Effect of various synthetic parameters on purity of $LiMn_2O_4$ spinel synthesized by a sol–gel method at low temperature

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Abstract

Spinel lithium manganese oxide, $LiMn_2O_4$, prepared by the sol–gel method using citric acid as a chelating agent under different (i) pH conditions, (ii) molar ratio of citric acid to total metal ion, (iii) amount of water, (iv) calcination temperature, and (vi) starting materials. The effects of various synthetic parameters on the purity of this oxide are analysed by means of X-ray diffraction measurements. The results show that pure $LiMn_2O_4$ can be prepared from nitrate salts as starting materials at a low temperature of $600^\circ C$. The optimum pH and molar ratio of chelating agent to total metal ions are 6.0 and 1.0, respectively. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Spinel lithium manganese oxides, $Li_xMn_2O_4$, have been widely studied as promising materials for the positive electrodes of rechargeable lithium batteries [1–4]. The main advantages of choosing this cathode material for lithium batteries are: manganese abundance, low price, ease of preparation, environmentally friendly characteristics [5,6]. $LiMn_2O_4$ powders are usually synthesised by a solid-state reaction of lithium and manganese salts [7–10]. Because of the several disadvantages of this method, viz. inhomogeneity, irregular morphology, larger particle size, broader particle size distribution, poor control of stoichiometry, and a longer period of calcination followed by extended grinding, a sol–gel method has been introduced for the synthesis of high-performance cathode active materials for rechargeable lithium batteries [11–15]. This latter method has several advantages such as low calcination temperature, shorter processing time and particles with sub-micron sizes and a narrow size distribution. The purity of $LiMn_2O_4$ powders synthesised by the sol–gel method is an important factor in achieving high battery performance. Usually, pure spinel powders are obtained at higher calcination temperature ($>700^\circ C$) [1,2]. Impurity peaks are always observed in

the X-ray diffraction (XRD) pattern at low calcination temperatures ($<700^\circ C$) [16].

Synthesis conditions are very important for the production of pure manganese oxide spinel. Several authors have synthesised the spinel under different conditions. Choy et al. [17] prepared the spinel by a modified citrate route at a pH of 6.4 using lithium carbonate and manganese nitrate as raw materials [17]. Lee et al. [1] prepared the spinel from an aqueous solution of acetate salts [1]. Sun [2] also produced the spinel from aqueous solution of acetate salts using glycolic acid as a chelating agent [2]. Although these data suggest the synthesis of pure $LiMn_2O_4$, no systematic study has been reported on the effect of various synthetic conditions on the purity of the spinel.

In this study, $LiMn_2O_4$ spinel powders are synthesised by a sol–gel method and the effect of various synthetic conditions on the purity of the spinel are analysed systematically by using XRD measurements.

2. Experimental

The $LiMn_2O_4$ powder was synthesised by the sol–gel method using citric acid as a chelating agent. The citrate precursor was obtained as follows. First, manganese acetate/nitrate was dissolved in demonised water to give a saturated solution. To this solution, lithium acetate/nitrate was added slowly with mild stirring. A saturated aqueous solution of

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citric acid was then added at different molar ratios with the total metal ions. The pH of the mixed solution was maintained by adding ammonium hydroxide solution. The solution was then heated at 80°C for 4 h with vigorous stirring to remove excess ammonia and water. The metal citrate precipitate so formed was dried in an air oven for 10 h at 100°C. After drying, the precursors were decomposed at 300°C for 6 h in air to eliminate organic contents. The decomposed powders were ground slightly and then calcined at 600°C in air. During heating and cooling, the temperature variation was fixed at 1°C/min. Powder X-ray diffraction (Rigaki) using Cu Kα radiation was used to analyse the purity of the spinel.

