

# Solvothermal Synthesis of Superfine $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ Powders

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Superfine  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  powders were successfully synthesized by the alcohol-thermal method using 0.01 mol of  $\text{MnO}_2$ , 0.01 mol of  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and 0.06 mol of  $\text{NaOH}$  as starting materials at 160–200°C. The products are characterized by XRD, TEM, ED, BET, and ICP. Results show that the  $\text{Li}_{0.74}\text{Mn}_2\text{O}_{3.74}$  powder prepared at 200°C has an average size of 180 nm with BET surface areas of 16.44 m<sup>2</sup>/g. A possible formation mechanism is proposed. It was concluded that the alcohol acts not only as the solvent but also as the reducing agent in the synthesis of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  powders. The effects of reaction temperature and the contents of  $\text{NaOH}$  and  $\text{LiOH}$  on the formation of single phase  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  were investigated. © 2002

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of the battery depends on packing density, specific surface area, and homogeneity of  $\text{LiMn}_2\text{O}_4$  powders. So, it is necessary to obtain submicron particles of uniform morphology with narrow size distribution and homogeneity. In order to improve the cycling performance, several low-temperature routes were developed such as sol-gel (6), coprecipitation (7), and the Pechini process (8). These methods show some improvement of the electrochemical properties of lithium manganese oxides, but some problems remain to be solved. For example, the presence of an impurity phase, the high processing cost, or the difficulty to operate and scale-up. The solvothermal method (9) is a soft chemistry method. However, little is reported on the synthesis of the spinel  $\text{LiMn}_2\text{O}_4$  by the solvothermal method. In this paper, ultrafine  $\text{LiMn}_2\text{O}_4$  powders were successfully synthesized by the alcohol-thermal method using  $\text{MnO}_2$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and  $\text{NaOH}$  as starting materials at 160–200°C.

## INTRODUCTION

Rechargeable lithium batteries (1,2) are under intensive development worldwide as a consequence of their high gravimetric and volumetric energy densities.  $\text{LiCoO}_2$  (3) has been used as a cathodic material for lithium ion batteries. Because of the high cost of cobalt and concerns about its structural stability when cells are fully charged, increasing interest has been placed on lithium manganese oxide spinel  $\text{LiMn}_2\text{O}_4$  (4) as an alternative electrode for lithium ion cells. The rechargeable capacity of  $\text{LiMn}_2\text{O}_4$  is 100–130 mAh/g, comparable to that of  $\text{LiCoO}_2$ . But the discharge capacity of  $\text{LiMn}_2\text{O}_4$  decreases with increasing number of charge-discharge cycles.  $\text{LiMn}_2\text{O}_4$  powders are usually prepared by solid-state reaction (5) which consists of grinding and calcination of hydroxides or carbonates such as  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Li}_2\text{CO}_3$ , and  $\text{MnCO}_3$ . Compared with wet-chemical methods, this method has several disadvantages: inhomogeneity, irregular morphology, larger particle size, broader particle size distribution, higher annealing temperatures, and longer periods of calcination. The performance

## EXPERIMENTAL SECTION

An amount of  $\text{MnO}_2$  powder,  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and  $\text{NaOH}$  were put into a Teflon-lined stainless steel autoclave with a 40 ml capacity that was filled with a solvent such as absolute alcohol, benzene, or deionized water up to 75% of the total volume. The autoclave was sealed and maintained at 160–220°C for 12 h, and then cooled to room temperature naturally. A gray-black precipitate was collected. After being washed with distilled water, the final product was dried in a vacuum box at 80°C for 2 h.

The annealing experiments of individual products were done in a muffle furnace. The as-prepared powders were placed into a pure alumina crucible, which is wide open to the air. The powder was heated in a muffle furnace at 350°C or 550°C for 8 h, and then cooled to room temperature naturally in the furnace. The black products were collected.

The as-prepared and annealed powders were characterized respectively by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), electron diffraction pattern (ED), BET, El-type elemental analysis, and inductively coupled plasma (ICP). The X-ray powder diffraction patterns were recorded by a Japan Rigaku D/max  $\gamma$ B X-ray

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diffractometer using  $\text{CuK}\alpha$  radiation operating at 40 kV and 30 mA with  $2\theta$  ranging from 10–70°. A transmission electron microscopy images were taken with a JEOL-2010CX transmission electron microscope. Nitrogen sorption analyses were carried out with a Micromeritics ASAP 2000 porosimeter at  $-196^\circ\text{C}$  on samples that had been degassed at  $180^\circ\text{C}$  under vacuum for at least 4 h. The data were analyzed according to a modified Broekhoff–de Boer method by using Hill's approximation for the thickness of the adsorbed gas layer. The lithium and manganese contents in the individual samples were determined by ICP after being dissolved in a dense hydrochloric acid solution. Hydrogen content analyses in the individual samples were carried out with a Germany Vario El-type elemental analyzer. The average oxidation state of manganese was determined by redox titration.

