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Short communication

Hydrothermal synthesis of orthorhombic $LiMnO_2$ nano-particles

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Abstract

Orthorhombic $LiMnO_2$ nano-particles were successfully prepared under mild hydrothermal conditions from $KMnO_4$ and $MnCl_2$ sources. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize the $LiMnO_2$ particles. The influence of the molar ratio of Li/Mn and of the holding temperature was studied. The synthesized nano-particles were found to be highly crystallized with a diameter of 50–100 nm.

Keywords: Hydrothermal synthesis; *o*-$LiMnO_2$; Cathode materials

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1. Introduction

Nowadays, secondary lithium-ion batteries are widely applied as a power supply for portable electronic devices, such as digital cameras, note computers, portable cells, and TV watches [1]. Lithium manganese oxides are almost the most attractive cathode materials. They have already received great attention owing to the low cost of raw materials and the fact that manganese is considered environmentally more friendly than the other transition metal oxide systems [2].

Several lithium manganese oxides have been studied [3–6], such as the spinels $LiMn_2O_4$, $Li_2Mn_4O_9$, $Li_4Mn_5O_{12}$ and the orthorhombic $LiMnO_2$. Among them, spinel-type $LiMn_2O_4$ with a three-dimensional framework structure is appealing. However, the material has a poor cyclability due mainly to the collective Jahn–Teller distortion when it cycles below 3 V. In contrast to $LiMn_2O_4$, the trivalent manganese compound $LiMnO_2$ exhibits a better cycle performance even between 2 and 4.5 V versus Li [7,8]. Since orthorhombic $LiMnO_2$ was prepared by Johnston and Keikes, tremendous efforts have been made in recent years to synthesize pure *o*-$LiMnO_2$ by different methods, such as conventional solid-state synthesis [9], reverse micro-emulsion preparation [10], and hydrothermal method [11].

Hydrothermal synthesis is usually carried out at a temperature lower than 300 °C and the products are single crystals or high crystalline materials with small particle size. In this paper, nanocrystalline *o*-$LiMnO_2$ particles were hydrothermally synthesized using $KMnO_4$ and $MnCl_2$ as the source of manganese.

2. Experimental

2.1. Preparation of the starting solution

Analytical reagents: $LiOH \cdot H_2O$ ($\geq$90%), $KMnO_4$ ($\geq$99.5%) and $MnCl_2$ ($\geq$98.0%) were used to prepare the starting solution. Firstly, a desired amount of $LiOH \cdot H_2O$ was dissolved in distilled water to obtain a lithium hydroxide aqueous solution. Then, an aqueous solution of $KMnO_4$ and $MnCl_2$ was prepared by dissolving $KMnO_4$ and $MnCl_2$ in the molar ratio of Mn(VII)/Mn(II) = 1:4 and added dropwise under vigorous stirring to the lithium hydroxide aqueous solution. The molar ratio of Li/Mn was varied from 10:1 to 50:1 for 4 M LiOH solution. The experimental conditions are shown in Tables 1 and 2.

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, hydrothermally treated at 140–220 °C for 10 h. After the final product was taken from the autoclave, it was filtered and

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Table 1
Hydrothermal experimental conditions with different Li/Mn ratios.

	Starting Li/Mn	Starting Li^+ (mol/L)	Soaking time (h)	Holding temperature (°C)
Group1	10	4	10	220
Group2	20	4	10	220
Group3	30	4	10	220
Group4	50	4	10	20

Table 2
Hydrothermal experimental conditions at different reaction temperatures.

	Starting Li/Mn	Starting Li^+ (mol/L)	Soaking time (h)	Holding temperature (°C)
Group1	30	4	10	140
Group2	30	4	10	160
Group3	30	4	10	180
Group4	30	4	10	200
Group5	30	4	10	220

washed with distilled water, and then dried at 80 °C for 3 h in air.

2.3. Characterization

The crystalline phase was characterized by X-ray powder diffraction (XRD; Model D/max, Rigaku Co., Japan) with Cu Kα radiation (40 kV, 150 mA) in the 2θ range from 10° to 80°. The morphology was characterized by transmission electron microscopy (TEM; Model JEM-840, JEOL Co., Japan).

3. Results and discussions

Fig. 1 presents the XRD patterns of the obtained products at different starting Li/Mn ratios. The XRD patterns in Fig. 1 are very similar to those reported in the literature [6,12], and also consistent with the JCPD card. It could be indexed as orthorhombic phase of o-$LiMnO_2$ with a space group of *Pmmn*. When Li/Mn = 50 (Fig. 1D), an impurity phase (*) appeared in the sample, which was indexed as Li_2MnO_3. When Li/Mn = 20 (Fig. 1B) and Li/Mn = 30 (Fig. 1C), an almost pure XRD pattern is obtained with a very small amount of the Li_2MnO_3 phase. Along with the Li/Mn ratio rise, a relatively small increase in the crystallinity was observed (Fig. 1A–C).

Fig. 2 shows the XRD patterns of $LiMnO_2$ synthesized at different holding temperatures. All the reflection peaks can be readily indexed to a pure orthorhombic crystalline phase of $LiMnO_2$ except the peak at about $2\theta = 24.8°$. For the 140 °C sample (Fig. 2A), all the peaks were weak. The peak intensity increased with temperature followed with the increase of crystallinity. For the 160 °C sample, the XRD pattern presents a strong Li_2MnO_3 impurity peak (*). At $T > 180$ °C, the final product was almost pure o-$LiMnO_2$ with trace amounts of Li_2MnO_3.

