# Electrochemical Properties of Spinel $LiMn_2O_{4-\delta}F_\delta$ for Cathode Materials of Secondary Lithium-ion Battery

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**Abstract:** The spinel $LiMn_2O_{4-\delta}F_\delta$ cathode materials were synthesized by solid-state reaction, with calculated amounts of $LiOH \cdot H_2O$, $MnO_2$(EMD), LiF. The results of electrochemical test demonstrated that these new materials exhibited excellent electrochemical properties. Its initial capacity reached ~115 mAh • $g^{-1}$ and reversible efficiency is about 100%. After 60 cycles, its capacity was still around 110 mAh • $g^{-1}$, with nearly 100% reversible efficiency.

**Keywords:** Spinel $LiMn_2O_{4-\delta}F_\delta$, cathode, materials.

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 $LiMn_2O_4$ with low toxicity and cost attract much attention. But the $LiMn_2O_4$ cathode material has the disadvantage of poor structural instability 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, but little reward has been received. We adopted anion substitution as a new method to reach this goal, and the new $LiMn_2O_{4-\delta}F_\delta$ cathode material exhibited excellent electrochemical properties.

The spinel $LiMn_2O_{4-\delta}F_\delta$ cathode materials were synthesized with the mixture of $LiOH \cdot H_2O$, $MnO_2$(EMD) and LiF. At first, this mixture was ball-milled in a planetary micro mill with stainless steel balls. Alcohol was added for dispersing to form a slurry which was ground overnight with combined action of shaking and rotation actions. After milling, the alcohol in the slurry precursors was evaporated. Finally, the precursors were calcined at 730°C for 36 h.

A series of spinel $LiMn_2O_{4-\delta}F_\delta$ compounds with different fluorine contents (0, 0.1, 0.2, 0.3) were synthesized as designed above.

The positive electrode consisted of 80wt% $LiMn_2O_{4-\delta}F_\delta$ and 15wt% acetylene black and 5wt% polytetrafluoroethylene(PTFE) as a binder, and metal Al was used as collector. The electrolyte solution consists of ethylene carbonate + diethylene carbonate (1:1)+1 mol/L $LiClO_4$. Lithium metal foil was used as the counter electrode during electrochemical measurements. All cell assemblies were put in a dry box filled with argon gas. All electrochemical tests were carried out in a DC-5 fully automatic program test instrument, with constant current.

X-ray power diffraction (XRD) was carried out by means of a Rigaku D/max-ra

with Cu Kα radiation and a graphite monochromator.

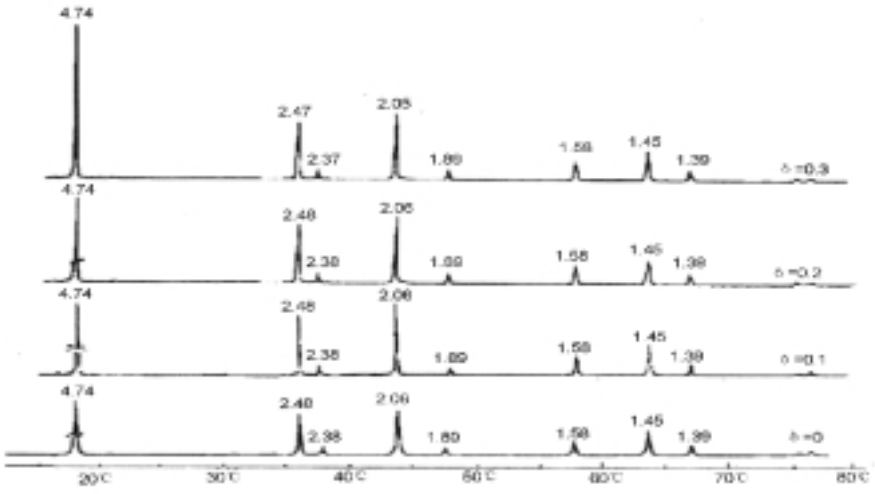
Transmission electron microscopy (TEM) was carried out using JEOL JEM-100CX microscope. The contents of fluorine (δ) was determined by chemical analysis (CA).

**Chemical Analysis (CA)**

In order to find out the relationship between the electrochemical properties and the contents of fluorine of the cathode material, a series of $LiMn_2O_{4-\delta}F_\delta$ with different fluorine contents were prepared. The chemical analysis indicated that the δ values in the samples were much smaller than the designed values. For example, the δ value found were 0, 0.016, 0.021, 0.04 corresponding to the designed values of 0, 0.1, 0.2, 0.3 respectively. It was caused by the fluorine loss at high calcination temperature.

**XRD and Structure**

**Figure 1** XRD patterns of $LiMn_2O_{4-\delta}F_\delta$ with different fluorine contents




The crystal structures of $LiMn_2O_{4-\delta}F_\delta$ were characterized by XRD, as shown in **Figure 1**. It is 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 $LiMn_2O_4$, except that at 2θ=58°, 64°, 66°. For F-inserted samples, these peaks

