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Synthesis of highly crystalline spinel $LiMn_2O_4$ by a soft chemical route and its electrochemical performance

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Abstract

Highly crystalline spinel $LiMn_2O_4$ was successfully synthesized by annealing lithiated MnO_2 at a relative low temperature of 600 °C, in which the lithiated MnO_2 was prepared by chemical lithiation of the electrolytic manganese dioxide (EMD) and LiI. The LiI/MnO_2 ratio and the annealing temperature were optimized to obtain the pure phase $LiMn_2O_4$. With the LiI/MnO_2 molar ratio of 0.75, and annealing temperature of 600 °C, the resulting compounds showed a high initial discharge capacity of 127 mAh g^{-1} at a current rate of 40 mAh g^{-1}. Moreover, it exhibited excellent cycling and high rate capability, maintaining 90% of its initial capacity after 100 charge–discharge cycles, at a discharge rate of 5 C, it kept more than 85% of the reversible capacity compared with that of 0.1 C.

Keywords: $LiMn_2O_4$; Lithiated manganese dioxide; Rechargeable lithium batteries; Cathode material; Highly crystalline

1. Introduction

The cathode materials for lithium-ion batteries are usually oxides transition metal due to their high electrochemical potentials during the highly reversible lithium insertion/deinsertion. It has been demonstrated that spinel structure lithium manganese oxides are the most promising cathodes because they are much lower in cost, richer in natural sources, more permissible in an environmental standard [1–8]. The details of the crystallinity, crystal structure, the deviation from theoretical stoichimetry of elemental composition, the grain size and grain size distribution, all play important and eventually decisive roles in the electrochemical performance of the $LiMn_2O_4$ spinel. Most of these parameters are decided by, or at least influenced by the synthesis process. $LiMn_2O_4$ was typically obtained by reaction of a mixture of lithium salt (e.g., Li_2CO_3) and manganese oxides at around 800 °C in air for many hours. The high temperature solid-state synthesis process could achieve a high crystalline spinel $LiMn_2O_4$, but suffers from a problem in controlling the stoichimetry, especially causing an oxygen deficiency, which was accompanied with a faster capacity fading during cycling [9–12]. On other hand, it has been demonstrated that the high crystallinity would improve the stability of crystallographic structure during charge–discharge cycles and thus enhance the cycling reversibility of the $LiMn_2O_4$ [13–15]. In recent years, several low-temperature preparation techniques such as sol–gel precipitation [16–18], Pechini process [19,20], electrochemical process [21,22], aqueous reduction method [23] and hydrothermal process [24] template method [25] have been developed in which all the components can been homogeneously distributed to the atomic scale, thus allowing a reduction of heating temperature and sintering time. In spite of that, most of resulting materials show either low discharge capacity or large capacity fading due to the presence of impurity phases and low crystallinity, and further heating treatments involving temperature as high as those used in ceramic route are always needed to enhance their electrochemical performance. Therefore, it is of great importance, but a challenge, to explore an alternative method, which could at a relative low temperature prepare well-crystalline $LiMn_2O_4$ spinel single phase having excellent electrochemical performance.

Pistoia et al. [26,27] have reported that various MnO_2 polymorphs can be lithiated with LiI solutions to give Li_xMnO_2, which would transform to spinel upon heating. In the present work, we explored the optimal conditions to obtain highly crys-

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talline $LiMn_2O_4$ spinel and employed thermo-gravimeter (TG), X-ray diffraction (XRD) and scanning electronic microscope (SEM) to characterize its composition, structure and morphology. Moreover, the relationships among the morphology, crystal structure and electrochemical performance were discussed in detail.

2. Experimental

Lithiated manganese oxide, Li_xMnO_2, was prepared by chemical lithiation of the electrolytic manganese oxide (EMD, Xiangtan Chemical Co.) and a LiI solution in acetonitrile. The preparation procedure can be simply described as follows: 0.1675 g LiI was dissolved in 25 mL of acetonitrile and then stirred at room temperature until the solution became clear. Different amounts of EMD (with molar ratios of LiI to EMD ranging from 0.5:1 to 1:1) were then added into the above solution. The suspension was heated to 70 °C under reflux for 24 h, followed by centrifugation. The resulting product was washed with acetonitrile several times, dried under vacuum at 200 °C for 1 day and then annealed at the temperature range of 200–800 °C for 2 h at a heating rate of 2 °C min^{-1} in air. For comparation, the $LiMn_2O_4$ was prepared by heating a stoichiometric mixture of LiOH and EMD with a Li/Mn molar ratio of 0.5 at 600 °C for 12 h in air.

XRD measurements were performed using a Rigaku D/MAX-IIA X-ray diffractometer using Cu Kα radiation. SEM images were obtained on Philip XL30 operated at 20 kV. The thermo-gravimetric (TG) analysis was carried out on a Perkin-Elmer TGA 7 thermal analyzer.

