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Synthesis and electrochemical properties of spinel LiMn_2O_4 prepared by the rheological phase method

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Abstract Pure-phase and well-crystallized spinel LiMn_2O_4 powders were successfully synthesized by a simple rheological phase method. The thermal behavior and structure properties of the powders prepared by the rheological phase method compared with the solid-state reaction were investigated by thermogravimetry, powder X-ray diffraction, scanning electron microscopy and transmission electron microscopy. According to the results of the electrochemical tests, it is obvious that the sample resulting from the rheological phase method shows higher discharge capacity and better cycling stability than one formed in the solid-state reaction. The cyclic voltammogram and columbic efficiency curves also confirm that the product by the rheological phase method has a good cycling performance due to its fine cubic spinel structure and morphology.

Keywords LiMn_2O_4 · Lithium-ion battery · Rheological phase method · Spinel · Cycling performance

Introduction

The rechargeable lithium-ion battery has been enjoying a significant commercial success as the most promising portable energy source in electronic products mainly due to their high working voltage, high energy density and long life. The transition metal oxides, especially LiMn_2O_4 , LiCoO_2 and LiNiO_2 have been studied extensively to use them as the cathode materials of lithium batteries. Among these cathode materials, spinel

LiMn_2O_4 and its derivatives are considered as the potential cathode materials because of its low cost, rich abundance of Mn resources, low toxicity of Mn ion and environmental friendly nature [1, 2]. The traditional synthesis method of LiMn_2O_4 is the solid-state reaction of mixing oxides or carbonates that contain lithium and manganese cations followed by extended grinding and calcining at high temperatures for a long time. This traditional method includes some disadvantages such as chemical in-homogeneity, broad particle size distribution and long reaction time or unwanted phases. In recent years, several chemical methods such as Sol-gel technique, Pechini method and combustion method have been developed to overcome the above-mentioned disadvantages caused by solid-state reaction. However, most of those methods involve complicated steps during the preparation—which is difficult for commercial applications [3, 4].

For this reason, pure cubic spinel LiMn_2O_4 powder has been synthesized by the rheological phase reaction method in this work. It's a simple and cost-saving way of preparing the compounds or materials from a solid-liquid rheological mixture. In the rheological phase system, the solid powders and liquid substances are uniformly distributed, so the surface area of the solid particles can be utilized more efficiently than in the solid state phase due to the close contact between the solid and liquid sections; also it is convenient for the heat exchange and should ease the diffusion of lithium into the material [5].

In this paper, the physical characteristics of LiMn_2O_4 powders synthesized by the rheological phase method in comparison to the conventional solid-state reaction have been investigated. Moreover, the electrochemical properties of the Li/ LiMn_2O_4 cells, which prepared by the two different methods, are also examined. The results reveal that the LiMn_2O_4 powders obtained from the rheological phase method have a larger initial capacity and show better reversibility than one formed in the solid-state reaction, due to its better crystallinity and morphology.

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Experimental

Preparation of LiMn_2O_4 powders

Rheological phase method

The starting materials lithium carbonate (Li_2CO_3), electrolytic manganese dioxide (EMD) were blended homogeneously with the Li:Mn atomic ratio of 1:2, and then were added to a mixed solution of alcohol and de-ionized water (volume ratio: 1:5) which is used as the dispersant to obtain the solid-liquid rheological state mixture. The mixture was under continuous stirring for 20 h. After that, the rheological body was first dried at 80 °C in the oven and then preserved under vacuum for 5 h at 100 °C to eliminate water adequately. The resulting precursors were preheated at 650 °C for 5 h and finally calcined at 750 °C for 12 h in air, then quenched to room temperature slowly. Figure 1 summarizes the experimental procedure.

Solid-state reaction

The LiMn_2O_4 powders were prepared by the solid-state reaction from stoichiometric mixture of Li_2CO_3 and MnO_2 (EMD). The well milled solid mixtures were preheated at 650 °C in air for 5 h and ground after cooling, and then treated at 800 °C in air for 24 h, followed by cooling to room temperature.

