

Preparation and characterization of $\text{LiMn}_{1.5}\text{Me}_{0.5}\text{O}_4$ (Me = Ti, Fe, Ni, Zn) for lithium-ion battery cathode materials^①

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Abstract: Based on synthesizing pure spinel type lithium manganese oxides, the derivations such as $\text{LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Fe}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Zn}_{0.5}\text{O}_4$ were prepared using solid-step sintering method. The structures were characterized by using XRD, SEM and laser granulometer. The electrochemical measurement results show that the element of iron or nickel can raise the discharging plateau voltage of LiMn_2O_4 , and element titanium improves the electrochemistry property of LiMn_2O_4 little, while element zinc destroys the electrochemistry property of LiMn_2O_4 . The influence of elements of titanium, iron, nickel, or zinc on the structure of LiMn_2O_4 pure phase was discussed from the viewpoint of structural chemistry.

Key words: lithium-ion battery; cathode material; lithium manganese oxide; derivations; characterization

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1 INTRODUCTION

Lithium-ion cells are the advanced rechargeable batteries following by nickel-cadmium cells and nickel-hydrogen cells, which are being used widely in the field of portable computer, mobile phone and the other modern electronic equipments^[1]. Moreover, the applications of the lithium-ion cells are increasing rapidly in uninterruptible power system, electric vehicle, cosmic space field, etc.^[2]. Therefore, as the key technique to this kind of cells, it is worthwhile developing lithium-ion battery materials with high performance-cost ratio.

At present, lithium cobalt oxides, lithium nickel oxides, and lithium manganese oxides are the rich-lithium transitions for the main lithium-ion battery cathode materials^[3]. Among them of LiCoO_2 has good thermo-stability, but with expensive synthesis and a little pollution. The preparation condition of LiNiO_2 is rather difficult, and its thermo-stability is unstable. While lithium manganese oxides are the more attractive materials with lower cost, little pollution, possessing three-dimension tunnel structure, fine thermal stability, and higher availability of discharge capacity^[4].

Based on synthesizing pure phase LiMn_2O_4 with solid-step sintering method, the derivations of lithium manganese oxides were prepared by adding certain amount of transition metal element and the products were characterized. From the viewpoint of structure chemistry, we analyze whether the transition metal

elements could weaken Jahn-Teller effect, which will do favor to the practice for lithium-ion battery with lower cost and high properties.

2 EXPERIMENTAL

2.1 Sample preparation

On the basis of differential thermal analysis experiment^[5], the mixture of $\text{LiOH} \cdot \text{H}_2\text{O}$, MnO_2 and transition metal oxides such as TiO_2 (or Fe_2O_3 , $\text{Ni}(\text{OH})_2$, ZnO respectively) with some certain molar ratio was ground, pressed and put into a corundum boat, then placed at Fe-Cr-Al wire horizontal furnace. The heating temperature was controlled by WZK type governing silicon temperature apparatus utilizing Ni-Cr/Ni-Si thermocouple. By the solid-step sintering method^[6], the samples such as LiMn_2O_4 , $\text{LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Fe}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Zn}_{0.5}\text{O}_4$ were synthesized in oxygen atmosphere.

2.2 Characterization

The derivations were determined by RIGAKU/MAX-3B type X-ray diffraction instrument, applying Ni-filter and $\text{Cu K}\alpha$ (50 kV \times 50 mA). The scanning rate and step of the half width value were $10^\circ/\text{min}$ and 0.02° , respectively. The particle size and distributions of the samples were determined using Malvern laser granulometer. The surface of the sample was coated with a layer of gold film using JFC-1100E type ion-sputtering device and the handled samples were

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observed by JSM-5800 type scanning electron microscope.

