Research Article

Structural and Electrochemical Investigation of $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{4-x}\text{F}_x$ ($x = 0, 0.08$) Synthesized by Solid-State Method

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To improve the cycle performance of spinel LiMn_2O_4 as the cathode of 4-V-class lithium secondary batteries, spinel phases $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{4-x}\text{F}_x$ ($x = 0, 0.08$) have been successfully prepared by a conventional solid-state method. The structure and physicochemical properties of this as-prepared powder were investigated by powder X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS), and galvanostatic charge-discharge test in detail. The results reveal that the multiple doping spinel $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{4-x}\text{F}_x$ have better electrochemical performance than the undoped or only metal-element doped material, which may be contributed to the multiple cation and anion doping to lead to a more stable spinel framework with good capacity retention rate.

1. Introduction

Spinel LiMn_2O_4 has been regarded as one of the most promising cathode materials for lithium-ion batteries in virtue of its obvious advantages such as the abundant and cheap resources, environmental benignity, safety, high voltage, and good rate of capability [1]. So it has been extensively investigated as a cathode material for lithium-ion batteries [2]. Although LiMn_2O_4 cycles well at room temperature, prolonged cycling at higher temperatures is accompanied by an unacceptable fading of capacity [3]. This severe capacity fading is mainly due to the Jahn-Teller distortion on the surface of spinel LiMn_2O_4 [4], the dissolution of manganese in the electrolyte solution [5, 6], the spinel LiMn_2O_4 with oxygen deficiency [7], and the decomposition of electrolyte solution on the electrode [8, 9]. To overcome this problem, many researchers have studied the mechanisms of capacity fading and many methods for the cyclability improvement of spinel cathodes have been suggested.

Doping is considered to be an effective path to improve the electrochemical performance of LiMn_2O_4 , so several attempts have been made for improving synthesis of lithium

manganese spinels by doping with various metals, such as Al, Mg, Co, Cr, Ni, Fe, and Cu. [10–15]. It may be expected that replacing part of the manganese with another metal could increase the stability of the spinel structure and improve the cycling performance of Li-Mn spinel when it is employed as the cathode active material [16]. Although such substitutions often result in enhanced stability of the spinel, the initial discharge capacity of the doped spinels decreases significantly and is lower than that of the parent compound. Single-ion-doped LiMn_2O_4 spinels could not counteract all the factors responsible for the capacity loss. The effect of multiple cation-substituted LiMn_2O_4 has been reported and it has been pointed out that codoping has a synergistic effect on the improvement of the cycling life of the materials as cathodes in lithium batteries [17]. It has been demonstrated that the cyclic stability of LiMn_2O_4 could be improved by doping anion F [18–21]. So in this work codoping cations and anion F has been designed to improve the properties of LiMn_2O_4 .

In this work, the cathode materials LiMn_2O_4 , $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, and $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ have been successfully prepared by the high temperature solid-state reaction. The physical characteristics and

FIGURE 1: The XRD patterns of (a) LiMn_2O_4 , (b) $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$, and (c) $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$ obtained by the high temperature solid-state reaction.

electrochemical properties of the synthesized products have also been investigated in detail.

2. Experimental Section

2.1. Materials Preparation. The spinel LiMn_2O_4 , $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, and $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ powders were prepared by a simple solid-state reaction. A stoichiometric amount of Li_2CO_3 , MnO_2 , $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, HF , $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was thoroughly ground in an agate mortar and pelletized. The pellets were heated at 700°C for 12 h to drive off CO_2 and then calcined in a muffle at 800°C for 20 h in air. The heating rate was 2°C min^{-1} and the cooling rate to room temperature was $-3^\circ\text{C min}^{-1}$. After cooling to room temperature, the pellets were ground again.

2.2. Structure and Morphology Characterization. The structure of products was characterized by an X-ray diffractometer (D/Max-3B, Japan) with $\text{CuK}\alpha$ radiation operating at 40.0 kV and 30.0 mA. XRD data were collected in the 2θ ranges from 10° to 80° .

2.3. Electrochemical Measurements. After mixing the active material (80 wt%) with acetylene black (12 wt%) and polyvinylidene fluoride (PVDF) binder (8 wt%) in N-methylpyrrolidinone (NMP) solvent, the mixed slurry was attained. The slurry was coated on an aluminum foil by a doctor blade technique in a vacuum oven at 100°C for 12 h. The cells were assembled in an Ar-filled glove box. The CR2032 coin cell comprises a cathode, a Celgard (2325) separator, and a Li-foil anode. The electrolyte was 1M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Charge-discharge characteristics were tested galvanostatically on a Land

TABLE 1: Lattice parameters of samples.

Samples	Lattice parameters volume ($\text{\AA}^3$)	Unit cell volume ($\text{\AA}^3$)
$\text{Li}_2\text{Mn}_2\text{O}_4$	8.246	560.279
$\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$	8.232	558.572
$\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$	8.237	559.132

CT2001A (Wuhan, China) between 3.0 and 4.5 V (versus Li/Li^+). Cyclic voltammetry measurements of the prepared powders were performed in the voltage range 3.0–4.5 V at a scan rate of 0.1 mV s^{-1} . The electrochemical impedance measurements were carried out in the frequency range from 100 KHz to 0.01 Hz with an AC voltage signal of $\pm 5\text{ mV}$.

