

## Electrochemical performance of SrF<sub>2</sub>-coated LiMn<sub>2</sub>O<sub>4</sub> cathode material for Li-ion batteries

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**Abstract:** SrF<sub>2</sub>-coated LiMn<sub>2</sub>O<sub>4</sub> powders with excellent electrochemical performance were synthesized. The electrochemical performance of SrF<sub>2</sub>-coated LiMn<sub>2</sub>O<sub>4</sub> electrodes was studied as function of the level of SrF<sub>2</sub> coating. With increasing the amount of the coated-SrF<sub>2</sub> to 2.0% (molar fraction), the discharge capacity of LiMn<sub>2</sub>O<sub>4</sub> decreases slightly, but the cycleability of LiMn<sub>2</sub>O<sub>4</sub> at elevated temperature is improved obviously. In view of discharge capacity and cycleability, the 2.0% (molar fraction) coated sample shows optimum cathodic behaviors. When being cycled at 55 °C, as-prepared LiMn<sub>2</sub>O<sub>4</sub> remains only 79% of its initial capacity after 20 cycles, whereas the 2.0% (molar fraction) coated sample shows initial discharge capacity of 108 mA·h/g, and 97% initial capacity retention.

**Key words:** lithium ion batteries; LiMn<sub>2</sub>O<sub>4</sub>; surface coating; SrF<sub>2</sub>

### 1 Introduction

Spinel LiMn<sub>2</sub>O<sub>4</sub>, with economical and environmental advantages, is considered to be one of the most promising cathode materials for rechargeable lithium-ion batteries. Its drawbacks include the significant capacity fading during cycling at elevated temperature due to several probabilities, e.g., manganese dissolution[1–2], Jahn-Teller distortion[3] and electrolyte decomposition[4]. Partial replacement of Mn in LiMn<sub>2</sub>O<sub>4</sub> by some low valent metal ions such as Li<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>3+</sup>, Al<sup>3+</sup> and Cr<sup>3+</sup>[5–9] can effectively enhance its cycleability. On the other hand, another appropriate method to reduce capacity fades of LiMn<sub>2</sub>O<sub>4</sub> is surface coating of the spinel to avoid Mn dissolution. Metal oxides, such as lithium boron oxide glass (LBO)[10], SiO<sub>2</sub>[11], ZnO[12], ZrO<sub>2</sub>[13], Al<sub>2</sub>O<sub>3</sub>[14] and TiO<sub>2</sub>[15], have been reported to be very interesting materials for this purpose. The coated metal oxides are insoluble in water, but cannot remain stable unfortunately under the corrosion of HF. Recently, SUN et al[16] reported the surface modification of LiCoO<sub>2</sub> by AlF<sub>3</sub>. The AlF<sub>3</sub> coating layer could reduce the formation of LiF films

that increase cathode/electrolyte interfacial impedance and also suppress Co dissolution by covering LiCoO<sub>2</sub> surface from HF attack, therefore improving the capacity retention of LiCoO<sub>2</sub> at 4.5V cut-off cycling.

It is very necessary to study the effects of fluoride-coating on the cycleability of LiMn<sub>2</sub>O<sub>4</sub>. To our best knowledge, there are still no literatures on this issue. In this study, SrF<sub>2</sub> that is insoluble in HF was investigated to be used as coating material of LiMn<sub>2</sub>O<sub>4</sub>. Herein, the effects of coated-SrF<sub>2</sub> amount on the structural and electrochemical properties were discussed.

### 2 Experimental

LiMn<sub>2</sub>O<sub>4</sub> sample was first prepared by annealing the well-ground mixture of stoichiometric EMD and Li<sub>2</sub>CO<sub>3</sub> at 800 °C in air for 20 h. For preparing the SrF<sub>2</sub>-coated LiMn<sub>2</sub>O<sub>4</sub> cathode material, the prepared LiMn<sub>2</sub>O<sub>4</sub> powders were suspended in the Sr(NO<sub>3</sub>)<sub>2</sub> solution, and then NH<sub>4</sub>F solution was dropped slowly into the suspended solution. After being stirred for 2 h, the coated LiMn<sub>2</sub>O<sub>4</sub> powders were filtrated and heated under N<sub>2</sub> for 5 h. The heat treatment temperature was 300, 400, 500, 600 and 700 °C, respectively. The amount of coated SrF<sub>2</sub>

corresponds to 0.5%, 1.0%, 2.0% and 4.0% (molar fraction) of the  $\text{LiMn}_2\text{O}_4$  powders. Powder X-ray diffraction (XRD7000) was used to characterize the structure of the powders. Particle morphology of the powders was observed using a scanning electron microscope (HITACHI-S3500). The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 88% coated or uncoated  $\text{LiMn}_2\text{O}_4$ , 6% carbon black, and 6% PVDF (mass fraction), a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1.15 mol/L  $\text{LiPF}_6/\text{EC}+\text{DMC}+\text{DEC}$  (3:3:1 in volume ratio). The charge-discharge tests were galvanostatically performed over 3.3–4.3 V at different current densities. AC-impedance measurements were performed using a CHI660B impedance analyzer over the frequency range from 100 kHz to 1 MHz with the amplitude of 10 mV.

