# Properties and Structure of Spinel Li-Mn-O-F Compounds for Cathode Materials of Secondary Lithium-ion Battery

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**The spinel Li-Mn-O-F compound cathode materials were synthesized by solid-state reaction from calculated amounts $LiOH\cdot H_2O$, $MnO_2$(EMD) and LiF. The results of the electrochemical test demonstrated that these materials exhibited excellent electrochemical properties. It's initial capacity is ~115 $mAh\cdot g^{-1}$ and reversible efficiency is about 100%. After 60 cycles, its capacity is still around 110 $mAh\cdot g^{-1}$ with nearly 100% reversible efficiency. The spinel Li-Mn-O-F compound possibly has two structure models: interstitial model $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$, in which the fluorine is located on the interstice of crystal lattice, and substituted model $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]O_{4-\delta}F_\delta$, which the fluorine atom substituted the oxygen atom. The electrochemical result supports the interstitial model $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$.**

**Keywords** Spinel Li-Mn-O-F compound, the interstitial model $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$, cathode materials

## Introduction

In recent years, with the development of all sorts of cellular phones, camcorders, laptop computers, the lithium-ion secondary batteries attracted much attention based on the use of manganese-lithium oxide $LiMn_2O_4$.[1,2] 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 *et al*. 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] Xia *et al*. also synthesized the Li-Mn-O-F compounds,[11] but they found that the adopted-fluorine helped to improve the stability of Li-Mn-O compounds, with a little sacrifice in capacity. Their results opposed to each other, for they have not made the detailed and reasonable explanation. We added fluorine to Li-Mn-O compounds and found that the Li-Mn-O-F compound cathode materials exhibited excellent electrochemical properties and the structural stability of Li-Mn-O compounds was attributed to the added fluorine, which was in agreement with Xia's results. Based on our experiments, we suggested a structural model for Li-Mn-O-F compounds and explained well our results by means of it.

## Experimental

### *Synthesis*

These spinel Li-Mn-O-F compound cathode materials were synthesized from the mixture of $LiOH\cdot H_2O$, $MnO_2$ (EMD) and LiF. 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℃ for 36 h.

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A series of spinel Li-Mn-O-F compounds with different δ (δ = 0, 0.1, 0.2, 0.3) were synthesized as designed above.

The positive electrode consisted of 80 wt% Li-Mn-O-F compound and 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) as a binder, and metal Al was used as collector. The electrolyte solution was EC + DEC (1:1) + $LiClO_4$(1 mol/L). Lithium metal foil was used as the counter electrode during electrochemical measurements. 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—4.35 V).

X-ray power diffraction (XRD) was carried out on a Rigaku D/max-rA with Cu $K_\alpha$ radiation and a graphite monochromator.

Transmission electron microscopy (TEM) was carried out on JEOL JEM-100CX microscope. The contents of fluorine (δ) were determined by chemical analysis (CA).

## Results and discussion

### *Chemical analysis*

In order to find out the relationship between the electrochemical property and the content of fluorine of the cathode material, we prepared a series of Li-Mn-O-F compounds with different fluorine content. The chemical analysis indicated that the δ values in the samples were much smaller than the designed values. For example, the δ values were 0, 0.016, 0.021, 0.04 corresponding to the designed values 0, 0.1, 0.2, 0.3 respectively. It may be caused by the fluorine loss at high calcination temperature.

### XRD *and structure*

The crystal structure of Li-Mn-O-F compound was characterized by XRD, as shown in Fig. 1. It was found that almost all of the diffraction peaks are attributable to the spinel structure of $LiMn_2O_4$. The crystal data of the samples are nearly the same as those of standard $LiMn_2O_4$.

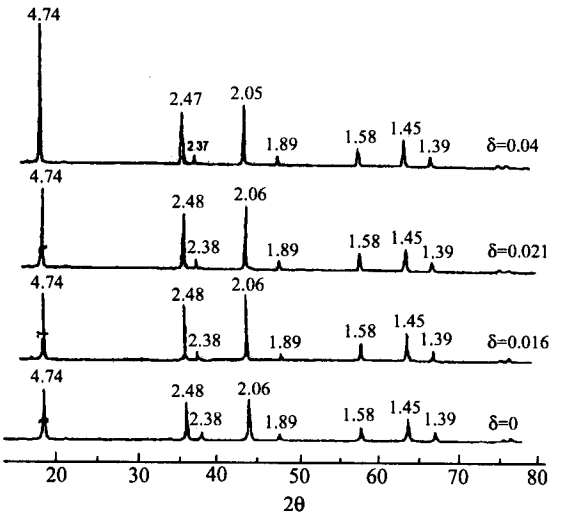


**Fig. 1** Powder XRD patterns of spinel Li-Mn-O-F compounds with different fluorine contents (δ).

### TEM *characterization of* Li-Mn-O-F *compounds*

Fig. 2 shows a typical TEM image of a series of spinel Li-Mn-O-F compounds with different fluorine content. It can be seen from Fig. 2 that these particles are all of regular forms. In Fig. 2, a is the image of pure spinel $LiMn_2O_4$, and the outer diameter is only 0.2 μm. With the fluorine increasing from 0.016 to 0.021 or 0.04, the particle diameter becomes gradually greater, from 0.8 μm to 1.0 μm or 1.2 μm.