3. Results and discussion

3.1. Effect of pH

To investigate the influence of pH on the purity of the $LiMn_2O_4$ spinel phase, the $LiMn_2O_4$ precursor was synthesised at different pH values namely 4.0, 5.0, 6.0, 6.5, and 7.0. The $LiMn_2O_4$ precursor was calcined at 600°C for 10 h. The molar ratio of citric acid to total metal ions is 1.0. To identify the impurity peaks, the XRD patterns of the synthesised spinel were compared with the JCPDS pattern of $LiMn_2O_4$ (Fig. 1A). As seen in Fig. 1B, the impurity peak due to Mn_2O_3 is observed at all pH conditions. The intensity of this peak is lower at pH 6.0 and 6.5 than at other pH values (Fig. 1C). Hence, it can be concluded that the pH range 6.0–6.5 is a suitable condition for the synthesis of $LiMn_2O_4$ spinel with a low quantity of impurity phase.

The reason why the purity of the $LiMn_2O_4$ spinel depends on pH can be explained as follows. In the lithium acetate–citric acid–water system, the possible precipitates are taken to be lithium hydroxide and lithium acetate. Lithium hydroxide is highly soluble in an aqueous solution. It can be precipitated only in a fairly basic region. The solubility of citric acid is expected to be increased by the presence of citric acid since this gives rise to the formation of soluble citrate complexes such as $LiC_6H_5O_7^{2-}$. In the manganese acetate–citric acid–water system, the aqueous solution of Mn^{2+} is hydrolysed and precipitated as $Mn(OH)_2$ at around pH 6.0 according to the isotherm for the $Mn(OH)_2$–citric acid–water system in the absence of citric acid [17]. The $Mn(OH)_2$ will precipitated around pH 8.0, since citric acid takes part in the complex formation of manganese. Considering the dissociation constant of citric acid, it is desirable to synthesise at pH values greater than 6.4. To obtain stable lithium–manganese citrate complexes, the pH should be maintained at <10.0.

3.2. Effect of molar ratio

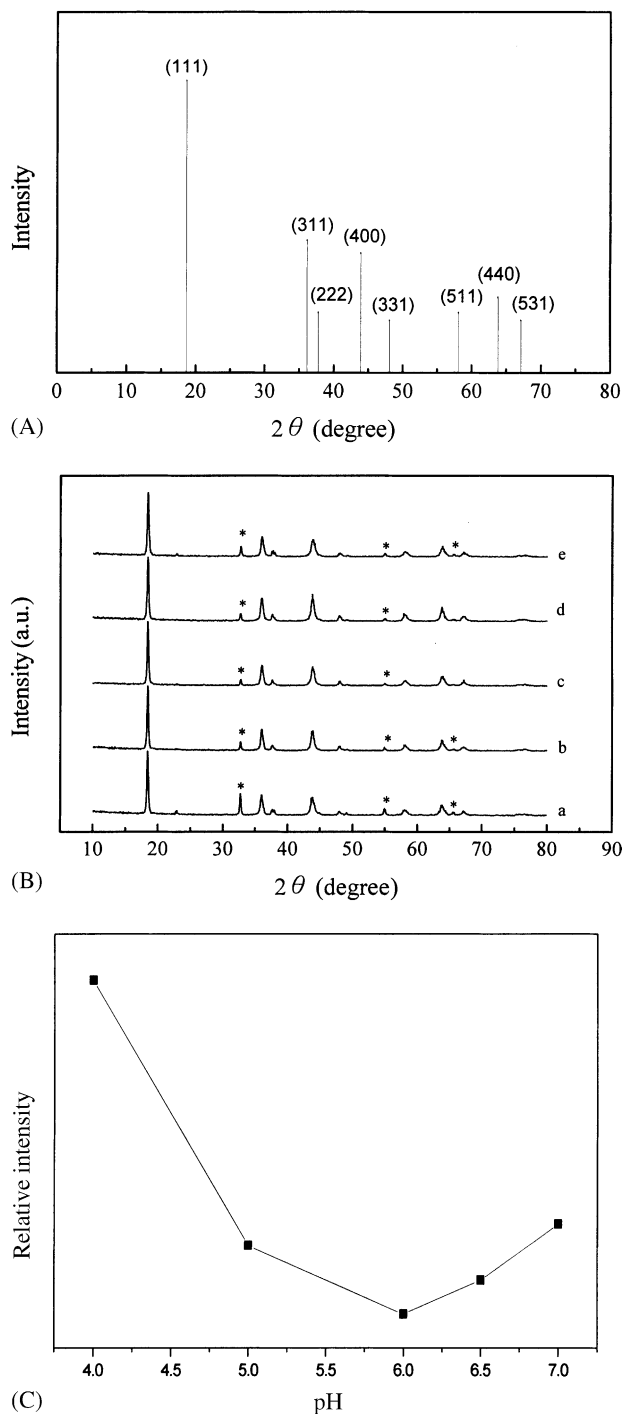In order to investigate the effect of the quantity of chelating agent on the purity of $LiMn_2O_4$ spinel, the

