

A combustion method to prepare spinel phase LiMn_2O_4 cathode materials for lithium-ion batteries

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Abstract

Spinel phase LiMn_2O_4 is of great interest as cathode materials for lithium-ion batteries. We describe here a new simplified technique (Combustion method) to synthesize LiMn_2O_4 directly from lithium nitrate, manganese nitrate and urea. The influence of the Li/Mn ratio of product, the mole ratio of urea to nitrate, the preset temperature of the furnace and the heat-treated time have been explored. The resultant LiMn_2O_4 synthesized under the optimum synthesis conditions shows perfect spinel structure, uniform particle size distribution and excellent electrochemical performances. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Over the past decade, the spinel LiMn_2O_4 has been studied extensively as a cathode material for rechargeable lithium and lithium-ion batteries due to its economical and environmental advantages [1–4]. Unfortunately, its practical application has been limited by a relatively low diffusion rate, low specific capacity and severe capacity fading with cycling in contrast to other cathode candidates, such as LiCoO_2 and LiNiO_2 .

For getting lithium manganese oxide with excellent electrochemical characteristics, several techniques, such as sol–gel [5–7], melt-impregnation [8–10] and the Pechini process [11,12] have been developed. Although these methods show some extent effect on the improvement of electrochemical properties of lithium manganese oxides, there are still some problems. For example, the presence of undesirable impurity phase, difficulty to operate or to scale-up.

In this study, a combustion method has been developed to synthesize spinel phase LiMn_2O_4 directly from lithium nitrate, manganese nitrate and urea. This synthesis method is inexpensive and simple. On the other hand, the resultant powders synthesized by this method show perfect spinel

structure, uniform particle size distribution and excellent electrochemical performances.

2. Experimental

The new method is based on the phenomenon that nitrate can act rapidly with carbamide (urea) $\text{CO}(\text{NH}_2)_2$. The flow chart of the synthesis procedure of the combustion method is shown in Fig. 1. The manipulation details are described as following:

LiNO_3 , $\text{Mn}(\text{NO}_3)_2$ (50 wt.% solution in water) and urea were mixed in a desired proportions and stirred until a uniform solution was formed. The solution was poured into a crucible, and then the crucible was put into a furnace, which was preset at a high temperature. A rapid reaction of urea with nitrate took place to form fine powder. Thus formed fine powders were heat-treated at 800°C for a period of time (2–48 h), and then cooled with furnace to room temperature. The spinel phase LiMn_2O_4 was thus obtained.

The chemical composition of these samples was analyzed by using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Model P-5200, Hitachi). The average valence of manganese of lithium manganese oxides was determined with a redox process using KMnO_4 as the titrant. The structure of thus obtained samples was characterized by X-ray diffraction (XRD) using a D/max-A diffractometer, Cu K_α radiation at 40

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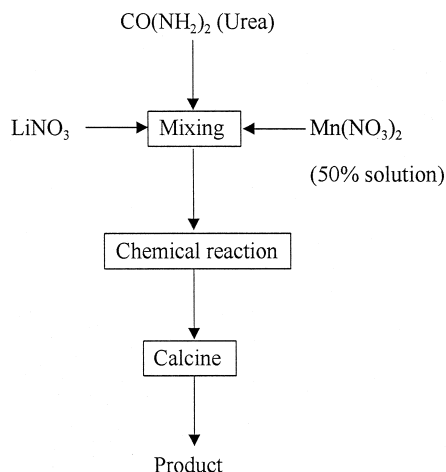


Fig. 1. The flow chart of combustion method.

kV and 10 mA. A centrifugal particle size analyzer (Model SA-CP3, Shimadzu) was used to determine the average particle size and particle size distribution.

The electrochemical properties of the products were investigated using two electrode test cells. Active material (85 wt.%) was mixed with 10 wt.% of acetylene black and 5 wt.% of PTFE emulsion, then rolled into films. The cathode films were dried in a vacuum below 1 Pa at 120°C for 24 h. 1 M LiClO₄ dissolved in ethylene carbonate (EC) and 1, 2-dimethylcarbonate (DMC) solution (1:1 ratio in volume) was used as the electrolyte, Celgard 2400 as the cell separator membrane, and lithium foil as the counter electrode. The test cells were assembled in an argon dry box.