2.3 Electrochemical measurement

For electrochemical evaluation, the cathode was made in the way as follows: lithium manganese derivation was mixed with carbon black and polyvinylidene fluoride in the mass ratio of 85: 10: 5, then the mixture was coated onto a d 12 mm \times 0. 2 mm nickel mesh collection and toasted, finally pressed as a positive electrode. The cathode loading was about 0. 25 g/cm². A metal lithium sheet with size of d 12 mm \times 0. 4 mm was made as a negative electrode. The separator used was Celgard 2 300 microporous membrane type polypropylene film. The electrolyte was 1 mol/L LiPF₆ in ethylene carbonate: dimethyl carbonate (1: 1 in volume) solution. The charge-discharge characteristic of the material was evaluated by using the experimental type batteries assembled in a glove box full of argon atmosphere with comparative humidity of 2%. The electrochemical tests were performed with DC-5 type electrochemistry properties instrument. The charge-discharge experiments were carried out under voltage limits within 2. 4 ~ 5. 0 V at a constant current under 0. 1c or 0. 2c multiplying factor.

3 RESULTS AND DISCUSSION

3.1 Phase analysis

The X-ray diffraction patterns of LiMn₂O₄, LiMn_{1.5}Ti_{0.5}O₄, LiMn_{1.5}Fe_{0.5}O₄, LiMn_{1.5}Ni_{0.5}O₄ and LiMn_{1.5}Zn_{0.5}O₄ are shown in Fig. 1. For

LiMn_{1.5}Me_{0.5}O₄ spinel derivations, the addition of transition elements Ti, Fe or Ni can all increase the crystal face value (d) of (111), (311), (222), (400), (331), (511), (440) and (531). For LiMn_{1.5}Zn_{0.5}O₄, the crystal face value (d) of (111), (311), (511) and (440) are bigger than those of LiMn₂O₄, but the d value of (400) and (531) are smaller. For LiMn_{1.5}Me_{0.5}O₄, the relative strength of (222), (331), (511), (440) and (531) crystal face is weaken compared with those of LiMn₂O₄. If adding element Ti, the relative strength of (311) and (400) is weaker, while adding element Fe or Zn, that of (111) and (400) crystal face is stronger. To LiMn_{1.5}Ni_{0.5}O₄, the relative strength of crystal face (400) is stronger than that of LiMn₂O₄, while that of crystal face (311) is weaker. For these derivations, if adding transition element Ti or Ni, the strongest peak of the corresponding sample is as the same as that of LiMn₂O₄, which is the crystal face (111), however adding element Fe or Zn, the strongest peak is crystal face (311). The phase structure of lithium manganese derivations LiMn_{1.5}Me_{0.5}O₄ is spinel type.

3.2 Granularity analysis

The granularity analysis of lithium manganese oxide derivations is shown in Fig. 2. The average granularity of LiMn₂O₄ is 2. 68 μ m, if adding transition element Ti or Fe, the average granularity is 2. 47, 2. 20 μ m, respectively, smaller than that of LiMn₂O₄. Adding element Ni or Zn, the average granularity is 8. 34, 11. 71 μ m, respectively, larger

