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Short communication

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

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Abstract

Ultrafine powders of $LiMn_xCo_{1-x}O_2$ ($x = 0.2$–0.9) cathode materials for lithium-ion secondary batteries are successfully prepared under mild hydrothermal conditions from $KMnO_4$, $MnCl_2$ and $Co(NO_3)_2\cdot 6H_2O$. The influence of the molar ratio of Mn/Co and the reacting temperature are studied. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Energy Dispersive Spectrometer (EDS) are used to characterize the obtained final particles. The final products are found to be well crystallized $LiMn_xCo_{1-x}O_2$ as the molar ratio of Mn/Co is less than 5/5. Transmission electron microscopies (TEM) revealed that the powders are composed of nanosized crystallites with ununiform shape and average size of 10–50 nm. It has been found that the cystallinity of the $LiMn_xCo_{1-x}O_2$ powders increased with the reacting temperature rise. And when Mn/Co = 4/6, the sample has good cation ordering.

Keywords: A. Powders: chemical preparation; Hydrothermal synthesis; $LiMn_xCo_{1-x}O_2$

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, various limitations, such as high toxicity and high cost of Co, narrow range of lithium extraction, have resulted in the search of alternative layered materials. Substitution of Co by Mn has been proposed as an attractive option, in terms of its low cost, high discharge capacity, long cycling stability and thermal safety [2–4]. The synthesis of these layered compounds is usually carried out either by high temperature methods [5] or by ion-exchange reactions from Na-based compounds [6].

Conventionally, $LiMn_xCo_{1-x}O_2$ is prepared by a solid-state route [7–10], which requires high calcining temperature and prolonged calcining time. Alternate routes have been explored to overcome these shortcomings, such as sol–gel method [11]. However, none of them have successfully reduced the calcination time less than 10 h with high performance. Furthermore, they contain multi-step and time-consuming processes to prepare precursors.

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

2. Experiments

2.1. Preparation of the starting solution

The starting materials are analytical grade reagents: $LiOH\cdot H_2O$ (≥90%), $KMnO_4$ (≥99.5%), $MnCl_2$ (≥98.0%), $Co(NO_3)_2\cdot 6H_2O$ (≥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 1/4. The molar ratio of Mn(II)/Co(II) is varied from 2/8 to 9/1. 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 for 4 M LiOH solution. The experiment conditions are shown in Table 1.

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Table 1
Hydrothermal experiment conditions (Li/(Mn + Co) = 50).

Groups	Starting Mn/Co	Starting Li^+ (mol/L)	Soaking time (h)	Holding temperature (°C)
Group A	2/8	4	10	220
Group B	3/7	4	10	220
Group C	4/6	4	10	220
Group D	5/5	4	10	220
Group E	6/4	4	10	220
Group F	7/3	4	10	220
Group G	8/2	4	10	220
Group H	9/1	4	10	220
Group I	4/6	4	10	140
Group J	4/6	4	10	160
Group K	4/6	4	10	180
Group L	4/6	4	10	200

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 140–220 °C for 10 h. After the final 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.

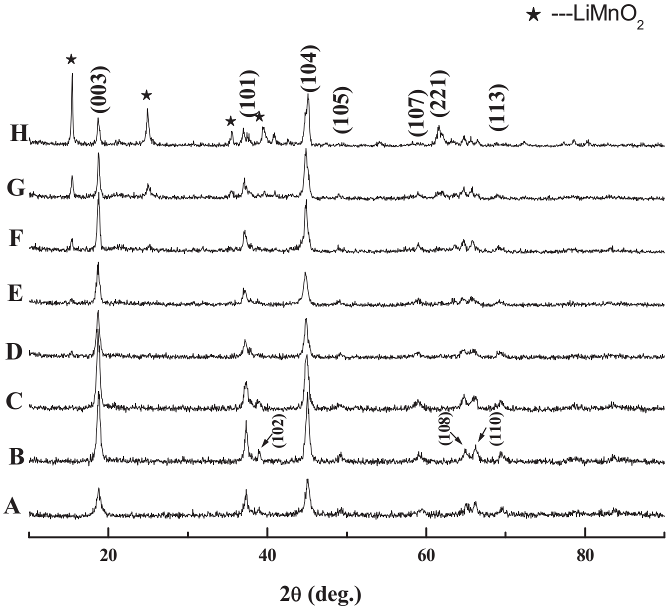

Fig. 1. XRD patterns of as-prepared powders with the molar ratio of Li/(Mn + Co) = 50 at 220 °C for 10 h (the molar ratio of Mn/Co: A = 2/8, B = 3/7, C = 4/6, D = 5/5, E = 6/4, F = 7/3, G = 8/2, H = 9/1).

