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The effect of $LaMnO_3$ with high electronic conductivity on the high rate charge-discharge performance of $LiMn_2O_4$

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ABSTRACT

The effect of $LaMnO_3$ with high electronic conductivity on the fast charge-discharge rate performance of $LiMn_2O_4$ is studied. X-ray diffraction patterns confirm the existence of $LaMnO_3$ and also indicate $LaMnO_3$ has no influence on the crystal structure of pristine $LiMn_2O_4$. The transmission electron microscopy (TEM) images indicate that $LaMnO_3$ coating layer, about 15 nm thickness, covers the surface of $LiMn_2O_4$ well. The electrochemical performances are evaluated by galvanostatic charge/discharge tests and electrochemical impedance spectroscopy (EIS). At 0.5 C/0.5 C, $LaMnO_3$ coated $LiMn_2O_4$ delivers an initial capacity of about 114 mAh g^{-1} along with the coulombic efficiency of 95.0%, which are higher than those of uncoated $LiMn_2O_4$ (106 mAh g^{-1} and 89.1%). Furthermore, $LaMnO_3$ coated $LiMn_2O_4$ can exhibit higher capacities at high charge-discharge rates than uncoated $LiMn_2O_4$. It can deliver about 90.6 mAh g^{-1} at 10 C/10 C and 68.0 mAh g^{-1} at 20 C/20 C, but there are only 53.6 mAh g^{-1} and 43.3 mAh g^{-1} for bare $LiMn_2O_4$. Electrochemical impedance spectroscopy (EIS) demonstrates that $LaMnO_3$ coating layer can effectively reduce the electrodes' resistances and improve the kinetics of electrodes. The improved high rate properties of $LaMnO_3$ coated $LiMn_2O_4$ are ultimately ascribed to the easier phase conversion from λ-MnO_2 to $Li_{0.5}Mn_2O_4$ which is related to $LaMnO_3$ coating layer with high electronic conductivity.

1. Introduction

As a major rechargeable batteries for small portable devices, Li-ion batteries (LIBs) are also expected to be used as large-scale energy storage devices for electric vehicles (EVs) as well as for hybrid electric vehicles (HEVs) [1]. When used in a high-energy and high-power assistant for EVs and HEVs, LIBs should store and deliver large quantities of energy rapidly in a short time [2]. This means excellent high rate charge-discharge performance and high energy density are needed for LIBs. Thus an enormous effort is taken to improve the high rate charge-discharge capability of LIBs.

There are various types of cathode materials for commercialized LIBs, such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, substituted transition metal oxides and so on. Among them, $LiMn_2O_4$ has been extensively investigated due to the obvious advantages of low cost, easy preparation, safety and environmental friendliness [3–5]. Especially, the good thermal stability of $LiMn_2O_4$ is a positive factor for being used in EVs and HEVs, because it is not necessary to equip expensive safety devices [6]. However, for bare $LiMn_2O_4$, the durability and the limited rate capability to some extent are still a lasting issue. Up to now, tremendous efforts have been devoted to overcome these obstacles, such as doping with foreign atoms [7], optimizing synthesis approaches [8], decreasing particle size [9,10], treating the surface of $LiMn_2O_4$ by coating electronically conductive agents [11] and so on.

Though great success in improving cycle stability has been achieved, few studies focus on high rate charge-discharge performance. The improvement on the high rate charge-discharge performance of $LiMn_2O_4$ is necessary before it can be used as cathode material of LIBs for EVs and HEVs. According to previous reports, the limited charge-discharge performance of bare $LiMn_2O_4$ is mainly ascribed to its low electronic and ionic conductivity, as well as slow diffusion of lithium ions at the cathode/electrolyte interface [12,13]. Surface modification has been proved to be an effective approach to improve the charge-discharge performance of $LiMn_2O_4$. Here, the coating layer can act as an electron-conducting media to facilitate the heterogeneous charge transfer process and reduce the inter-particle resistance on the cathode surface [14]. Furthermore, it can also provide the extra electron-conducting pathways between material particles and current collector, as well as among the particles [15].