Characterization

The thermal decomposition behavior of LiMn_2O_4 was analyzed by means of thermogravimetry (TG) which was performed on DuPont TGA1090B with $\alpha\text{-Al}_2\text{O}_3$ as the reference substance at a heating rate of 10 °C min^{-1} . The crystal structure of the prepared samples were all characterized by X-ray diffractometer (D/max-2400 Rigaku, Japan) using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) operating at 40.0 KV and 60.0 mA and the datum were collected in the 10 °–80° 2 θ range. The particle size and morphology were investigated by transmission electron

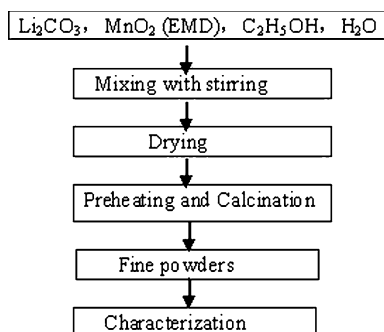


Fig. 1 Schematic diagram for experimental procedure of the rheological phase method

microscopy (TEM, Hitachi600, Japan) and scanning electron microscopy (SEM, JSM-5600LV, Japan).

The electrochemical characterization was carried out by a test two-electrode cell, which consisted of a cathode and a lithium metal anode separated by a Celgard 2,400 porous polypropylene film. A commercial 1 M LiPF_6 solution in a 1:1 mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) was used as the electrolyte. The cathode materials consisted of a mixture of LiMn_2O_4 powders, acetylene black as conductor and polyvinylidene fluoride (PVDF) as binder in a ratio of 75:15:10 by weight. The mixture was coated onto an aluminum disk sheet, and then dried at 100 °C for 24 h in a vacuum oven before use. This disk and a foil of lithium metal were used as the working and counter electrodes, respectively. All the cells were assembled in an argon filled glove box and tested at room temperature. The galvanostatic charge/discharge cycle was performed using a LAND BT-10 cycle life tester (China) with current density of 40 mA/g in the voltage range between 3.0 V and 4.4 V vs. Li/Li^+ . Cyclic voltammetry was conducted using CHI660 electrochemical workstation (Chenhua, Shanghai) for a sweep rate of 0.1 mV/s between 3.0 V and 4.7 V vs. Li/Li^+ .

Results and discussion

Thermal behavior

Figure 2 shows the TG curve for the thermal decomposition of the precursor prepared by the rheological phase method. Weight loss occurs in four temperature region: (1) room temperature–200 °C (2) 200–350 °C (3) 350–650 °C (4) 650–800 °C. The first step from room temperature to 200 °C may be attributed to the evaporation of residual water; as the heating continues, a

