

# Synthesis and Electrochemical Performance of Spinel $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$ Cathode Materials

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The spinel  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  compound cathode materials were synthesized by solid-state reaction of the calculated amounts of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{MnO}_2$  and  $\text{MnSO}_4$ . The results of the electrochemical test demonstrated that these materials exhibited excellent electrochemical properties. The highest reversible capacity of these series of cathode materials was  $\sim 120$  mAh/g, and after 50 cycles, this reversible capacity was still around 116 mAh/g with nearly 100% reversible efficiency, which revealed that doped sulfate ion could improve the structural stability of spinel.

**Keywords** spinel  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$ , cathode material, lithium ion secondary battery

## 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 lithium-manganese-oxide  $\text{LiMn}_2\text{O}_4$ <sup>1,2</sup> have attracted much attention. But the  $\text{LiMn}_2\text{O}_4$  cathode material has a disadvantage of structural instability<sup>3,4</sup> as a result of the Jahn-Teller effect caused by  $\text{Mn}^{3+}$ . Many efforts have been made to improve its structural stability by cation substitution,<sup>5-7</sup> but little reward has been received. Amatucci and Strobel synthesized Li-Mn-O-F compounds by means of anion addition, and in their experiments, when  $\text{F}^-$  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.<sup>8-10</sup> In this paper, sulphate ions were

added to Li-Mn-O compounds and it was found that the  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  compound cathode materials could improve the structural stability of the spinel compounds. Based on above experiments, some explanation was suggested for it.

## Experimental

These series of spinel  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  compound cathode materials were synthesized from the mixture of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{MnO}_2$  (electrolytic manganese dioxide), (EMD) and  $\text{MnSO}_4$ . These mixtures were ball-milled in a planetary micro-mill with stainless steel balls. Then, a dispersing liquid, alcohol, was added to form a slurry, which was ground overnight through combined shaking and rotation. After that, the fully mixed precursor slurry was dried to evaporate the alcohol under an infrared lamp. Finally, the precursors were calcinated at 730 °C for 36 h.

A series of spinel  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  compounds with different content of sulfate ion ( $x = 0, 0.025, 0.05, 0.1$ ) were synthesized as designed above.

The positive electrode consisted of 80wt% of  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  compound and 15wt% of acetylene black and 5wt% of polytetrafluoroethylene (PTFE) as a binder, and metal Al was used as the collector. The electrolyte solution was ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1) + 1 mol/L  $\text{LiClO}_4$ . Lithium metal foil was used as the counter electrode during

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the electrochemical measurements. All cell assemblies were completed in a dry box filled with argon gas. All electrochemical tests were carried out in a set of DC-5 fully automatic program test instrument at room temperature, with the constant current density of 0.353 mA/cm<sup>2</sup> and the potential range of 3.0 to 4.5 V.

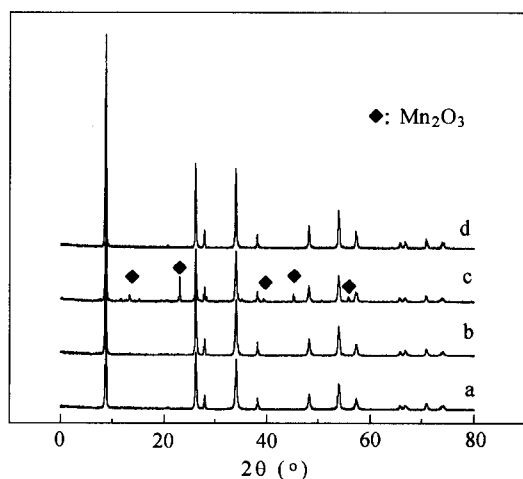
X-ray powder diffraction (XRD) was carried out on a Rigaku D/max-rA with Cu K<sub>α</sub> radiation and a graphite monochromator.

Transmission electron microscopy (TEM) was carried out on a JEOL JEM-100CX microscope.