### 3 Results and discussion

#### 3.1 Structural variation after $\text{SrF}_2$ -coating

XRD patterns of the 4.0%  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  sample heat-treated at 300, 400, 500, 600 and 700 °C respectively for 5 h under  $\text{N}_2$  are shown in Fig.1. It is obvious that all samples show main peaks attributed to well-defined spinel phases and small amount of  $\text{SrF}_2$  peaks as impurity. The  $\text{SrF}_2$  peaks become sharp with increasing the heat-treated temperature from 300 to 700 °C. This indicates that the coated  $\text{SrF}_2$  exists as a separate phase, and  $\text{SrF}_2$  crystallization extent enhances with increasing heat-treated temperature. The crystal lattice constants of the coated samples, as listed in Table 1, clearly reveal that the values remain almost unchanged at 300–500 °C and decrease obviously over 600 °C. This indicates a possible surface reaction between  $\text{SrF}_2$  and

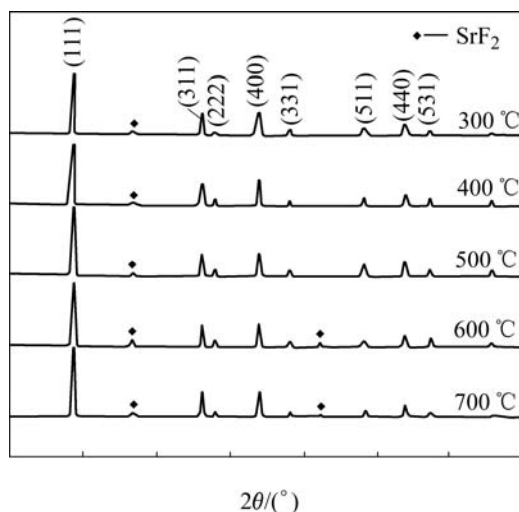


Fig.1 XRD patterns of 4.0%  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  samples

Table 1 Lattice parameters of 4.0%  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  sample heat-treated at different temperatures

Heat-treated temperature/°C	<i>a</i> /nm
300	0.822 98
400	0.823 01
500	0.823 09
600	0.822 47
700	0.822 31

$\text{LiMn}_2\text{O}_4$  during firing over 600 °C, which may result in the formation of a thin  $\text{LiMn}_{2-x}\text{Sr}_x\text{O}_{4-y}\text{F}_y$  solid-solution layer. In order to avoid the reaction between  $\text{SrF}_2$  and  $\text{LiMn}_2\text{O}_4$ , the heat-treated temperature of the following studied  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  samples are selected to be 400 °C.

XRD patterns of 0, 0.5%, 1.0%, 2.0% and 4.0%  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  samples are shown in Fig.2. The  $\text{SrF}_2$  peaks can be detected when the coated  $\text{SrF}_2$  amounts are up to 2.0%, and become stronger with increasing the coated  $\text{SrF}_2$  amounts to 4.0%. However, the lattice parameters of  $\text{LiMn}_2\text{O}_4$  show no detectable changes before and after coating, supporting the postulate that  $\text{SrF}_2$  exists as a separate phase on the  $\text{LiMn}_2\text{O}_4$  particle surface.

