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Short Communication

Synthesis and Electrochemical Performance of Co-doped LiMn2O4 by Mg and F with One Improved Soild-State Method

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A series of spinel $Li_{1.02}Mg_xMn_{1.98-x}O_{4-y}F_y$ materials as cathode materials for Li-ion battery have been synthesized by one improved solid-state reaction method. Their structures and electrochemical performances are studied by XRD, CV and charge-discharge tests. Results show that the specific capacities of the materials have been increased with the co-doping of Mg and F, the stability of spinel structure and cycle performance were also improved by F^-, Mg^{2+} and Li^+ multiplex doping. The charge-discharge tests reveal that $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ has the best cycling performance. Its first specific discharge capacity is 115.9mA.g^{-1} and 116.5 mAh.g^{-1} at 25°C and 55 °C,respectively. The capacity retention ratios are 96.5% and 90.6% after 40 cycles at 25 °C and 55 °C, respectively.

Keywords: lithium-ion battery; cathode material; high temperature performance; Li-Mn spinel;Co-doping

1. INTRODUCTION

Li-Mn spinel $LiMn_2O_4$ has been considered to be one of the most promising cathode materials to substitute for $LiCoO_2$, because it is resource abundant, very cheap, safe, environment friendly and easy to recover with high working voltage[1,2]. However, its low specific discharge capacity, specially its fast capacity fading at high temperature limits its application in large scale. Although the fading mechanism is not yet very clear, it has been agreed that there are three main reasons to claim for the capacity fading: (1) manganese dissolution from $LiMn_2O_4$ into electrolyte solution[3], (2) the decomposition of electrolyte solution in the higher voltage region [4,5] ,(3) the Jahn-Teller effect out of the deep discharging to distort the crystal lattice[6] by more Mn^{3+}. Doping by metal element (Li,Mg,Ni,Al,Cr,Fe, and so on) or by anion ions (Cl and F) has been proved to be one very good method to improve the cycling stability of $LiMn_2O_4$ [7-12] . Co-doping $LiMn_2O_4$ by metal element and anion ion would be more effective in improving the stability of $LiMn_2O_4$. In this work, a series of spinel $Li_{1.02}Mg_xMn_{1.98-x}O_{4-y}F_y$ materials have been synthesized and investigated.

2. EXPERIMENTAL

2.1 Preparation of materials

The spinel $LiMn_2O_4$, $Li_{1.02}Mg_xMn_{1.98-x}O_{4-y}F_y$ powders were prepared by an improved solid-state reaction. A stoichiometric amount of Li_2CO_3, MnO_2, $Mg(NO_3)_2{\cdot}6H_2O$ and HF were thoroughly ground in an agate mortar and pelletized. The pellets were heated between 200- 600 ^oC with a heating rate 5 $^oC\ min^{-1}$ and then kept at 700 ^oC for 8h to drive off CO_2, then increased the temperature to 800 ^oC with the heating rate 2 $^oC\ min^{-1}$ and calcined in a muffle at 800 ^oC for 12h in air. Then the samples were cooled to the room temperature with cooling rate -3 $^oC\ min^{-1}$. After cooling to room temperature, the pellets were ground.

2.2. Structure characterization

The structure of products was characterized by an X-ray diffractometer (D/Max-3B, Japan) with Cu Kα radiation operating at 40.0kV and 30.0mA. XRD data were collected in the 2θ ranges from 10 to 80°.

2.3. Electrochemical measurements

After mixing the active material (80 wt%) with acetyleneblack (12 wt%) and polyvinylidene fluoride (PVDF) binder (8 wt%) in N-methylpyrrolidinone (NMP) solvent, the mixed slurry was obtained. The slurry was coated on an aluminum foil by a Doctor-blade technique, followed by drying in a vacuum oven at 100 ^oC overnight. The cells were assembled in in an Ar-filled glove box. The complete cell comprises a cathode, a Celgard (2325) separator, and a Li-foil anode. The electrolyte was 1 M $LiPF_6$ in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC). Then some CR2032 coin cells were made. Charge-discharge characteristics were tested galvanostatically on a Land CT2001A (Wuhan, China) between 3.0 and 4.5V (versus Li/Li^+) with different rates at 25 ^oC and 55 ^oC, respectively . Cyclic voltammetry measurements of the prepared powders were performed in the voltage range 3.0-4.5V at a scan rate of 0.1mV s^{-1}.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Fig.1 presents the XRD pattern of $LiMn_2O_4$, (b) $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and (c) $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$. All samples were identified as a pure spinel phase with a space group Fd3m where lithium ions occupy the tetrahedral sites (8a) and manganese and substituting metal ions reside at the octahedral (16d) sites.