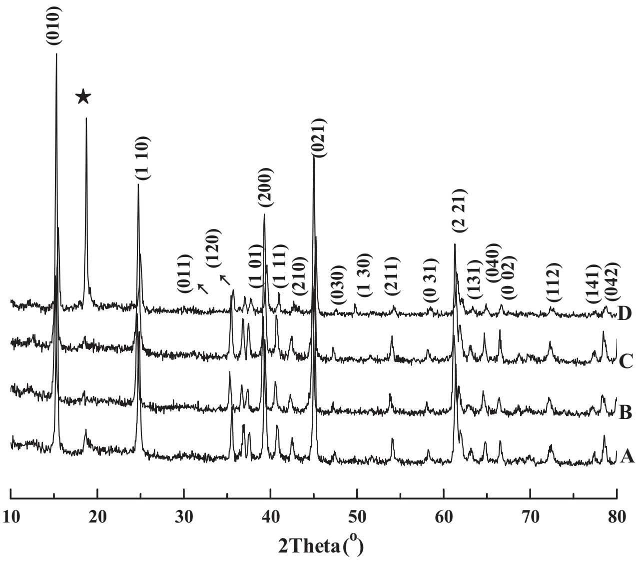

Fig. 1. XRD patterns of powders synthesized with different Li/Mn ratios (A = 10, B = 20, C = 30, and D = 50).

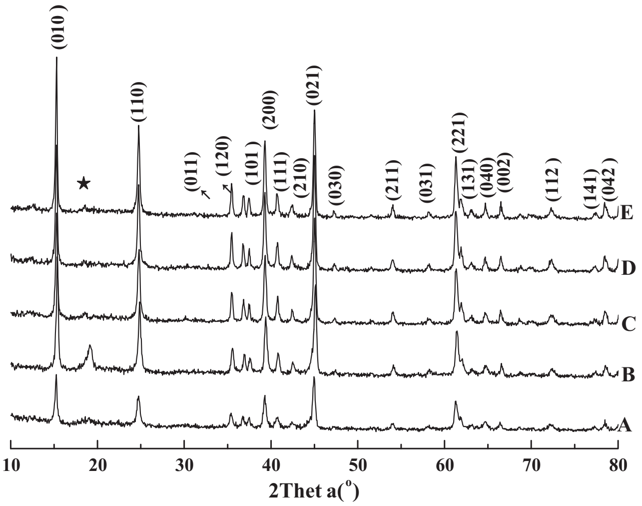

Fig. 2. XRD patterns of powders synthesized at different temperatures with stating Li/Mn = 30 (A = 140 °C, B = 160 °C, C = 180 °C, D = 200 °C, and E = 220 °C).

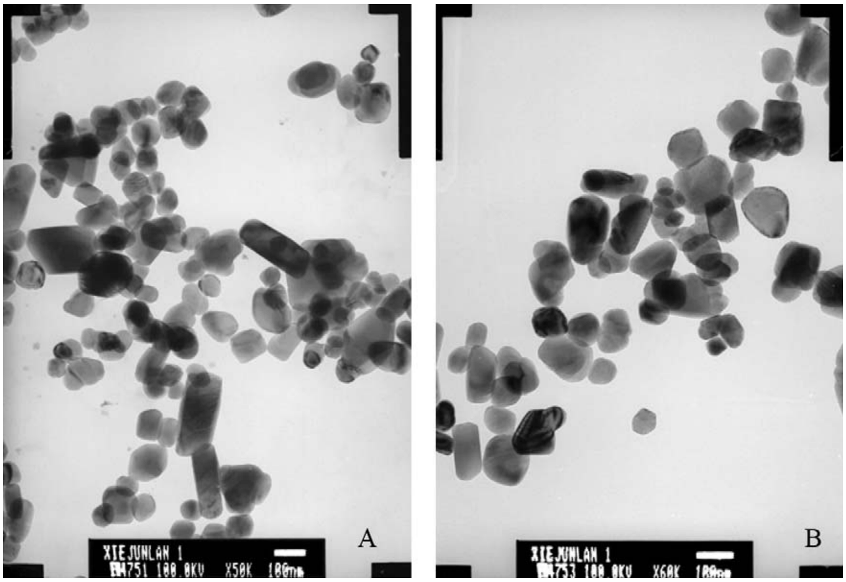

Fig. 3. TEM images of $LiMnO_2$ powders prepared at 220 °C for 10 h with starting Li/Mn = 30.

TEM images of $LiMnO_2$ powders prepared at 220 °C for 10 h (Fig. 3) show well-dispersed near-spherical and short-columnar nano-particles about 50–100 nm in size, which is consistent with the sharp peaks in the XRD patterns (Figs. 1 and 2).

4. Conclusions

o-$LiMnO_2$ nano-particles were successfully synthesized by the hydrothermal method using $KMnO_4$ and $MnCl_2$ as manganese source. The Li/Mn ratio and the holding temperature influenced the phase composition and the crystallinity of the final products. The samples prepared with Li/Mn = 20 and Li/Mn = 30 at 220 °C were almost pure *o*-$LiMnO_2$ nano-particles with a very small amount of Li_2MnO_3. When the temperature was above 180 °C and Li/Mn = 30, all the reflection peaks could be readily indexed to a pure orthorhombic $LiMnO_2$ crystalline phase with trace amounts of Li_2MnO_3. The crystallinity of *o*-$LiMnO_2$ nano-particles increased slowly with the rise of Li/Mn ratio and the holding temperature.

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