Facile synthesis of spherical spinel $LiMn_2O_4$ nanoparticles via solution combustion synthesis by controlling calcinating temperature

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ABSTRACT

Spherical $LiMn_2O_4$ nanoparticles were successfully prepared via solution combustion synthesis by controlling calcinating temperature. XRD results indicate that high purity $LiMn_2O_4$ can be fabricated by calcinating the precursor above 600 °C. SEM results reflect that $LiMn_2O_4$ calcinated lower than 600 °C are composed of nanoparticles about 100 nm. Therefore, $LiMn_2O_4$ calcinated at 600 °C possess high purity and nanoparticles, which ensure the most excellent electrochemical performance among the precursor as well as $LiMn_2O_4$ calcinated at 500 °C, 600 °C and 700 °C. $LiMn_2O_4$ calcinated at 600 °C even can deliver a capacity of 103.8 mA h g^{-1} at 10 C, which is the 83.6% of the capacity at 0.2 C. It also displays excellent capacity retention ratio of 95.1% for 100 cycles at constant current rate of 1 C.

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1. Introduction

With the expansions of lithium-ion batteries (LIBs) to the fields of electric vehicles (EV), hybrid electric vehicles (HEV) and grid-scale energy storage systems, high power LIBs are increasingly demanded [1–3]. As the key component of LIBs, cathode materials directly determine the power density and energy density. Designing and developing nano-structured cathode materials is an essential route to increase the power density of LIBs. Due to the short distances for lithium ions transport within the nano-structured active material as well as the large contact area between the cathode active materials and electrolyte, nano-structured cathode materials usually exhibit the capability of rapid electrochemical reactions suiting for high power use.

Spinel $LiMn_2O_4$ have received particular attention for application in EV and HEV due to their intrinsic merits such as abundant Mn resource, lower cost, better safety, environmental benignity and high working voltage [4–8]. However, their application as cathode materials for LIBs have been hindered by their inherent drawbacks like serious capacity fading due to the Jahn–Teller distortion of Mn^{3+} ions and structure change during charge–discharge cycles such as formation of two cubic phases, loss of crystallinity as well as development of micro-strain [1,4–8]. Just like other nano-

structured cathode materials [2,3], nano-structured $LiMn_2O_4$ exhibit excellent electrochemical performance such as high specific capacity, high power density and long cycling life because nano-structured $LiMn_2O_4$ can effectively overcome their inherent drawbacks [4]. Therefore, great deals of efforts have been devoted in preparation and characterization of nano-structured $LiMn_2O_4$. So far, various $LiMn_2O_4$ nanostructures such as nanochains [8], nanowires [9], nanoparticles [1,10,11], nanorods [12,13] and nanotubes [14] have been prepared and used as the cathode materials for LIBs. Among those nano-structured $LiMn_2O_4$, $LiMn_2O_4$ nanoparticles have been mostly concerned because of their easy synthesis compared with those nanowires, nanorods and nanotubes.

Solid state synthesis is a traditional method to prepare $LiMn_2O_4$ [15]. For solid synthesis, high temperatures for a long period are needed to form the $LiMn_2O_4$ crystals because of the long-range diffusion of atoms. Compared with solid state synthesis, solution combustion synthesis can be performed at comparatively low temperatures for a short period because all the components have been homogeneously distributed at the atomic-molecular level [16]. Solution combustion synthesis usually contains two steps. Firstly, metal nitrate oxidant as well as the other suitable fuel reductant such as urea [16–20], poly vinyl alcohol [21], poly(acrylic acid) [22], glycol [23], glycol and citric acid [24], urea and citric acid [25], triethanolamine (TEA) [26] and hexamethylenetetramine (HMTA) [27] are homogeneously mixed together. And then, the mixture is evaporated and auto-ignited combusted above 250 °C to get the nano powder precursor. Secondly, the nano powder precursor is calcinated at high temperature to get final $LiMn_2O_4$

[16–27]. How to utilize the nano powder precursor to get $LiMn_2O_4$ nanoparticles in the second step is rarely concerned. In the previous study, we investigated the effects of NO_3^-/CH_3COO^- ratio on the structure and electrochemical performance of ultrafine $LiMn_2O_4$ [5]. In a continuation of our previous study, we choose the suitable NO_3^-/CH_3COO^- ratio to prepare nano powders precursor and then sinter the precursor to obtain spherical spinel $LiMn_2O_4$ nanoparticles by controlling calcinating temperature. The structure and electrochemical performance of the $LiMn_2O_4$ nanoparticles were also investigated.