## Results and discussion

### XRD and structure

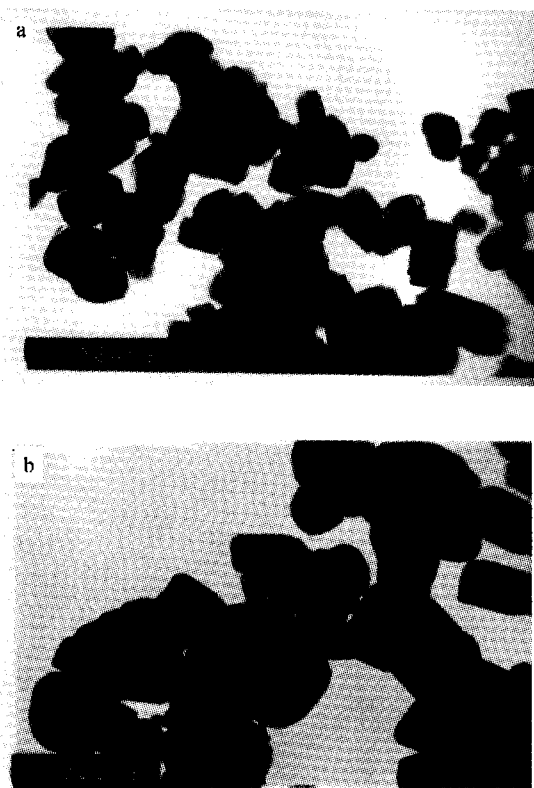
The crystal structure of LiMn<sub>2</sub>O<sub>4-x</sub>(SO<sub>4</sub>)<sub>x</sub> compounds with different contents of SO<sub>4</sub><sup>2-</sup> was characterized by XRD, as shown in Fig. 1. It was found that almost all of the diffraction peaks were attributable to the spinel structure of LiMn<sub>2</sub>O<sub>4</sub> in Fig. 1. The crystal data of the samples were nearly the same as those of standard LiMn<sub>2</sub>O<sub>4</sub>, and it could be concluded that when the content of SO<sub>4</sub><sup>2-</sup> was lower, pure spinel LiMn<sub>2</sub>O<sub>4-x</sub>(SO<sub>4</sub>)<sub>x</sub> could be easily synthesized. But in Fig. 1-c, there were some other peaks, which were attributed to Mn<sub>2</sub>O<sub>3</sub>. So a conclusion could be reached that when the content of SO<sub>4</sub><sup>2-</sup> was as high as 0.1, it was very difficult to prepare the pure LiMn<sub>2</sub>O<sub>4-x</sub>(SO<sub>4</sub>)<sub>x</sub>.



**Fig. 1** XRD patterns of LiMn<sub>2</sub>O<sub>4-x</sub>(SO<sub>4</sub>)<sub>x</sub> compounds with different contents of sulfate ion (a,  $x = 0.025$ ; b,  $x = 0.05$ ; c,  $x = 0.1$ ; d,  $x = 0$ ).

### TEM characterization of LiMn<sub>2</sub>O<sub>4-x</sub>(SO<sub>4</sub>)<sub>x</sub> compounds

Typical TEM images of pure LiMn<sub>2</sub>O<sub>4</sub> and spinel LiMn<sub>2</sub>O<sub>3.95</sub>(SO<sub>4</sub>)<sub>0.05</sub> compounds were shown in Fig. 2, where it could be seen that these particles were all of regular forms. Comparing the images of doped and undoped-sulfate ion LiMn<sub>2</sub>O<sub>4</sub>, it could be found that the particle diameter of the doped sample was larger than that of the undoped sample, which helped to decrease the dissolution of manganese and improve the cycle life of the materials.



**Fig. 2** TEM images of LiMn<sub>2</sub>O<sub>4</sub> (a) and LiMn<sub>2</sub>O<sub>3.95</sub>(SO<sub>4</sub>)<sub>0.05</sub> (b).

### Electrochemical test and discussion

The relations between the initial reversible capacity and sulfate ion contents of spinel LiMn<sub>2</sub>O<sub>4-x</sub>(SO<sub>4</sub>)<sub>x</sub> compounds with different sulfate ion contents were shown in Fig. 3. The initial reversible capacity of prepared materials gradually became lower with the sulfate ion-content increasing.