3. Results and Discussion

3.1. X-Ray Diffraction. Figure 1 presents the XRD pattern of LiMn_2O_4 , $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$, and $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$. All samples were identified as a pure spinel phase with a space group $\text{Fd}3\text{m}$ where lithium ions occupy the tetrahedral (8a) and manganese and substituting metal ions reside at the octahedral (16d) sites [22]. This fact may indicate that the Mn site in LiMn_2O_4 is substituted fully by Al-, Cr-, and Fe-, respectively, and no other phase is formed.

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 Table 1. 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^+ (0.059 nm), Al^{3+} (0.054 nm), Cr^{3+} (0.0615 nm), and Fe^{3+} (0.064 nm) as compared with the larger Mn^{3+} ion (0.066 nm) [23]. The decrease in cell volume should increase the stability of the spinel structure during the insertion and deinsertion of lithium [16], and thereby the electrochemical cycle stability of the sample could be improved. In addition, the $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ has a little larger lattice parameter than the $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, which is due to the fact that monovalent fluorine substitutes for divalent oxygen reduce 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 $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ compared to that of $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$ and elevate the initial specific capacity.

3.2. Charge-Discharge Characteristics. Figure 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 4.5 V. 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

FIGURE 2: The charge-discharge curves of cells (a) $\text{Li/LiMn}_2\text{O}_4$, (b) $\text{Li/Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, and (c) $\text{Li/Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$.

into the material [24]. Compared with the pure LiMn_2O_4 , the charging plateau potential for the doped samples rises and the discharge plateau potential drops. This may mainly be due to the stronger chemical bond of Al–O, Fe–O, and Cr–O than Mn–O, which can reinforce the lattice energy of the doped samples, which needs expending more energy for lithium ions to extract or to insert.

The initial capacity of $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$ or $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ is lower than that of pure LiMn_2O_4 . The initial discharge capacity of LiMn_2O_4 , $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, and $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ is 121.5, 115.6, and 117.8 $\text{mAh}\cdot\text{g}^{-1}$, respectively. This decrease of initial capacity is because the composition of the substituting spinel can be written as $\text{Li}_{1.02}^{1+}\text{Al}_{0.02}^{3+}\text{Fe}_{0.02}^{3+}\text{Cr}_{0.02}^{3+}\text{Mn}_{0.96}^{3+}\text{Mn}_{0.96}^{4+}$

$\text{O}_{3.92}^{2-}\text{F}_{0.08}^{1-}$ and $\text{Li}_{1.02}^{1+}\text{Al}_{0.02}^{3+}\text{Fe}_{0.02}^{3+}\text{Cr}_{0.02}^{3+}\text{Mn}_{0.88}^{3+}\text{Mn}_{1.04}^{4+}\text{O}_4^{2-}$, respectively. Compared with the initial composition of $\text{Li}^{1+}\text{Mn}^{3+}\text{Mn}^{4+}\text{O}_4^{2-}$, 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 .

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 4.5 V. The variations of the discharge capacity with the cycle number for LiMn_2O_4 , $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, and $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ are shown in Figure 3. It is obviously found that the cyclabilities of $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$ and $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ have been significantly improved. Although the

FIGURE 3: Cycle performance of cells (a) Li/LiMn₂O₄, (b) Li/Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄, and (c) Li/Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} at room temperature.

pure LiMn₂O₄ had the highest initial discharge capacity, its capacity retention ratio was 82.1% after 50th cycle. However, the capacity retention ratio of Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} is 96.8% after 50th cycle. The capacity retention ratio of Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄ is 91.5% after the 50th cycle. Moreover, spinel Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} shows better cycle performance and a slightly higher capacity than the spinel Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄ because the substitution of Mn by Cr, Fe, Al, and Li decreases the unit cell volume and the decrease of Mn³⁺ concentration reduces the Jahn-Teller distortion and also stabilizes the structure integrity of the active. In addition, the Cr, Fe, Al, Li, and F codoping in LiMn₂O₄ increases the binding energy in the octahedral MO₆ sites. Thus, the simultaneous cation and anion substitution of LiMn₂O₄ with Cr, Fe, Al, Li, and F improves the cycling performance of spinel LiMn₂O₄ more than cation-only substitution of LiMn₂O₄ with Cr, Fe, Al, and Li.

Figure 4 shows the cycling performance of the Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} electrode at 25 and 55°C in voltage range of 3.0–4.5 V, respectively. To investigate the rate capability upon cycling, various current densities of C/3 and 1C were applied to the working electrode. From Figure 4, it can be seen that the synthesized Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} material exhibits excellent cycling stability at room and elevated temperature even at high current densities. For the electrode cycled at 25°C, the initial discharge capacity is 117.5 and 111.8 mAh·g⁻¹ at C/3, 1C rate, respectively. At 55°C, the initial discharge capacity is 118.1 and 111.5 mAh·g⁻¹ at C/3, 1C rate, respectively. The capacity retention ratio is 96.8% and 91.7% after the

50th cycle at 25°C and 55°C at C/3 rate and 94.7% and 88.1% after the 90th cycle at 1C rate, respectively. It is well known that high rate discharge capability and cycle stability are the most important electrochemical parameters for battery applications [25]. Therefore, the results obtained above confirm that the Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} sample is an attractive material for practical applications.

