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Electrochemical performance of LBO-coated spinel lithium manganese oxide as cathode material for Li-ion battery

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Abstract

Surface treatment of the lithium manganese oxide cathode material coated by lithium borate glass ($\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$) with improved electrochemical cyclability and structural stability was conducted in this study. The lithium manganese oxide powder doped with various weight percentages of LBO glass was calcined to form a fine powder with single spinel phase, exhibiting different particle size, size distribution and morphology. The surface area decreased with the content of the LBO glass. The average particle size was in the range of 3–8 μm . Cyclic charge/discharge testing of the coin cells, fabricated by lithium manganese oxide and 0.4 wt.% LBO-coated lithium manganese oxide as cathode material, provided the initial discharge capacity of 95.57 and 119.79 mAh/g, respectively. Furthermore, the 0.4 wt.% LBO-coated lithium manganese oxide powder retained 93% of its original capacity after 10 cycles, showing much better cyclability than the uncoated lithium manganese oxide. It is demonstrated that the LBO-coated lithium manganese oxide cathode material exhibited high discharge capacity and the fading rate was evidently decreased after cyclic test.

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1. Introduction

The Li-ion rechargeable batteries based on carbon as anode, non-aqueous electrolyte and cathode with high energy density and power capability have been extensively studied. They are widely used in the electronic portable devices, such as cellular phones, notebooks and personal digital assistance (PDA) devices.

Different types of cathode materials in Li-ion rechargeable batteries with low cost, high stability and good electrochemical performance, such as LiCoO_2 [1] and LiNiO_2 [2] with R3m layer structure, LiNiVO_4 and LiCoVO_4 [3] with inverse Fd3m spinel structure and LiMn_2O_4 [4] with Fd3m spinel structure have been considered in the research. Among these candidate cathode materials, LiMn_2O_4 was proposed to satisfy the field-use

requirements and has become a promising cathode material for commercial usage. However, there are some drawbacks associated with the poor electrochemical performance of LiMn_2O_4 cathode material, such as Jahn–Teller distortion [5], manganese dissolution and electrolyte decomposition [6]. The first factor could be significantly improved by partial substitution of manganese cations with monovalent lithium ions [7], or transition metal like Ni, Co, Cr Cu and Fe [8–12] and substitution of oxygen with fluorine [13,14]. The dissolution of manganese and the electrolyte decomposition could be overcome by altering the surface chemistry of the cathode electrode particles by inorganic materials and metal oxide, such as lithium boron oxide glass and zinc oxide [15,16].

In this study, a surface modification approach was used to provide satisfactory electrochemical property for Li-ion rechargeable batteries. In order to simplify the synthesis process and to increase the yield of the product, the utilization of solid-state method for surface modification was employed. The effect of LBO glass coating layer on the

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electrochemical performance at higher charge–discharge voltage and structural stability of the base commercial LiMn_2O_4 electrode were investigated.

2. Experimental procedure

2.1. Powder preparation

The precursor of LBO glass, LiOH and H_3BO_3 , were mixed with a molar ratio of 1:2 in methanol, and then heated and gently stirred at 50–70 °C until the solvent was completely evaporated. The base commercial LiMn_2O_4 , km110 (Kerr-McGee, Oklahoma City, USA) was coated with the LBO glass by solid-state method. The solid-state method is described as follows. First, the mixture of the precursor of LBO glass with various weight percentages and km110 were blended by a pulverizer. The mixed powders were then calcined at 500 °C for 10 h. The weight percentage of the precursor of LBO glass was between 0 and 1 wt.% before calcination, and in the range of 0–0.5 wt.% after the heat treatment.

2.2. Characterization and analysis

The compositions of the calcined powder were analyzed with an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkin Elmer, Optima 3000 DV, USA), and were furthermore evaluated with an electron probe

microanalyzer (EPMA, JXA-8800 M, JEOL, Japan). Since lithium could not be detected by EPMA, the content of manganese and oxygen were first evaluated through ZAF technique in EPMA and then the amount of lithium was obtained by difference and normalization approach. The phase and crystal structure of the heat-treated powders were analyzed with an X-ray diffractometer operated at 30 kV and 20 mA from 15 to 70 °C (Rigaku, D/MAX-B, Japan) with a wavelength of $\text{CuK}\alpha$ ($\lambda=1.5406$ Å). The particle size and distribution of the precursor and spinel LiMn_2O_4 powder were examined by laser scattering (Horiba, LA 300, Japan). The particle morphology was observed using a field scanning electron microscope (FESEM, JSM-6500F, JEOL) at an accelerating voltage of 15 kV.