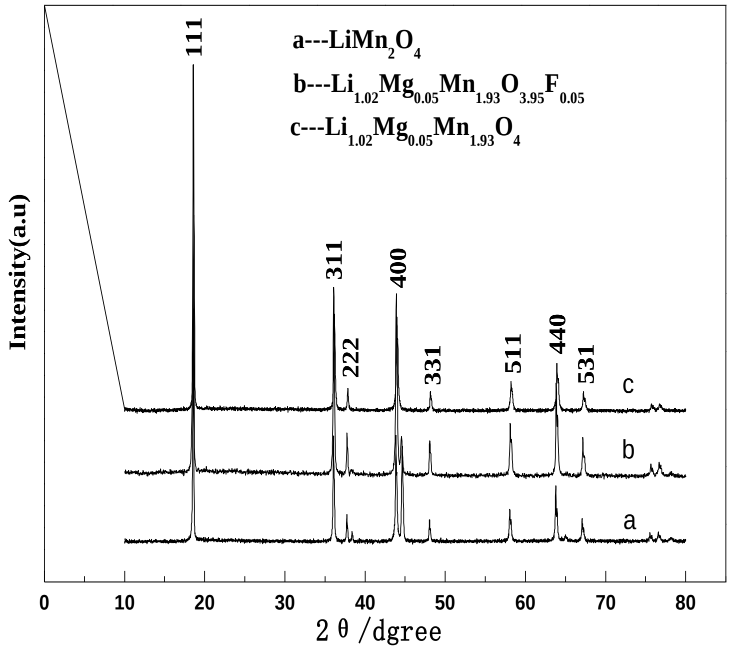

Figure 1. The XRD patterns (a) $LiMn_2O_4$, (b) $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and (c) $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ obtained by the high temperature solid-state reaction.

The lattice parameters, which were calculated from the diffraction data through the least-squares method, and the unit cell volumes of the samples are given in Table1.

Table 1. Lattice parameters of samples

Samples	Lattice parameters (Å)	Unit cell volume (Å^3)
$LiMn_2O_4$	8.246	560.699
$Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$	8.230	557.442
$Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$	8.235	558.458

It could be found that all the substituted samples have lattice parameters values smaller than those of $LiMn_2O_4$. This is due to the smaller size of the substituting ions Li^+ (0.059nm), Mg^{2+} (0.062nm), as compared with the larger Mn^{3+} ion (0.066nm). The decrease in cell volume should increase the stability of the spinel structure during in sertion and deinsertion of lithium, and thereby the electrochemical cycle stability of the samples is improved. In addition, the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ has a little larger lattice parameter than the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$,which is due to that monovalent fluorine substitute for divalent oxygen reduces Mn^{4+} to Mn^{3+} and thus increase the quantity of the larger trivalent manganese Mn^{3+}. The increase of Mn^{3+} will slightly increase the unit cell volume of the

$Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ compared to that of $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ and elevate the initial specific capacity.