(A)

(B)

(C)

Fig. 1. (A) JCPDS pattern of $LiMn_2O_4$; (B) XRD patterns of $LiMn_2O_4$ precursors prepared at various pH: (a) 4.0, (b) 5.0, (c) 6.0, (d) 6.5, (e) 7.0, and a calcination temperature of 600°C (* indicates Mn_2O_3 impurities); (C) plots of relative intensity of impurity peak (around $2\theta = 33°$) with (1 1 1) peak vs. pH.

precursor materials were prepared with different molar ratios of citric acid to total metal ions. Fig. 2A shows XRD patterns for $LiMn_2O_4$ precursors calcined at 600°C for 10 h. For materials prepared at all molar ratios, namely, 0.7, 1.0, 1.5 and 2.0, impurity peaks due to Mn_2O_3 are
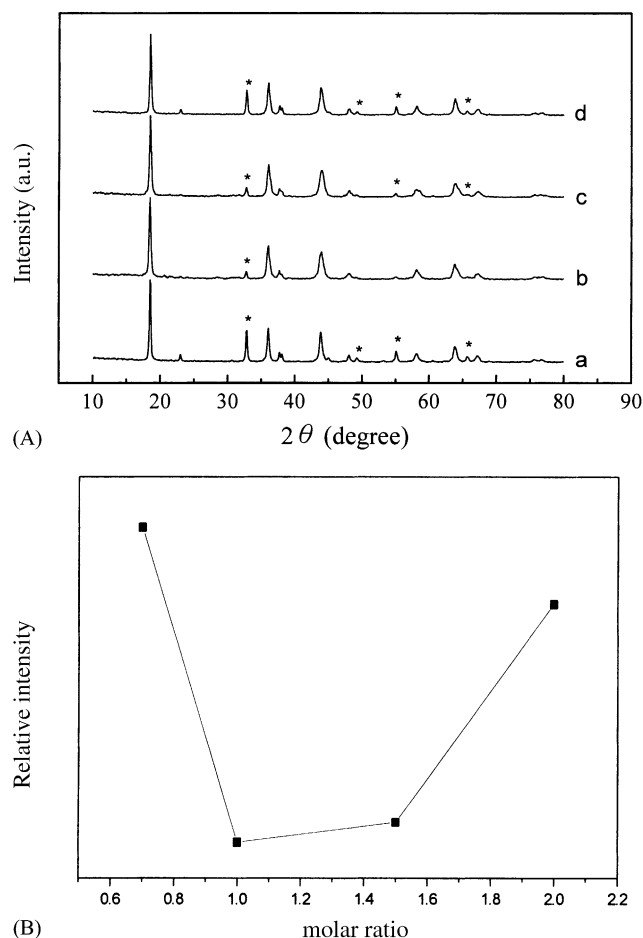
Fig. 2. (A) XRD patterns of LiMn$_2$O$_4$ precursors prepared with different molar ratio of citric acid to metal ion: (a) 0.7, (b) 1.0, (c) 1.5, (d) 2.0 and a calcination temperature of 600°C (∗ indicates Mn$_2$O$_3$ impurities); (B) plots of relative intensity of impurity peak (around $2\theta = 33°$) with (1 1 1) peak vs. molar ratio.

observed. A closer examination of the data, however, indicates that the ratio of the quantity of LiMn$_2$O$_4$ phase to that of impurity Mn$_2$O$_3$ phase is higher at molar ratios of 0.7 and 2.0. As can be seen in Fig. 2B, the LiMn$_2$O$_4$ precursor synthesised at a molar ratio of 1.0 is crystallised into LiMn$_2$O$_4$ spinel with the lowest amount of impurity. Hence, a molar ratio of citric acid to total metal ions of 1.0 is chosen for further studies.