### *Electrochemical test and structural model*

Fig. 3 shows the relation between the initial reversible capacity and fluorine contents of spinel Li-Mn-O-F compounds with different fluorine content. The initial reversible capacity of prepared materials gradually becomes lower with the F-content increasing. It was well known that the reversible capacity is determined by the amount of reversible lithium-ion. While charging, the lithium ion deintercalates from the cathode materials, leading to $Mn^{3+}$ change to $Mn^{4+}$, and leading to the improvement of the potentials. So we can make use of the amount of $Mn^{3+}$ to evaluate the initial charge capacity. It was well known that the initial capacity decreases and that the structural stability increases with the amount of $Mn^{3+}$ decreasing. The rule shown in Fig. 3 supports the F-interstitial model $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$. If fluorine adopts the F-substituted model, because the fluorine is −1 valence, it must lead to the average valence of Mn lower than 3.5. It means that the amount of $Mn^{3+}$

increases and the Jahn-Teller effect become remarkable. According to the analysis above, with the fluorine content increasing, the initial charge capacity of cathode materials will increase gradually, and stability will be gradually decreased. But it is just opposed to that. Instead, when fluorine adopt the F-interstitial model $[Li]-[Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$, the average valence of Mn is higher than 3.5 and total negative valence become greater. It means to the decreasing of $Mn^{3+}$, so it suppresses the Jahn-Teller effect, and stability is improved. According to the above analysis, the initial charge capacity of positive materials will decrease and stability will gradually increase with the fluorine content increasing. This is confirmed by the result. So the electrochemical test results support the F-interstitial model $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]-O_4F_\delta$.

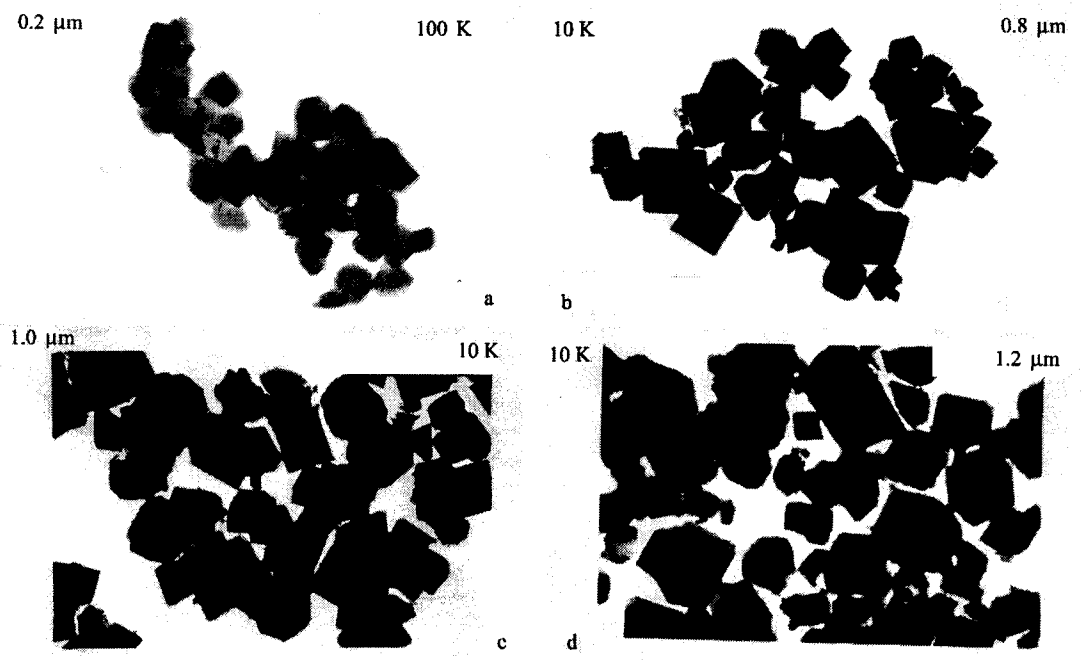


**Fig. 2** TEM images of the spinel Li-Mn-O-F compounds with different fluorine contents (δ) (a—δ = 0, b—δ = 0.016, c—δ = 0.04).