3.2. Charge-discharge characteristics

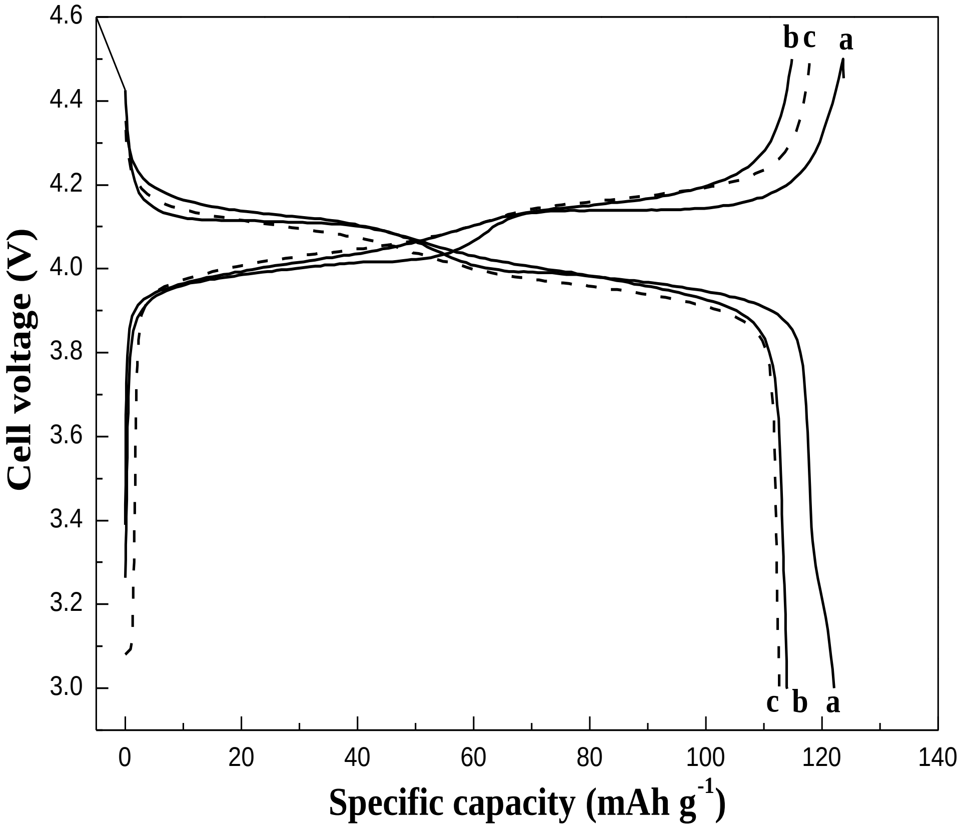

Figure 2. Initial charge-discharge curves of cells (a) Li/$LiMn_2O_4$, (b) Li/$Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and (c) Li/$Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$.

Fig.2 shows the initial charge-discharge curves of the prepared samples at room temperature and a constant current density of C/3 in the potential range from 3.0 to 4.5V. It can obviously be seen that the charge-discharge curves of all the samples have two distinctive voltage plateaus, characteristic of the well-defined spinel $LiMn_2O_4$ cathode, which implies that there are two steps for lithium intercalating and deintercalating into the material . Compared with the pure $LiMn_2O_4$, the charging plateau potential of the doped samples rises and the discharge plateau potential drops**.** This may mainly due to the stronger chemical bond of Mg-O than Mn-O, which can reinforce the lattice energy of the doped samples, so as to need expending more energy for lithium ions extraction or insertion**.**

The initial discharge capacities of $LiMn_2O_4$, Li/$Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and Li/$Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ are 121.5, 115.9 and 113.9 mAh.g^{-1}, respectively. This decrease of initial capacity is due to that the number of Mn^{3+} ions in the substituted spinel phase is decreased. In fact, only the Mn^{3+} contributes to the charge-discharge capacity during the intercalation-deintercalation of Li^+ in $LiMn_2O_4$.

