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Short Communication

Synthesis and Improvement of Li-Mn Spinel by Multiple Co-doping

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Cathode material Li-Mn spinel materials $LiZn_{0.03}Mg_{0.03}Mn_{1.94}F_{0.05}$, $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ and $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$ for Li-ion battrry have been successfully synthsized by a citric acid sol-gel method. Their cycling performances have been improved by multiple co-doping with Zn,Mg and F elements. The effects of the ratios of Li/Mn on electrochemical performance of the modified $LiMn_2O_4$. are also investigated. The crystal structures of the materials were characterized by X-ray powder diffraction(XRD). Electrochemical properties were characterized by cyclic voltammetry and galvanostatic charge and discharge methods. The CV curves of the as-prepared materials show two typical redox couples of spinel $LiMn_2O_4$. The galvanostatic charge and discharge test results show that the $LiZn_{0.03}Mg_{0.03}Mn_{1.91}O_4F_{0.05}$ has the best electrochemical performance.

Keywords: Lithium-ion battery, Li-Mn spinel ,cathode material, multiple co-doping, improvement

1. INTRODUCTION

Li-Mn spinel $LiMn_2O_4$ has been demonstrated 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 prepare with high working voltage[1-3]. So for almost more than 20 years, it has been widely studied as a promising cathode material for lithium-ion batteries [1-10]. Also this kind of material has been researched in our laboratory over more than 10 years[1-3]. 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, [4,5]; (2) the decomposition of electrolyte solution in the higher voltage region [6];(3) the Jahn-Teller effect[7,9,10] out of the deep discharging to distort the crystal lattice by more

Mn^{3+}. Especially, the Jahn-Teller effect is the most prominent factor to reduce the electrochemical performance for Li-Mn spinel . 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 $LiMn_2O_4$ [8,9, 11-22]. Co-doping $LiMn_2O_4$ by metal element and anion ion would be more effective in improving the stability of $LiMn_2O_4$. The F element doping has been proved to be favourable for the cycling stability of Li-Mn spinel[2,17,21]. Also in consideration of that both the element Mg and the element Zn are cheaper than the Mn element. In this work, mutiple co-doping Li-Mn spinel materials $LiZn_{0.03}Mg_{0.03}Mn_{1.94}F_{0.05}$, $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ and $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$, have been synthesized and investigated. Also the effects of Li/Mn ratios on the electrochemical performances have been checked. All the materials have been synthesized by a citric acid sol-gel method.

2. EXPERIMENTAL

2.1 Preparation of materials

The stoichiometrical reagents $LiNO_3$ (A.R grade), $Mn(CH_3COO)_2\cdot4H_2O$ (A.R. grade), $Mg(NO_3)_2\cdot6H_2O$ (A.R. grade) , $Zn(NO_3)_2\cdot6H_2O$ and LiF were dissolved into deionized water. The resulting solution was heated to 80 °C, then a proper amount of citric acid (A.R grade) was dissolved into it. The pH value of the solution was adjusted to about 7.0 by adding concentrated $NH_3 \cdot H_2O$. After 3-5 h, the sol-gel was formed. After the sol-gel was dried in a dessicator at 85 °C, it was heated at 300 °C for 6 h and 500 °C for 6 h. Then the sample was calcined at 750 °C for 12h. Finally, the doped spinel cathode materials $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$, $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ and $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$ were obtained.

2.2. Structure characterization

X-ray diffraction (XRD) for the materials were measured by the instrument Bruker D-8 with Cu Kα radiation at 3 °/min in $2\theta = 10 \sim 90°$ with the step 0.02°.

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 °C 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 used is LB-315 (1M $LiPF_6$ in m(DMC):m(EMC):m(EC)=1:1:1).

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 °C. Cyclic voltammetry (CV) measurements of the prepared powders were performed in the voltage range 3.0-4.5V at a scan rate of 0.1mV s^{-1}. The CV measurements were by one ZAHNER-IM6 instrument made in Germany.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Fig.1(a) presents the XRD patterns of $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$, $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ and $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$.

