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Synthesis and modification of non-stoichiometric spinel ($Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$) for lithium-ion batteries

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ABSTRACT

A non-stoichiometric spinel phase ($Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$) was synthesized using a natural polymer sol–gel method. It was characterized by X-ray diffraction. The particle size and shape of the as-prepared compounds were observed by scanning electron microscope. The new compound was coated with $LiBO_2$, and the effects of the $LiBO_2$ coating on $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ spinel phase were investigated. The results showed that pure $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ had good electrochemical properties, however, the non-stoichiometric spinel coated with $LiBO_2$ showed better electrochemical performance at both room temperature and high temperature (50 °C) than pure $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$. The initial discharge capacity of the $LiBO_2$-coated non-stoichiometric spinel was 118 mAh g^{-1} at a current density of 1 mA cm^{-2} over the voltage range from 3.0 to 4.4 V. The discharge capacity was about 99.2% of the initial capacity after 100 cycles at room temperature and about 95.2% after 50 cycles at high temperature (50 °C). The modification of spinel with $LiBO_2$ effectively improved the electrochemical properties of non-stoichiometric spinel as a cathode material.

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1. Introduction

Secondary lithium batteries have been studied for the past several decades, as they exhibit the highest specific energy among all the battery systems. Much effort has been devoted to developing some new lithium-ion battery systems in order to meet the demands of the market. Among the cathode materials for these batteries (such as $LiCoO_2$, $LiNiO_2$, $LiCo_xNi_{1-x}O_2$, and $LiMn_2O_4$), Li–Mn-spinel is one of the most promising candidates, in terms of its low cost, easy preparation, and lack of toxicity. However, the loss of capacity in the Li–Mn-spinel lithium-ion battery system has been remarkable upon cycling, which is believed to be mainly a result of the Jahn–Teller effect and slow dissolution of Mn(III) ions into the electrolyte. Much research has been done to improve the properties of Li–Mn-spinel, including synthesis of spinel with smaller specific surface areas, partially replacing oxygen with fluorine or elemental sulfur, or coating the spinel with some particular compounds. Many other efforts have also been devoted to stabilizing its structure by doping with metal ions such as Li^+, Co^{3+}, Cr^{3+} and Ni^{2+} [1–7]. In this work, a novel synthesis and modification for non-stoichiometric spinel phase ($Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$) are reported. It also provides not only the electrochemical properties for non-stoichiometric spinel ($Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$), but also the beneficial effects of $LiBO_2$-coated non-stoichiometric spinel on its electrochemical properties.

2. Experimental

The samples ($Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$) were prepared by a natural polymer sol–gel method. Lithium acetate ($LiAc_2{\cdot}2H_2O$), manganese acetate, Y_2O_3, and LiF were taken in the molar ratio of 1.05:1.90:0.01:0.15 and ground well to form a solid powder mixture. Konjac powders (a natural polymer, Konjac Glucomannan $(C_6H_{10}O_5)_n$, FM ≈ 10^6) were dissolved in water to form a sol–gel. The solid powder mixture was added to the Konjac sol–jel and mixed fully to form a rheological state mixture, which was then kept at 95 °C for 12 h to form the precursor. The final product was obtained by a two-step calcination of the precursor at suitable temperatures (first time at 550 °C for 2 h and second time at 750 °C for 6 h). The product obtained was coated with $LiBO_2$ by dispersing the product together with $LiBO_2$ (weight ratio of $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ to $LiBO_2$ of 93 to 7) in ethyl alcohol. After the evaporation of the solvent ethanol at 70 °C, the powders coated with $LiBO_2$ were annealed at 600 °C for 2 h. X-ray diffraction (XRD) analysis of the resultant product was carried out on a Shimadzu XRD-6000 diffractometer, using $CuK\alpha_1$ radiation. The particle morphology was observed by scanning electron microscopy techniques (JEOL JSM 6460A SEM). The relative content of Mn(IV) and Mn(III) was determined by X-ray photoelectron spectroscopy (XPS). The composition of the expected compound was determined by the inductively coupled plasma (ICP) analysis technique. The fluorine content in the spinel phase was detected by fluorine ion selective electrode analysis method.

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Positive electrodes for testing were prepared by mixing spinel powders (64–70 wt.%), acetylene black (20–24 wt.%), and polytetrafluoroethylene (PTFE) (10–12 wt.%). 8–15 mg of the mixture was pressed onto a nickel grid. Prior to use, the positive electrodes were dried at 125 °C in a vacuum furnace for 24 h. Lithium foil was used as the anode. The test cells were assembled in a glove box under argon atmosphere. The electrolyte used was a solution of 1 mol L^{-1} $LiClO_4$ in ethylene carbonate/propylene carbonate (EC–PC; 1:1). For long-term cycling experiments, the cells were charged and discharged over the voltage range of 4.4–3.0 V (vs. Li/Li$^+$), using particular current densities.

3. Results and discussion

The XRD pattern (Fig. 1) of the compound formed at 750 °C indicates that the spinel phase compound was formed. All diffraction lines can be indexed just the same as $LiMn_2O_4$. The lattice constant of the new spinel compound formed at 750 °C was calculated from the XRD data: $a = 0.8210$ nm. The a lattice parameter was found to be smaller than that of Li–Mn-spinel ($LiMn_2O_4$, $a = 0.8241$ nm) [8]. SEM investigations revealed that each particle takes on a cubic shape, as shown in Fig. 2. The particle sizes were distributed in the range from 100 to 300 nm. From Fig. 2, it can be seen that the particles of $LiBO_2$-coated $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ (No. 0179) have a more regular shape than $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ (No. 0181). Fig. 2 (bottom panel) is the energy dispersive spectroscopy (EDS) B mapping of $LiBO_2$-coated $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$, which shows the distribution of B atoms in the $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ compound.