## RESULTS AND DISCUSSION

Table 1 lists the characteristics of products synthesized using  $\text{MnO}_2$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and  $\text{NaOH}$  as starting materials in various media.

From Table 1, it can be found that molar ratios of starting materials and reaction temperature play important roles in determining the phase of products. Through the adjustment of the molar ratios of starting materials and the change of reaction temperature, the single phase lithium manganese spinel was obtained using 0.01 mol of  $\text{MnO}_2$ , 0.01 mol of  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and 0.06 mol of  $\text{NaOH}$  as starting materials at  $200^\circ\text{C}$  for 12 h. The XRD patterns are shown in Fig. 1c.

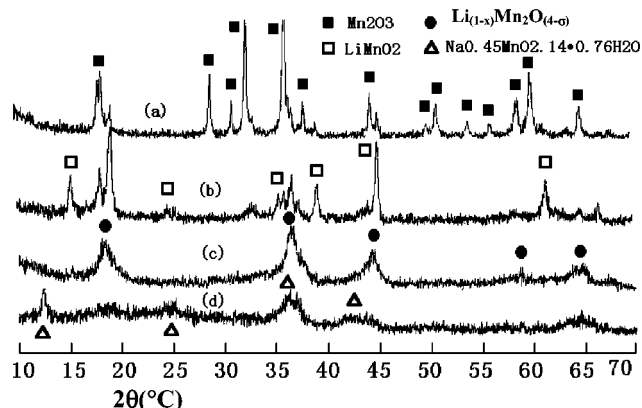
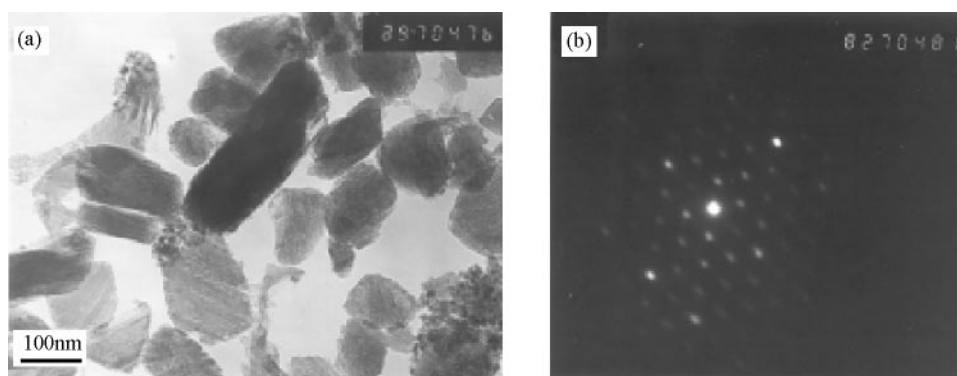


FIG. 1. XRD patterns of powders prepared using 0.01 mol of  $\text{LiOH}$ , 0.01 mol of  $\text{MnO}_2$ , and  $\text{NaOH}$  with the following molar numbers as starting materials at  $200^\circ\text{C}$ : (a) 0; (b) 0.045 mol of  $\text{NaOH}$ ; (c) 0.06 mol of  $\text{NaOH}$ ; (d) 0.075 mol of  $\text{NaOH}$ .

It was found that all the diffraction peaks could be indexed as the cubic spinel  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  phase. This result was confirmed by the selected-area electron diffraction (ED) patterns. The  $\text{Li}/\text{Mn}$  ratio was determined by elemental chemical analysis and found to be 0.37. The oxygen content was calculated via the average oxidation state of manganese, which is determined by the redox titration and found to be 3.37. Vario El-type elemental analysis shows that hydrogen content in the samples is near 0.00 wt%. It indicates that the lithium in tetrahedral sites is not replaced by hydrogen. Thus the formula of the sample can be expressed