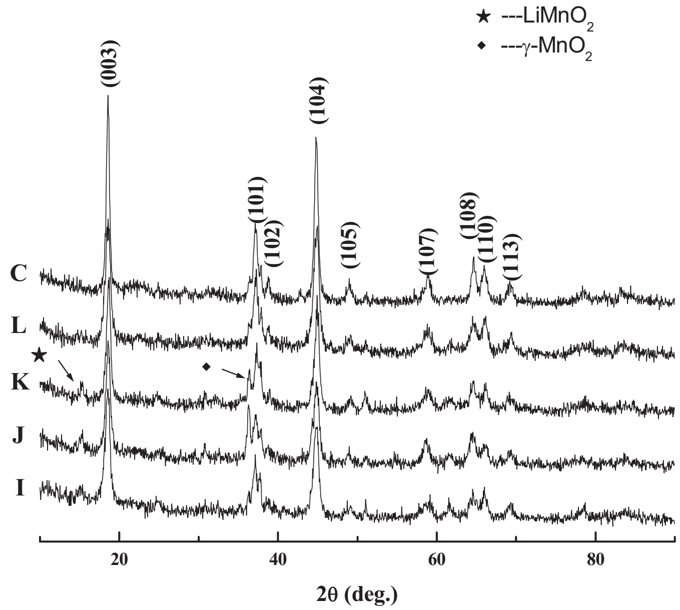

Fig. 2. XRD patterns of powders synthesized at different temperatures for 10 h with starting Li/Mn = 50 and starting Mn/Co = 4/6 (I = 140 °C, J = 160 °C, K = 180 °C, L = 200 °C, C = 220 °C).

3. Results and discussions

Fig. 1 presents the XRD patterns of the as-prepared samples from different ratio of Mn/Co prepared at 220 °C for 10 h, and the molar ratio of Li/(Mn + Co) = 50. When the content of Mn is low, the reflection peaks can be readily indexed to a crystalline phase of $LiMn_xCo_{1-x}O_2$ (Fig. 1A–D). Along with the Mn/Co ratio rise, an impurity phase appears in the sample, noted as asterisk, which are assigned to $LiMnO_2$ phase (Fig. 1E–H). There is a good agreement with the reported results so far [12,13]. It simply means ultra-fine powder on the basis of its broad and weak diffraction peak. The mean crystal size of the products is about 10–50 nm estimated by Scherrer equation. When Mn/Co = 2/8–5/5 (Fig. 1A–D), it exhibits an almost pure XRD pattern. When Mn/Co = 4/6, the I(0 0 3)/I(1 0 4) ratio reaches a maximum. According to Gao et al. [14],

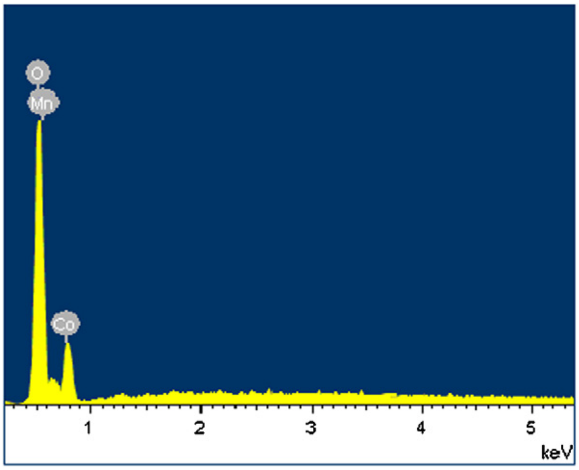

Fig. 3. EDS spectrum of powders with starting Li/(Mn + Co) = 50 and Mn/Co = 4/6 at 220 °C for 10 h.