A CR2016 coin type cell was fabricated to test its electrochemical performance with metallic lithium as counter electrode. The working electrode was prepared by compressing a mixture of active materials ($LiMn_2O_4$), conductive material (acetylene black, AB) and binder (polytetrafluoroethylene, PTFE) in a weight ratio of $LiMn_2O_4$/AB/PTFE = 16:3:1 onto an aluminum grid at 10 MPa. The electrode was punched in disk form with a typical diameter of 12 mm and dried at 120 °C for 12 h before assembly. Typical mass loading of the active material was about 10 mg cm^{-2}. The cell was assembled in a glovebox filled with pure argon. The electrolyte solution was 1 M $LiPF_6$/ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1, v/v). The cell was galvanostatically cycled between 3 and 4.3 V versus Li/Li^+ at various current densities at 25 °C. Lithium insertion into $LiMn_2O_4$ electrode was referred to as discharge and extraction as charge. The cell capacity was determined by only the weight of the positive active material. Cyclic voltammograms (CV) were characterized using a three-electrode cell; the metallic lithium was used both as a counter and reference electrodes. The experiments were performed using a Solartron Instrument Model 1287 electrochemical interface at a scanning rate of 0.1 mV s^{-1}.

3. Results and discussion

Firstly, the formation mechanism for spinel was studied by thermo-gravimeter (TG), and differential thermal analysis (DTA). The DTA and TG traces for the transformation of $Li_xMn_2O_4$ from the lithiated Li_xMnO_2 in air are displayed in Fig. 1. The weight loss until 200 °C was due to the loss of the adsorbed water. From the TG and DTA traces, and the transformation of the defected $Li_xMn_2O_{4+y}$ from Li_xMnO_2 (if $x = 0.5$) may occur from 200 to 500 °C. The reaction can be described as follows:

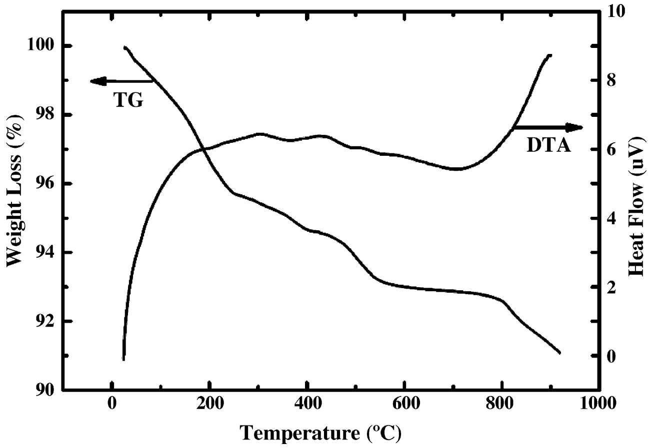

Fig. 1. TG and DTA curves for lithiated MnO_2 recorded over the temperature range from ambient to 900 °C at a heating rate of 10 °C min^{-1} in air at 100 ml min^{-1} flow rate.

$$2Li_{0.5}MnO_2(\text{orthorhombic}) + 0.5yO_2 = LiMn_2O_{4+y}(\text{cubic})$$

The transformation from a defect to a well-ordered spinel proceeds *via* a loss of oxygen was occurred at 500 °C. The following reaction clearly corresponds to an exothermic peak on DTA curve:

$$LiMn_2O_{4+y}(\text{defect}) \rightarrow LiMn_2O_4(\text{well-ordered}) + 0.5yO_2$$

Weight loss over 800 °C was also observed on TG curve. That was also accompanied by the formation of oxygen deficient spinel:

$$LiMn_2O_4(\text{cubic}) \rightarrow LiMn_2O_{4-y}(\text{tetragonal}) + y/2O_2$$

All above results suggest that optimum synthesis conditions for the transformation of well-ordered spinel from lithiated Li_xMnO_2 was occurred performed between 500 and 800 °C.

Fig. 2 gives the XRD pattern of EMD, lithiated MnO_2 heat-treated at different temperatures. Fig. 2a reveals that γ-MnO_2 is relative low degree of crystallinity with broad, low-density peaks, which is a common feather of commercial EMD materials widely used in primary batteries. Fig. 2b and c shows the XRD patterns of the lithiated EMD with Li/Mn = 0.75 after heat treatment at 200 and 400 °C, respectively. Both curves are similar to that of the above mentioned pristine EMD, but most peaks continuously shift toward a lower diffraction angle and the intensity increases correspondingly. This feather confirms that lithium intercalation was occurred in the EMD in a topotactic manner without much distribution in its structure [27]. In addition, diffraction peaks from spinel $LiMn_2O_4$ can also been found in Fig. 2c, suggesting that $LiMn_2O_4$ was initially formed by heat treatment of lithiated EMD at 400 °C. Upon further heating treatment at 600 and 800 °C, all the diffraction peaks could be