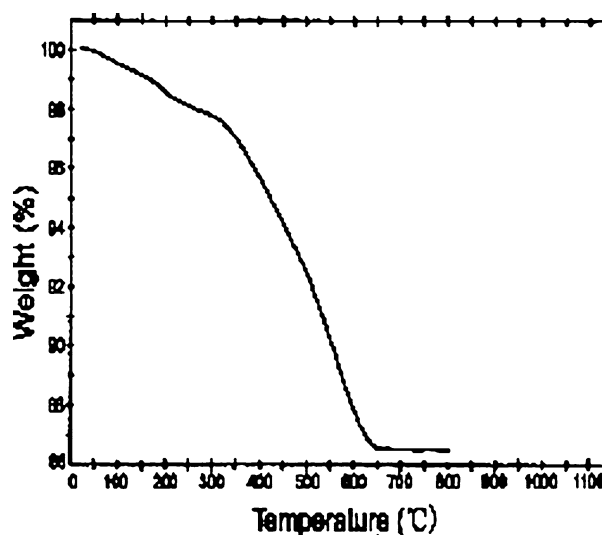


Fig. 2 TG curve of the precursor prepared by the rheological phase method

slight weight loss occurs in the second region which indicates that not all of the water of crystallization in the precursor can be removed in the first region. The occluded water in MnO_2 is lost during this step [6]. In the third region, there is a noticeable weight loss in the TG curve. It is believed that the reaction of Li_2CO_3 with MnO_2 occurs in this region. So preheating in this temperature region is useful for the crystallization of LiMn_2O_4 phase. In the last region, the TG curve becomes flat, which indicates that no phase transformation occurs, and that further heating could only make the structure of the products more crystalline. The TG curve of the precursor by the solid-state reaction is mostly the same as the rheological phase method.

Structure analysis

Figure 3 shows the XRD patterns of LiMn_2O_4 synthesized by the two different methods. The main peaks for spinel LiMn_2O_4 are labeled with hkl indexes. It can be clearly seen that the diffraction peaks of all the samples correspond to a single-phase cubic spinel structure of $\text{Fd}3\text{m}$ space group, in which the lithium ions occupy the tetrahedral sites (8a); Mn^{3+} and Mn^{4+} ions reside at the octahedral sites (16d); and O^{2-} ions are located at 32e sites [3]. For simplicity, these structures can be expressed as $[\text{Li}^+]_{\text{tetrahedral}} [\text{Mn}^{3+} \text{Mn}^{4+}]_{\text{octahedral}} [\text{O}_4^{2-}]$ [7]. The stronger and narrower peaks of the sample obtained from the rheological phase method indicate that the crystallinity of the compound obtained by the rheological method is better than that of the sample obtained by the solid-state method.

Since the particle size is also an important factor for cycling performance of the $\text{Li}/\text{LiMn}_2\text{O}_4$ cells, particle morphology and particle size were examined by SEM and TEM, respectively. Fig. 4 presents the SEM micrographs of LiMn_2O_4 prepared by the two different methods. Comparing Fig. 4a with 4b, it could be seen that the

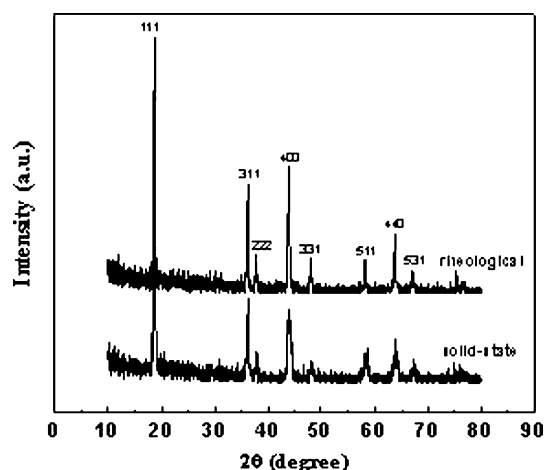


Fig. 3 X-ray powder diffraction patterns obtained from LiMn_2O_4 spinel prepared by the two different methods