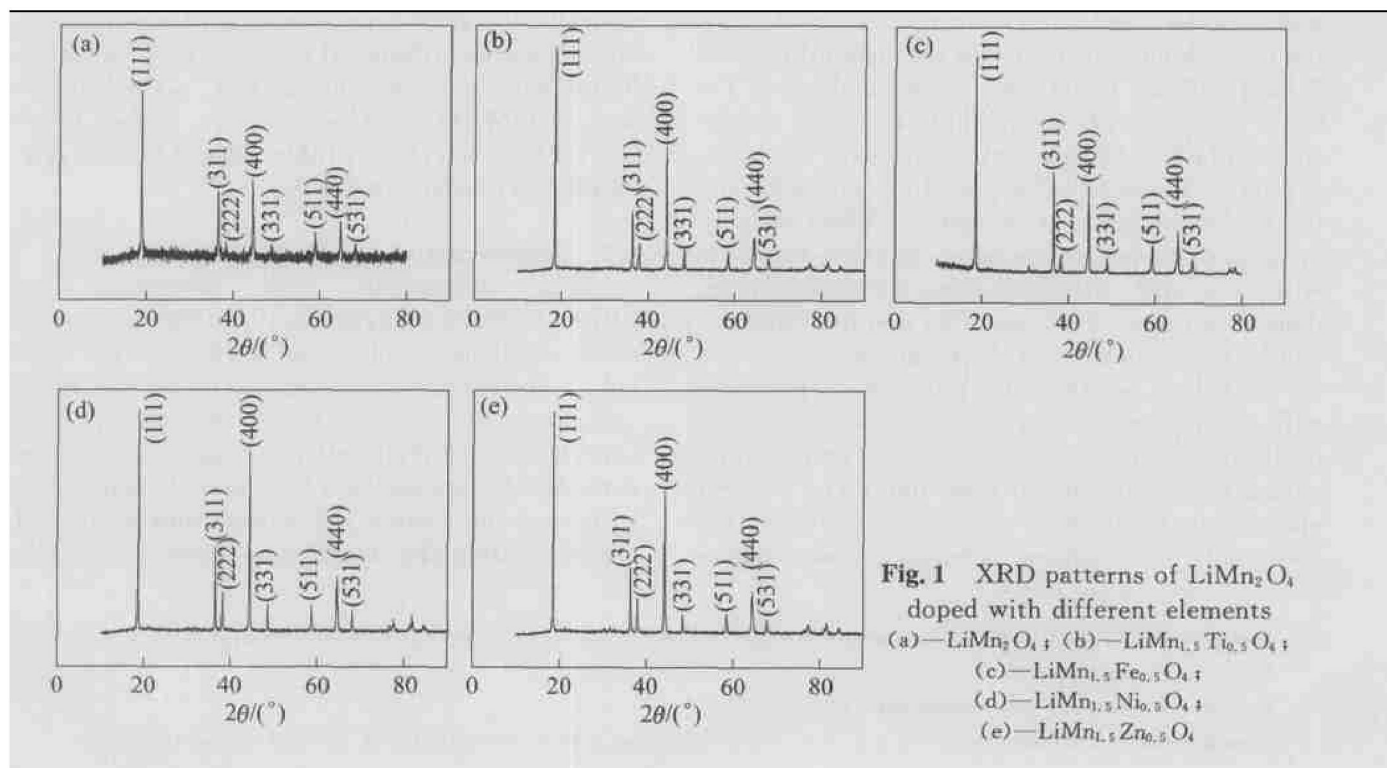


Fig. 1 XRD patterns of LiMn₂O₄ doped with different elements
(a)—LiMn₂O₄; (b)—LiMn_{1.5}Ti_{0.5}O₄;
(c)—LiMn_{1.5}Fe_{0.5}O₄;
(d)—LiMn_{1.5}Ni_{0.5}O₄;
(e)—LiMn_{1.5}Zn_{0.5}O₄

than that of LiMn_2O_4 .