The test cell performance was measured on a charge/discharge apparatus controlled by a computer. The test cells were charged and discharged with a constant current density of 0.3 mA/cm² within a voltage range between 3.3 V and 4.35 V (vs. Lithium).

3. Results and discussion

3.1. Effect of Li/Mn ratio on the structure and electrochemical characteristics

Products with different Li/Mn ratio have been synthesized from different starting mole ratio of LiNO₃ to Mn(NO₃)₂. The chemical composition and the average valence of manganese of the products were measured with ICP-AES and redox titration methods, respectively. The results are listed in Table 1.

The X-ray diffraction patterns of the products are shown in Fig. 2. Li₂MnO₃ phase appeared for the product with the Li/Mn ratio of 1.15/2, and Mn₂O₃ phase became visible when the Li/Mn ratio was 0.90/2. When the Li/Mn ratio was between 0.95/2 and 1.10/2, there was no other phase detected by XRD besides spinel phase.

Table 1

Chemical composition and the average valence of manganese of products

Product number	Results of ICP-AES chemical analyses			Average valence of manganese
	Li wt.%	Mn wt.%	Li/Mn ratio	
A	4.35	59.9	1.15/2	3.523
B	4.16	60.1	1.10/2	3.516
C	4.01	60.5	1.05/2	3.506
D	3.86	60.9	1.00/2	3.498
E	3.69	61.4	0.95/2	3.471
F	3.51	61.6	0.90/2	3.452

However, we cannot make sure whether products were of nonstoichiometric spinel structure (Li-rich Li_{1+x}Mn₂O₄ or Li-poor Li_{1-x}Mn₂O₄) when the Li/Mn ratio was between 0.95/2 and 1.10/2 because the accuracy of X-ray diffraction method is not very high. If the amount of impurity phase is less than 5%, it is difficult to identify the impurity with XRD. So the average valence of manganese in products measured with the redox titration was employed to determine the composition of products jointly.

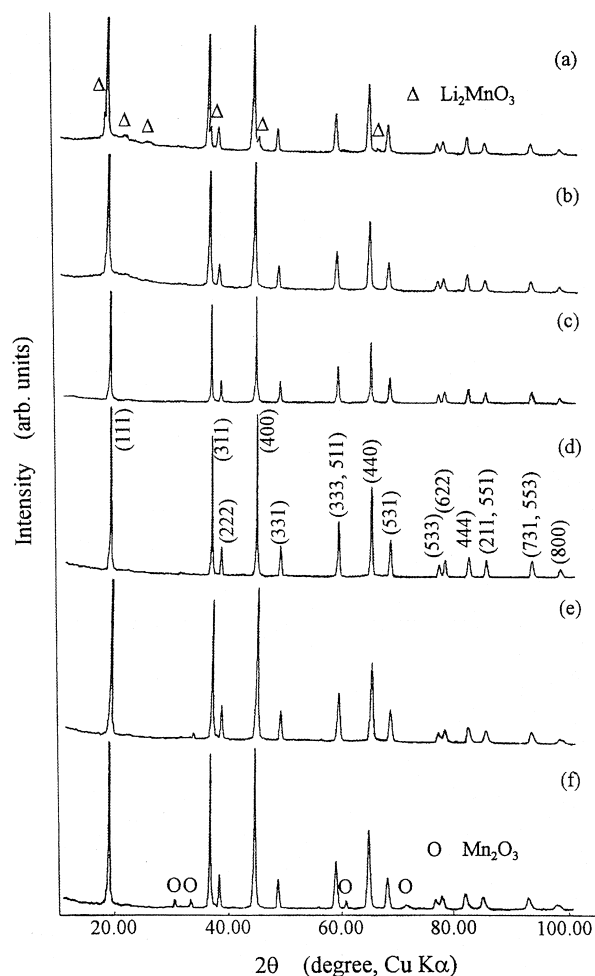


Fig. 2. The X-ray diffraction patterns of products with different Li/Mn ratio. (a) to (f) stand for products A to F in Table 1 respectively.