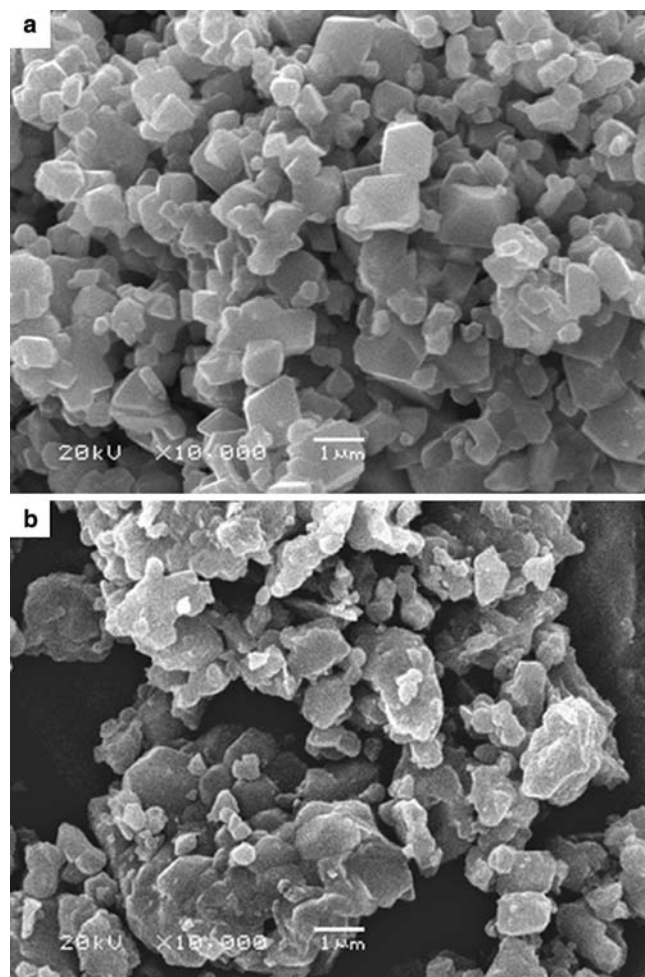


Fig. 4 SEM photographs of LiMn_2O_4 synthesized by a rheological phase method b solid-state reaction

LiMn_2O_4 powders synthesized by the rheological phase method have a narrower particle size distribution and most of the prepared particles are cubic spinel structure shapes (Fig. 4a). However, the particles of the products prepared by the solid-state reaction are larger and non-uniform (Fig. 4b). This fact is also demonstrated by TEM photograph in Fig. 5. It can be found that the average diameter of the cubic structure particles prepared by the rheological phase method is 80–150 nm and the size distribution is narrow (Fig. 5a). In contrast, the average diameter of the particles obtained from solid-state reaction is about 100–300 nm and there is a certain agglomeration in these particles (Fig. 5b).

From the SEM and TEM results, it is apparent that this rheological phase method leads to the formation of fine cubic spinel structure particles that are narrowly distributed.

Electrochemical properties

The electrochemical performance of LiMn_2O_4 as the cathode of the lithium-ion battery was examined as

