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Short communication

Hydrothermal synthesis of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ for lithium rechargeable batteries

Junlan Xie, Xiang Huang *, Zhibin Zhu, Jinhui Dai

Institute of Materials Science and Engineering, Ocean University of China, No. 238 Songling Road, Qingdao 266100, China

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Abstract

Ultrafine powders of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode materials for lithium-ion secondary batteries were prepared under mild hydrothermal conditions. The influence of the molar ratio of Li/(Ni + Co + Mn) was studied. The products were investigated by XRD, TEM and EDS. The final products were found to be well crystallized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ with an average particle size of about 10 nm.

Keywords: Hydrothermal synthesis; $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$; 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, the toxicity and high cost of cobalt represent some of the problems of this material. Therefore extensive research has been carried out to find alternative positive electrode materials [2].

Recently, layered $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ developed by Ohzuku and Makimura [3] has been considered as an attractive candidate of next-generation cathode materials to replace $LiCoO_2$ for rechargeable lithium-ion batteries due to its capacity and stable structure [4]. Because a solid-state reaction method easily leads to impure phase and unsatisfactory cell performance [5], various other synthesis methods have been tried to improve the electrochemical performance, such as hydroxide co-precipitation route [6,7], hydrothermal synthesis [8], radiated polymer gel method [9], carbonate co-precipitation route [10,11], and thermal polymerization [12]. However, some of them contain multi-step and time-consuming processes to prepare precursors.

In this study, we have succeeded in preparing $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders via the mild hydrothermal method. It does not need troublesome processes such as preparation of precursors and heat treatments.

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%), $KMnO_4$(≥99.5%) and $MnCl_2$(≥98.0%). The hydrothermal synthesis process was carried out as follows. Firstly, a desired amount of $LiOH{\cdot}H_2O$ was dissolved in distilled water to obtain a lithium hydroxide aqueous solution. The aqueous solution of $NiCl_2$, $Co(NO_3)_2$, $KMnO_4$ and $MnCl_2$ was prepared by dissolving $NiCl_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $KMnO_4$ and $MnCl_2$ in the molar ratio of Ni(II)/Co(II)/Mn(VII)/Mn(II) = 5:5:3:2. Then the mixed solution was added dropwise under vigorous stirring to the lithium hydroxide aqueous solution. The molar ratio of Li/(Ni + Co + Mn) was varied from 10:1 to 50:1 for 4 M LiOH solution, respectively. The experiment conditions are shown in Table 1.

2.2. Preparation of samples

The as-prepared starting suspension was rapidly poured into a Teflon-lined autoclave with 0.8 filling factor and sealed,

* Corresponding author. Tel.: +86 532 66781690; fax: +86 532 66786519.
E-mail address: sunny_huangx@yahoo.cn (X. Huang).

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Table 1
Hydrothermal experiment conditions.

	Statring Li/(Ni + Co + Mn)	Starting Li^+ (mol/L)	Soaking time (h)	Holding temperature (°C)
Group 1	10	4	10	220
Group 2	20	4	10	220
Group 3	30	4	10	220
Group 4	50	4	10	220

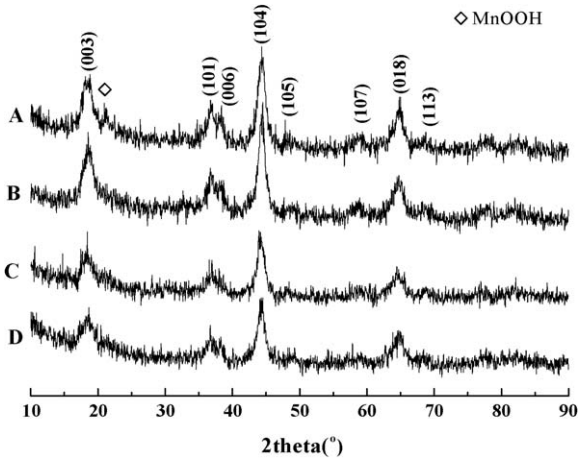


Fig. 1. XRD patterns of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders. (The molar ratio of Li/(Ni + Co + Mn): *A* = 50, *B* = 30, *C* = 20, *D* = 10.)

hydrothermally treated at 220 °C for 10 h. After the sample was cooled, the brown precipitate was washed with distilled water to remove unreacted lithium. It was then dried at 80 °C for 3 h in air.