In this paper, in order to improve the high rate charge-discharge performance, the surface of $LiMn_2O_4$ is modified by perovskite-type oxide

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$LaMnO_3$ particles, which has much higher electronic conductivity than $LiMn_2O_4$. The effect of $LaMnO_3$ coating layer on enhancing the electrochemical performance of $LiMn_2O_4$ is also investigated.

2. Experimental

Commercial $LiMn_2O_4$ powder was utilized as bare material (Tianjin Huaxia Hongyuan industrial Co., ltd.). The other raw materials were analytical-grade.

The raw material of $La(NO_3)_3 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ were dissolved in distilled water, and the molar concentration of La^{3+} and Mn^{2+} was 0.1 $mol \cdot L^{-1}$, respectively. Then $C_6H_8O_7 \cdot H_2O$ (complexation agent, 0.3 $mol \cdot L^{-1}$) was added into the reaction vessel, after which $NH_3 \cdot H_2O$ was dropwise added to adjust pH of the solution to 3. Subsequently, the commercial $LiMn_2O_4$ powders were added into the above solution, and the obtained mixture was heated at 60 °C under continuous stirring until it became a homogeneous sol (the amount of $LaMnO_3$ in the sol was 3 wt.% $LiMn_2O_4$). At last, the resulting mixture was dried at 120 °C for 10 h, calcined at 400 °C for 4 h and 700 °C for 10 h in sequence to obtain $LaMnO_3$ coated $LiMn_2O_4$ powders.

The crystal structures of the prepared samples were studied by Powder X-ray diffraction (XRD, D/max 2500 V/PC, Rigaku, 40 kV, 150 mA) using Cu-Kα radiation (λ = 1.5405 Å) and a bent graphite monochromatic with a scanning rate of 2° min^{-1} in the 2θ range 15–80°. The morphologies and microstructures of the samples were observed by transmission electron microscopy (TEM, JEM-2100F, JEOL) at an accelerating voltage of 200 kV.

The cathode slurry was prepared by homogeneously mixing active material, carbon black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 8:1:1 in *N*-methyl-2 pyrrolidence (NMP) solvent, after which it was cast uniformly onto aluminum foil and dried at 120 °C for 12 h to obtain the dried electrode which was further punched into round disks with a diameter of 1.2 cm. Subsequently, by using lithium metal as anode, the prepared electrode as cathode and 1 M $LiPF_6$ in ethylence carbonate (EC)/ethyl methyl carbonate (EMC)/dimethyl carbonate (DEC) (1:1:1 by volume) as electrolyte, the cells were assembled in an argon-filled glove box where the moisture and oxygen content were less than 1 ppm. The electrochemical properties of the cells were measured by a battery testing system (CT2001A, LAND) at different charge-discharge rate from 0.5 C to 20 C (1 C = 120 mA g^{-1}) at room temperature. Electrochemical impedance spectroscopy (EIS) were recorded using an electrochemical workstation PARSTAT 2273 in the frequency range from 10 mHz to 100 kHz and a ±5 mV AC signal.

3. Results and discussion

The XRD patterns of bare $LiMn_2O_4$ and $LaMnO_3$ coated $LiMn_2O_4$ are presented in Fig. 1. In Fig. 1a, the main diffraction patterns of both samples can be well indexed to a standard cubic spinel structure with $Fd\overline{3}m$ space group (JCPDS Card No. 35-0782) [16]. Furthermore, the sharp diffraction peaks of both patterns indicate that both samples have good crystal structure. Besides $LiMn_2O_4$ phase, the XRD patterns for $LaMnO_3$ coated sample in Fig. 1a also present some weak peaks of a second phase (marked as *) between 30° and 50°. Fig. 1b is the amplified pattern in the 2θ range of 30–50° for $LaMnO_3$ coated $LiMn_2O_4$. The (110), (104) and (204) diffraction peaks of $LaMnO_3$ (JCPDS Card No. 54-1275) in Fig. 1b, which correspond to a rhombohedral structure with $R\overline{3}c$ space group [17], can be observed. So the above weak peaks indicate the existence of $LaMnO_3$ particles in the composite. Because the diffraction peaks of $LiMn_2O_4$ after coating $LaMnO_3$ have no obvious change, $LaMnO_3$ coating layer has no obvious influence on the spinel structure of $LiMn_2O_4$ bulk.