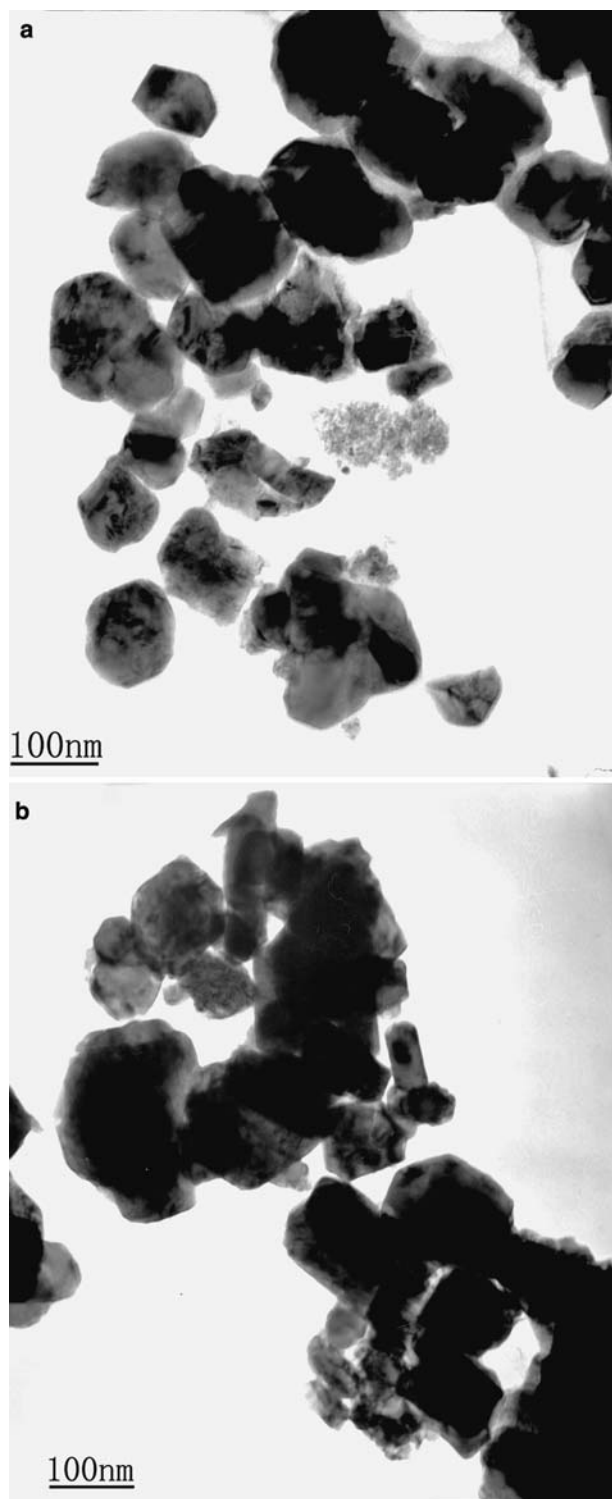


Fig. 5 TEM images of LiMn_2O_4 prepared by **a** rheological phase method **b** solid-state reaction

follows. Fig. 6 plots the relationships between the charge-discharge capacity and the cycle number for LiMn_2O_4 prepared by the two different methods. The $\text{Li}/\text{LiMn}_2\text{O}_4$ cells were charged and discharged at a current rate of $1/3\text{ C}$ (40 mA/g) between 3.0 V and 4.4 V

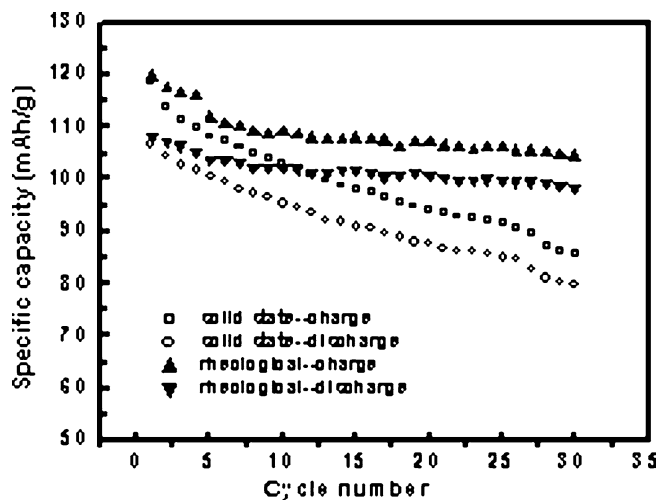


Fig. 6 Relationships between the capacity and cycle number of the $\text{Li}/\text{LiMn}_2\text{O}_4$ cells prepared by the two different methods

at room temperature. The initial charge and discharge capacity for the sample prepared by the rheological phase method can reach 119 mAh/g and 108 mAh/g , respectively. And the sample prepared by solid-state reaction had the first charge capacity of 118 mAh/g and discharge capacity of 106 mAh/g . After 30 cycles, the discharge capacity for LiMn_2O_4 obtained from rheological method faded from 108 mAh/g to 98 mAh/g with the capacity retention rate of 90.74% , whereas that of LiMn_2O_4 prepared via solid-state reaction was only 74.5% . These results indicate that the rheological phase method has a better cycle stability, which is believed to be related with its better crystallinity and structure morphology, also this comment is well consistent with the SEM and TEM results mentioned above. Accordingly, the rheological phase method is suitable for synthesizing the spinel LiMn_2O_4 with a good cycling performance.

