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Effect of Calcination Temperature on the Electrochemical Properties of Spinel $LiMn_2O_4$ Prepared by Solid-State Combustion Synthesis

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In this research, spinel $LiMn_2O_4$ with high crystallinity was rapidly prepared by a solid-state combustion synthesis, which is a feasible process of decreasing calcination temperature and shortening reaction time. Lithium carbonate and manganese carbonate were used as the raw materials, and β-cyclodextrin (5 wt%) was a fuel. The effect of calcination temperature on the structures and electrochemical properties of spinel $LiMn_2O_4$ was investigated. The phase composition and micro-morphology of the products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD data suggested that pure $LiMn_2O_4$ was synthesized for 1 h when the reactants were calcinated at 500 °C and 600 °C. SEM investigation indicated that the as-prepared powders were 50-200 nm in size when calcination temperatures were 400-500 °C, but the products grew up to 300-1500 nm when calcination temperature increased to 600-700 °C. Electrochemical performance tests indicated that the sample synthesized at 500 °C showed the highest initial discharge specific capacity as well as the capacity retention. The initial discharge capacity and the capacity retention after 40 cycles of the sample synthesized at 500 °C were 110.5 mAh/g and 90.14 % at 0.2 C rate, respectively.

Keywords: Solid-state combustion synthesis; spinel $LiMn_2O_4$; lithium-ion battery

1. INTRODUCTION

Nowadays, spinel lithium manganese oxide compound $LiMn_2O_4$ with three-dimensional tunnel structure as the cathode material for secondary lithium ion batteries is widely investigated as an alternative material to substitute the conventional power sources due to its high-energy density, environmentally benign, stable cycling lifespan, excellent voltage profile characteristics, low cost and good rate capability [1-4].

It is well documented that the electrochemical performances of cathode materials are strongly linked with its structure, particle size and grain morphology. Therefore, experimental synthesis is the conclusive element for the physico-chemical properties of the target products [5,6]. Pechini [7], sol-gel method [8], electrochemical precipitation method [9], hydrothermal method [10], solid-state reaction [11] and combustion synthesis [12] are the representative processes to prepare $LiMn_2O_4$. Among those, solid-state reaction is the simplest and easiest one [13]. However, it is hard to get single phase $LiMn_2O_4$ at low temperature in a short time, due to the low reaction rate of solid state reaction. In our previous investigations, it is reported that the rate of solid state reaction can be enhanced by adding a moderate amount of glucose as fuel into the mixed raw materials [14]. In brief, adding fuel into the raw materials can uniformly, rapidly, and sufficiently promote the solid state reaction, and the single phase of $LiMn_2O_4$ will be obtained in a short time at a relatively low temperature. This method is the so called solid-state combustion synthesis.

In this research, we selected β-cyclodextrin as a fuel to synthesize spinel $LiMn_2O_4$ by solid-state combustion synthesis. The effect of calcination temperature on the electrochemical performance of $LiMn_2O_4$ cathode materials was investigated in details.

2. EXPERIMENTAL

2.1. Preparation of the samples

The experiments on synthesizing compounds $LiMn_2O_4$ were carried out by solid-state combustion synthesis. Lithium carbonate (AR, Sinopharm) and manganese carbonate (AR, Tianjin Kemiou) are used as the metal source materials, and β-cyclodextrin (AR, Emerging) is the fuel. Firstly, lithium carbonate and manganese carbonate were weighted at a stoichiometric atomic ratio of Mn : Li = 2 : 1, and then the metal carbonates were put into a 500 mL polytetrafluoroethylene jar with the ethanol medium. Secondly, a given amount of 5 wt% β-cyclodextrin was added into the mixture and the raw materials together with fuel were ball-milled thoroughly by planetary ball mill, then the obtained precursor was put into an oven to evaporate the solvent. Thereafter, the mixture was ground into white powder which is like flour, and about 5 g powder combusted in a muffle furnace for 1 h. Ultimately, the alumina crucible with starting materials was taken out, and the targeted product $LiMn_2O_4$ was obtained after the starting materials spontaneously cooled down to the ambient temperature. To explore the impact of calcination temperature on the electrochemical properties of $LiMn_2O_4$, diverse temperatures of 400 °C, 500 °C, 600 °C and 700 °C were chosen as the research objects.

