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Short communication

Hydrothermal synthesis of $LiMn_{0.4}Co_{0.6}O_2$ cathode materials

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Abstract

In this study, orthorhombic $LiMn_{0.4}Co_{0.6}O_2$ nano-particles are successfully prepared under mild hydrothermal conditions. The source of manganese is $KMnO_4$ and $MnCl_2$, and the source of cobalt is $Co(NO_3)_2\cdot 6H_2O$. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) are used to characterize the obtained $LiMn_{0.4}Co_{0.6}O_2$ particles. The synthesized nano-particles are found to be highly crystallized with an average size of 20 nm.

Keywords: Hydrothermal synthesis; $LiMn_{0.4}Co_{0.6}O_2$; Cathode materials

1. Introduction

Nowadays, the secondary lithium-ion batteries have widely been applied as a power supply for portable electronic devices, such as digital cameras, notebooks, portable cells, and TV set [1]. The common electrode material of present day commercial lithium batteries is $LiCoO_2$ [2], but this material suffers from high cost, toxicity and relatively low practical capacity (about 140 mA h/g, around half of its theoretical capacity), which limits its further application. Intensive research for new cathode materials has been carried out in recent years [3,4]. One of the most promising candidates to replace the actually commercialized $LiCoO_2$ is the layered $LiMn_{1-y}Co_yO_2$ ($0 < y < 1$) due to its less toxicity, lower cost and higher reversible capacity [5].

Conventionally, $LiMn_xCo_{1-x}O_2$ is prepared by a solid-state route [6–9], which requires high calcining temperature and prolonged calcining time. Alternate routes have been explored to overcome these shortcomings, such as sol–gel method [10]. However, none 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.

Hydrothermal synthesis is usually carried out at a low temperature of less than 300 °C and the products are single crystals or high crystalline materials with smaller particle size. In this study, we have succeeded in preparing $LiMn_{0.4}Co_{0.6}O_2$ powders via the mild hydrothermal method. It does not need troublesome processes such as preparation of precursors and heat treatments.

2. Experiments

2.1. Preparation of the starting solution

The starting materials are analytical reagents: $LiOH\cdot H_2O(\geq 90\%)$, $KMnO_4(\geq 99.5\%)$, $MnCl_2(\geq 98.0\%)$, $Co(NO_3)_2\cdot 6H_2O(\geq 99.0\%)$. The hydrothermal synthesis process is carried out as follows. Firstly, a desired amount of $LiOH\cdot H_2O$ is dissolved in distilled water to obtain a lithium hydroxide aqueous solution. The aqueous suspension of manganese and cobalt is prepared by dissolving $KMnO_4$, $MnCl_2$ and $Co(NO_3)_2\cdot 6H_2O$, and the molar ratio of Mn(VII)/Mn(II)/Co(II) is 1:1:3. Then the mixed suspension is added dropwise under vigorous stirring to the lithium hydroxide aqueous solution. The molar ratio of Li/(Mn + Co) is 50:1 and 30:1 for 4 M LiOH solution, respectively. The experiment conditions are shown in Tables 1 and 2.

2.2. Preparation of samples

The as-prepared starting suspension is rapidly poured into a Teflon-lined autoclave with 0.8 filling factor and sealed, hydrothermally treated at 220 °C for 4–24 h. After the final

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product is taken from the autoclave, it is filtered and washed with distilled water, and then dried at 80 °C for 3 h in air.

2.3. Characterization

The crystalline phase, chemical composition and morphology are 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 shows the XRD patterns of as-prepared powders synthesized at different soaking time. Almost all of the reflection peaks can be readily indexed to a pure orthorhombic crystalline phase of $LiMn_{0.4}Co_{0.6}O_2$. There is a good agreement with the reported results so far [11,12]. Diffraction peaks are relatively wide and weak, index of ultrafine powders. The mean crystal size of the products is about 20 nm estimated by Scherrer equation. For the 4 h sample (Fig. 1A), all the peaks are weak. Along with the temperature rise, the peak intensity increases, which indicates the better crystallinity. For the 24 h sample (Fig. 1F), the XRD pattern presents a $LiMnO_2$ impurity peak notes as asterisk. When the soaking time is under 10 h, the $I(0\,0\,3)/I(1\,0\,4)$ ratio is less than 1. When the soaking time is above 10 h, the $I(0\,0\,3)/I(1\,0\,4)$ ratio is more than 1. According to Gao et al. [13], an increase in the $I(0\,0\,3)/I(1\,0\,4)$ ratio indicates that the sample had good cation ordering. The good cation ordering is also evident from the well-separated (1 0 8) and (1 1 0) reflections [14,15].