It is known that chelating agent also provides the combustion heat required for the synthesis of LiMn$_2$O$_4$ powders [1,2]. Therefore, if the citric acid quantity is too small, more segregation of cations occurs and the combustion heat becomes insufficient for the synthesis of LiMn$_2$O$_4$. On the other hand, if the citric acid quantity is too large, it can raise the temperature too high in a short period of time and decrease the partial pressure of oxygen near LiMn$_2$O$_4$ due to the formation of CO or CO$_2$ from the decomposition of citric acid. The formation of a large amount of carbon in the form of CO will reduce the manganese ions and favour the formation of Mn$_2$O$_3$ [18].
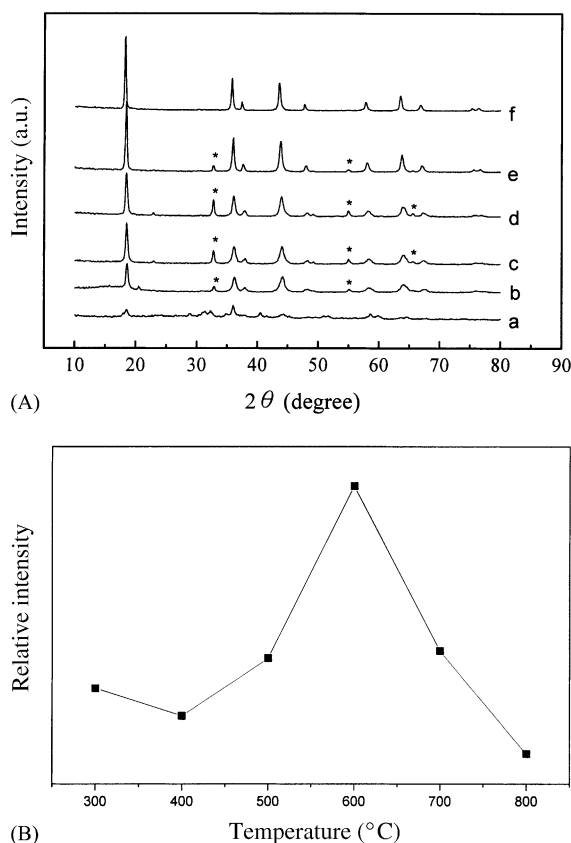

Fig. 3. (A) XRD patterns of LiMn$_2$O$_4$ precursors prepared at various calcination temperatures: (a) 300, (b) 400, (c) 500, (d) 600, (e) 700, (f) 800°C (∗ indicates Mn$_2$O$_3$ impurities); (B) plots of relative intensity of impurity peak (around $2\theta = 33°$) with (1 1 1) peak vs. temperature.

3.3. Effect of temperature

The XRD patterns for the LiMn$_2$O$_4$ precursors calcined at various temperatures for 10 h in air are presented in Fig. 3A. The molar ratio of citric acid to total metal ions and the pH of the solution are 1.0 and 6.5, respectively. Impurity peaks are observed at all calcination temperatures, except at 800°C Better crystallinity and sharper intensities of the diffraction peak of the LiMn$_2$O$_4$ are observed at a calcination temperature of 800°C. The variation of relative intensity of the impurity peak (around $2\theta = 30°$C) with temperature is shown in Fig. 3B. The relative peak intensity of the impurity peak increases up to 600°C and then decreases with increasing temperature. No impurity peaks are observed at 800°C.