Figure 7 shows the variations of voltage vs. charge/discharge capacity curves at the 1st, 10th, 20th and 30th cycle for LiMn_2O_4 synthesized by the two different methods. For these curves, the voltage range is $3.0\text{--}4.4\text{ V}$ and the current density is 40 mA/g . Usually there are two distinctive voltage plateaus in the charge/discharge curves, characteristic of the well-defined spinel LiMn_2O_4 cathode, which implies that there are two steps for lithium intercalating and deintercalating into the material [8]. As can be seen in Fig. 7, the charge/discharge curves of the rheological method indeed has two obvious voltage plateaus (Fig. 7a) indicating its pure and good spinel crystal structure, while that of the solid-state method is relatively blurry. Besides, the sharp capacity fading also occurred after several cycles in the solid-state reaction which is attributed to its unstable structure and severe distortion of the unit cell during charging and discharging (Fig. 7b). Hence, the better crystallinity and finer cubic spinel structure of LiMn_2O_4 prepared by the rheological phase method, compared

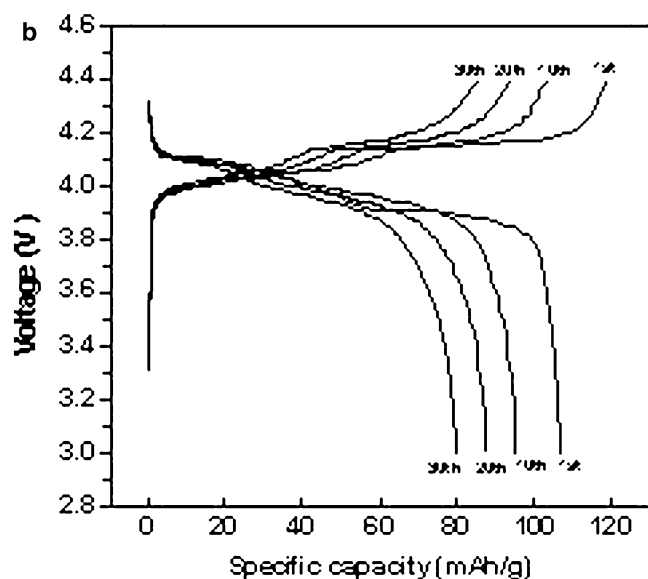
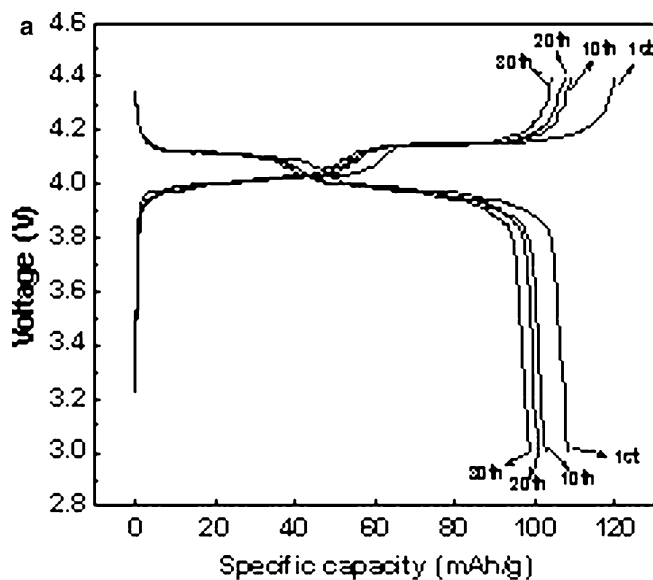


Fig. 7 Charge/discharge Curves vs. cycle number (1st, 10th, 20th, 30th) for LiMn_2O_4 cathode materials prepared by **a** rheological phase method **b** solid-state reaction

with that prepared by the solid-state reaction, are considered to lead to the larger capacities and better cycling behavior.