2. Experimental

2.1. Preparation of $LiMn_2O_4$ nanoparticles

$LiNO_3$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and 50% $Mn(NO_3)_2$ solution were used as starting materials. All the chemicals are analytical grade and without any further purified. We have proved the 3:2 of NO_3^-/CH_3COO^- ratio is fit to prepare ultrathin $LiMn_2O_4$ with best performance by calcinating at 700 °C [5]. Thus, $LiNO_3$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Mn(NO_3)_2$ in a mole ratio of 1:1:1 were dissolved into ethanol in a 200 ml porcelain evaporating dish. According to the previous study [5], we prepared the precursor and obtained ultrathin $LiMn_2O_4$ with average particle size of 210 nm when the precursor was sintered at 700 °C. Therefore, in order to get $LiMn_2O_4$ nanoparticles, the precursor was calcinated at 500 °C and 600 °C in air filled muffle furnace for 8 h and then cooled to the room temperature. In order to compare, the precursor calcinated at 700 °C (ultrafine $LiMn_2O_4$) was also choosed to be as a counterpart.

2.2. Characterization

The precursor, $LiMn_2O_4$ samples obtained at 500 °C, 600 °C and 700 °C were performed at X-ray diffraction (XRD) using a Rigaku RINT2000 X-ray diffractometer over with Cu Kα radiation (λ = 0.154 nm) to determine their crystal structure. The scanning angle was from 10° to 90° (2θ) and the scanning rate was 4 min^{-1}. Then, a JSM-6701F scanning electron microscopy (SEM) was used to further examine the morphology of the four samples.

Coin-type CR2032 cells were used to measure the electrochemical performance of the $LiMn_2O_4$ samples. All the cells consist of a lithium flake anode, a composite cathode, a Celgard 2400 microporous polypropylene separator and 1 mol/L $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl–methyl carbonate (EMC) (1:1:1 volume; Shenzhen Capchem Chemicals) as electrolyte. The composite cathode was prepared as follows. Firstly, 80 wt.% $LiMn_2O_4$ samples, 10 wt.% conductive carbon black (Super P) and 10 wt.% aqueous LA132 binder (Chengdu Indigo power sources CO., Ltd.) were mingled in an agate mortar to obtain the viscous slurry. Secondly, the slurry was coated on a 20 μm aluminum foil and split to 12 mm circular disks (composite cathode). Thirdly, the composite cathode was dried in a vacuum drying oven at 100 °C for 8 h and then weighed. Finally, CR2032 cells were assembled by using the weighed composite cathode, lithium flake anode, Celgard 2400 separator, and electrolyte in an argon-filled glove box.

Galvanostatic charge–discharge tests between the voltage ranges of 3.3–4.4 V were carried out using a LAND CT2001A battery testing system (Wuhan LAND Electronics Co., Ltd.) at room temperature. Cyclic voltammetry (CV) studies were carried out using ZF-100 electrochemical workstation (Shanghai Zhengfang Instruments Co., China).