2.3. Electrochemical characterization

The electrochemical behavior of commercial LiMn_2O_4 powder was examined by using two-electrode test cells consisting of a cathode, metallic lithium anode, polypropylene separator and an electrolyte of 1 M LiPF_6 in a 1:1 (volume ratio) mixture of EC/DMC (ethylene carbonate/dimethyl carbonate). All procedures in fabricating the cells were carried out in a specially designed chamber with low oxygen pressure and low moisture. Details of the set-up were reported elsewhere [7]. The coin cells were cycled within the potential range of 3.0–4.2 V at 0.1 C rate for the first cycle and then at 0.2 C rate from the 2nd to the 16th cycle.

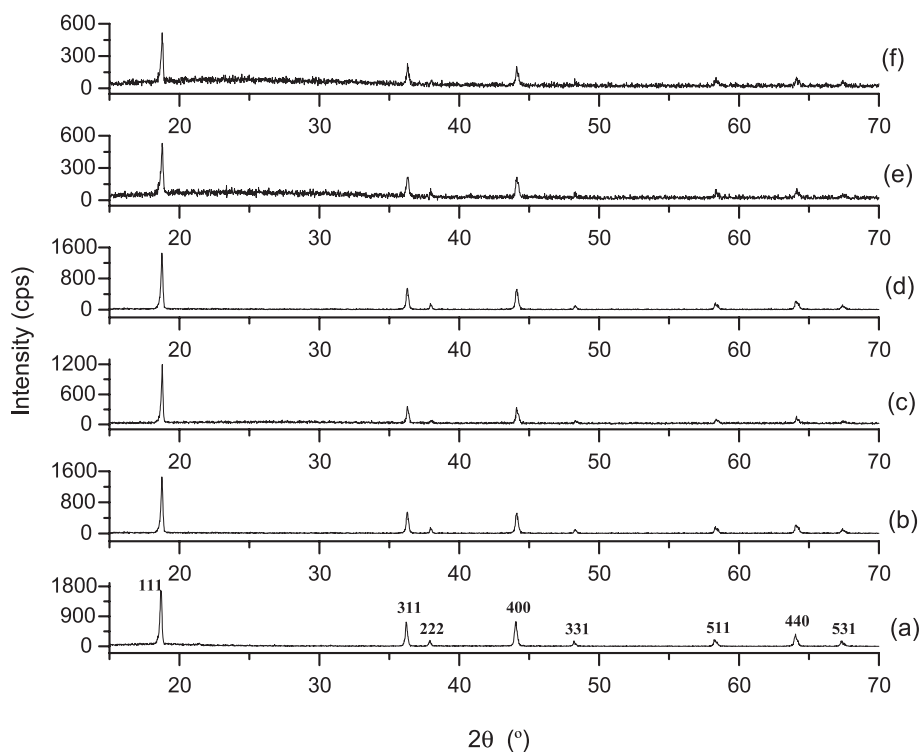


Fig. 1. XRD pattern of km110 coated with various weight percentages of LBO glass calcined at 500 °C for 10 h (a) base km110, (b) 0.1 wt.%, (c) 0.2 wt.%, (d) 0.3 wt.%, (e) 0.4 wt.%, and (f) 0.5 wt.%.

3. Results and discussion

3.1. Phase identification

The X-ray diffraction patterns of the km110 coated with the various weight percentages of LBO glass derived from solid-state method calcined at 500 °C for 10 h are shown in Fig. 1(a) to (f), respectively. In Fig. 1(b) to (f), it is apparent

