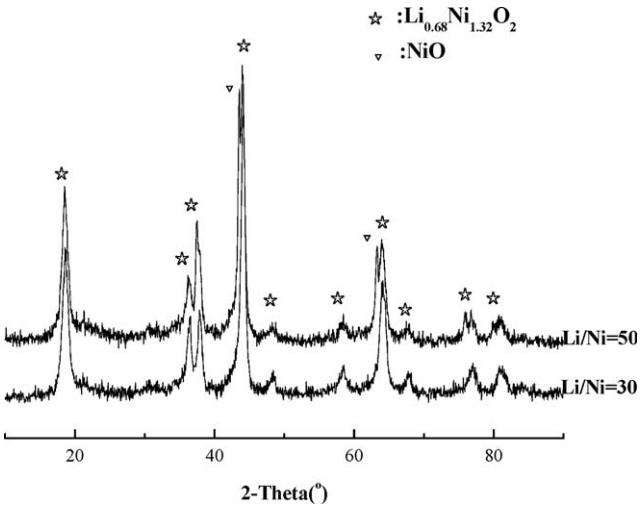


Fig. 2. XRD patterns of $LiNiO_2$ powders from different starting Li/Ni.

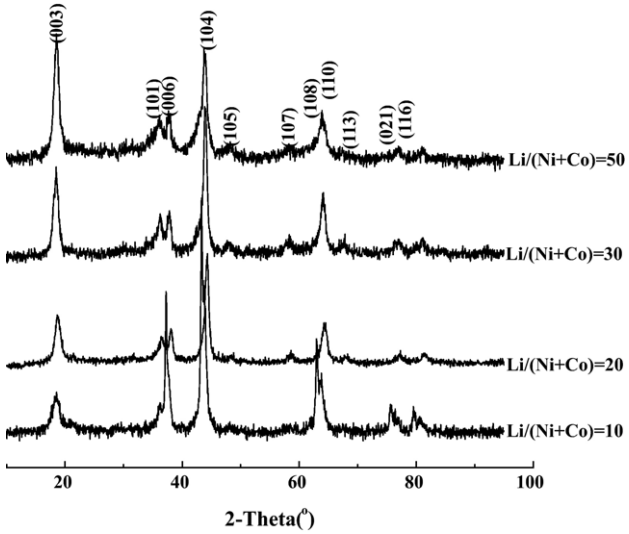
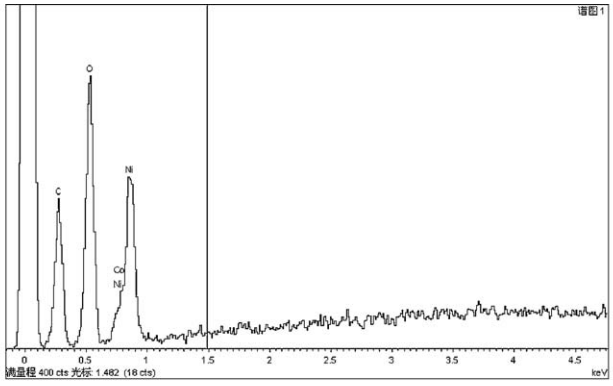


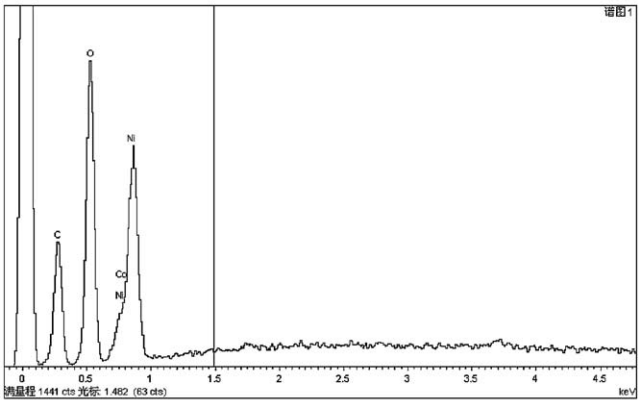
Fig. 3. XRD patterns of $LiNi_{0.9}Co_{0.1}O_2$ powders from different starting Li/(Ni + Co).

3. Results and discussions

The XRD patterns of the as-prepared products are shown in Figs. 1–3. Fig. 1 revealed the formation of $LiCoO_2$. All the XRD patterns had sharp peaks indicated a high degree of crystallinity. Especially the group of Li/Co = 20, the XRD patterns displayed the hexagonal doublets (0 0 5)/(1 0 8), (0 0 9)/(1 0 7) and (1 0 8)/(1 1 0) with a clear splitting, which



Ni：Co=25.28：2.96=8.54



Ni：Co=39.23：4.28=9.16

Fig. 4. EDS of $LiNi_{0.9}Co_{0.1}O_2$ powders with Li/(Ni + Co) = 50.