In order to compare the differences of the charge/discharge behavior between the samples prepared by the two different methods more clearly and directly, we picked out the 30th cycle charge and discharge curves of the two different products and presented them in Fig. 8. From this figure, it is obvious that the voltage plateaus of the sample obtained by the rheological phase method are much longer and flatter than that of the sample obtained by the solid-state reaction, therefore, the material obtained from the rheological phase method has a larger charge and discharge capacity. Besides, it is apparent that the sample prepared by the rheological

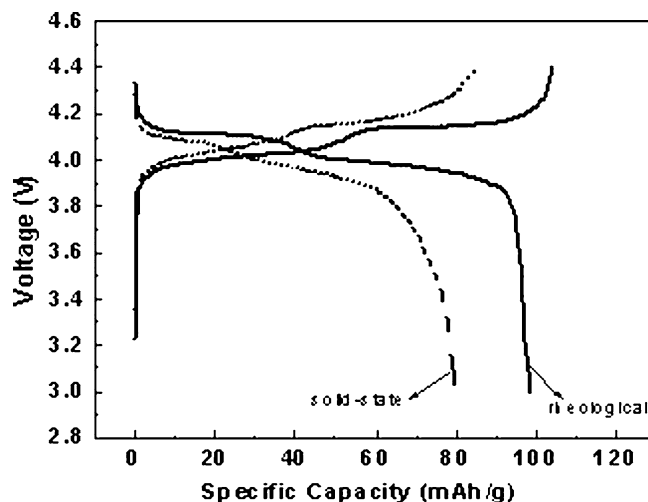


Fig. 8 The 30th cycle charge and discharge curves of LiMn_2O_4 synthesized by the two different methods

phase method possesses a higher discharge voltage plateau than that obtained by the solid-state reaction, which indicates that the material by the rheological phase method has a better battery performance.

With the purpose of further investigating the electrochemical properties of the rheological phase method, a typical first cyclic voltammogram (CV) at a scan rate of 0.1 mv/s is shown in Fig. 9. As depicted in Fig. 9, two pairs of clearly separated peaks which represent two redox reactions for LiMn_2O_4 are located at 3.96, 4.06 and 4.08, 4.17 V. (The peak potentials are labeled in the curves). These results correspond to the typical two-step reversible intercalation/de-intercalation processes of lithium ion. In the spinel LiMn_2O_4 , the oxygen ions form a cubic close-packed array, tetrahedral (8a) sites

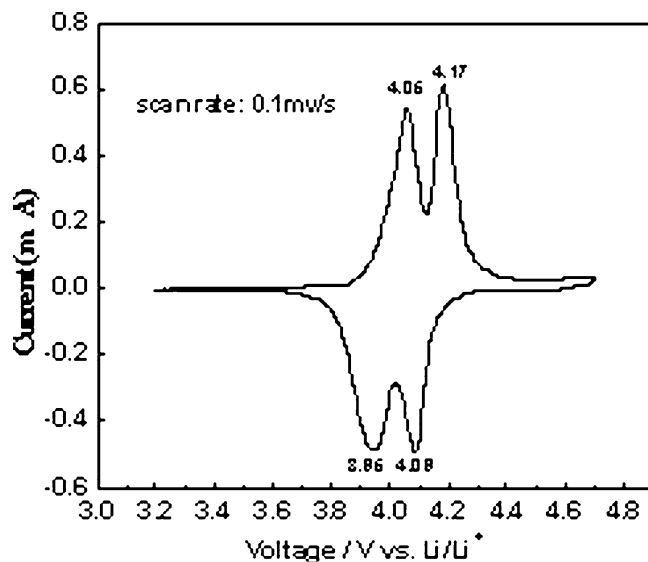


Fig. 9 First cycle of cyclic voltammogram for LiMn_2O_4 synthesized by the rheological phase method. (Scanning rate: 0.1 mv/s. Voltage range: 3.0–4.7 V)