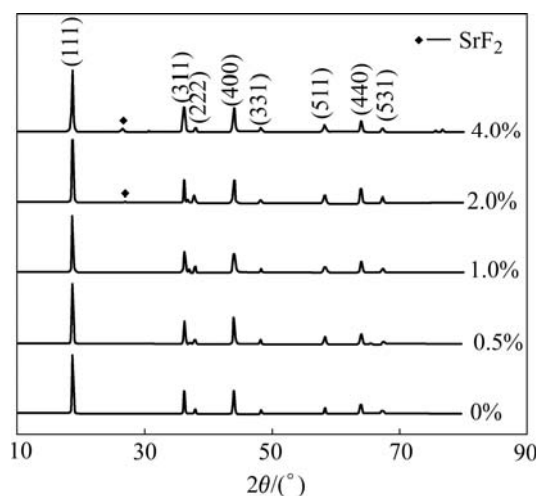


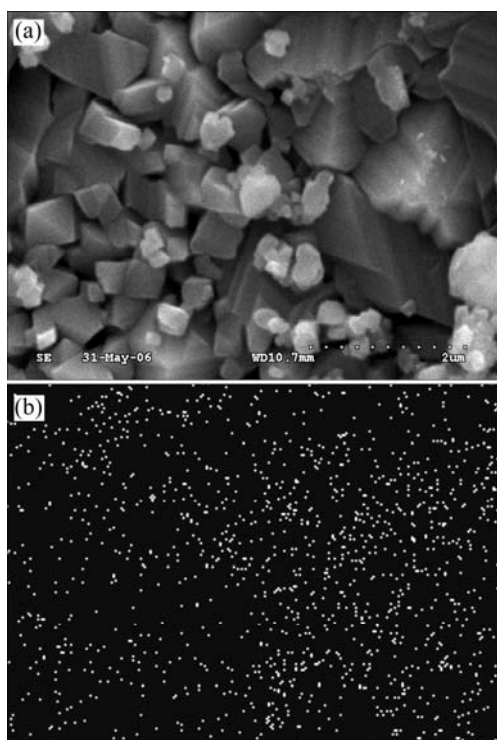
Fig.2 XRD patterns of  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  samples

#### 3.2 Morphology of $\text{SrF}_2$ -coated $\text{LiMn}_2\text{O}_4$

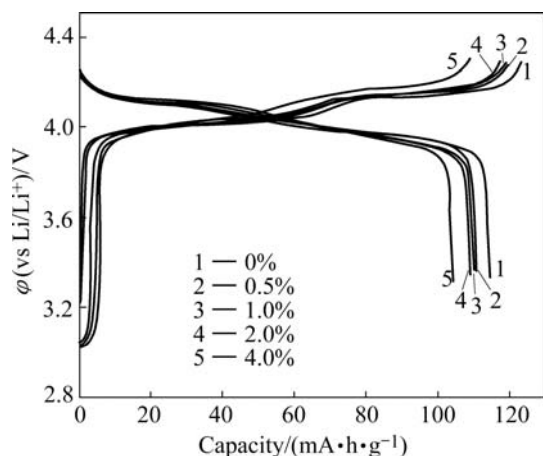
Fig.3 shows SEM micrograph and EAX(energy dispersed X-ray analysis) image of 2.0%  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$ . The powders are agglomerated, consisting of many small crystal particles. As can be seen in EPMA image, the distribution of Sr on the powder is fairly uniform.

#### 3.3 Electrochemical characteristics of $\text{SrF}_2$ -coated $\text{LiMn}_2\text{O}_4$

Fig.4 shows charge-discharge curves for the as-prepared  $\text{LiMn}_2\text{O}_4$  and various amounts of  $\text{SrF}_2$ -coated



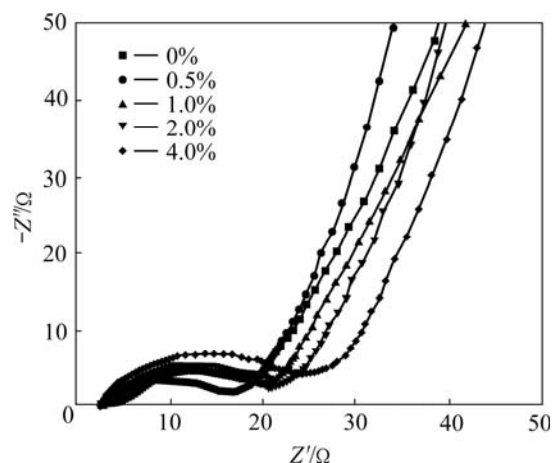
**Fig.3** Scanning electron micrograph of 2.0%  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  (a) and Sr-distribution map obtained by energy dispersed X-ray analysis (b)



**Fig.4** Charge-discharge curves of  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  samples

$\text{LiMn}_2\text{O}_4$  at room temperature. The as-prepared  $\text{LiMn}_2\text{O}_4$  shows discharge capacity of 114.6  $\text{mA}\cdot\text{h}/\text{g}$ , which is very close to the data reported in Refs.[11–15]. Compared with the base one, the  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  samples show lower capacity. The discharge capacity decreases slightly with increasing amount of  $\text{SrF}_2$  coating to 2%, but reduces remarkably to 104.4  $\text{mA}\cdot\text{h}/\text{g}$  with increasing amount of the  $\text{SrF}_2$  coating to 4%. With increasing amount of the  $\text{SrF}_2$  coating, the polarization (voltage difference between the charge and the discharge curves) enhances. Because the  $\text{SrF}_2$  coating is inactive, it

can be speculated that the coating may increase the contact resistance between inter-particles and the charge-transfer resistance, leading to the decrease of the capacity. The supposition can be confirmed by the EIS spectra of the as-prepared  $\text{LiMn}_2\text{O}_4$  and various amounts of  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$ , as shown in Fig.5.



