

Low-Temperature Refluxing Synthesis of Nanosized LiMn_2O_4 Cathode Materials

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(Received July 1, 2005; CL-050849)

Nanosized spinel LiMn_2O_4 particles were synthesized from Na-birnessite precursor by a LiBr refluxing method in hexanol at temperature as low as 80 °C. TEM tests showed that the average crystallite size is about 50 nm with a fairly narrow size-distribution. The electrochemical experiments showed that after post-treatment under vacuum, the initial discharge capacity of the as-prepared spinels could reach 125 mAh g^{-1} with good cycle-ability.

Lithium ion batteries have attracted more and more attention in recent years because of their high energy density and long cycle life. Recently, LiMn_2O_4 spinels have been extensively investigated as the cathode materials for lithium ion batteries because of their low cost and limited environmental impact.^{1–4} Traditionally, LiMn_2O_4 spinels were synthesized by solid-state reaction which requires reaction temperature over 700 °C.^{5,6} This method has several disadvantages: inhomogeneity, larger particle size, broader particle size distribution, higher annealing temperatures, and longer periods of calcinations. Thus, low temperature techniques, referred to as soft chemistry synthesis such as hydrothermal method,^{7–10} sol-gel,^{11–13} and coprecipitation^{14,15} have caught much attention. But, these methods also face the problems such as long reaction time, expensive reagents and so on. In this paper, we for the first time report the refluxing synthesis of nanocrystalline LiMn_2O_4 with the average size of 50 nm at the temperature as low as 80 °C. The electrochemical properties of the product were also studied.

All the reagents are of analytical purity and have been received from commercial sources. Na-birnessite was synthesized following the method proposed by Stanton Ching¹⁶ and was used as the precursor to synthesize nanocrystalline LiMn_2O_4 after drying at 80 °C in air for 10 h. To synthesize nanocrystalline LiMn_2O_4 , the prepared Na-birnessite precursor powders (2 g) were introduced into the mixed solution of hexanol (50 mL) and lithium bromide ($\text{LiBr}\cdot\text{H}_2\text{O}$; 10 g). The refluxing reaction was carried out at 80–100 °C for 12–24 h in a batch reactor equipped with a refluxing condenser. After the reaction, the solution was filtrated. The remaining powders were washed with alcohol and distilled water for several times. The washed powders were dried at 80 °C for 12 h in air.

The XRD analyses were carried out on a Philips X'Pro Super diffractometer with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The data were collected in a 2θ range of 10–80° at a scanning rate of 0.02°/s. The morphology and particle size of the samples were investigated by transmission electron microscopy (TEM, Hitachi, Model H-800) with an accelerating voltage 200 kV. Fourier transform infrared spectroscopy (FT-IR) was conducted with a Magna IR-750FT spectrometer at room temperature using KBr pellets as self-supporting

wafers. Teflon cells were made to study the electrochemical properties of the product. The positive electrode consisted of the prepared LiMn_2O_4 (80 wt %), carbon black (10 wt %), and polyvinylidene (PVDF, 10 wt %). The cells were assembled in an argon-filled glove box in which both the moisture and the oxygen levels were less than 1 ppm. The electrochemical tests were made in the voltage range of 3.0–4.5 V at a current density of 0.2 mA cm^{-2} .

Figure 1 shows the XRD patterns of Na-birnessite precursors and the product prepared using LiBr refluxing method at different temperature for various lengths of time. It can be observed that at the temperature 100 °C, spinel LiMn_2O_4 can be synthesized after 12 h of LiBr refluxing reaction. For the temperature 80 °C, the 12 h refluxing product shows typical peak at 6.9 Å, a little lower than the characteristic peak at 7.1 Å for Na-birnessite. The product still shows the characteristic layered structure, but the intensity of the characteristic peaks of layered structure reduces considerably. With the refluxing time increasing to 24 h, the Na-birnessite precursors totally transform into spinel LiMn_2O_4 . According to our best knowledge, the synthesis of spinel LiMn_2O_4 under 100 °C is rarely reported. Herein, we first apply the refluxing method to the synthesis of spinel and successfully synthesized LiMn_2O_4 spinels at temperature as low as 80 °C. The hexanol used in our method can be recycled, which is very economical.

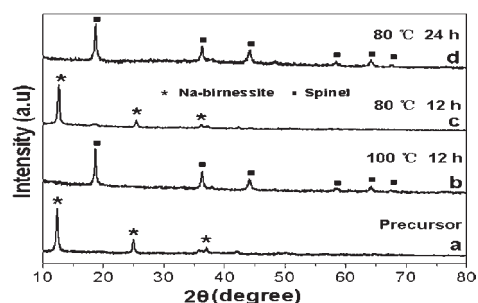


Figure 1. XRD patterns of the precursor and products.