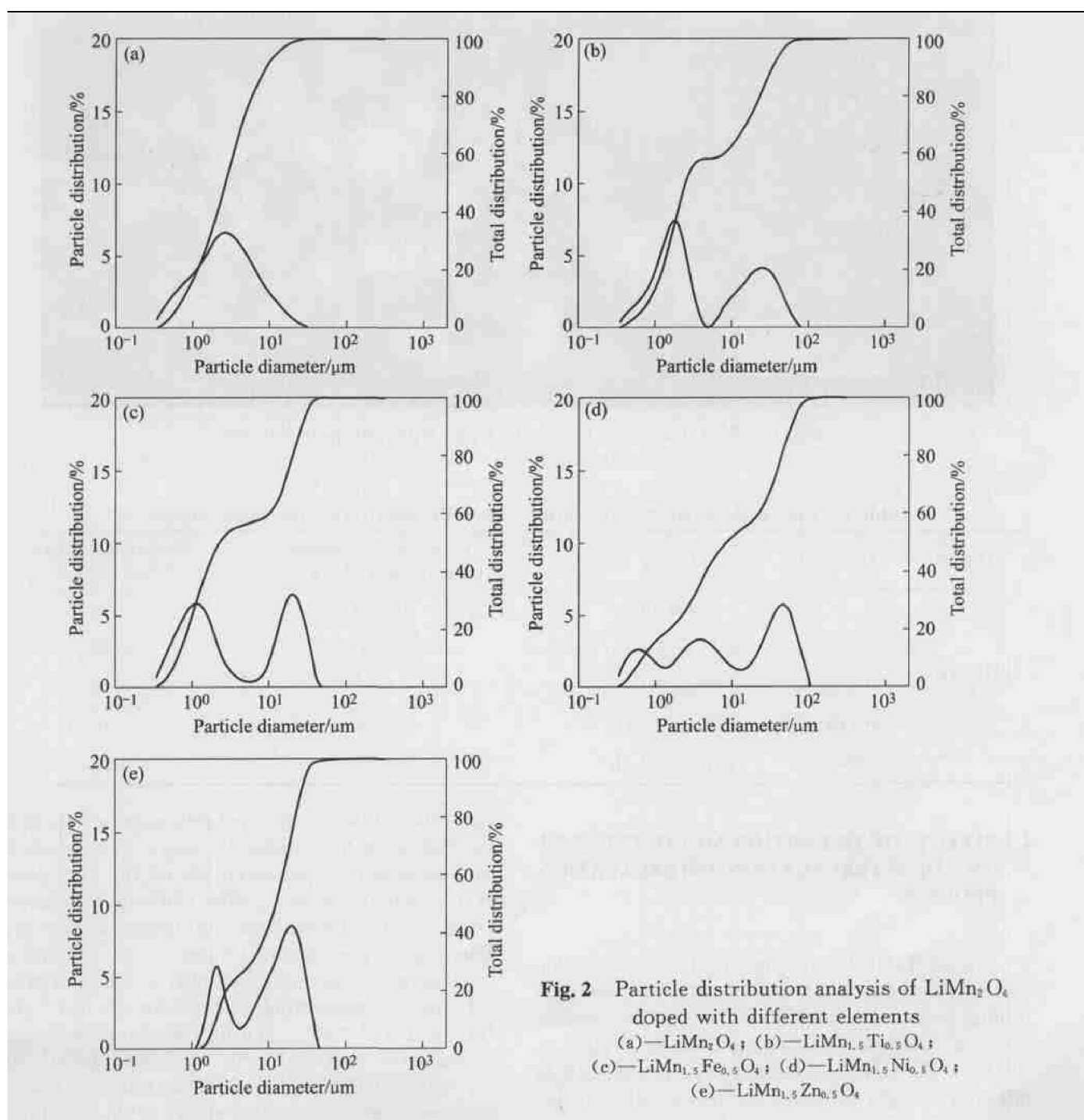
3.3 SEM analysis

The SEM images of the derivations are shown in Fig. 3. From Fig. 3, we can see that, for the derivations such as $\text{LiMn}_{1.5}\text{Fe}_{0.5}\text{O}_4$ or $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, their surface is regular, while for $\text{LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$ more grains are minute with few grains, especially for $\text{LiMn}_{1.5}\text{Zn}_{0.5}\text{O}_4$, the shape is complex with flake and club-shaped phase.

3.4 Electrochemistry measurements result

The experimental type batteries made with

positive material as LiMn_2O_4 , $\text{LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Fe}_{0.5}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Zn}_{0.5}\text{O}_4$ were tested respectively. The electrochemical measurements of $\text{LiMn}_{1.5}\text{Me}_{0.5}\text{O}_4$ derivations are shown in Table 1. Adding element Fe or Ni improves the beginning discharge capacity little, but higher discharge voltage plateau of LiMn_2O_4 , contributes to more effective rate of 3 V discharge plateau. The beginning discharge ratio capacity of $\text{LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$ is 96.37 mA·h/g, higher than that of $\text{LiMn}_{1.75}\text{Ti}_{0.25}\text{O}_4$ ^[7]. If adding element Zn, the electrochemical properties of LiMn_2O_4 is destroyed strongly.