**Fig.5** EIS spectra of  $\text{SrF}_2$ -coated  $\text{LiMn}_2\text{O}_4$  samples

The cycleability of the spinels was tested at 55  $^{\circ}\text{C}$ , using a voltage window of 3.3–4.3 V and a current density of 110  $\text{mA}/\text{g}$ . The resulting data are plotted in Fig.6. When being charge-discharged for 20 cycles at 55  $^{\circ}\text{C}$ , the as-prepared  $\text{LiMn}_2\text{O}_4$  sample shows very fast capacity fading, and only 79% of its initial capacity remains. With increase of the amount of the coated  $\text{SrF}_2$  from 0% to 2.0%, the discharge capacity of  $\text{LiMn}_2\text{O}_4$  decreases slightly, but the cycleability of  $\text{LiMn}_2\text{O}_4$  is improved obviously. As mentioned in other papers, surface coating of  $\text{LiMn}_2\text{O}_4$  by some stable substances, e.g.  $\text{SiO}_2$ [11],  $\text{ZrO}_2$ [13] and  $\text{Al}_2\text{O}_3$ [14], can prevent the direct contact between  $\text{LiMn}_2\text{O}_4$  particles and electrolyte, and hence lessen the possibility of spinel dissolution and electrolyte decomposition that are the major cause of capacity loss. The  $\text{AlF}_3$  coating layer of  $\text{LiCoO}_2$  also have been reported to reduce the formation of  $\text{LiF}$  films that increase the cathode/electrolyte interfacial impedance and also suppress Co dissolution by covering  $\text{LiCoO}_2$  surface from HF attack[16].  $\text{SrF}_2$  is very stable even in HF, so it can be speculated that the surface coating of  $\text{LiMn}_2\text{O}_4$  by  $\text{SrF}_2$  can improve the cycleability of  $\text{LiMn}_2\text{O}_4$  cathode due to the same reason. 2.0% coated sample exhibits the best electrochemical performance. This shows initial discharge capacity of 108  $\text{mA}\cdot\text{h}/\text{g}$ , and 97% initial capacity retention after 20 cycles. Although 4.0% coated sample also shows very good cycleability, its lower capacity is unsatisfied due to higher impedance resulted from too much coated  $\text{SrF}_2$ . The 2.0% coated sample shows optimum cathodic behaviors in view of discharge capacity and cycleability.

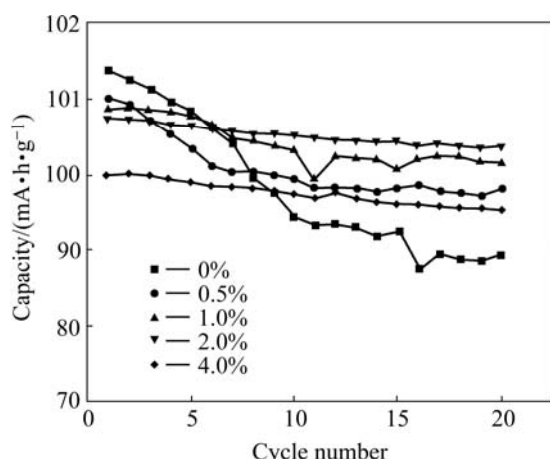


Fig.6 Cycleability of SrF<sub>2</sub>-coated LiMn<sub>2</sub>O<sub>4</sub> samples at 55 °C

## 4 Conclusions

1) SrF<sub>2</sub> is coated uniformly on the surface of LiMn<sub>2</sub>O<sub>4</sub> particles by using chemical deposition, followed by heat-treatment at 400 °C.

2) Significant improvement of the electrochemical performance of LiMn<sub>2</sub>O<sub>4</sub> is achieved by coating SrF<sub>2</sub>. With increasing the amount of the coated SrF<sub>2</sub>, the discharge capacity of LiMn<sub>2</sub>O<sub>4</sub> decreases slightly, but the cycleability of LiMn<sub>2</sub>O<sub>4</sub> at elevated temperature is improved obviously.

3) In view of discharge capacity and cycleability, the 2.0% coated sample shows optimum cathodic behaviors. It shows initial discharge capacity of 108 mA·h/g, and 97% initial capacity retention after 20 cycles at 55 °C.

4) The SrF<sub>2</sub> coating is favorable to improving the cycleability of LiMn<sub>2</sub>O<sub>4</sub> at elevated temperatures.

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