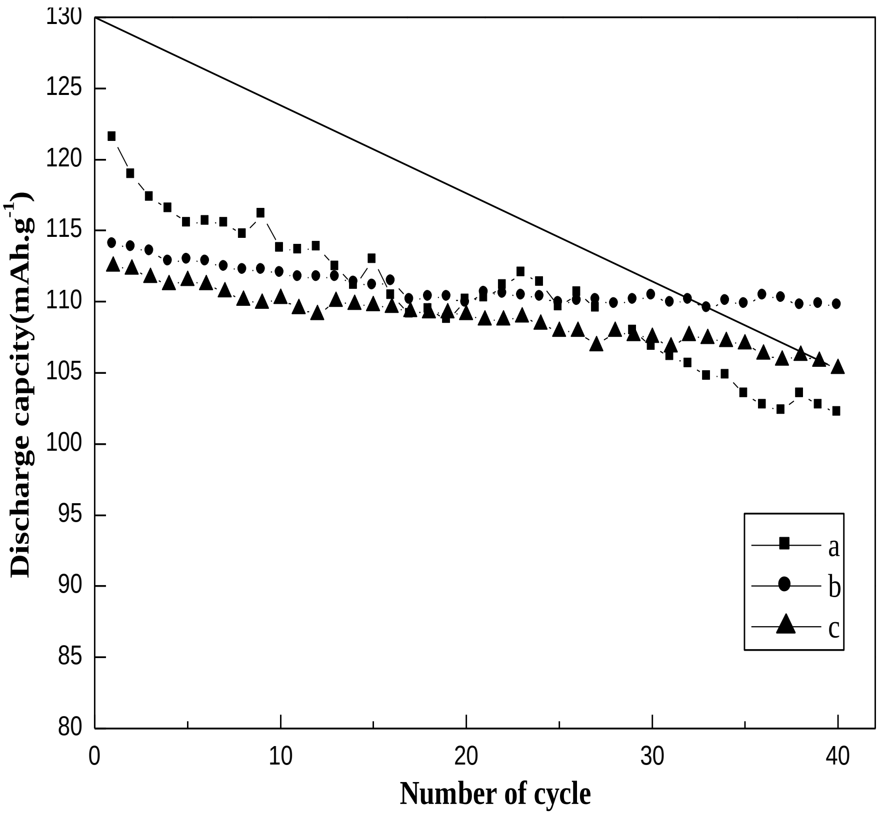

Figure 3. Cycle performance of cells (a) Li/$LiMn_2O_4$, (b) Li/$Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and (c) Li/$Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ at room temperature

In order to study the influence of doping ions on the cyclability, the cells were tested at a charge-discharge current density of C/3 between 3.0 and 4.5V at room temperature 25 ^oC. The variations of the discharge capacity with the cycle number for $LiMn_2O_4$, $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ are shown in Fig. 3. It is obviously found that the cyclibilities of $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ are significantly improved. Although the pure $LiMn_2O_4$ has the highest initial discharge capacity, its capacity retention ratio was 84.1% after 40 cycles. However, the capacity retention ratio of $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ is 93.2% after 40 cycles. Moreover, spinel $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ shows slightly better cycle performance and a slightly higher capacity compared with spinel $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$. The capacity retention ratio of $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ is 96.5% after 40 cycles. Because substitution of Mn by Mg and Li decreases the unit cell volume and the decrease of Mn^{3+} concentration reduces the Jahn-Teller distortion and also stabilizes the structure integrity of the active material. In addition, Mg , Li and F codoping in $LiMn_2O_4$ increases the binding energy in the octahedral MO_6 sites. Thus, the simultaneous cation and anion substitution of $LiMn_2O_4$ with Mg, Li and F improves the cycling performance of spinel $LiMn_2O_4$ more than cation-only substitution of $LiMn_2O_4$ with Mg and Li. Also the co-doping increases the ability of Li-Mn spinel against the attack of HF in eletrolyte so as to increase the cycling performance[13].

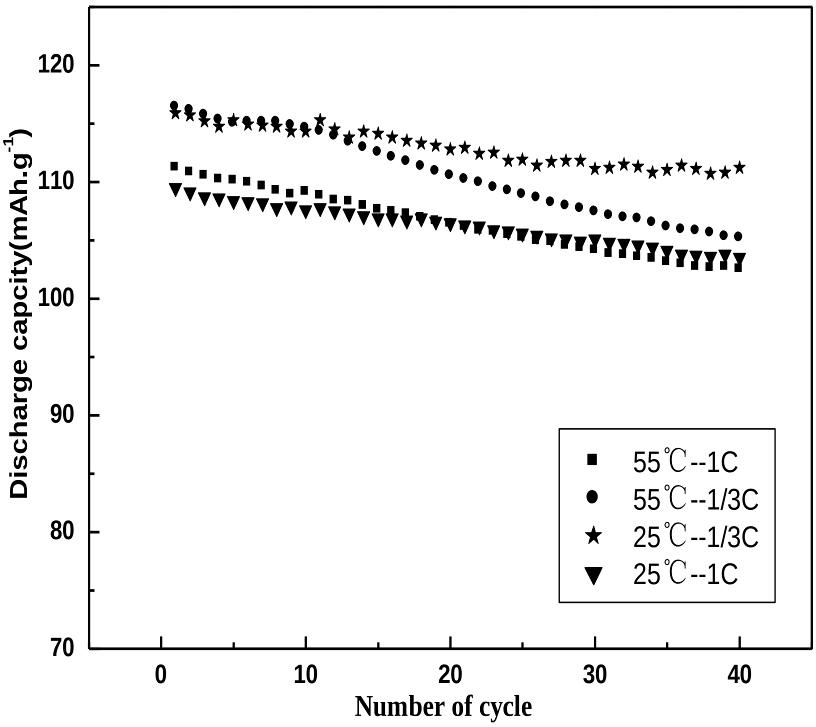

Figure 4. Cycle performance of $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$