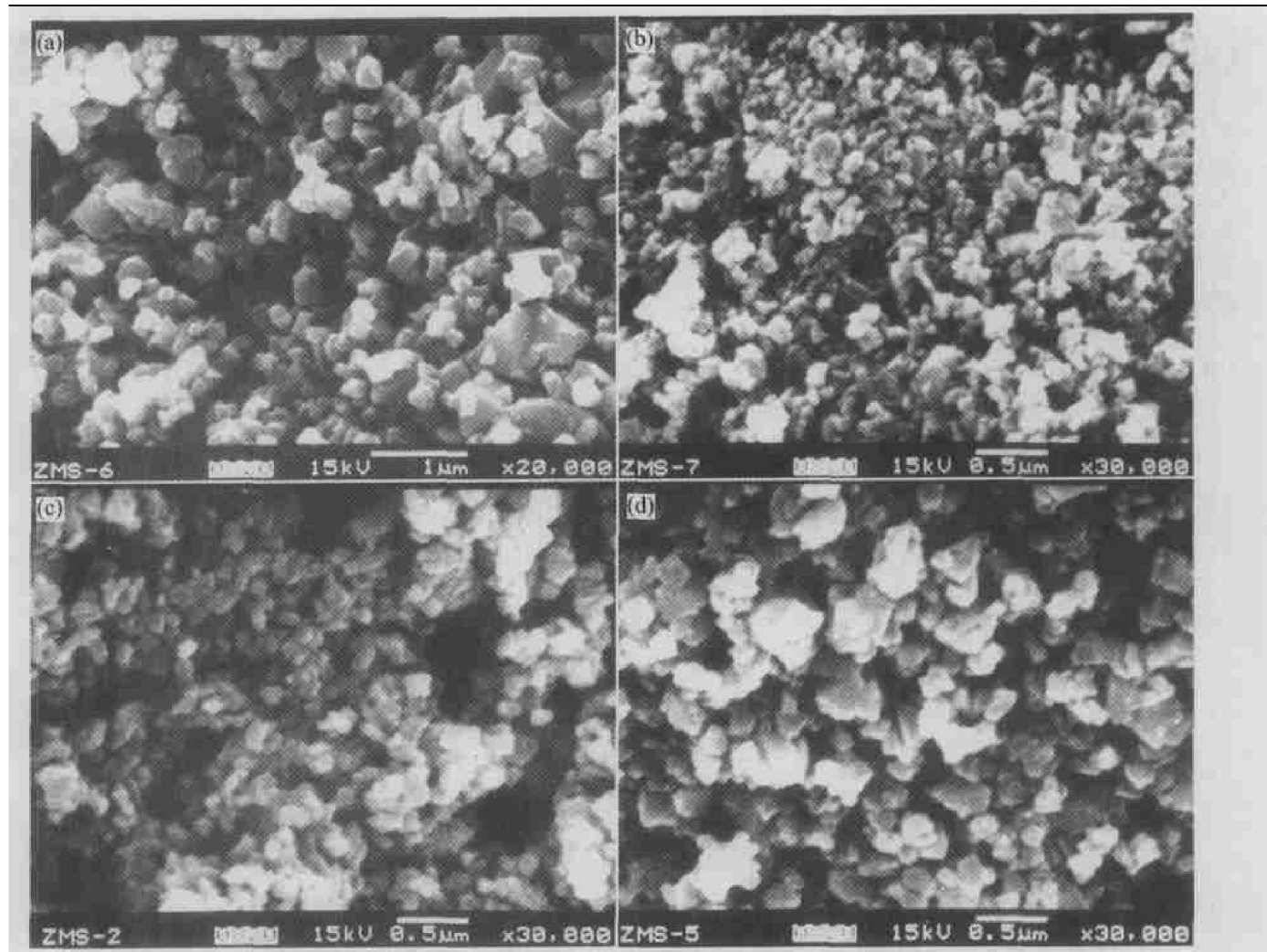


Fig. 3 SEM images of LiMn_2O_4 doped with different elements
(a) —Ti; (b) —Fe; (c) —Ni; (d) —Zn