The average manganese valence of a perfect spinel structure of LiMn_2O_4 is 3.5. Half of manganese atoms are of three valences, and half of four valences. If we suppose that nonstoichiometric compound $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ presents in Li-rich products, the average valence of manganese would be $3.5 - x/2$, i.e., the average valence of manganese is lower than 3.5. For Li-poor products, the nonstoichiometric compound $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, shows the average valence of $3.5 + x/2$, i.e., higher than 3.5.

However, the average valences of manganese in products measured by redox titration method (shown in last column of Table 1) are on the contrary to the above analysis. For Li-rich products the average valences of manganese were higher than 3.5, and for Li-poor products the average valences of manganese were lower than 3.5.

So it is suggested that when the Li/Mn ratio of the products is higher than 1:2 (Li-rich), the impurity phase of Li_2MnO_3 is in existence, although it may not be detected by X-ray diffraction method. The valence of manganese in Li_2MnO_3 is four, so the Li-rich products show the average valence larger than 3.5. Otherwise, when the Li/Mn ratio is less than 1:2 (Li-poor), the impurity phase of Mn_2O_3 is in presence. The valence of manganese in Mn_2O_3 is three, so the Li-poor products exhibit the average valence less than 3.5. As the amount of Li_2MnO_3 or Mn_2O_3 is limited when the Li/Mn ratio slightly deviates from 1:2, they could not be found by the X-ray diffraction.

The cycling characteristics of products with different Li/Mn ratio are shown in Fig. 3. When the Li/Mn ratio of product is 1:2, the specific capacity is the highest and the cycleability is the best. So we can say that the purer the spinel LiMn_2O_4 , the better the cycle characterization.

Using LiMn_2O_4 synthesized under the optimum condition as cathode and mesocarbon microbeads (MCMB) as anode, lithium-ion batteries were assembled and tested. The capacity fading was only 22% after 640 cycles (The details will be reported later). So it suggested that the capacity fading of the above two electrode test cell is due to lithium foil anode. Because all the experiments were carried out under the same experimental conditions, the

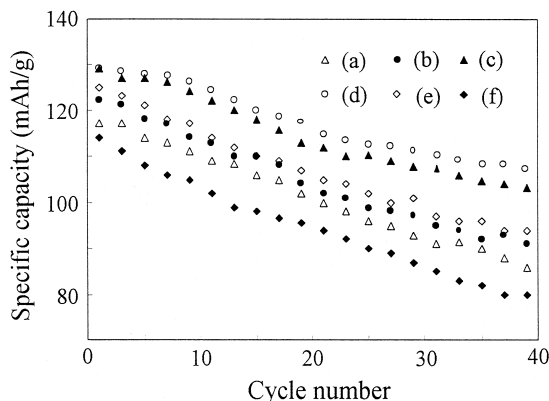


Fig. 3. The cycle characteristics of products with different Li/Mn ratio. (a) to (f) stand for products A to F in Table 1 respectively.

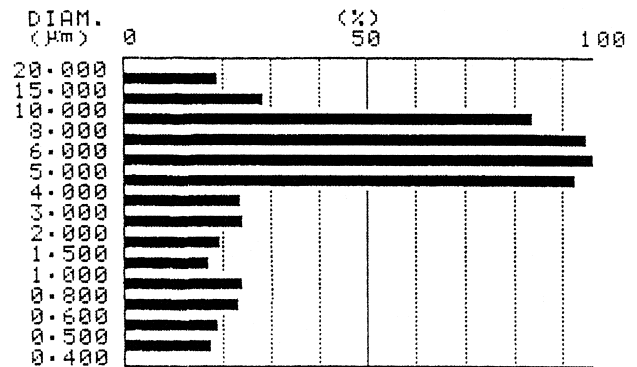


Fig. 4. The particle size analyses result of product synthesized with mole ratio of urea to nitrate 0.6 and preset temperature 600°C.

defined optimum condition to synthesize LiMn_2O_4 according to the above experiments is believable.