Fig.4 shows the cycling performance of the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ at different rates in voltage range of 3.0-4.5V at 25 ^oC and 55 ^oC, respectively. To investigate the rate capability upon cycling, various current densities of C/3 and 1C were applied to the working electrode. From Fig.4, it can be seen that the synthesized $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ material exhibits excellent cycling stability not only at room temperature ,but also at elevated temperature even at higher current density. For the electrode cycled at 25 ^oC, the initial discharge capacity is 115.9 and 109.5 $mAh.g^{-1}$ at C/3 and 1C rate, respectively. At 55 ^oC, the initial discharge capacity is 116.5 and 112.0 $mAh.g^{-1}$ at C/3 and 1C rate, respectively. The capacity retention ratio is 96.5%, 90.4% after 40 cycles at C/3 rate at 25 ^oC and 55 ^oC, respectively;and 94.5%, 91.4% after 40 cycles at 1C rate at 25 ^oC and 55 ^oC, respectively. It is well known that high-rate discharge capability and cycle stability are the most important electrochemical parameters for battery applications. Especially for the Li-Mn spinel material the cycling stability at high temperature is a very important characteristic for practical application. Therefore, the results obtained above confirm that the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ sample is an attractive material for practical application.

3.3. Cyclic voltammetry

The cycle voltammogram properties of the cells $LiMn_2O_4$ and $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ were tested. Cyclic voltammograms (sweep rate: 0.1mV s^{-1}) in the potential region of 3.0-4.5 V are presented in Fig. 5. For both cyclic voltagram curves, there are two pairs of reversible peaks, oxidation and reduction peaks corresponding to Li^+ extraction and insertion, which reflect the typical Mn^{3+}/Mn^{4+}

redox process of the spinel structure in the 4V domain. That all the peaks are sharp shows that these two spinel materials have excellent lattice structurs[14,15].

The difference between the two samples is that the redox peaks of the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ electrode are sharp and show well-defined splitting, which indicates that the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ powder are more crystalline than pure $LiMn_2O_4$. This strongly demonstrates that the cycling performance of the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ electrode is significantly improved.

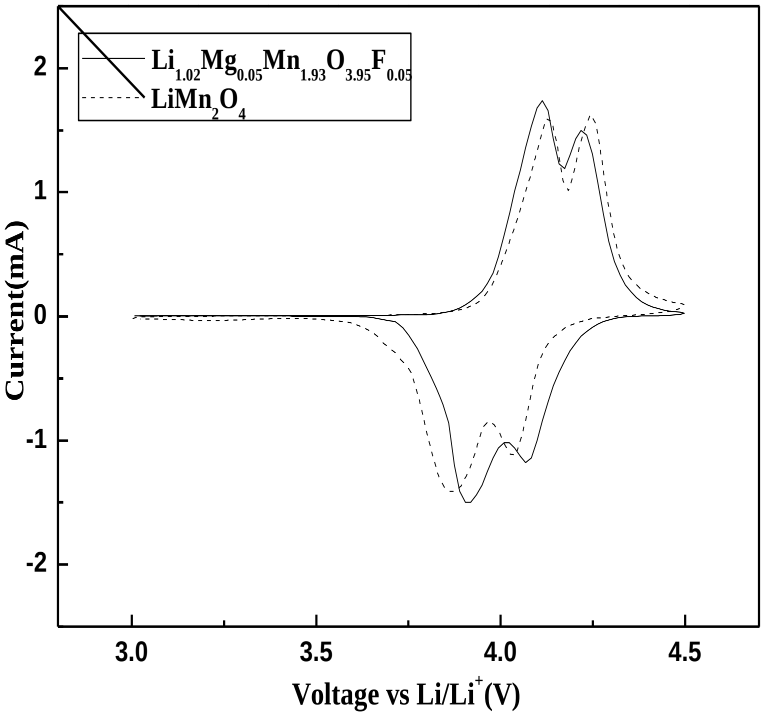

Figure 5. The cyclic voltammograms of $LiMn_2O_4$ and $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$

4. CONCLUSIONS

A good quality $LiMn_2O_4$, $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ and $Li_{1.02}Mg_{0.05}Mn_{1.93}O_4$ were successfully synthesized by a improved simple solid state reaction. Among these synthesized materials, the $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ sample shows the best cycle performance at room and elevated temperature even at high current density. The improvement in cycling performance might be attributed to the stabilization in the spinel structure and the suppression of Jahn–Teller distortion by the doped metal cations. In addition, the Mg, Li and F codoping in $LiMn_2O_4$ increases the binding energy in the octahedral MO_6 sites. The $Li_{1.02}Mg_{0.05}Mn_{1.93}O_{3.95}F_{0.05}$ sample is a promising cathode material for Li-ion battery in practical application.

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