Table 1 Electrochemistry of derivations with different transition metal elements

Material	Additive	Sample	Beginning discharging capacity/($\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$)	Discharging plateau voltage/V
$\text{LiOH} \cdot \text{H}_2\text{O} + \text{MnO}_2$		LiMn_2O_4	140.00	2.70
	TiO_2	$\text{LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$	96.37	2.62
	Fe_2O_3	$\text{LiMn}_{1.5}\text{Fe}_{0.5}\text{O}_4$	119.5	2.90
	$\text{Ni}(\text{OH})_2$	$\text{LiMn}_{1.75}\text{Ni}_{0.5}\text{O}_4$	95.42	2.76
	ZnO	$\text{LiMn}_{1.5}\text{Zn}_{0.5}\text{O}_4$	23.98	2.58

4 EFFECTS OF TRANSITION METAL ELEMENT ON DE-INTERCALATION/INTERCALATION PROCESS

Spinel LiMn_2O_4 belongs to face-center-cubic structure system. There are 56 atoms containing 8 lithium atoms, 16 manganese atoms and 32 oxygen atoms in a crystal cell whose Pearson symbol is

CF56^[8]. We can consider that one crystal cell is made up of eight second-cubic crystal cells, including four octahedron gaps and eight tetrahedron gaps where lithium atom possesses the tetrahedron gap and manganese atoms possesses the octahedron gap, moreover oxygen atom lies on the knot place of face-centered cubic^[9]. Spinel lithium-manganese oxide is three-dimensional lithium ion conductor. The original positions of lithium ion are located at tetrahedral interstice space which could be separated into two space groups

such as $4a(0, 0, 0)$ and $4c(1/4, 1/4, 1/4)^{[10]}$. During the charge-discharge process, the back and forth movement for lithium ion within half-tetrahedron slack could be divided into two steps as de-intercalation and intercalation. When charging, lithium ion was de-intercalating from $4c$ location, while discharging, due to increasing amount of Mn^{4+} positive ion, it could apply more energy which comes from strong exclusion force for lithium ion to intercalate into $4a$ gap. If adding some certain transition metal element into LiMn_2O_4 , it may strengthen its structure stability. Our experiment results show that Fe or Ni can improve discharge plateau voltage of LiMn_2O_4 , while Zn weakens the electrochemical properties of LiMn_2O_4 .

Table 2 Electron negativity, atom radius and arrange of some certain transition metal elements^[11-13]

Adding element	Electron negativity		Atom radius/ nm	Orbit electron arrange mode
	4s	3d		
Mn	0.54	2.87	0.127	$3d^5 4s^2$
Ti	0.46	1.22	1.470	$3d^2 4s^2$
Fe	0.57	3.80	1.260	$3d^6 4s^2$
Ni	0.65	5.22	1.246	$3d^8 4s^2$
Zn	0.69	—	1.332	$3d^{10} 4s^2$

Table 2, we know that electron negativity of 4s or 3d orbit electron for Fe or Ni is larger than that of Mn. For LiMn_2O_4 , if we replace some atoms of Mn with those of Fe or Ni, its attracting electrons ability is much bigger, which benefits lithium ions to de-intercalate or intercalate during the spinel structure, and improves the electrochemical characteristics of pure phase LiMn_2O_4 . This means that adding Fe or Ni could improve the discharge plateau voltage of LiMn_2O_4 . The atom radius of Fe or Ni is smaller than that of Mn, when displacing some atoms of Mn with those of Fe or Ni, correspondingly three dimensions tunnel space of LiMn_2O_4 can be increased. This is advantageous for lithium ion to intercalate and de-intercalate in the spinel structure, and favorable to electrochemical properties of LiMn_2O_4 . To element titanium, its atom radius is bigger than that of manganese atom, and its electron negativity of 4s or 3d orbit electron is smaller than that of Mn, thus the attracting atom capability is weakened, which is disadvantageous for lithium ion to de-intercalate or intercalate. After adding titanium element into LiMn_2O_4 , the discharge ratio capacity is reduced and discharge plateau voltage of LiMn_2O_4 is lowered. To element zinc, its atom radius is larger than that of manganese, and while displacing some atoms of Mn with Zn, the three dimensions tunnel space of LiMn_2O_4 is corre-

spondingly lowered. In addition, it is disadvantageous for lithium ion to intercalate and deintercalate in the spinel structure, which is not favorable to electrochemical properties of LiMn_2O_4 ^[14, 15].