TEM images of bare and coated $LiMn_2O_4$ before cycling are given in Fig. 2. It can be employed to further investigate the microstructure of coating layer. In contrast to the smooth surface of bare $LiMn_2O_4$ (Fig. 2a), $LaMnO_3$ coating layer, with a thickness of approximately 10 nm, forms a compact and uniform film on the surface of $LiMn_2O_4$ in Fig. 2b, which is beneficial to forming a good core-shell structure. Furthermore, the interlayer spacing of 2.7 Å between the lattice fringes in the inset of Fig. 2b corresponds to the (104) plane of $LaMnO_3$ crystallites (JCPDS card No. 54-1275). The above result demonstrates that $LaMnO_3$ layer with high crystallinity has covered the surface of $LiMn_2O_4$ well.

Fig. 3 compares the initial charge-discharge curves of both samples at 0.5 C. Both cells were firstly charged to 4.3 V at 0.5 C, held at 4.3 V until the current drops to 0.2 C, then discharged to 3.0 V at 0.5 C. $LaMnO_3$ coated $LiMn_2O_4$ delivers an initial discharge capacity of about 114 mAh g^{-1} with an initial coulombic efficiency of 95.0%, which are higher than those of bare $LiMn_2O_4$ (106 mAh g^{-1} and 89.1%). So $LaMnO_3$ coating is beneficial to increasing the discharge capacity and coulombic efficiency of $LiMn_2O_4$, which can be attributed to the high electronic conductivity of $LaMnO_3$ [18]. In general, the initial coulombic efficiency is related to the total sum of lithium ion available in the subsequent cycling, and a higher coulombic efficiency stands for the less loss of lithium ion. So the result indicates that $LaMnO_3$ coating layer is beneficial to decreasing the irreversible capacity loss of $LiMn_2O_4$.

But, compared with bare $LiMn_2O_4$, the charge-discharge curves of $LaMnO_3$ coated $LiMn_2O_4$ show two more typical plateaus approximately at 4.1 V and 4.0 V, which correspond to the two characteristic steps during Li^+ intercalation for well-defined spinel $LiMn_2O_4$, namely, phase transformation of λ-MnO_2 to $Li_{0.5}Mn_2O_4$ and the coexistence of two

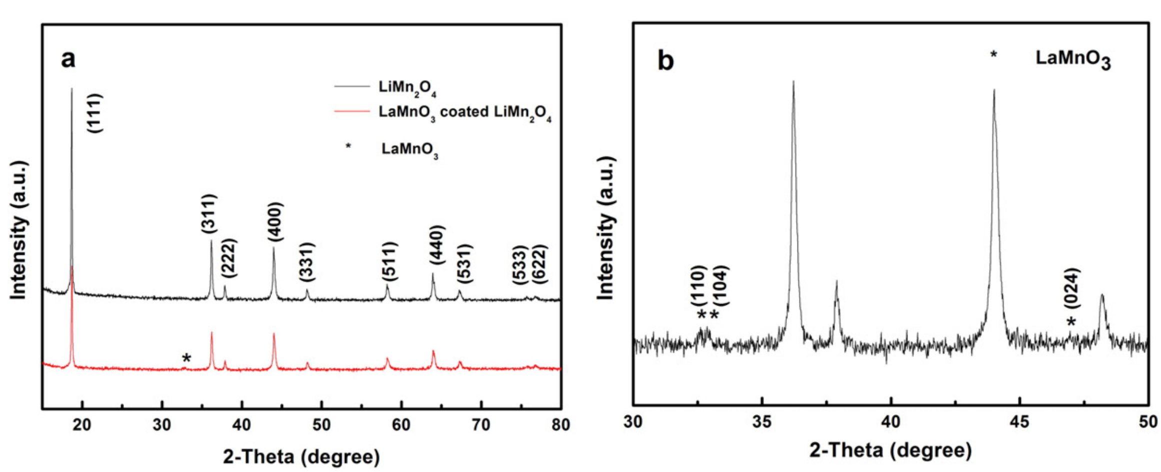

Fig. 1. XRD patterns of (a) uncoated $LiMn_2O_4$ and $LaMnO_3$ coated $LiMn_2O_4$, (b) partially magnification of 30–50° of $LaMnO_3$ coated $LiMn_2O_4$.