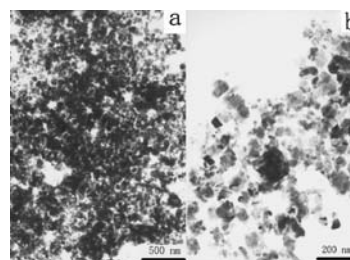


Figure 2. TEM images of LiMn_2O_4 nanoparticles prepared at 80 °C.

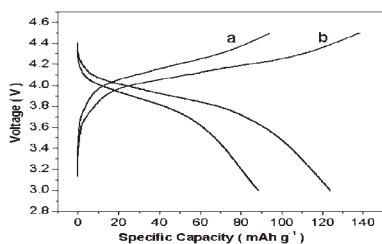


Figure 3. Charge–discharge curves of Li/LiMn₂O₄ (product of 80 °C) a: The original sample; b: The sample dried in vacuum at 120 °C.

Figure 2 shows the TEM bright-field images of the spinel LiMn₂O₄ prepared at 80 °C using refluxing method. It can be observed from the TEM pattern that the crystals are of flake-like shape with the average particle size of 50 nm and the size distribution is fairly narrow. The TEM results suggest that the refluxing method may be a satisfying low-temperature synthesis method of nanocrystalline spinel LiMn₂O₄.

The formation of the spinel phase by refluxing method at low temperature may be explained by the following mechanism. The sodium ions and water molecules in the interlayer galleries of Na-birnessite can be exchanged by other cations. During the exchanging process, the layered structure of Na-birnessite will collapse and change into the tunneled structure. Spinel LiMn₂O₄ can be assigned as a (1 × 3) tunnel structure.⁷ In our refluxing method, during the refluxing of the Na-birnessite precursor in the mixed solution of LiBr·H₂O and hexanol, the sodium ions and water molecules in the interlayer galleries of Na-birnessite are exchanged by Li⁺. Since the ionic radius of Li⁺ is smaller than that of Na⁺, the layered structure of Na-birnessite begins to contract, which can be validated from the reduction of *d* spacing in the XRD pattern after 12 h of refluxing at 80 °C. As the ion exchange proceeds, the contract finally leads to the collapse of layered structure into the (1 × 3) tunnel structure of spinel LiMn₂O₄. The reaction time for the complete transformation is critical. The product after 12 h of refluxing at 80 °C still remains the layered structure. Only after 24 h of reaction, spinel LiMn₂O₄ can be obtained, as shown in Figure 1d.

Figure 3 shows the charge–discharge curves of Li/LiMn₂O₄ (product of 80 °C) cells at a constant charge–discharge rate of 0.2 mA cm⁻² over the voltage range of 3.0–4.5 V. Here, the original product was divided into two halves. One half was made into cells directly, and the other half was dried at 120 °C for 12 h in vacuum before being made into cells. It can be observed that for the original product, the electrochemical property is quite poor, the initial discharge capacity is less than 90 mAh g⁻¹. For the sample dried in vacuum at 120 °C, the initial discharge capacity reaches 125 mAh g⁻¹. The similar phenomenon can be observed for all the refluxing product at 100 °C. Cycle tests were also taken on the two samples, the air-dried sample lost 60% of its initial capacity after 30 cycles. For the vacuum-dried sample, 80% of the initial capacity remained after 30 cycles. The reason for this phenomenon may be that in the original product, a lot of organic substance is left inside the (1 × 3) tunnel structure of spinel LiMn₂O₄. With the process of vacuum post-treatment, the organic remainder is driven out, leading to the improvement of electrochemical property of the product. FT-IR study gives strong support to this explanation. The results of FT-IR study are shown in Figure 4. It can be clearly observed

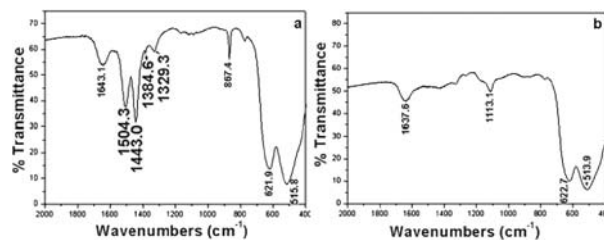


Figure 4. FT-IR spectra of the LiMn₂O₄ products. a: dried in air; b: dried in vacuum.

that in the spinel LiMn₂O₄ dried in air, there are four bands at 1329.3, 1384.6, 1443.0, and 1504.3 cm⁻¹ in the IR spectra, respectively, which can be assigned to the organic residues in the spinel structure. After vacuum post-treatment, these bands totally disappear, which causes the improvement of electrochemical property.

In summary, the refluxing synthesis may be an original and attractive low-temperature synthesis route of spinel LiMn₂O₄. The electrochemical property of the product is studied. The initial discharge capacity of the as-prepared spinels reached 125 mAh g⁻¹ with fairly good cycleability. The possible mechanism on the formation of the nanocrystallites and the mechanism for the electrochemical property improvement by vacuum post-treatment were discussed.

This work is partly supported by the Ministry of Science and Technology of China (No. 2002BA322C). We acknowledge the assistance from the Highstar Chemical Power Source Company Limited.

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