3.4. Effect of water content

In order to find out the effect of water content, LiMn$_2$O$_4$ precursors were prepared from raw materials dissolved in (i) saturated water and (ii) 50% excess water. After drying and calcination, XRD measurements were performed. LiMn$_2$O$_4$ spinel phase prepared from saturated water shows a spinel phase without impurity, whereas that prepared from excess amount of water has some impurity peaks. The reason for

this latter behaviour is that, when raw materials are dissolved in an excess of water, there is a possibility of solvation of metal ions by water molecules and thus the distance between lithium and manganese ions increases. Hence, during calcination, lithium oxides and manganese oxides are also formed in addition to $LiMn_2O_4$ spinel phase.

3.5. Effect of sintering periods

To understand the influence of sintering period on the grain size, $LiMn_2O_4$ samples were prepared at 800°C with sintering for 10, 15 or 20 h. The grain size increases with increasing in sintering period. The grain size (t) is calculated from XRD patterns using the Scherrer formula

$$t = \frac{0.9\lambda}{B \cos \vartheta}$$

where λ is the wavelength of the X-ray used, B the width at an intensity equal to half I_{max}, and ϑ the Bragg angle of the diffraction peak considered. The grain size is found to be 44.4, 48.0 and 49.7 nm for a sintering period 10, 15 and 20 h, respectively. Hence, $LiMn_2O_4$ powders with various grain size can be prepared by controlling the sintering period. Optimisation of grain size is an important determinant of the performance of lithium rechargeable batteries.

3.6. Effect of raw materials

In order to find out the reason for the impurity peaks observed at lower calcination temperatures, different raw materials were used for the synthesis of $LiMn_2O_4$ precursors. Acetate and nitrate salts were chosen. The pH and molar ratio of citric acid to total metal ions were maintained at 6.0 and 1.0, respectively. The XRD patterns for $LiMn_2O_4$ spinel obtained from lithium nitrate and manganese acetate, and for lithium nitrate and manganese nitrate raw materials are shown in Fig. 4a and b, respectively. The precursors were calcined at 600°C. The results show a pure $LiMn_2O_4$ powder can be synthesised by using nitrate salts as raw materials.
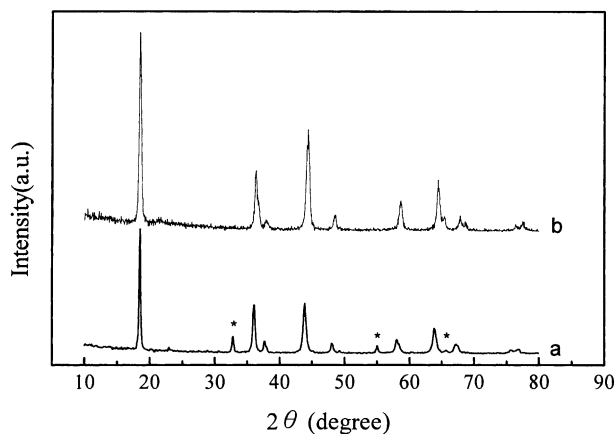

Fig. 4. XRD patterns of $LiMn_2O_4$ precursors prepared from different metal ions sources: (a) lithium nitrate and manganese acetate; (b) lithium nitrate and manganese nitrate (∗ indicates Mn_2O_3 impurities).

From the XRD pattern presented in Figs. 1–4, it can be concluded that the use of carbon-containing precursors for the synthesis of $LiMn_2O_4$ spinel by the sol–gel method leads to the formation of Mn_2O_3 impurity below 700°C, compared with the use of carbon-free precursors. It appears that the large amount of carbon present in the precursor tends to reduce the manganese ions and favour the formation of Mn_2O_3 impurity. This is consistent with the results obtained from the effect of molar ratio as discussed previously.

4. Conclusions

In this work, a pure spinel $LiMn_2O_4$ has been prepared by the sol–gel method at a low temperature of 600°C. The optimum conditions to prepare a pure spinel $LiMn_2O_4$ are as follows: (i) pH should be maintained at 6.5; (ii) molar ratio of chelating agent to total metal ions should be 1.0; (iii) a saturated aqueous solution of raw materials should be used; (iv) carbon-free raw materials, such as lithium nitrate and manganese nitrate, should be used as sources of metal ions.

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