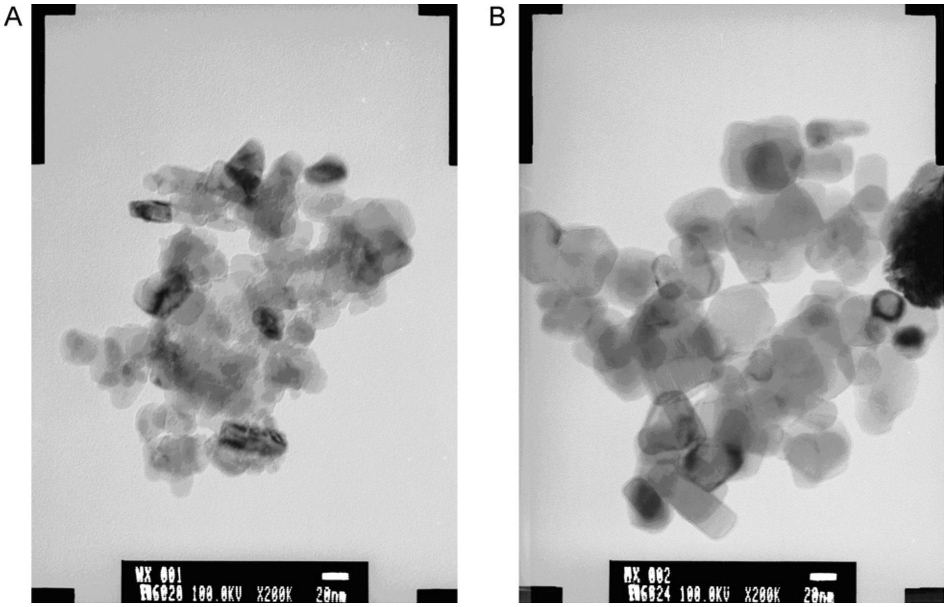

Fig. 4. TEM of $LiMn_xCo_{1-x}O_2$ powders with starting Li/(Mn + Co) = 50 at 220 °C for 10 h ((A) Mn/Co = 4/6, (B) Mn/Co = 3/7).

an increase in the I(0 0 3)/I(1 0 4) ratio indicates that the sample has good cation ordering. The good cation ordering is also evident from the well-separated (1 0 8) and (1 1 0) reflections [15,16].

Fig. 2 shows the XRD patterns of as-prepared powders synthesized at different temperatures. Almost all of the reflection peaks can be readily indexed to a pure orthorhombic crystalline phase of $LiMn_xCo_{1-x}O_2$. Along with the temperature rise, the peak intensity increase which indicated that the crystallinity become better and better. For the 140 °C, 160 °C and 180 °C sample, XRD pattern presents a $LiMnO_2$ impurity peaks and a γ-MnO_2 impurity peak, noted as asterisk and ◆, respectively (Fig. 2I–K). When the temperature is above 180 °C, the final products are almost pure $LiMn_xCo_{1-x}O_2$ (Fig. 2L and C).

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 EDS results correspond to the XRD results, further demonstrating that the final product is $LiMn_{0.6}Co_{0.4}O_2$.

Fig. 4 shows the transmission electron microscopy (TEM) images of the $LiMn_xCo_{1-x}O_2$ powders prepared at 220 °C for 10 h. The powders are composed of nanosized crystallites with ununiform shape and average size of 10–50 nm. These results are in good agreement with the characteristic of wide and weak peaks in XRD pattern in Fig. 1 (crystal size of 10–50 nm estimated by Scherrer equation).

4. Conclusions

Ultrafine powders of $LiMn_xCo_{1-x}O_2$ are successfully synthesized by hydrothermal method. The ratio of Mn/Co and holding temperature influence the phase composition and the crystallinity of the final products, respectively. When Mn/Co = 4/6, the I(0 0 3)/I(1 0 4) ratio reaches a maximum. Along with the temperature rise, the peak intensity increases indicating the better crystallinity of the samples.

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