2.2. Characterization of the samples

Powder X-ray diffraction (XRD, D/max-TTRIII, Japan) with Cu Kα radiation is used to identify the crystalline phase of the prepared powders. XRD data were collected at 2θ = 10-70 °, with a step width of 0.02 °, a scan speed of 4 °/min, an operation current of 30 mA and voltage of 40 kV. The morphologies of the as-prepared powder were determined by scanning electron microscopy (SEM, QUANTA 200, America FEI).

2.3. Electrochemical evaluations

Electrochemical performance was tested using CR2025 coin-type cells assembled in a glove box (MBraun, Germany) filled with high purity argon gas. The positive electrodes were prepared by homogeneously coating the syrupy of the N-methyl-pyrrolidone (NMP) solution which is composed of 80 wt% active material, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) onto cleaned and polished aluminium foil by doctor-blade technique. In order to eliminate the solvent the film was dried at 80 °C for 4h in an oven, then it was cut into small wafers with 16 millimetre diameter under certain pressure and before assembling cells these small wafers were dried at 120 °C under a vacuum condition for 12 h. Lithium metal foil, 1 M $LiPF_6$ dissolved in ethylene carbonate (EC) - diethyl carbonate (DEC) (1 : 1, v / v) and Celgard 2320-type membrane were used as counter electrode, electrolyte and micro-porous polypropylene separator. The assembled cells were aged for 12 h before the electrochemical measurements.

At room temperature, charge-discharge experiments were carried out galvanostatically in a cut-off voltage limit of 3.2-4.35 V (versus Li / Li^+) at 0.2 C by the Land electric test system CT2001A (Wuhan Jinnuo Electronic Co., Ltd). The cyclic voltammogram (CV) measurement was tested under room temperature on ZAHNER Zennium IM6 Electrochemical Workstation (ZAHNER-elektrik GmbH & Co. KG, Kronach, Germany) at a scan rate of 0.0 5mV s^{-1} and the voltage range from 3.6 to 4.5 V (versus Li / Li^+).

3. RESULTS AND DISCUSSION

3.1. Structures and morphologies of $LiMn_2O_4$

Fig. 1 shows XRD patterns of the as-synthesized $LiMn_2O_4$ calcined at various temperatures for 1 h. As can be seen, the diffraction peaks of all the samples emerged at 2θ =18.6 °, 36.1 °, 37.7 °, 43.9 °, 48.0 °, 58.1 °, 63.8 ° and 67.1 ° which agree well with the (1 1 1), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (5 1 1), (4 4 0) and (5 3 1) crystal planes of the stoichiometric spinel $LiMn_2O_4$ with a cubic unit cell and Fd3m space group (JCPDS, No. 35-0782), implying that the main phase of all products was spinel $LiMn_2O_4$. However, some weak diffraction peaks can be also found at 2θ = 28.9 °, 32.4 ° and 59.9 ° from Fig.1a and 1d, standing for the characteristic diffractions of Mn_3O_4 (PDF, No. 80-0382). It suggested that the impurity phase of Mn_3O_4 appeared in the products prepared at 400 °C and 700 °C.

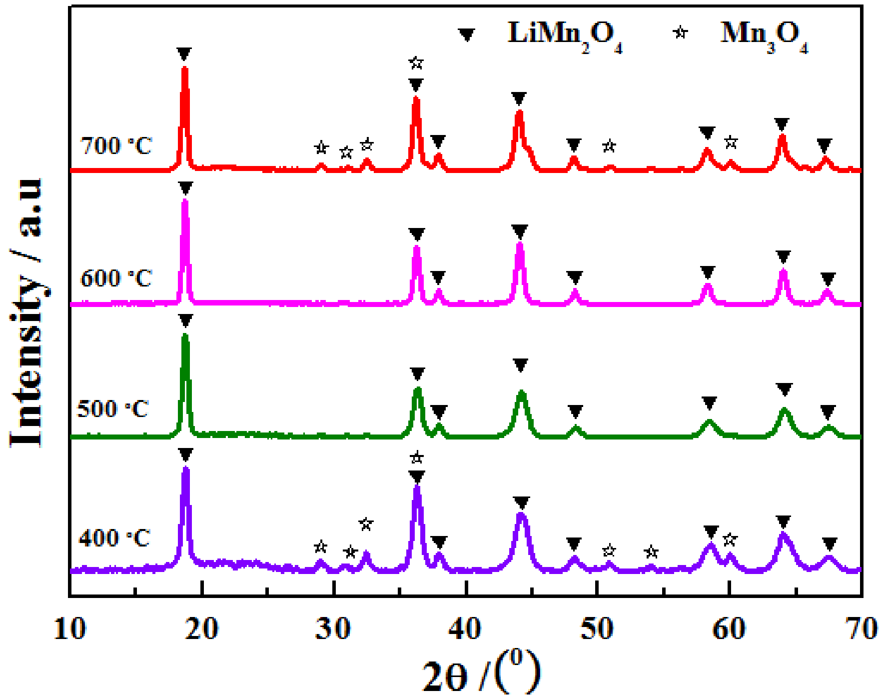

Figure 1. XRD patterns of the as-synthesized $LiMn_2O_4$ calcined at various temperatures