TABLE 1  
Characteristics of Products Prepared by the Solvothermal Synthesis Method

| Sample no. | $\text{MnO}_2$ (mol) | $\text{LiOH}\cdot\text{H}_2\text{O}$ (mol) | $\text{NaOH}$ (mol) | Temp. ( $^\circ\text{C}$ ) | Reaction medium | Phase  |
|------------|----------------------|--|---------------------|----------------------------|-----------------|--|
| 1          | 0.01                 | 0  | 0                   | 200                        | Alcohol         | $\gamma\text{-Mn}_2\text{O}_3$   |
| 2          | 0.01                 | 0.005                                      | 0.06                | 200                        | Alcohol         | $\text{Na}_{0.45}\text{MnO}_{2.14}\cdot 0.76\text{H}_2\text{O}$ ,<br>$\gamma\text{-Mn}_2\text{O}_3$  |
| 3          | 0.01                 | 0.01                                       | 0.06                | 200                        | Alcohol         | $\text{Li}_{0.74}\text{Mn}_2\text{O}_{3.74}$   |
| 4          | 0.01                 | 0.01                                       | 0.075               | 200                        | Alcohol         | $\text{Na}_{0.45}\text{MnO}_{2.14}\cdot 0.76\text{H}_2\text{O}$ ,<br>$\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$   |
| 5          | 0.01                 | 0.01                                       | 0.045               | 200                        | Alcohol         | $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ , $\text{LiMnO}_2$ ,<br>$\gamma\text{-Mn}_2\text{O}_3$   |
| 6          | 0.01                 | 0.01                                       | 0                   | 200                        | Alcohol         | $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ , $\gamma\text{-Mn}_2\text{O}_3$   |
| 7          | 0.01                 | 0.01                                       | 0.06                | 220                        | Alcohol         | $\text{Na}_{0.45}\text{MnO}_{2.14}\cdot 0.76\text{H}_2\text{O}$ ,<br>$\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ , $\gamma\text{-Mn}_2\text{O}_3$ ,<br>$\text{LiMnO}_2$        |
| 8          | 0.01                 | 0.01                                       | 0.06                | 160                        | Alcohol         | $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  |
| 9          | 0.01                 | 0.01                                       | 0.06                | 200                        | Deionized water | $\text{MnO}_2$   |
| 10         | 0.01                 | 0.01                                       | 0.06                | 200                        | Benzene         | $\text{Na}_4\text{Mn}_{14}\text{O}_{27}\cdot 9\text{H}_2\text{O}$ ,<br>$\text{Na}_4\text{Mn}_9\text{O}_{18}$ , $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ ,<br>$\text{MnO}_2$ |
| 11         | 0.01                 | 0.01                                       | —                   | 200                        | Benzene         | $\text{MnO}_2$   |
| 12         | 0.01                 | —  | —                   | 200                        | Benzene         | $\text{MnO}_2$   |



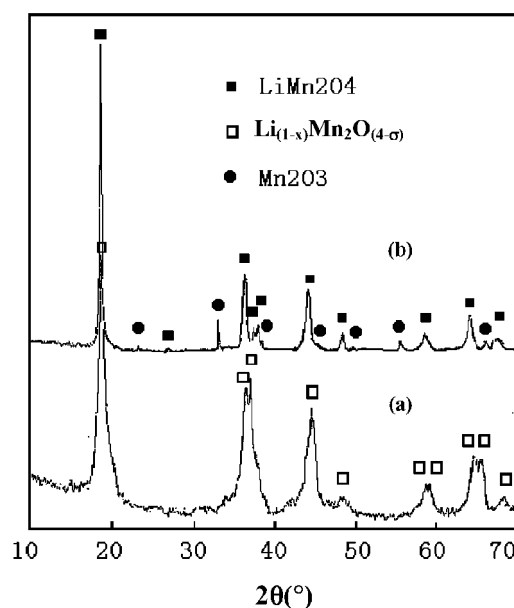
**FIG. 2.** TEM photograph (a) and ED pattern (b) of powders prepared using 0.01 mol of LiOH, 0.01 mol of  $\text{MnO}_2$ , and 0.06 mol of NaOH as starting materials in absolute alcohol at  $200^\circ\text{C}$ .

as  $\text{Li}_{0.74}\text{Mn}_2\text{O}_{3.74}$ .  $\text{N}_2$  adsorption measurement reveals that the BET surface area of this sample is  $16.44 \text{ m}^2/\text{g}$ . Moreover, it was also seen from Fig. 1c that the diffraction peaks of the powders are greatly broadened. Assuming that the peak broadening is due only to the particle size factor, an average size of 36 nm was obtained from Scherrer's formula on the basis of the XRD half-width. However, the TEM photograph of this sample shows that the size of the particles is about 180 nm, as shown in Fig. 2a. The particle size discrepancy between TEM and XRD results may come from the crystallinity of the particles.