The curves of cycle-capacity of spinel LiMn<sub>2</sub>O<sub>4-x</sub>(SO<sub>4</sub>)<sub>x</sub> compounds with different contents of sulfate ion

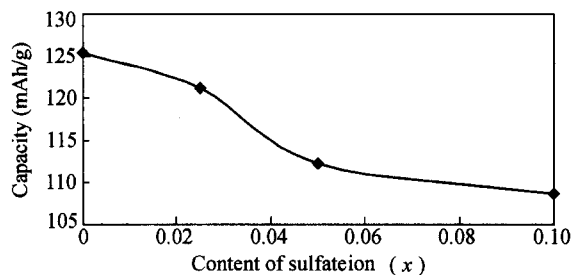


Fig. 3 Relation between the highest reversible capacity and the content of doped sulfate ion ( $x$ ).

were shown in Fig. 4. It was found that the pure spinel  $\text{LiMn}_2\text{O}_4$  as cathode materials cycled 20 times at a large capacity loss. Whereas, the spinel  $\text{LiMn}_2\text{O}_{3.975}(\text{SO}_4)_{0.025}$  exhibited excellent stability. After cycling 50 times, the reversible capacity exhibited only slight loss, and the reversible capacity was still around 116 mAh/g. The rate of capacity fade of the pure  $\text{LiMn}_2\text{O}_4$  was cal-

culated from Table 1 after 20 cycles and was up to 15.6%, while from Table 2, only a slight capacity fade was observed after 50 cycles. Thus, the results confirmed that the doped-sulfate ion improved the stability of  $\text{LiMn}_2\text{O}_4$ .

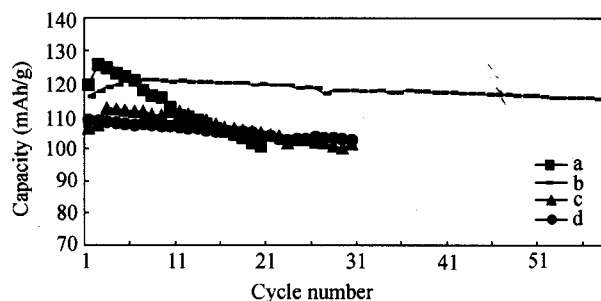


Fig. 4 Curves of reversible capacity against cycle number of  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  compounds with different contents of sulfate ion (a,  $x = 0$ ; b,  $x = 0.025$ ; c,  $x = 0.05$ ; d,  $x = 0.1$ ).

Table 1 Reversible efficiency of  $\text{LiMn}_2\text{O}_4$

Cycle number	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Efficiency (%)
1	135.9	119.5	87.9
5	130.0	122.1	95.0
10	119.6	112.8	94.3
15	112.0	106.1	94.7
20	104.0	100.5	96.6

Table 2 Reversible efficiency of  $\text{LiMn}_2\text{O}_{3.975}(\text{SO}_4)_{0.025}$

Cycle number	Charge capacity (mAh/g)	Discharge capacity (mAh/g)	Efficiency (%)
1	119.2	115.8	97.1
10	121.4	120.6	99.3
20	120.4	119.7	99.3
30	119.3	117.8	98.7
40	117.9	117.3	99.5
50	116.8	116.1	99.4

Depending on the results of electrochemical test, it was confirmed that when  $x = 0.025$ , the capacity and stability of the cathode material reached the best state. The reversible efficiency was about 100% in the first 50 cycles calculated in Table 2.

From above results it was easily found that adoptable amount of sulfate ion helped to suppress the capacity fade. Two plausible reasons could be suggested; (1) the doped sulfate ion can arrest the  $\text{H}^+$  produced

during the course of cycling. Since the  $\text{H}^+$  content was decreased, the dissolution of manganese was suppressed. Thus the cycle performance of  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  was improved; (2) after substitution of sulfate ion, the bond between  $\text{SO}_4^{2-}$  and  $\text{Li}^+$  was weaker than that between oxygen and lithium ion, and  $\text{Li}^+$  could move in and out more easily without destroying the spinel structure.

## Conclusion

When the content of  $\text{SO}_4^{2-}$  was lower, pure spinel  $\text{LiMn}_2\text{O}_{4-x}(\text{SO}_4)_x$  could be easily synthesized. Otherwise, when the content of  $\text{SO}_4^{2-}$  was as high as 0.1, the synthesis was very difficult. When  $x = 0.025$ , the best electrochemical performance was obtained. And after 50 cycles only a slight capacity fade was observed for this material.

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