3.2. Effect of the mole ratio of urea to nitrate and the preset temperature

Experiments with different starting mole ratio of urea to nitrate (0.4 to 0.7) and different preset temperature of the furnace (400°C to 700°C) were carried out. When the solution in a crucible was put into a furnace preset at a high temperature, after a while of waiting for heating the crucible and solution the reaction took place and brown smoke was generated. It has been found that the mole ratio of urea to nitrate and preset temperature show considerable effect on the waiting time, the particle size and particle size distribution of the final products.

The particle size analyses result of product synthesized with mole ratio of urea to nitrate 0.6 and preset temperature 600°C is shown in Fig. 4. The particle size analyses results of products synthesized with different mole ratio of urea to nitrate and different preset temperature are summarized in Table 2.

Table 2

Average particle size (upper) and particle distribution range^a (lower) of products synthesized with different mole ratio of urea to nitrate and different preset temperature

Mole ratio of urea to nitrate	Preset temperature of the furnace (°C)			
	400	500	600	700
0.4		1.61	2.12	2.67
		0.7–7.0 ^a	0.9–9.0	1.7–9.0
0.5	2.54	3.04	3.48	3.96
	1.2–9.0	1.7–9.0	2.5–9.0	3.5–9.0
0.6	3.89	4.54	5.06	5.62
	2.5–9.0	3.5–9.0	4.5–9.0	4.5–12.5
0.7	5.18	5.87	6.65	
	3.5–9.0	4.5–12.5	5.5–12.5	

^a80% particles are within this range.

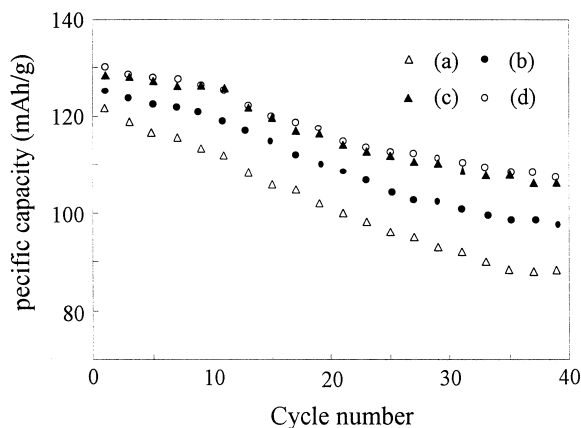


Fig. 5. The cycle characteristics of products with different heat-treated time. (a) 2 h, (b) 12 h, (c) 24 h and (d) 48 h.

With the mole ratio of urea to nitrate increasing or the preset temperature of the furnace raising, the waiting time became short and the particle size distribution become uniform. However, if the mole ratio of urea to nitrate or the preset temperature of the furnace is too high, the reaction of urea with nitrate will become too violent to control. According to the current experimental conditions, when the mole ratio of urea to nitrate is 0.60 and the preset temperature of the furnace is 600°C, the resultant powders show perfect spinel structure and uniform particle size distribution.

3.3. Effect of the heat-treated time

Fine powders thus obtained with preset temperature of 600°C were heat-treated at 800°C for a period time, such as 2, 12, 24 and 48 h, respectively, and then cooled with furnace to room temperature. The cycling characteristics of thus obtained spinel LiMn_2O_4 with different heat-treated times are shown in Fig. 5. It is seen that the longer the heat-treated time, the better the cycle characterization. Because the difference of the cycleability of samples heat-

treated for 24 h and 48 h is quite small, we think that 24 h of heat treatment is enough.

4. Conclusion

The combustion method is an effective technique for the synthesis of spinel phase LiMn_2O_4 . The Li/Mn ratio of product, the mole ratio of urea to nitrate, the preset temperature of the furnace and the heat-treated time at 800°C are the key factors to obtain LiMn_2O_4 with perfect spinel structure and uniform particle size distribution. When the mole ratio of urea to nitrate is 0.60, the preset temperature of the furnace is 600°C, and heat-treated at 800°C for 24 h, the product shows perfect spinel structure, uniform particle size distribution and excellent electrochemical properties.

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