A New Spinel $LiMn_2O_{4-x}(SO_4)_x$ Compounds for Cathode Materials

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The spinel $LiMn_2O_{4-x}(SO_4)_x$ compound cathode materials for lithium ion secondary battery were synthesized by solid-state reaction among the calculated amounts of $LiOH{\cdot}H_2O$, MnO_2 (EMD) and $MnSO_4$. The results of the electrochemical test demonstrated that these materials exhibited excellent electrochemical properties. It's highest reversible capacity of these series of cathode materials is ～120 $mAh{\cdot}g^{-1}$, and after 50 cycles, its capacity is still around 116 $mAh{\cdot}g^{-1}$ with nearly 100% reversible efficiency, which reveals that doped sulfate ion can improve the structure stability of spinel.

Keywords Spinel $LiMn_2O_{4-x}(SO_4)_x$, cathode materials, lithium-ion secondary battery

1. Introduction

In recent years, with the development of all sorts of cellular phones, camcorders, laptop computers, the lithium-ion secondary batteries based on the use of manganese-lithium oxide $LiMn_2O_4$[1, 2] attracted much attention. But the $LiMn_2O_4$ cathode material has a disadvantage of structural instability[3, 4] as a result of the Jahn-Teller effect caused by Mn^{3+}. Many researchers have made great efforts to improve its structural stability by cation substitution[5-7], but little reward has been received. Amatucci and Strobel synthesized Li-Mn-O-F compounds, and in their experiments, when fluorine was added, the capacity of Li-Mn-O-F compounds was clearly higher than that of Li-Mn-O compounds with some penalty in stability[8-10]. We added sulphate to Li-Mn-O compounds and found that the $LiMn_2O_{4-x}(SO_4)_x$ compound cathode materials exhibited excellent structural stability during charge-discharge actions. Based on our experiments, we suggested some explanation for it.

2. Experimental

These spinel $LiMn_2O_{4-x}(SO_4)_x$ compound cathode materials were synthesized from the mixture of $LiOH{\cdot}H_2O$, MnO_2 (EMD) and $MnSO_4$. In the first, these mixtures were ball-milled in a planetary micro-mill with stainless steel balls. A dispersing liquid, alcohol, was added to form an slurry which was ground overnight through combined shaking and rotation. After milled, these fully mixed precursor slurry were dried to evaporate the alcohol under infrared lamp. Finally, the precursors were calcined at 730°C for 36 h.

A series of spinel $LiMn_2O_{4-x}(SO_4)_x$ compounds with different x (x=0, 0.025, 0.05, 0.1) were synthesized as designed above. All cell assemblies were completed in a dry box filled with argon gas. All electrochemical tests were carried out in a DC-5 fully automatic program test instrument at room temperature, with constant current (0.265~0.353 mA/cm^{-2}, 3.0-4.5 V).

3. Results and discussion

Fig. 1 shows the relation between the initial reversible capacity and sulfate ion contents of spinel $LiMn_2O_{4-x}(SO_4)_x$ compounds with different sulfate ion contents. The initial reversible capacity of prepared materials gradually becomes lower with the sulfate ion -contents increasing.

Fig. 2 shows the cycle-capacity of spinel $LiMn_2O_{4-x}(SO_4)_x$ compounds with different sulfate ion contents. From Fig. 4 we can find that the pure spinel $LiMn_2O_4$ as cathode material cycled 20 times at a large capacity loss. Whereas, the spinel $LiMn_2O_{3.975}(SO_4)_{0.025}$ exhibits excellent stability, after cycling 50 times, the reversible capacity does not almost exhibit any loss, and the reversible capacity is still around 116$mAh{\cdot}g^{-1}$. These results confirm the fact that the doped-sulfate ion improved the electrochemical stability of $LiMn_2O_4$ and when x = 0.025, the cycling behavior reaches the best state.

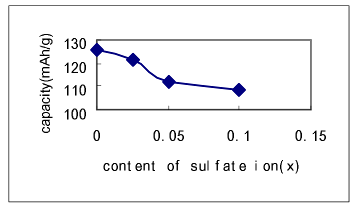

Fig. 1 Relation between the highest reversible capacity and the content of doped sulfate ion(x)

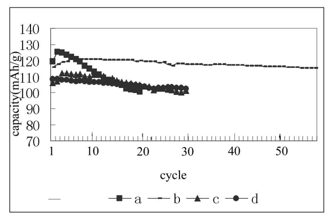

Fig. 2 Curves of reversible capacity against cycle of $LiMn_2O_{4-x}(SO_4)_x$ compounds with different content of sulfate ion (a: x=0, b: x=0.025, c: x=0.05, d: x=0.1).

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