3.3. Cyclic Voltammetry. The cycle voltammogram properties of the cells LiMn₂O₄ and Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄F_{0.08} after 2 and 50 cycles were tested. Cyclic voltammograms with the sweep rate of 0.05 mV s⁻¹ in the potential region of 3.0–4.5 V are presented in Figures 5(a) and 5(b), respectively. For both cyclic voltammograms, there are two pairs of reversible peaks, oxidation and reduction peaks, corresponding to Li⁺ extraction and insertion, which reflect the typical Mn³⁺/Mn⁴⁺ redox process of the spinel structure in the 4 V domain [26].

The difference between the two samples is that the redox peaks of the Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄F_{0.08} electrode are sharp and show well-defined splitting, which indicates that the Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄F_{0.08} powder is more crystalline than pure LiMn₂O₄. In addition, the peak current of pure electrode for the 50th cycle is much lower than that for the 2nd cycle, which indicates that the cycling leads to a distinct capacity fading. In comparison, the peak current of Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄F_{0.08} with cycling almost does not decrease, and the curve for the 50th cycle is approximately the same as that for the 2nd cycle. This strongly demonstrates that the cycling performance of the Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄F_{0.08} electrode is significantly improved.

3.4. EIS Studies the Spinel Electrodes. AC impedance spectroscopy is a powerful technique for determining the kinetic parameters of the electrode process [27]. The Nyquist plots obtained at the CV peak potential (4.16 V) for LiMn₂O₄, Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄, and Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} spinels are shown in Figure 6. All the Nyquist plots show two semicircles and a Warburg impedance associated with the diffusion of lithium ions in the oxide matrix. The first semicircle is associated with the passivation layer on the electrode. The second one is associated with the charge-transfer resistance coupled with a capacitance at the surface film/cathode particle interface arising from surface-adsorbed species.

From the Nyquist plots, it can be found that in comparison with semicircles of pure LiMn₂O₄, the first and second semicircles of doped LiMn₂O₄ decrease, which indicates that the surface layer resistance (R_{sei}) and the charge transfer resistance (R_{ct}) of doped LiMn₂O₄ are smaller than those of pure LiMn₂O₄. In addition, the minimum R_{ct} values of Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} mean a lower electrochemical polarization, and this leads to a higher electrochemical performance. These EIS phenomena might be able to explain the excellent high rate performance of the spinel Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O_{3.92}F_{0.08} [28]. Also, it can be seen from Figure 6 that total resistance (R_{cell}) of LiMn₂O₄ and Li_{1.02}Mn_{1.92}Al_{0.02}Fe_{0.02}Cr_{0.02}O₄

FIGURE 4: Cycling performance of the $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ electrode at different current densities in voltage range of 3.0–4.5 V at 25°C and 55°C.

FIGURE 5: Cyclic voltammograms of cells containing (a) LiMn_2O_4 and (b) $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ after 2 and 50 cycles.

evidently increases after 50 cycles, especially for pure LiMn_2O_4 . Compared with pure LiMn_2O_4 , the resistance of the spinel $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ almost does not change after 50 cycles. The electrochemical impedance is a major part of internal resistance of a battery and the cycle life of a battery decreases as its internal resistance increases after repeated charge and discharge. Hence,

the electrochemical impedance characteristics of the spinel $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ explains the enhanced cycle life of the multiple doping spinel compared to the pure one. Also, from the EIS property comparison, it could be concluded that $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ has better electrochemical performance than $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$.

FIGURE 6: AC impedance experiments measured for the spinel (a) $\text{Li/LiMn}_2\text{O}_4$, (b) $\text{Li/Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, and (c) $\text{Li/Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ electrodes at the potential $E = 4.16$ V before and after 50 cycles.

4. Conclusions

Spinel materials LiMn_2O_4 , $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_4$, and $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ were successfully synthesized by the simple solid-state reaction. Among these synthesized materials, the $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ sample shows the best cycle performance at room and elevated temperature even at high current densities. The improvement in cycling performance might be attributed to the stabilization in the spinel structure and the suppression of Jahn-Teller distortion by the codoped metal cations and anion

F. In addition, the Cr, Fe, Al, Li, and F codoping in LiMn_2O_4 increases the binding energy in the octahedral MO_6 sites. It could be seen that codoping is an effective way to improve the stability of LiMn_2O_4 . $\text{Li}_{1.02}\text{Mn}_{1.92}\text{Al}_{0.02}\text{Fe}_{0.02}\text{Cr}_{0.02}\text{O}_{3.92}\text{F}_{0.08}$ is one promising cathode material for Li-ion battery.

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