The chemical composition of the new spinel phase was checked by ICP analysis. The molar ratio of the elements (Li, Mn, Y) was 1.02:1.90:0.02. The relative content of Li ions showed a small loss during synthesis, but the relative content of the elements Mn and Y was nearly the same as that in the reactant mixture. The fluorine content in the spinel phase was detected by fluorine ion selective electrode analysis method, it was found that the content of fluorine in spinel was about 54.5% of the fluorine's moles designed in the raw material. Hence the experimental chemical formula of the new compound was $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$. The relative quantities of Mn(III) and Mn(IV) were determined by XPS. The content of Mn(III) was 36.89% of total Mn, and the content of Mn(IV) was 63.11% of total Mn. According to the electric charge balance, the value of y was calculated as about 0.1 [9].

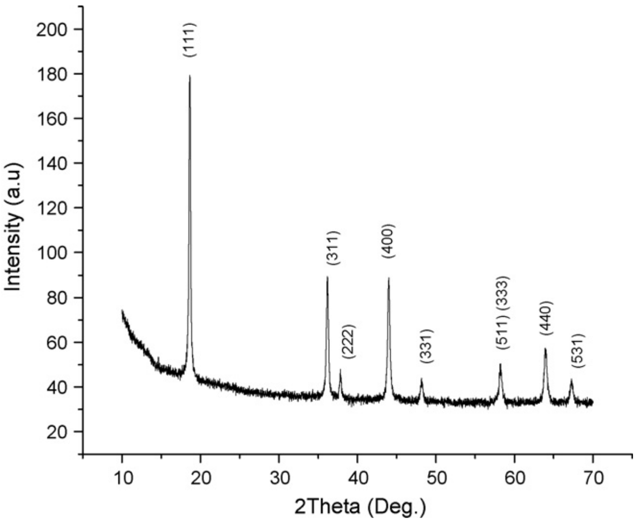

Fig. 1. XRD of Li–Mn-spinel powders ($Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$).

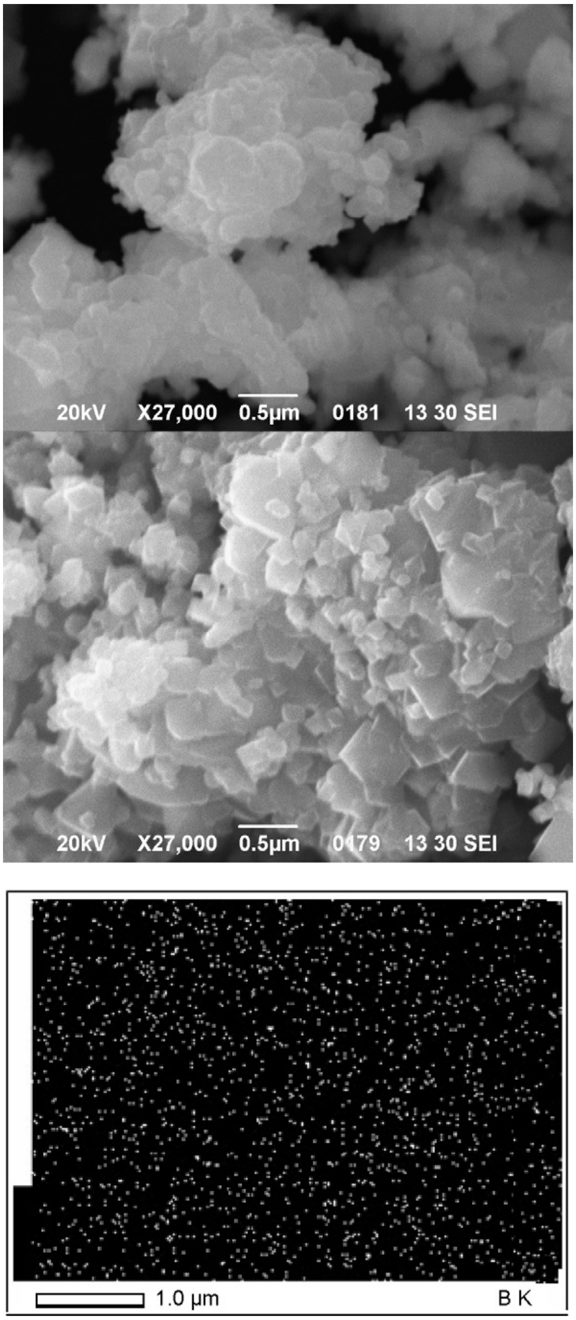

Fig. 2. SEM of $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ (0181), $LiBO_2$-coasted $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ (0179) powders and EDS mapping of B element in spinel $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$.

Fig. 3 shows that having a certain weight of $LiBO_2$ coating on the surface of the $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ powders (7 wt.%) did not change its spinel structure. Both $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ and $LiBO_2$-coated $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ have the same crystal structure, but peaks of $LiBO_2$ in the coated $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ were not detected. We therefore believe that $LiBO_2$ was present on the surface of $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ and formed a thin layer of $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08\times z}$ $LiBO_2$. The lattice constant of $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ was 0.8210 nm. The lattice constant of $LiBO_2$-coated $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$ kept unchanged, which proved that the $LiBO_2$ coated on the surface of the spinel had not reacted with the spinel to form a new phase and just been absorbed on the surface of spinel in state of non-crystal powders. Fig. 2 (BK) is EDS B element mapping of $LiBO_2$-coated $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$. It can be seen that B atoms are distributed uniformly in the $LiBO_2$-coated non-stoichiometric $Li_{1.02}Mn_{1.90}Y_{0.02}O_{4-y}F_{0.08}$.

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