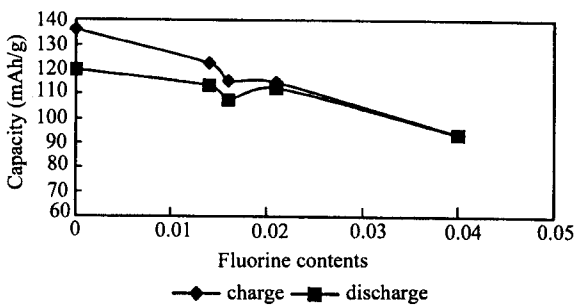


**Fig. 3** Relation between the initial capacity and flourine contents of the spinel Li-Mn-O-F compounds with different fluorine contents (δ).

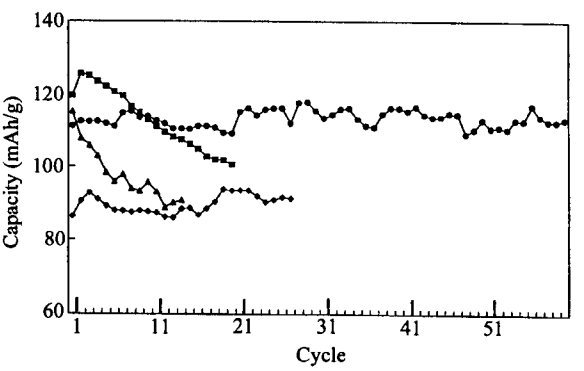


**Fig. 4** Reversible capacity against cycle number of the spinel Li-Mn-O-F compounds with different fluorine content (δ: ◆ 0.04, ● 0.021, ▲ 0.016, ■ 0).

Fig. 4 shows the cycle-capacity of spinel Li-Mn-O-F compounds with different fluorine contents. From Fig. 4 we can find that the pure spinel $LiMn_2O_4$ as cathode materials cycled 20 times at a large capacity loss. The spinel $LiMn_2O_4F_{0.021}$ exhibits excellent stability, after cycled 60 times, the reversible capacity has not exhibited any loss, and the reversible capacity is still around 110 $mAh \cdot g^{-1}$. In Table 2, we can calculate that after 20 cycles, the capacity fade of the pure $LiMn_2O_4$ is up to 15.6%; while in Table 1, we almost can not find any

capacity fade. So, the results conform to the fact that the added-fluorine improved the stability of $LiMn_2O_4$.

**Table 1** Reversible efficiency of $LiMn_2O_4F_{0.021}$

| Cycle (times) | Charge capacity (mAh/g) | Discharge capacity (mAh/g) | Efficiency (%) |
|---|---|---|---|
| 1 | 111.1 | 111.0 | 99.9 |
| 10 | 115.0 | 113.7 | 98.9 |
| 20 | 112.1 | 109.0 | 97.2 |
| 30 | 117.2 | 115.3 | 98.4 |
| 40 | 116.9 | 116.0 | 99.2 |
| 50 | 114.1 | 112.7 | 98.8 |
| 60 | 115.0 | 112.9 | 98.2 |

**Table 2** Reversible efficiency of $LiMn_2O_4$

| Cycle (times) | Charge capacity (mAh/g) | Discharge capacity (mAh/g) | Efficiency (%) |
|---|---|---|---|
| 1 | 135.9 | 119.5 | 87.9 |
| 4 | 132.7 | 123.6 | 93.1 |
| 8 | 123.5 | 116.5 | 94.3 |
| 12 | 115.4 | 109.4 | 94.8 |
| 16 | 111.0 | 104.8 | 94.4 |
| 20 | 104.0 | 100.5 | 96.6 |

From the results of electrochemical test, we can draw a conclusion that when $\delta = 0.021$, the capacity and stability of the cathode materials reach to the best state. Tarascon[8] considered that $LiMn_2O_{3.8}F_{0.2}$ is the most excellent composition. It seems to be opposed to our results. But Tarascon has not made the elementary analysis. Under high temperature, the fluorine may be lost. The elementary analysis shows that the sample $LiMn_2O_4F_{0.021}$ is closed to the sample $LiMn_2O_{3.8}F_{0.2}$ designed by Tarascon.

We can know that the reversible efficiency is about 100% in the first 60 cycles from Table 1. As is well known that during the first cycle, about 20% of the capacity can be lost, a part of lithium ion can not reinserted into the positive material.[12] In the cathode material, we do not only find the capacity loss, but also find the efficiency is about 100%. It seems that the cathode material is still suitable to reinsert lithium ion. We think that interstitial fluorine lead to the partial micro-zone with negative electricity, which is suitable to lithium ion insertion. Due to the high efficiency of the positive material, it reduces reversible capacity loss and improves its cycle life. So the micro-zone negative electricity is the fundament reason of excellent reversible efficiency, and the efficiency about 100% supports the F-interstitial model $[Li]]Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$.