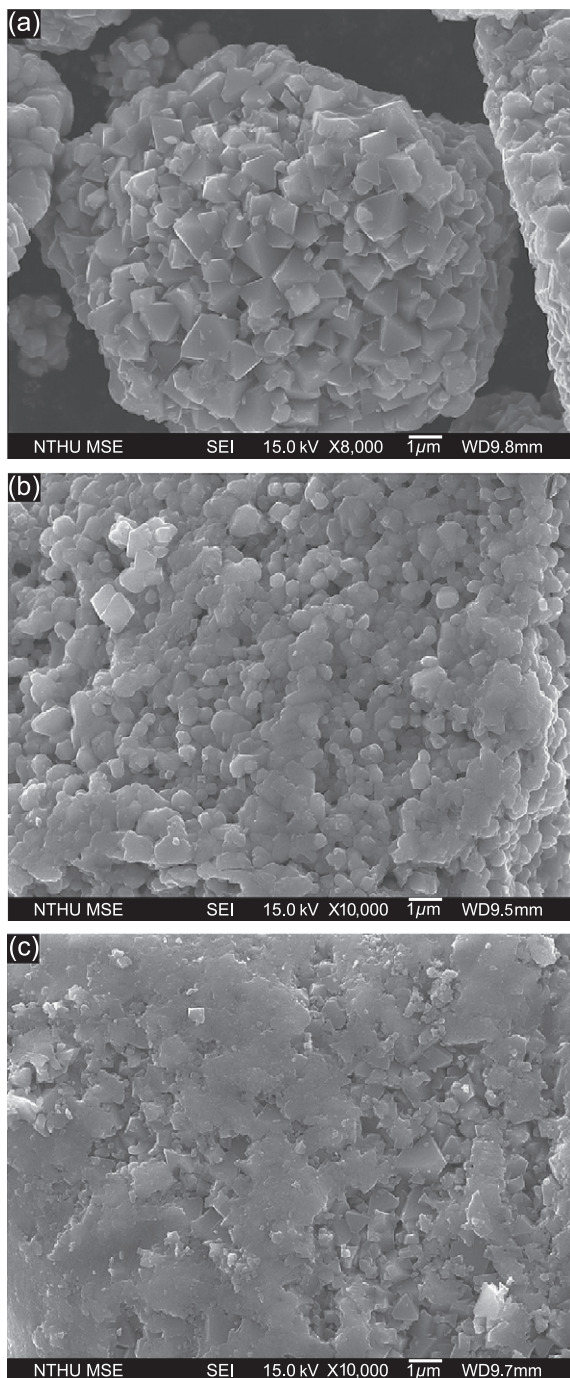


Fig. 2. FESEM images of km110 coated with various weight percentages of LBO glass calcined at 500 °C for 10 h (a) base km110, (b) 0.1 wt.%, and (c) 0.5 wt.%.

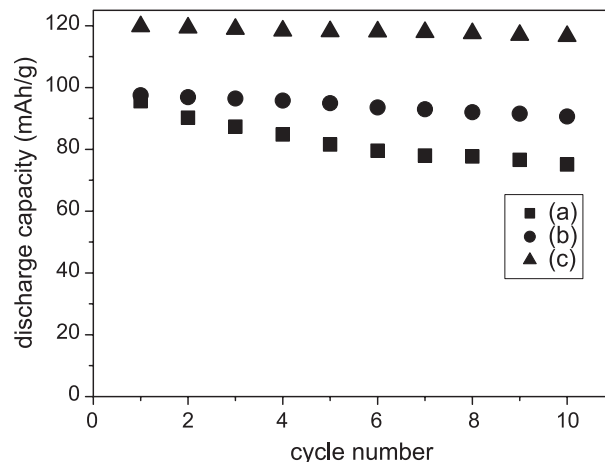


Fig. 3. Specific discharge capacity of various powders calcined at 500 °C for 10 h (a) base km110 and (b) 0.4 wt.% LBO of km110 at 4.2 V, and (c) 0.4 wt.% LBO of km110 at 4.5 V.

that the position of the peaks for the surface-modified km110 is almost the same as that for the base km110, as shown in Fig. 1(a). A pure spinel structure was revealed for all the XRD patterns. Since no other XRD peaks show up, it is believed that amorphous LBO glass well coated the surface of the km110 and did not penetrate into the spinel matrix.