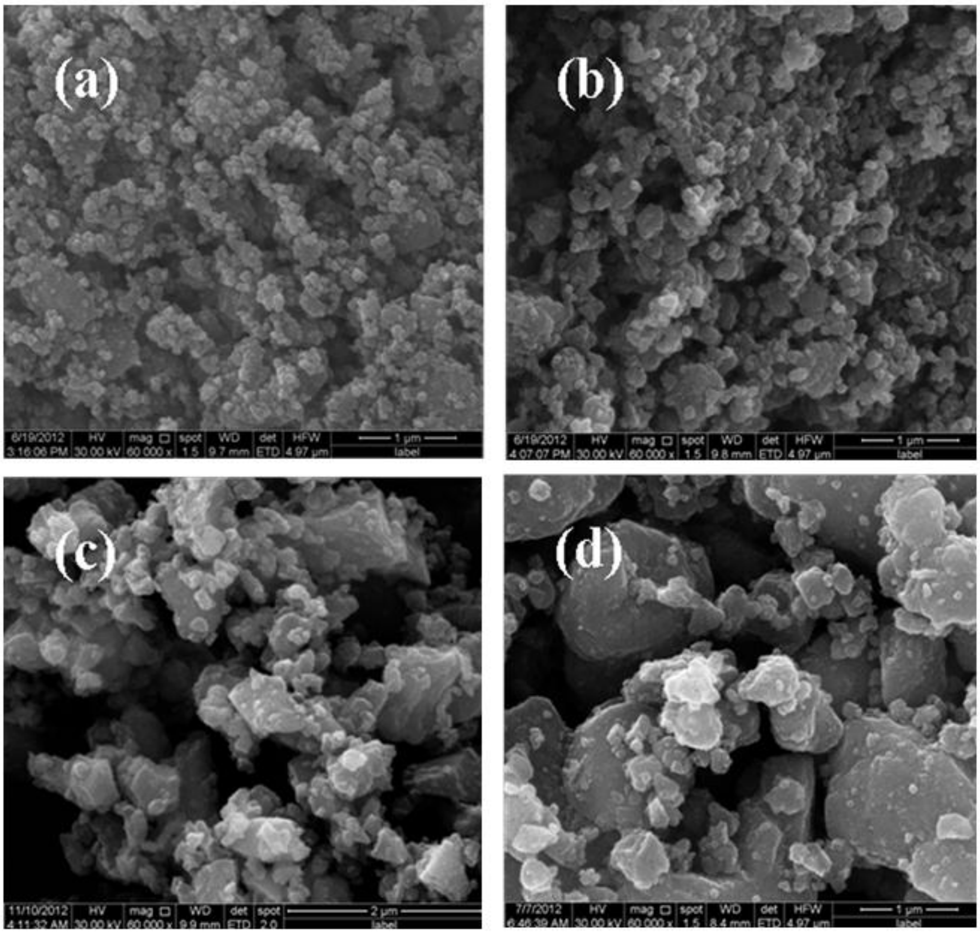

Figure 2. SEM images of products (a: 400 °C, b: 500 °C, c: 600 °C and d: 700 °C)

The reason was that at 400 °C, the calcination temperature was not high enough to achieve perfect crystallization of $LiMn_2O_4$, while at 700 °C, the acute burning of fuel released heat, so that the reaction temperature reached or even exceeded the decomposition temperature of spinel $LiMn_2O_4$ [15]. At 500 °C and 600 °C, no impurity peaks could be observed, suggesting that single phase spinel $LiMn_2O_4$ with cubic structure and Fd3m space group was obtained. It indicated that the optimal calcination temperature was from 500 °C to 600 °C [16, 17].