Fig. 5 and Fig. 6 show respectively the cyclic voltammograms of Li/EC-DEC-$LiClO_4$/$LiMn_2O_4$ and Li/EC-DEC-$LiClO_4$/$LiMn_2O_4F_{0.021}$ cells in the potential range of about 3.4 to 4.4 V *vs*. Li. In Fig. 5 there are two redox couples between 3.4 and 4.4 V which are typical of a two-step reversible transformation of the spinel. These voltammetric features agree well with the observation of Liu.[13] In Fig. 6, two pairs of clearly separated redox peaks were also observed indicating that the reversibility of $Li^+$ deintercalation/intercalation reaction in the spinel host between 3.4 and 4.4 V (*vs*. Li) was not compromised by fluorine addition. However, the peak at 3.9 V is higher than that at 4.05 V on the cathodic scan in Fig. 6 while it is the contrary in the Fig. 5. It supports that the $LiMn_2O_4F_{0.021}$ cathode makes the second lithium-ion intercalation easier. According to the mechanism of the electrochemical lithium intercalation, the lower voltage plateau corresponds to the second step lithium intercalation. The upper plateau region of discharge represents a two-phase region equilibrium between $\lambda$-$MnO_2$ and $Li_{0.5}Mn_2O_4$, and the lower plateau an equilibrium between $Li_{0.5}Mn_2O_4$ and $LiMn_2O_4$. During lithium intercalation, lithium ions would first fill over other available tetrahedral site (8a) in the spinel structure, until half of the sites were filled. When a small number of $Li^+$ ions are moved into the tetrahedral sites of the spinel structure, the repulsion between adjacent lithium is weak. With increase of $Li^+$ ions moving into the tetrahedral sites, the activity of each $Li^+$ ion will be influenced by the four $Li^+$ ions that surround it. Through the comparison between Fig. 5 and Fig. 6, we can draw a conclusion that the fluorine-intercalation would reduce the second step lithium intercalation repulsion from the adjacent lithium ions, so it makes the second step lithium intercalation easier and the first lithium deintercalation more difficulty. It conforms to the fact that the reversible capacity is lower than that of standard $LiMn_2O_4$ and the efficiency is about 100%.

According to above analysis, we can explain that why $LiMn_2O_4F_{0.021}$ is excellent in stability and capacity:

(1) $LiMn_2O_4F_{0.021}$ adopts the F-interstitial model $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$. In this model, the average va-

lence of the Mn is higher than 3.5, that is to say, the amount of $Mn^{3+}$ is less than usual, and the Jahn-Teller effect is suppressed and stability is improved;

(2) In the $LiMn_2O_4F_{0.021}$, the partial micro-zone is with negative electricity, which makes the lithium ion insertion easier and the efficiency is about 100%.

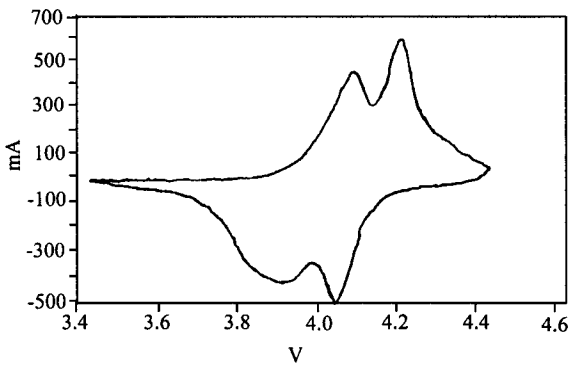


**Fig. 5** Cyclic voltammogram of $LiMn_2O_4$.

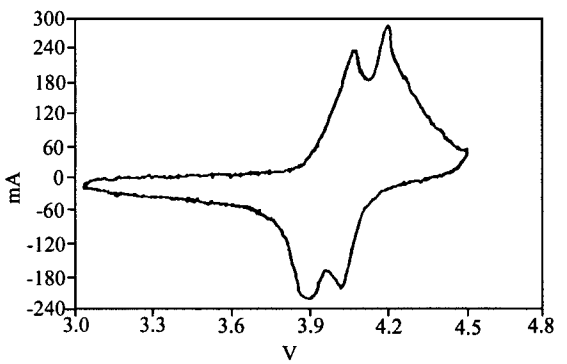


**Fig. 6** Cyclic voltammogram of $LiMn_2O_4F_{0.021}$.

## Conclusion

We can draw these conclusions according to above analysis and results:

(1) The spinel Li-Mn-O-F compounds adopted the F-interstitial $[Li][Mn_x^{3+}Mn_{2-x}^{4+}]O_4F_\delta$ model ($0 < \delta < 0.05$);

(2) The cathode material is of about 100% reversible efficiency;

(3) The cathode material is still suitable to reinsert lithium ion;

(4) $LiMn_2O_4F_{0.021}$ has excellent electrochemical properties.

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