3.2. Particle size and morphology

Fig. 2(a) to (c) demonstrate the SEM micrographs of the base km110, 0.1 wt.%, and 0.5 wt.% LBO-coated km110 derived from solid-state method calcined at 500 °C for 10 h. Particle size analysis revealed that the first and the second particle size of the km110 was in the range of 300–700 nm and 9–13 μm, respectively. In Fig. 2(a), the km110 exhibited well-defined crystal faces and regular shape of octahedral. The SEM micrograph of 0.1 wt.% LBO doped sample, as indicated in Fig. 2(b), showed similar surface morphology as compared to the undoped km110 matrix. It appears that the amount of 0.1 wt.% LBO was not sufficient to alter the angular features of particles as shown in Fig. 1(a) for the km110-based materials. However, the surface morphology of 0.5 wt.% LBO doped sample was quite distinct. As shown in Fig. 2(c), the surface of the km110 was obviously coated by a layer of the LBO glass. From the SEM morphology of the LBO-coated km110 and the fact that no other phases revealed in the XRD pattern, it is believed that the LBO glass layer was amorphous rather than crystalline [17].

3.3. Electrochemical performance

The fading rate test of the base km110 and LBO-coated km110 calcined at 500 °C for 10 h, represented in Fig. 3, was measured galvanostatically at elevated charge–discharge voltage from 3 to 4.2 V and 3 to 4.5 V with the assembly of Li/EC+DMC+LiPF₆/LiMn₂O₄ at the rate of 0.1 C. The

Table 1

The discharge capacity of the first and tenth cycle and the capacity fading percentage of the initial discharge capacity of the base km110 and LBO-coated km110

Sample	Discharge capacity after the first cycle (mAh/g)	Discharge capacity after 10 cycles (mAh/g)	Capacity fading after 10 cycles (%)
Base km110 at 4.2 V	95.57	75.22	21.3
0.4 wt.% LBO glass at 4.2 V	97.5	90.63	7.05
0.4 wt.% LBO glass at 4.5 V	119.79	116.64	2.63

discharge capacity after the first and 10 cycles are evaluated and recorded in Table 1. Also listed in Table 1 is the calculated capacity fading rate after 10 cycles for the base cathode as well as the LBO doped sample.

The km110 assembly delivered a value of 95.57 mAh/g at the first cycle and decayed to 75.22 mAh/g after 10 cycles. The discharge capacity of the 0.4 wt.% LBO-coated km110 was 97.5 mAh/g in the initial cycle and remained 93% of its origin value after 10 cycles. This was much better than that of the initial discharge capacity fading of 79% for the uncoated one. Furthermore, as the charge–discharge voltage was raised to 4.5 V, the 0.4 wt.% LBO-coated km110 showed very good electrochemical property of highly initial capacity of 119.79 mAh/g and great retention of 97.4%, as shown in Fig. 3.

In literature, the main reason for the capacity loss observed for the conventional LiMn_2O_4 spinel cathode material is suggested to the HF formation resulting from the reaction of fluorinated anions with residual H_2O , and the HF contents play a vital role in MnO dissolution [15]. Therefore, it is possible that Mn dissolution could be reduced by decreasing HF contents at the cathode surface. The electrochemical data obtained in this study demonstrated that the improvement of the cycling performance of LiMn_2O_4 spinel electrode by LBO dopant was evident. This was attributed to the surface modification accustomed in the glassy film offering high diffusion rates and sintering of the particulate surfaces, thereby decreasing the interface area between the cathode and the electrolyte as well as the HF content at the cathode surface. This would then reduce the electrolyte oxidation and dissolution of Mn_2O_3 [18]. Recently, Sun et al. [19] reported the formation of a rock salt Li_2MnO_3 phase resulting from the dissolution of MnO from LiMn_2O_4 into electrolyte. The surface modification employed in this study is presumed to protect the electrolyte from the catalytic effects of LiMn_2O_4 formation and thus prevents the cathode from corrosion by the non-aqueous electrolyte.

The achievements in this study demonstrate that the LBO-coated spinel lithium manganese oxide cathode materials prepared by solid-state method exhibit relatively good stability and electrochemical properties.

4. Conclusion

1. The $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glass can be deposited successfully on the surface of the commercial LiMn_2O_4 with various weight percent by solid-state approach.
2. The pure spinel XRD pattern of the LBO-coated km110 without any other phases indicated that the LBO glass may form an amorphous film on the surface of the cathodic powder only but not into the spinel structure. An amorphous $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ glass film was also revealed on the km110 surface.
3. The 0.4 wt.% LBO-coated glass showed the best electrochemical performance in the studied deposit concentration range. The specific area of the cathode powder can thus be reduced to depress the electrolyte oxidation by surface-modification.

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