Fig. 2 presents the SEM images of the $LiMn_2O_4$ calcined at serious temperatures for 1 h. It was evident that with the increasing calcination temperature, the particles size became larger, varying from tens of nanometers to several microns. When calcination temperature was ≤ 500 °C, the particles dispersed uniformly. The particle size of the products prepared at 400 °C and 500 °C were about 50-100 nm and 100-200 nm, respectively. On the other hand, when the temperature was ≥ 600 °C, the products were badly agglomerated. The agglomeration size of the products prepared at 600 °C and 700 °C were in the range of 300 nm and 1.5 μm, respectively. It's obvious that the particles agglomerated seriously at relatively higher temperature, especially for the materials prepared at 700 °C.

3.2. Galvanostatic cycling

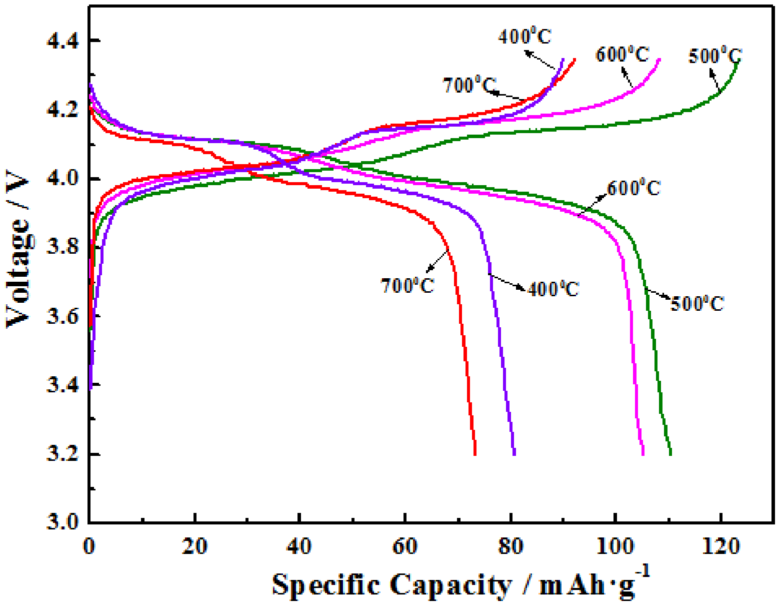

Figure 3. The first galvanostatic charge-discharge curves of obtained $LiMn_2O_4$

Fig. 3 illustrates the first galvanostatic charge-discharge capacity curves of the $LiMn_2O_4$ products, in the voltage range of 3.2-4.35 V (vs. Li / Li^+) at 0.2 C under room temperature. All of the samples manifested two well defined voltage plateaus during charge-discharge process, which coincided with Li^+ insertion and extraction at two different tetragonal 8a sites in the spinel framework [18]. Table 1 presents the discharge specific capacity and capacity retention of the $LiMn_2O_4$ products. From table 1 and Fig. 3, it can be found that the initial discharge specific capacity of the $LiMn_2O_4$

products prepared at 400 °C was fairly low, and this may be caused by the poor crystallinity with the presence of much Mn_3O_4 impurity. The initial discharge specific capacity reached to a maximum value when calcination temperature increased to 500 °C, and then it gradually decreased with the increased calcination temperature. Appropriate enhancement of calcination temperature benefited better crystallinity as well as satisfactory discharge specific capacity. Additionally, under exorbitant temperature, particles easily transformed into sinter which effortlessly generated Jahn — Taller distortion, resulting in bad cycling performance [19-21].

Cycling performances of $LiMn_2O_4$ synthesized through the solid-state combustion synthesis in the voltage range of 3.2-4.35 V at room temperature are represented in Fig. 4. As depicted in Fig. 4 and table 1, the capacity retentions after 40 cycles were about 83.40 %, 90.14 %, 88.98 % and 87.62 % for the $LiMn_2O_4$ products calcined at 400 °C, 500 °C, 600 °C and 700 °C, respectively. It indicated that the best cycling performance was obtained at 500 °C. This result was in accordance with the homogeneous particles from SEM [22].