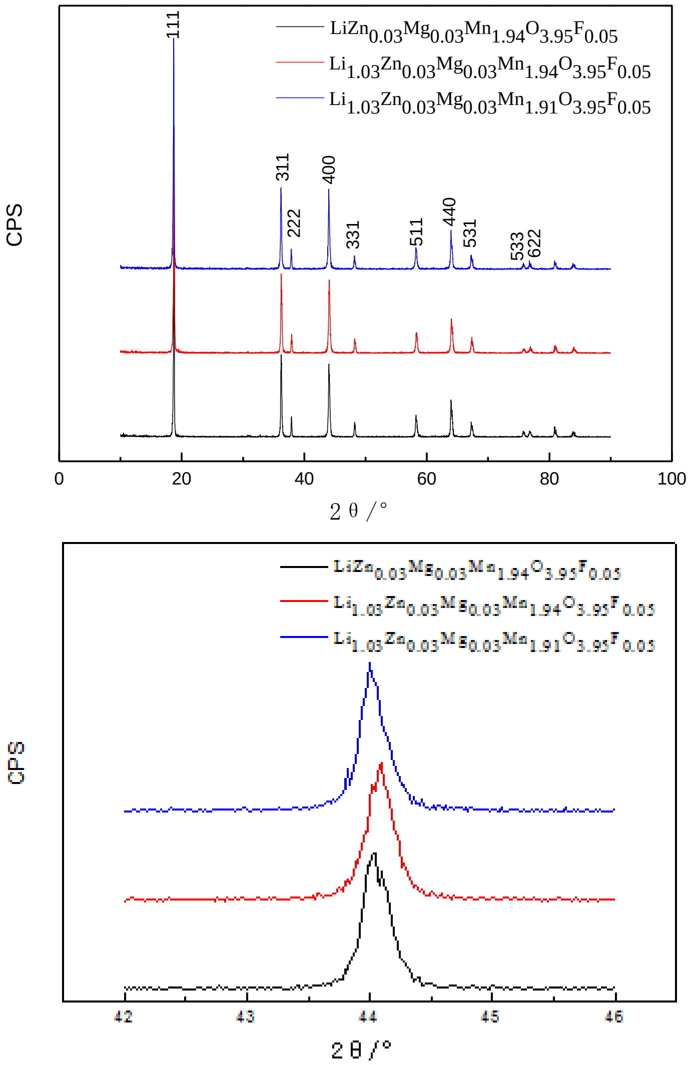


Figure 1. XRD patterns (a) and their selective enlargemengts (b) of the as-prepared materials

Fig.1(b) shows their selective enlargemengts on the position of 2θ = 44°. It can be seen that all the XRD patterns of the materials show typical spinel phase. It could be considered that the doped metal elements occupy some 16d positions of Mn in the crytals. From Fig.1(b), it could be found that the FWHM value of I_{400} peak for $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ is the lowest, which may predict that it should have the best electrochemical performance among the three materials.

The lattice parameters, which were calculated from the diffraction data through the least-squares method, together with the FWHM values of I_{400} peaks for the samples are given in Table1. The lattice parameters decrease with the increase of Li/Mn ratio. All lattice parameters are smaller than the lattice parameter of standard $LiMn_2O_4$ material with a_0=8.236 Å（JCPS88-1026）. So they should have better electrochemical performances.

Table 1. Lattice parameters and FWHM value of peak (111) of the as-prepared materials

samples	Li/Mn	lattice parameter (Å)	I_{400} FWHM
$LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$	1/1.94	8.2285	0.201
$Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$	1.03/1.94	8.2280	0.218
$Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$	1.03/1.91	8.2274	0.204

3.2. Charge-discharge characteristics

Fig.2 shows the initial charge-discharge curves of the prepared samples at room temperature and a constant current density of 0.2mA/cm^2 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 . The charging voltage plateau appears in 4.0V~4.2V and discharging voltage plateau appears in 4.12V~3.98V.