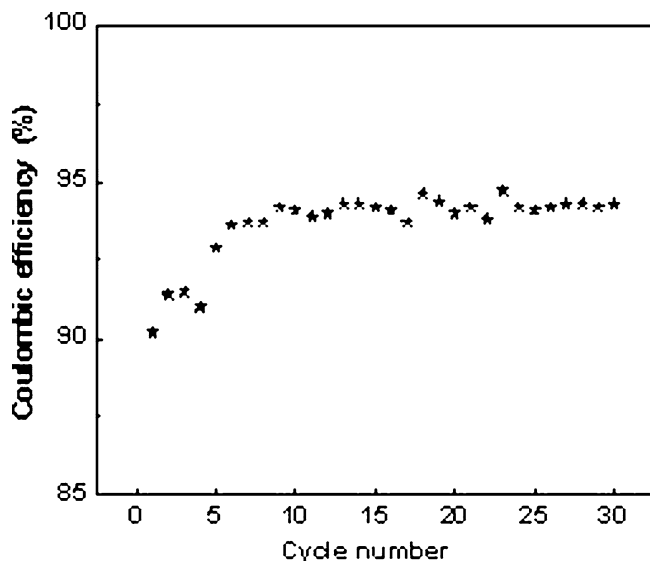


Fig. 10 Plot of Charge/discharge coulombic efficiency vs. cycle number for LiMn_2O_4 synthesized by the rheological phase method

share face with vacant octahedral sites (16c), so ions can intercalate/de-intercalate through these channels during the electrochemical reaction. In the oxidation process, the first peak around 4.06 V is believed to be the removal of Li ions from half of the tetrahedral sites, while the second peak at about 4.17 V is attributed to the removal of Li ions from the residual tetrahedral sites [9]. The results obtained in this experiment are consistent with those reported previously [7, 10, 11]. The measured value of the ratio for peak currents i_{pa}/i_{pc} is nearly 1 which demonstrates that Li ions are intercalation and de-intercalation relatively reversibly in this compound.

The results obtained from the CV plot are also in good agreement with the charge-discharge curves illustrated in Fig. 7a. As shown in Fig. 7a, the charge-discharge curves show two pairs of distinct voltage plateaus around 4.0 V and 4.1 V related to the two pairs of redox peaks in the CV, indicating the typical electrochemical characteristics of LiMn_2O_4 . As in the discharge curve, it is reported that the upper plateau region of discharge curve stands for two-phase equilibrium between λMnO_2 and $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$, while the second plateau represents a phase equilibrium between $\text{Li}_{0.5}\text{Mn}_2\text{O}_4$ and LiMn_2O_4 [12].

The charge/discharge coulombic efficiency of LiMn_2O_4 synthesized by rheological phase method is also presented in Fig. 10. The efficiency values all above 90% reveals that the sample obtained via rheological phase method has good charge-discharge reversibility

because of its fine cubic spinel structure, and this is also consistent with the cyclic voltammogram results above.

Conclusions

Using Li_2CO_3 , MnO_2 (EMD) as the starting materials, uniform LiMn_2O_4 powders have been synthesized successfully by an easy-control and cost-saving rheological phase method. It is believed that in the rheological phase system, the solid powders and liquid substances are distributed uniformly, so the surface area of the solid particles can be utilized more efficiently than in the solid state phase, which is good for the heat exchange and should ease the diffusion of lithium into the material to form fine spinel structure. The structure and electrochemical properties are also examined. The experiments results reveal that the rheological phase reaction leads to the formation of good crystallinity LiMn_2O_4 powders, which consist of cubic spinel structure particles. Compared with the LiMn_2O_4 prepared by the solid-state reaction, the product obtained from the rheological phase method yields a higher initial specific capacity for both charge (119 mAh/g) and discharge (108 mAh/g) process and also shows a better cycling performance with the capacity retention rate of 90.74% after 30 cycles. Therefore, the rheological phase method could be employed to synthesize the cathode materials for lithium-ion battery as a promising method.

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