In order to improve the crystallinity of the particles, the sample was annealed in air at different temperatures for 8 h. It can be found that the phase of the sample changes with increasing annealing temperature. After the sample was heated in air at  $350^\circ\text{C}$ , the diffraction peaks diverged, indicating that the cubic spinel  $\text{Li}_{0.74}\text{Mn}_2\text{O}_{3.74}$  phase is transformed into tetragonal spinel phase  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  (10). After the sample was heated in air at  $550^\circ\text{C}$ , reflections corresponding to  $\text{LiMn}_2\text{O}_4$  and a small amount of orthorhombic phase  $\text{Mn}_2\text{O}_3$  were observed in the X-ray diffraction pattern, as shown in Fig. 3. The above result shows that the  $\text{Li}_{0.74}\text{Mn}_2\text{O}_{3.74}$  phase is not stable at  $550^\circ\text{C}$ . Moreover, it can also be seen from Fig. 3 and Fig. 1c that the air-annealed samples show sharp reflections and become much sharper with increasing annealing temperature, indicating the increase of particle size and the remarkable improvement of crystallinity.

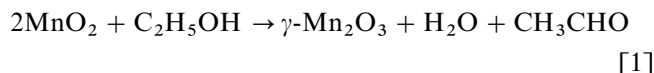
The effect of reaction medium on the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  is investigated. The experiments were carried out using 0.01 mol of  $\text{MnO}_2$ , 0.01 mol of  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and 0.06 mol of NaOH as starting materials at  $200^\circ\text{C}$  for 12 h. It can be found that in the benzene solution, the phases of obtained powders are  $\text{Na}_4\text{Mn}_{14}\text{O}_{27}\cdot 9\text{H}_2\text{O}$ ,  $\text{Na}_4\text{Mn}_9\text{O}_{18}$ , and a small amount of  $\delta\text{-MnO}_2$  and  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ ; in pure alcohol, the single phase  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  is obtained; however, in the aqueous solution, the reaction does not proceed and the phase of pow-

ders is  $\text{MnO}_2$ . The above results indicate that  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  can be formed in the benzene or alcohol medium, not in the aqueous solution. The alcohol and benzene act as the reducing agent as well as the solvent in the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  particles. In order to further elucidate the effect of alcohol and benzene in the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  particles, the experiments are done using only  $\text{MnO}_2$  powder as starting material in the alcohol or benzene medium at  $200^\circ\text{C}$  for 12 h, as shown in samples 1 and 12. The results indicate that the phase of powder after treatment in the benzene medium is  $\text{MnO}_2$ ; the phase of powder after treatment in the alcohol medium is  $\gamma\text{-Mn}_2\text{O}_3$ , not  $\text{MnO}_2$ . The above results confirm that the alcohol acts as reducing agent in the synthesis of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  and

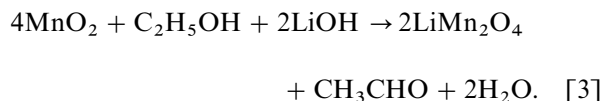


**FIG. 3.** XRD patterns of  $\text{Li}_{0.74}\text{Mn}_2\text{O}_{3.74}$  powders (a) after heating in air at  $350^\circ\text{C}$  and (b) after heating in air at  $550^\circ\text{C}$ .

indicate that the benzene has no reductive power in the absence of NaOH. On the basis of the above analysis, the possible reaction mechanism in alcohol medium is a reductive recombination pathway, in which  $\text{MnO}_2$  was reduced to  $\gamma\text{-Mn}_2\text{O}_3$  and  $\text{CH}_3\text{CHO}$  by alcohol (11). The processes can be described in terms of Eqs. [1] and [2].



So the overall reaction can be expressed as



The metastable  $\gamma\text{-Mn}_2\text{O}_3$  is easily formed through step [1], but the single phase of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  is not easily obtained through step [2], which is related to the reaction conditions such as the content of NaOH and LiOH and the reaction temperature.

In order to investigate the effect of the change of NaOH on the formation of single phase  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ , the molar numbers of LiOH and  $\text{MnO}_2$  are kept at 0.01 mol in the experiments. The XRD patterns of samples 3–6 are shown in Fig. 1. It was found that NaOH has a critical effect in the transformation of  $\gamma\text{-Mn}_2\text{O}_3$  to  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ . When no NaOH exists in the medium, there is an amount of metastable  $\gamma\text{-Mn}_2\text{O}_3$  in the product, and only a little  $\gamma\text{-Mn}_2\text{O}_3$  is transmitted to  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ ; when 0.045 mol of NaOH is added in the medium, an amount of metastable  $\gamma\text{-Mn}_2\text{O}_3$  is transmitted into  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ ; when the molar number of NaOH is 0.06 mol, the  $\gamma\text{-Mn}_2\text{O}_3$  is completely transmitted into  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  phases; when it was 0.075 mol, the  $\text{Na}_{0.45}\text{MnO}_{2.14} \cdot 0.76\text{H}_2\text{O}$  phase (12) appeared as well as  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ . As is well known, NaOH is very soluble in alcohol at 25°C. The concentration of NaOH in the alcohol increases with increasing content of NaOH. The above results show that the increase in the concentration of NaOH favors the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  in the alcohol. But when the molar number of NaOH is up to 0.075 mol, some of the  $\text{MnO}_2$  reacts with NaOH to form  $\text{Na}_{0.45}\text{MnO}_{2.14} \cdot 0.76\text{H}_2\text{O}$  because of the increase of the reaction rate of  $\text{MnO}_2$  with NaOH.