3. Results and discussion

3.1. XRD analysis

Fig. 1 is the XRD patterns of the precursor and prepared $LiMn_2O_4$ samples. There are typical Mn_3O_4 impurity peaks in the XRD patterns of the precursor. When the precursor was calcinated at 500 °C, the intensity of Mn_3O_4 impurity peaks obviously decrease compared with that of the precursor. When calcinated at 600 °C and 700 °C, high purity $LiMn_2O_4$ can be obtained. It indicates that increasing the calcinating temperature can greatly decrease the Mn_3O_4 impurity and obtain high purity $LiMn_2O_4$. The lattice parameter, crystallite size and unit cell volume of $LiMn_2O_4$ prepared at different temperatures are illustrated in Table 1. The lattice parameter a and unit cell volume increase with the calcinating temperature increasing except for the $LiMn_2O_4$ calcinated at 700 °C. It generally believe that a significant fraction of
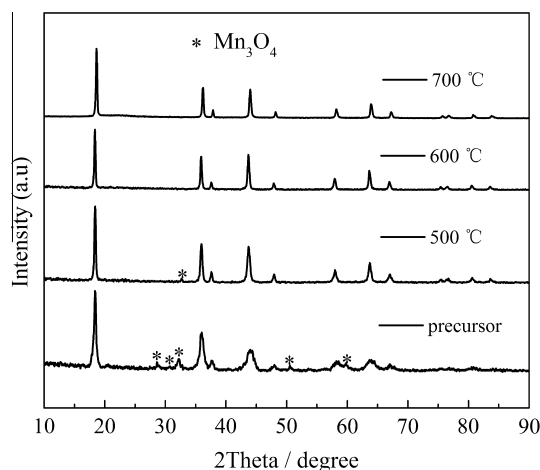

Fig. 1. XRD patterns of the precursor and prepared $LiMn_2O_4$ samples.

manganese ions are present in the Mn^{4+} state in the low-temperature products because of the greater stability of Mn^{4+} ions at low temperatures [19,26]. The bigger Mn^{3+} (Mn^{4+}: 0.60 Å; Mn^{3+}: 0.68 Å) leads to increased value a and unit cell volume. Calculated from the Scherrer's equation, the crystallite sizes are listed in Table 1. All the samples are made up of nanocrystallite $LiMn_2O_4$ and the crystallite size increases clearly with the calcinating temperature increasing. It is a common sense that high calcinating temperature can ensure the nanocrystallite growing larger. In addition, the crystallite size of the precursor is greatly lower than that of $LiMn_2O_4$ obtained at different temperatures which is very according with the distinctly wider peak of the precursor.

3.2. SEM analysis

Fig. 2 is the SEM images of the four samples. Spherical nanoparticles about 100 nm are observed in the SEM images of the precursor, $LiMn_2O_4$ calcinated at 500 °C and 600 °C. While, irregular submicro-particles about 200 nm are found in the SEM image of $LiMn_2O_4$ calcinated at 700 °C. Obviously, the particle character of $LiMn_2O_4$ calcinated at 700 °C is different from the rest three samples, which may be responsible for the abnormal value a and unit cell volume. The particle size of $LiMn_2O_4$ calcinated at 600 °C is nearly as big as that $LiMn_2O_4$ calcinated at 500 °C, while the particle size of the two samples are both smaller than that of the precursor. It indicates that the particle size become smaller with the crystallization degree increasing when calcinating temperature is lower than 600 °C. Considering the XRD results, high purity spherical $LiMn_2O_4$ nanoparticles can be obtained when calcinated at 600 °C. However, when the calcinating temperature is higher than 600 °C, for instance 700 °C, the nanoparticles fuse and form large submicro-particles.

3.3. Electrochemical tests

Fig. 3 presents the rate performance of the precursor and prepared $LiMn_2O_4$ samples. The four samples are all charge–discharged three cycles at every rate. The prepared $LiMn_2O_4$ samples exhibit similar discharge capacity at 0.2 C except the precursor and the difference of the discharge capacities of different samples become clear with the current rate increasing. $LiMn_2O_4$ calcinated at 600 °C shows the best rate capability among the four samples. Its third discharge capacity at 0.2 C is 124.2 mA h g^{-1} and a high discharge capacity of 103.8 mA h g^{-1} even can be maintained at 10 C. The ratio of discharge capacity at 10 C to that at 0.2 C is 83.6%. The rate capability of $LiMn_2O_4$ calcinated at 700 °C