2.3. Characterization

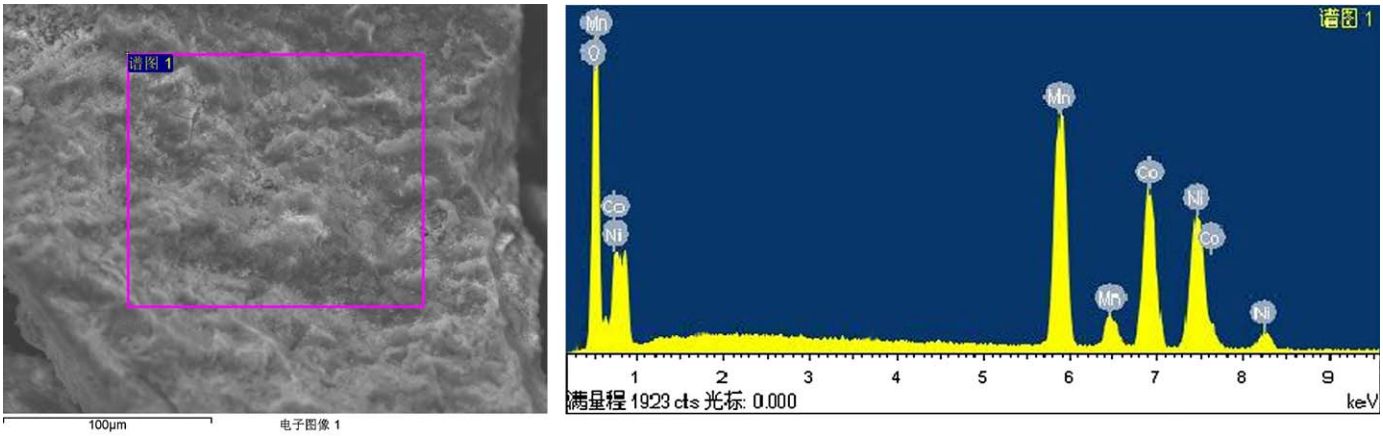
The crystalline phase, chemical composition and morphology were characterized by X-ray powder diffraction (XRD; Model D/max, Rigaku Co., Japan) with Cu Kα radiation (40 kV, 150 mA), energy dispersive X-ray spectroscopy (Oxford Instruments' INCA EDS system), and transmission electron microscopy (TEM;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

3. Results and discussions

Fig. 1 presents the XRD patterns of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ samples from different ratio of Li/(Ni + Co + Mn) prepared at 220 °C for 10 h. All the reflection peaks can be readily indexed to a crystalline phase of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ while a trace amount of impurity, MnOOH was observed in sample A. There was a good agreement with the reported results so far [12,13]. Diffraction peaks were relatively wide and small, index of ultrafine powders. The mean crystal size of the products was about 10 nm estimated by Scherrer equation. Along with the Li/(Ni + Co + Mn) ratio rise, a relatively small increase in the cystallinity was observed.

The EDS spectra of the synthesized powders in Fig. 2 show presence in the final products of Ni, Co, Mn and O (Li could not be detected by EDS), and there are no other impurity peaks in the spectra. The Ni/Co/Mn ratio was approximately equal to 1:1:1. The EDS results agreed with the XRD results, further demonstrating that the final product was $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$.

Fig. 3 shows the transmission electron microscopy (TEM) images of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders prepared at 220 °C for 10 h. The powders were composed of nanosized crystallites with ununiform shape. These results were in good agreement with the characteristic of wide peaks in XRD pattern in Fig. 1 (corresponding to the mean crystal size of 10 nm estimated by Scherrer equation).



Ni: Co: Mn = 11.19: 11.28: 11.24≈1: 1: 1

Fig. 2. EDS of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders with starting Li/(Ni + Co + Mn) = 50.

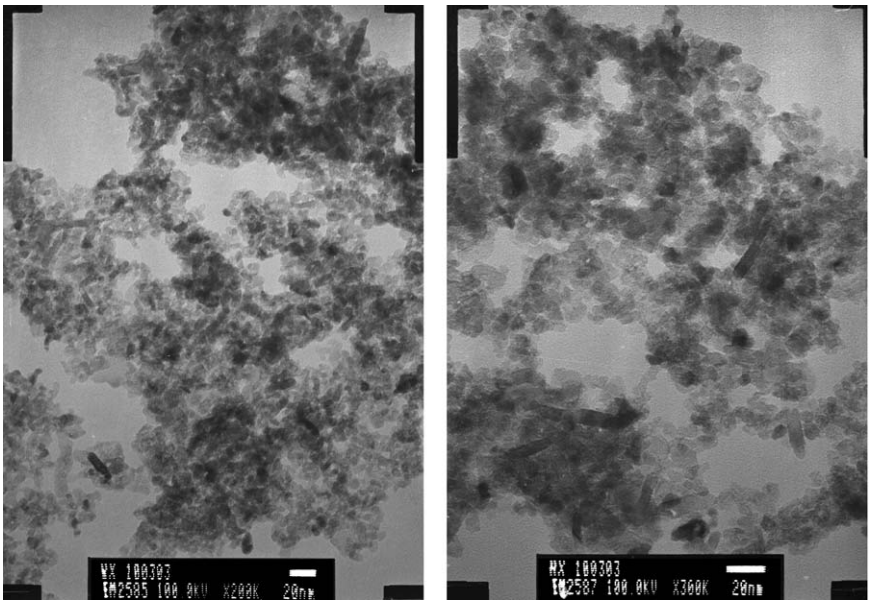


Fig. 3. TEM of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders with starting Li/(Ni + Co + Mn) = 50.

4. Conclusions

Ultrafine powders of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ were successfully synthesized by hydrothermal method at 220 °C for 10 h. The product was pure and well crystallized $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ which had an average size of about 10 nm. The cystallinity of the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ powders increased slowly with the Li/(Ni + Co + Mn) ratio rise.

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