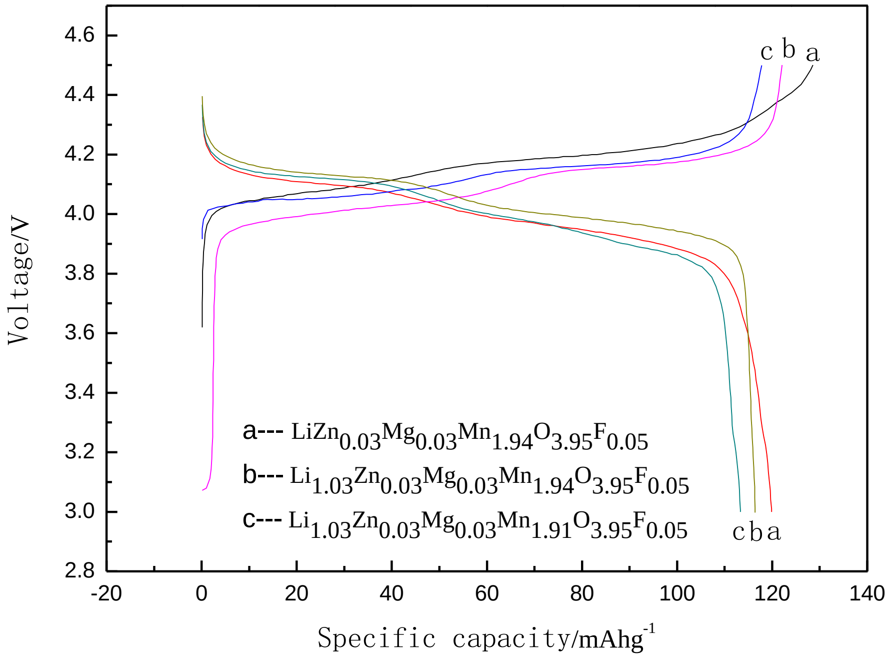


Figure 2. Initial charge /discharge curves of the as-prepared materials ,

3.3 Cycling Performance

Fig.3(a) shows the cycling performance of the three materials at C/3 rate in voltage range of 3.0-4.5V at 25 ^{o}C. It can be seen that all the three synthesized materials exhibit excellent cycling stabilities. This may be ascribed to the co-doping. The $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ material has the highest discharge capacity of 120.1 mAh/g and the best cycling performance. Ralatively the $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ material has the lowest discharge capacity of 113.4 mAh/g.

Fig.3(b) presents the cycling performance of the three materials at different rates in voltage range of 3.0-4.5V at 25 ^{o}C. Each cell was charged with a 1/3C rate and then dischared at 1/3C，0.5C，1C，2C and 3C ,respectively. For every discharging current, the cycling is for 10 cycles. It can be confirmed again that $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ material has the best cycling performance and rate capability. Perhaps the difference of Li/Mn ratio may affect the electrochemical performance. The lower Li/Mn ratio may result in a better electrochemical performance.

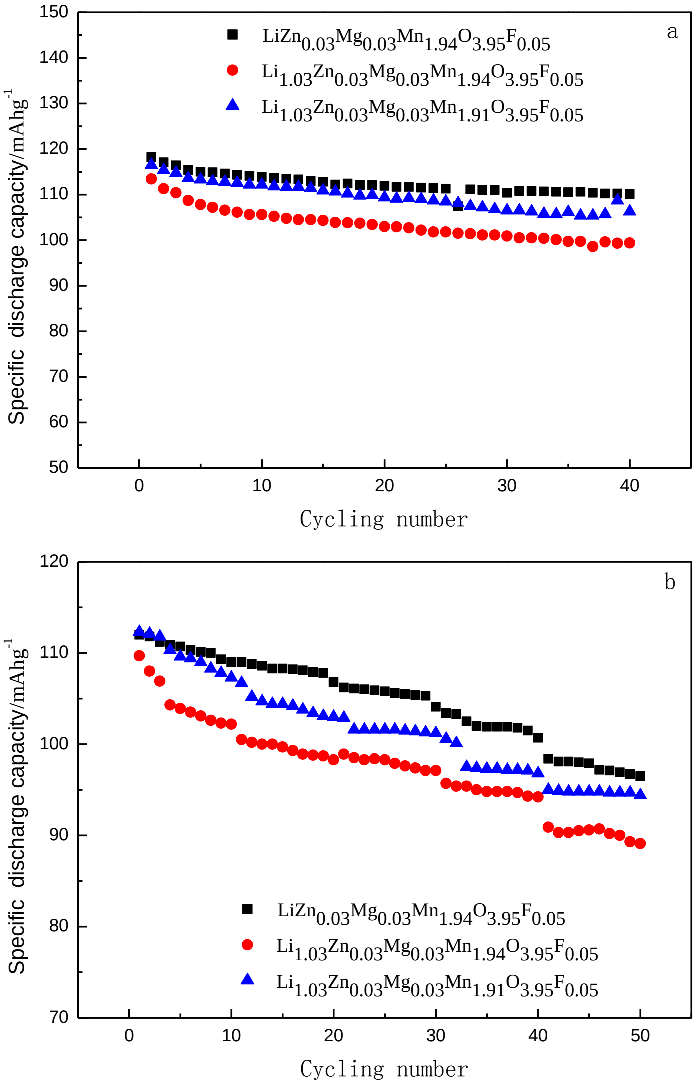
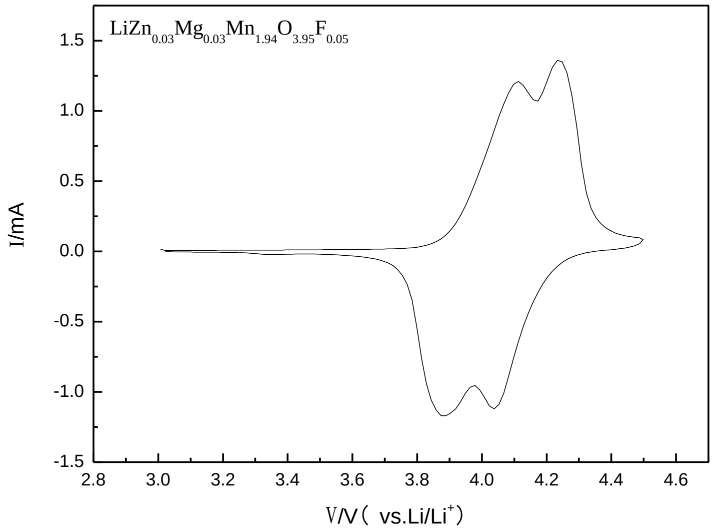