At the same time, the effect of the content of LiOH in alcohol on the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ , while  $\text{MnO}_2$  and NaOH were kept constant at 0.01 mol and 0.06 mol respectively, was shown in samples 2 and 3. Results show that the content of LiOH has a large effect on the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  particles. When the molar number of LiOH is decreased to 0.005 mol from 0.01 mol, the phases of

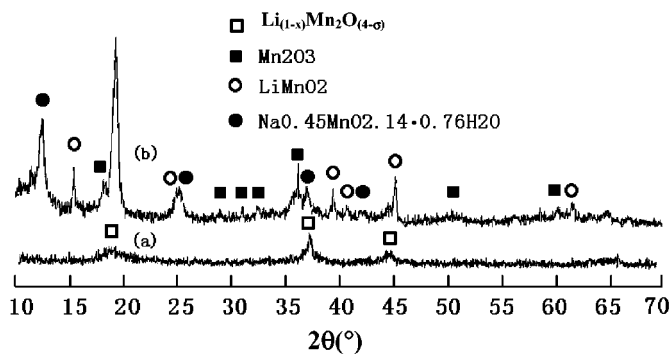


FIG. 4. XRD patterns of powders prepared using 0.01 mol of LiOH, 0.01 mol of  $\text{MnO}_2$ , and 0.06 mol of NaOH as starting materials at (a) 160°C and (b) 220°C.

powders are  $\text{Na}_{0.45}\text{MnO}_{2.14} \cdot 0.76\text{H}_2\text{O}$  and  $\gamma\text{-Mn}_2\text{O}_3$ , not  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ . It is common knowledge that the LiOH is slightly dissolved in deionized water at 25°C. It is possible that 0.01 mol of LiOH is completely dissolved in 30 ml of alcohol at 160–200°C. Thus, the formation rate of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  decreases with the decrease of the molar number of LiOH from 0.01 mol to 0.005 mol because the concentration of LiOH decreases in alcohol. It leads to the occurrence of  $\text{Na}_{0.45}\text{MnO}_{2.14} \cdot 0.76\text{H}_2\text{O}$  and  $\gamma\text{-Mn}_2\text{O}_3$ . The above results indicate that the relative concentration of LiOH and NaOH in alcohol is an important factor in the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ .

Moreover, the reaction temperature is a critical factor in the synthesis of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  as shown in the samples 3, 7, and 8. When the temperature is 220°C, the  $\text{Na}_{0.45}\text{MnO}_{2.14} \cdot 0.76\text{H}_2\text{O}$ ,  $\gamma\text{-Mn}_2\text{O}_3$ ,  $\text{LiMnO}_2$ , and  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  phases occur; at 160–200°C, the pure  $\text{LiMn}_2\text{O}_4$  phase is obtained. The XRD patterns are shown in Fig. 4. They are due to the difference in the relative formation rate of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  and  $\text{Na}_{0.45}\text{MnO}_{2.14} \cdot 0.76\text{H}_2\text{O}$  and reduced power of alcohol at the different temperatures.

## CONCLUSION

In summary, superfine  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  particles were successfully synthesized through a mild solvothermal process based on the reaction between  $\text{MnO}_2$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$ , and  $\text{C}_2\text{H}_5\text{OH}$ . The relative concentration of LiOH and NaOH in absolute alcohol and the reaction temperature are important factors in the synthesis of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$ . The single phase  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  powders can be obtained using 0.01 mol of  $\text{MnO}_2$ , 0.01 mol of  $\text{LiOH} \cdot \text{H}_2\text{O}$ , and 0.06 mol of NaOH as starting materials at 160–200°C for 12 h. In the formation of  $\text{Li}_{1-x}\text{Mn}_2\text{O}_{4-\sigma}$  particles,  $\text{C}_2\text{H}_5\text{OH}$  is not only a solvent, but also a reducing agent, which directly takes part in the whole solvothermal processes.

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