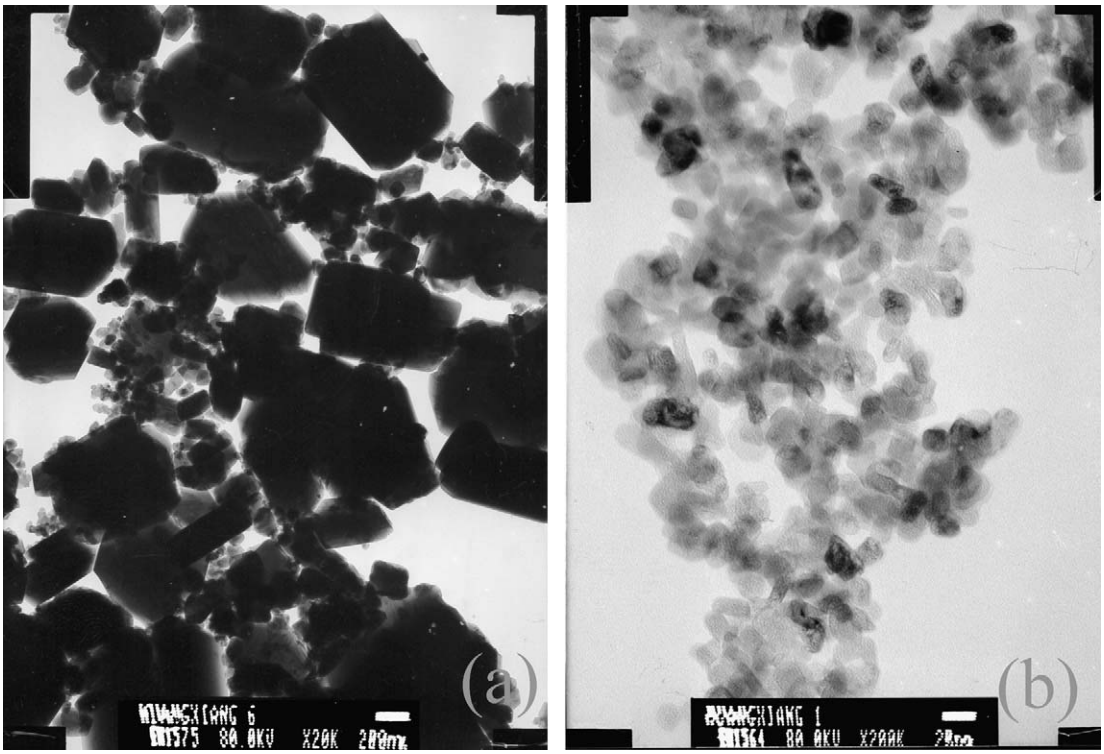


Fig. 5. TEM of $LiCoO_2$ (a) and $LiNi_{0.9}Co_{0.1}O_2$ (b) powders.

indicated a high degree of crystallinity and good hexagonal ordering (Fig. 1). The synthesis experiment of $LiNiO_2$, instead of stoichiometric $LiNiO_2$, nonstoichiometric $LiNiO_2$ and NiO (Fig. 2) were obtained. Consequently it was very difficult to synthesize stoichiometric $LiNiO_2$ under mild hydrothermal conditions. Fig. 3 presents the X-ray diffraction patterns of $LiNi_{0.9}Co_{0.1}O_2$ powders. Pure $LiNi_{0.9}Co_{0.1}O_2$ phase was obtained which had almost identical XRD patterns. There was a good agreement with the reported results so far [13,14]. The adding of Co(II) ion conduced to synthesize stoichiometric $LiNiO_2$ under mild hydrothermal conditions. 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. According to Gao et al. [15], 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 (Fig. 3) [16,17].

The EDS spectra of the synthesized $LiNi_{0.9}Co_{0.1}O_2$ powders were displayed in Fig. 4. According to that, the final products consisted of Ni, Co, and O (Li could not be detected by EDS), the spectra of carbon were 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 morphology of $LiCoO_2$ and $LiNi_{0.9}Co_{0.1}O_2$ powders observed by TEM were shown in Fig. 5. The particle shape of $LiCoO_2$ powders was ununiform as shown in Fig. 5(a). They had an average particle size of 100 nm. The $LiNi_{0.9}Co_{0.1}O_2$ powders had regular shape with an average particle size of 10 nm (Fig. 5(b)).

4. Conclusions

$LiCoO_2$, nonstoichiometric $LiNiO_2$ and $LiNi_{0.9}Co_{0.1}O_2$ powders were successfully synthesized by hydrothermal method at 220 °C for 10 h. The test results of XRD, EDS and TEM indicated that under mild hydrothermal conditions ultrafine $LiCoO_2$ and $LiNi_{0.9}Co_{0.1}O_2$ powders could be obtained. The adding of Co(II) ion was good for the synthesis of stoichiometric $LiNiO_2$ while only received nonstoichiometric $LiNiO_2$ or mixture of nonstoichiometric $LiNiO_2$ and NiO when Co(II) ion was absent. The final products $LiNi_{0.9}Co_{0.1}O_2$ had regular shape and homogeneous size while the $LiCoO_2$ powders were ununiform. The I(0 0 3)/I(1 0 4) ratio increased with the Li/(Ni + Co) ratio indicated that the sample $LiNi_{0.9}Co_{0.1}O_2$ had good cation ordering.

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