Fig. 2 presents the XRD patterns of the obtained products at different starting Li/(Mn + Co) ratios. When Li/(Mn + Co) = 50, it exhibits an almost pure XRD pattern of $LiMn_{0.4}Co_{0.6}O_2$ (Fig. 2G). There is a good agreement with the ICSD #50784 pattern and the reported results so far [11,12]. When Li/(Mn + Co) = 30, the XRD pattern presents a $LiMnO_2$ impurity peak and a γ-MnO_2 impurity peak notes as asterisk and ◆, respectively(Fig. 2H).

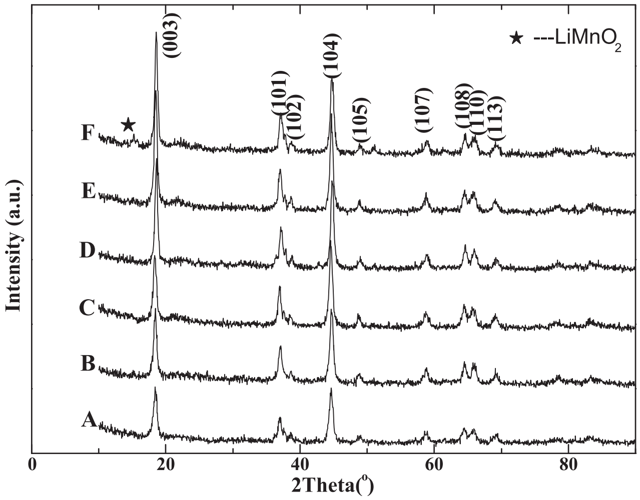

Fig. 1. XRD patterns of powders synthesized at different times with starting Li/Mn = 30 (A = 4 h, B = 6 h, C = 8 h, D = 10 h, E = 12 h and F = 24 h).

The EDS spectra of the synthesized powders in Fig. 3 show presence in the final products of Mn, Co, and O (Li could not be detected by EDS detector), and there are no other impurity peaks in the spectra. The similar as-obtained sample in this study is tested. The EDS results corresponded to the XRD results, further demonstrating that the final product is $LiMn_{0.4}Co_{0.6}O_2$.

Fig. 4 shows the transmission electron microscopy (TEM) images of the $LiMn_{0.4}Co_{0.6}O_2$ powders prepared at 220 °C for 10 h. The powders are composed of nanosized crystallites with ununiform shape and average size of 20 nm. These results are in good agreement with the characteristic of wide and weak peaks in XRD pattern in Fig. 1 (crystal size of 20 nm estimated by Scherrer equation).

Table 1
Hydrothermal experiment conditions at different soaking time.

	Starting Mn/Co	Starting Li$^+$ (mol/L)	Soaking time (h)	Holding temperature (°C)
Group A	4:6	4	4	220
Group B	4:6	4	6	220
Group C	4:6	4	8	220
Group D	4:6	4	10	220
Group E	4:6	4	12	220
Group F	4:6	4	24	220

Table 2
Hydrothermal experiment conditions at different starting Li/(Mn + Co) ratios.

	Starting Li/(Mn + Co)	Starting Li$^+$ (mol/L)	Soaking time (h)	Holding temperature (°C)
Group G	50:1	4	10	220
Group H	30:1	4	10	220

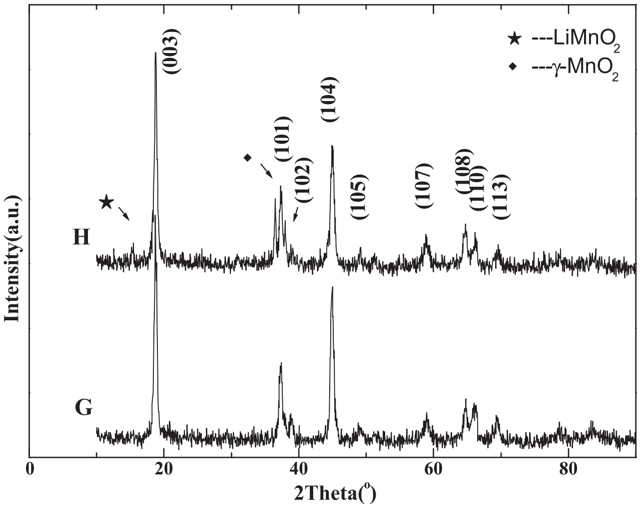

Fig. 2. XRD patterns of powders synthesized from different starting Li/(Mn + Co) (G: Li/(Mn + Co) = 50; H: Li/(Mn + Co) = 30).