**Figure 2** Initial charge-discharge capacity and fluorine contents in $LiMn_2O_{4-\delta}F_\delta$

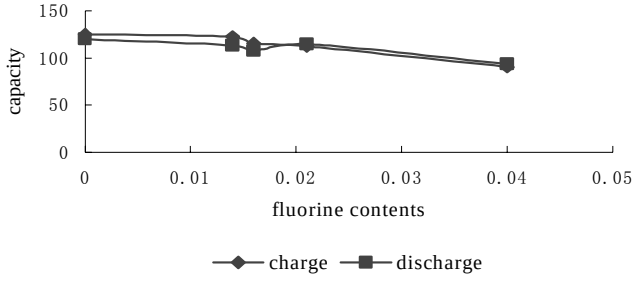
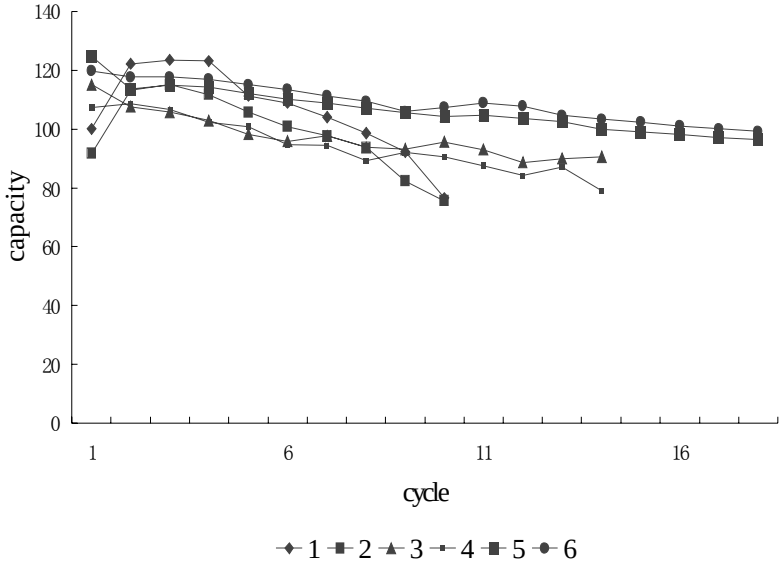
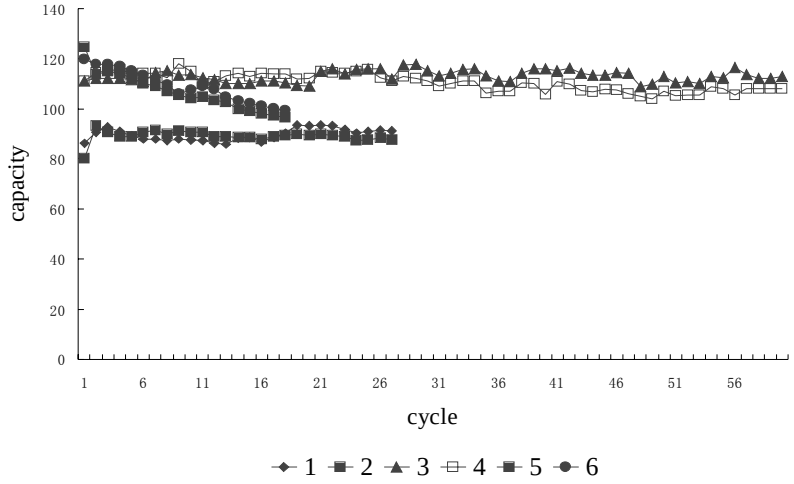


**Figure 3-1** Figure of capacity




1 and 2, the charge-discharge cycle figure of $LiMn_2O_{4-\delta}F_\delta$ with $\delta$=0.016; 3 and 4, the charge-discharge cycle figure of $LiMn_2O_{4-\delta}F_\delta$ with $\delta$=0.014; 5 and 6, the charge-discharge cycle figure of $LiMn_2O_{4-\delta}F_\delta$ with $\delta$=0.

**Figure 3-2** Figure of capacity-cycle




1 and 2, the charge-discharge cycle figure of $LiMn_2O_{4-\delta}F_\delta$ with $\delta$=0.040; 3 and 4, the charge-discharge cycle figure of $LiMn_2O_{4-\delta}F_\delta$ with $\delta$=0.021; 5 and 6, the charge-discharge cycle figure of $LiMn_2O_{4-\delta}F_\delta$ with $\delta$=0.

split into two peaks with different intension and width. Tarascon[1] discovered that the lattice constant of F-inserted lithium manganese spinels gradually increased with increasing fluorine contents. We consider that there is a tensile force between fluorine ion and oxygen ion with negative charge, it leads to the increase of the lattice parameters.

**Electrochemical test and structural model**

**Figure 2** shows the relation between the initial charge -discharge capacity and fluorine contents in spinel $LiMn_2O_{4-\delta}F_\delta$. The initial charge-discharge capacity of samples is gradually becoming lower with increasing F-content.

**Figure 3** shows the cycle-capacity of spinel $LiMn_2O_{3.979}F_{0.021}$with different fluorine contents. We can find that the spinel $LiMn_2O_{3.979}F_{0.021}$ exhibits excellent stability. After cycling for 60 times, the capacity has not exhibited any loss, and the charge-discharge capacity is still around 110 mAh • $g^{-1}$.

From the results of electrochemical test, we can draw the conclusion that when $\delta$=0.021, the capacity and stability of the cathode materials reached to the best state, its initial capacity reached ～115 mAh • $g^{-1}$ and reversible efficiency was about 100%, after 60 cycles, its capacity was still around 110 mAh • $g^{-1}$, with nearly 100% reversible efficiency. It seems that the new positive material is still suitable to reinsert lithium ion. We think that the inserted fluorine could stabilize the high oxide state of $Mn^{4+}$ and then inhibit the Jahn-Teller effect.

**Reference**

1. Glenn. G. Amatueci. Raritani, Jean-Marie Tarascon. *United States Patent* Number 5674645.

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