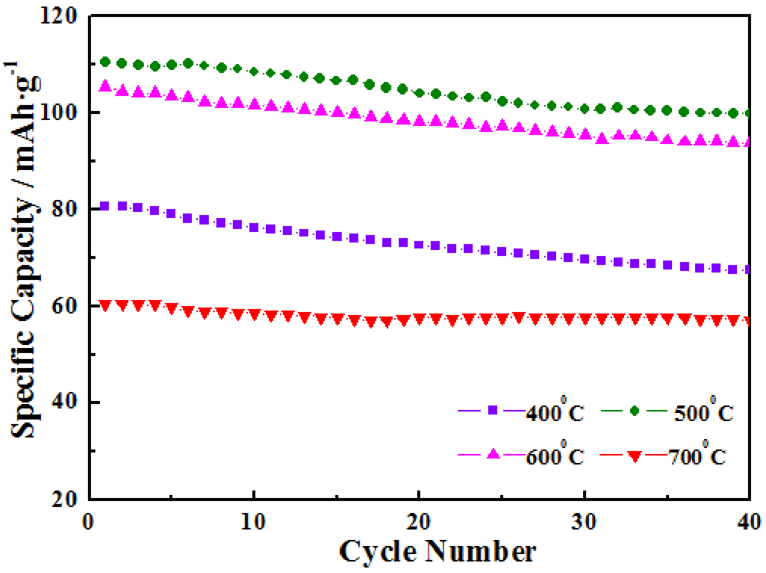

Figure 4. Cycling performances of the $LiMn_2O_4$ electrodes

Table 1. Discharge specific capacity and capacity retention of $LiMn_2O_4$ products calcined at various temperatures

Temperature (°C)	Discharge specific capacity (mAh/g)		Capacity retention (%)
	First cycle	40th cycle	
400	80.7	67.3	83.40
500	110.5	99.6	90.14
600	105.3	93.7	88.98
700	60.6	53.1	87.62

3.3. Cyclic voltammogram

Fig. 5 describes the cyclic voltammogram (CV) of $LiMn_2O_4$ calcined at various temperatures for 1 h with the scan rate of 0.05 mV/s. Two pairs of redox peaks were expressly observed from all the CV curves at about 4.08/3.91 V and 4.21/4.06 V, respectively, implying that the insertion and extraction of lithium-ions were a two-step process [23]. In addition, two couples of redox peaks presented in the cyclic voltammogram which were consistent with the two plateaus in the first galvanostatic charge-discharge curves as Fig. 3 shown. It can be seen that, among all the products, spinel $LiMn_2O_4$ synthesized at 500 °C possessed two well-separated and symmetrical peaks, indicating excellent reversibility. Besides, its highest peak current and peak area revealed a good electrochemical activity. Both the anodic and cathodic peaks of samples calcinated at other temperature became lower, implying they had inferior reversibility and decreased electrochemical performance.

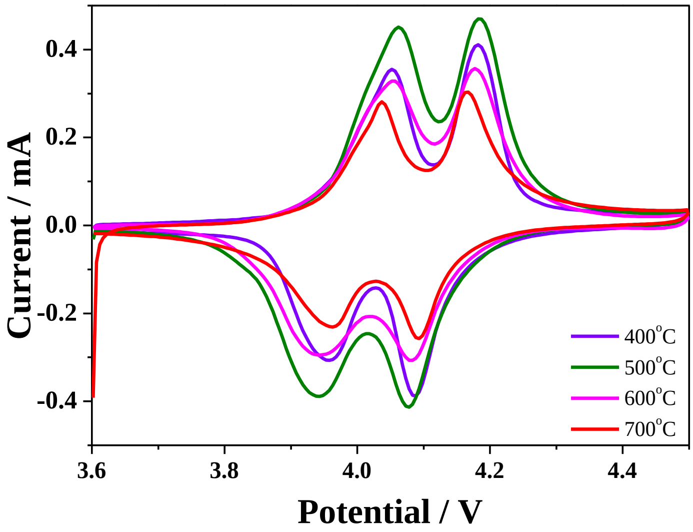

Figure 5. The cyclic voltammogram of the 10th cycle for the $LiMn_2O_4$ electrodes

4. CONCLUSIONS

(1) Pure spinel $LiMn_2O_4$ was rapidly synthesized by solid-state combustion synthesis using β-cyclodextrin (5 wt%) as a fuel, lithium carbonate and manganese carbonate as raw materials. When the calcination temperatures were 500 °C and 600 °C, the as-synthesized powders were spinel $LiMn_2O_4$ with single phase. However, at 400 °C and 700 °C, minor amount of Mn_3O_4 impurities emerged in the combustion resultants.

(2) With increasing combustion temperature, the crystallinity of products became better and the particle size tardily agglomerated to a comparatively larger scale. The particles' diameter of 400-500 °C were about 50-200 nm, whereas the particles of 600-700 °C were agglomerates varying from 300 nm to 1500 nm.

(3) In consideration of the initial discharge capacity and discharge capacity retention, the electrochemical properties of the sample calcined at 500 °C were the best. For the sample calcined at 500 °C, its initial discharge specific capacity was 110.5 mAh/g, and the capacity retention after 40 cycles was 90.14 %.

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