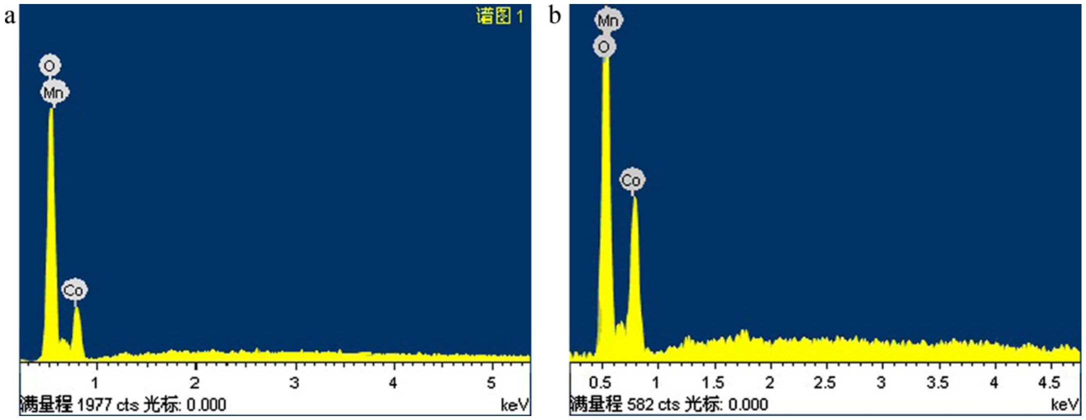

Fig. 3. EDS spectra of powders with starting Mn/Co = 4/6 at 220 °C for 10 h. (a) Li/(Mn + Co) = 50; (b) Li/(Mn + Co) = 30.

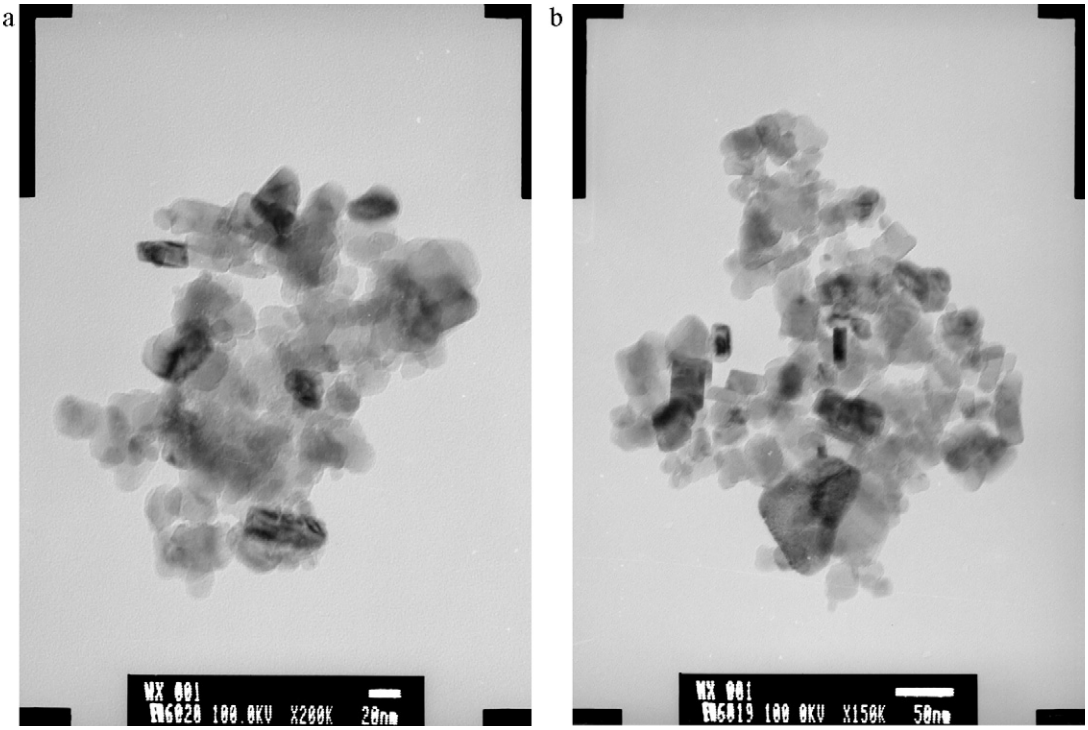

Fig. 4. TEM images of $LiMn_{0.4}Co_{0.6}O_2$ powders with starting Li/(Mn + Co) = 50 at 220 °C for 10 h.

4. Conclusions

Ultrafine powders of $LiMn_{0.4}Co_{0.6}O_2$ are successfully synthesized by hydrothermal method. The ratio of Li/(Mn + Co) and soaking time influence the phase composition and the crystallinity of the final products, respectively. When the soaking time is above 10 h and Li/(Mn + Co) = 50, it exhibited an almost pure XRD pattern of $LiMn_{0.4}Co_{0.6}O_2$.

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