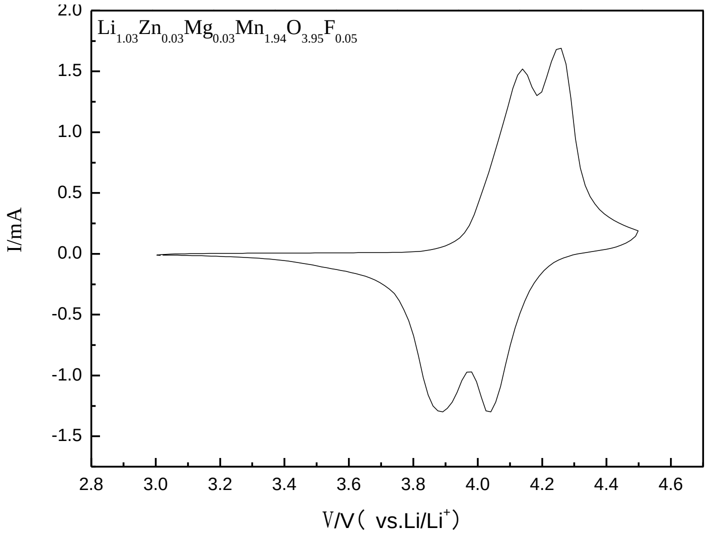
Figure 3. Cycle performance of the as-prepared materials (a) at the same current density,(b) at the different current densities

3.4. Cyclic voltammetry

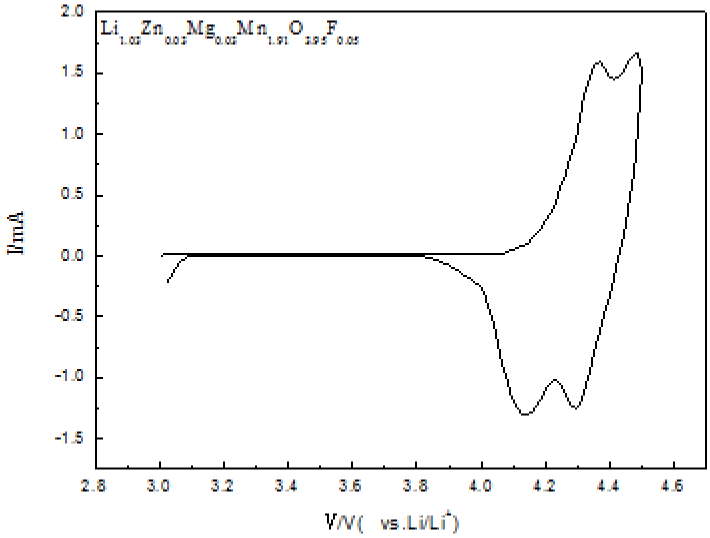
The cycle voltammogram properties of the three samples were tested. Cyclic voltammograms (sweep rate: 0.1mV s^{-1}) in the potential region of 3.0-4.5 V are presented in Fig. 4. For all cyclic voltagram curves, there are two pairs of reversible peaks, oxidation and reduction peaks corresponding to Li^+ 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 spinel materials have excellent lattice structurs [23,24]. The peak positions of sample (c) $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$ move toward higher voltages compared to those of sample (a) $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ and sample (b) $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$, which may show that sample (c) needs more energy for Li+ to move. Also it may be due to that there is less Mn^{3+} in (c) $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$ material.



(a) Sample $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$;



(b) Sample $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$



(c) Sample $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$

Figure 4. Cyclic voltammetric curves of the first cycles of the as-prepared materials

4. CONCLUSIONS

The Li^+ , Zn^{2+}, Mg^{2+}, and F^- co-doped Li-Mn spinel cathode materials $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$, $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.91}O_{3.95}F_{0.05}$ and $Li_{1.03}Zn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ have been successfully synthesized by a sol-gel method calcined at 750 °C. All these three materials present very good cycling stability. Among all the materials synthesized in this work, $LiZn_{0.03}Mg_{0.03}Mn_{1.94}O_{3.95}F_{0.05}$ shows the best electrochemical performance. At room temperature, it has a very high initial discharge capacity of 120.1 mAh·g^{-1} and a high capacity retention of 98.5% after 40 cycles . Also it has an excellent rate capability. It could be concluded that co-doping is a good way to improve the stability of Li-Mn spinel $LiMn_2O_4$. It has also been found that the Li/Mn ratio is one key factor in designing good Li-Mn spinel materials.

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