For globular cation centered with six anions or dipole ions, ortho-octahedron is the most favorable arrangement. This situation is not suitable for ions not full of electrons on d layer orbit. Because this ion is not characteristic as globular symmetry, ortho-octahedron is no longer the most stable arrangement. In order to reduce the system energy, the structure must distort. This means static electricity deformation called Jahn-Teller dimio effect^[11].

For manganese atom, the energy level of d orbit splits for Mn^{3+} or Mn^{4+} . Whether Mn^{3+} ion was at any distortion situation, it would be steadier on that deformation than on the ortho-octahedral coordination location, since Mn^{3+} ion gets extra stabilizing energy from coordination location. In the spinel structure, the deformation of Mn coordination ion must influence Li tetrahedron shape, and make it change into irregular tetrahedron, which is not beneficial for lithium ion to intercalate or de-intercalate, finally lead to discharge capacity decline for LiMn_2O_4 cathode material. In an octahedral structure, the configuration of Fe^{3+} is $(d_{xy})^2(d_{xz})^2(d_{yz})^1$. In the viewpoint of heterogeneous force, the shielding at orbit d_{yz} is weaker than that at orbit d_{xy} or d_{xz} , so Fe^{3+} ion has stronger force field. It means that the attractive force for central ion to coordination ions at orbit d_{yz} is stronger than that at orbit d_{xy} or d_{xz} , and the central ion tightens four coordination ions distributing at xy or xz plane, then the situation is that four longer bonds appearing at plane xy or xz while two shorter bonds at axis y or z . The shorter bonds at yz plane lead to force field intensive. For this reason, it weakens Jahn-Teller dimio effect of Mn, and reduces irregular tetrahedral numbers due to Mn ion leading to Jahn-Teller dimio effect, more favorable lithium ion to de-intercalate or intercalate. As the same analysis, the configuration of Ni^{2+} ion is $(t_{2g})^6(e_g)^2$, that is $(d_{xy})^2(d_{yz})^2(d_{xz})^2(d_{x^2-y^2})^1(d_{z^2})^1$. Compared to Mn^{3+} and Mn^{4+} , it can also weaken Mn ion leading to Jahn-Teller dimio effect. The configuration of Zn^{2+} is $(d^{10})(t_{2g})^6(e_g)^4$. Comparing to Mn^{3+} and Mn^{4+} , it can strengthen Jahn-Teller dimio effect of Mn ion, which is disadvantageous to electrochemistry of LiMn_2O_4 . The electron configuration of Ti^{4+} ion is (d^0) , and the chosen location energy of entering an octahedral for Ti^{4+} ion is zero^[11]. So-called chosen location energy means that stability energy difference for a transition metal ion between octahedral and tetrahedral. Ti^{4+} ion can't change Jahn-Teller dimio effect of Mn ion.

5 CONCLUSIONS

1) Laser granulometer analysis shows that the average grain size of lithium manganese derivations adding TiO_2 or Fe_2O_3 is smaller than that of LiMn_2O_4 . If adding $\text{Ni}(\text{OH})_2$ or ZnO , the grain size is larger than that of LiMn_2O_4 .

2) The phase structure of $\text{LiMn}_{1.5}\text{Me}_{0.5}\text{O}_4$ ($\text{Me} = \text{Ti, Fe, Ni, Zn}$) is spinel AB_2O_4 type. Lithium manganese derivations of $\text{LiMn}_{1.5}\text{Fe}_{0.5}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ have regular appearance, and $\text{LiMn}_{1.5}\text{Ti}_{0.5}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Zn}_{0.5}\text{O}_4$ have complex appearance.

3) Adding Fe_2O_3 or $\text{Ni}(\text{OH})_2$ can improve discharge plateau voltage, adding TiO_2 reduces the discharge ratio capacity of lithium manganese oxides and discharge plateau voltage, while adding ZnO destroys the electrochemistry property of LiMn_2O_4 .

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