

Structure and electrochemical properties of LiMn_2O_4

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Abstract: LiMn_2O_4 , a cathode material of lithium ion battery, was prepared by the citric acid complexing method using lithium acetate and manganese acetate as raw materials. The type of atom location confused degree, the confused degree and judgement method in LiMn_2O_4 were analyzed. The effect of sintering temperature on structure and electrochemical properties of LiMn_2O_4 was also investigated. The results show that the atom location confused degree increases with the decrease of the X-ray diffraction peak intensity ratio of LiMn_2O_4 , I_{111}/I_{311} . The type of atom location confused degree depends on the variation tendency of I_{111}/I_{311} and I_{311}/I_{400} value. If the variation tendency is the same, it belongs to the 16c type location confusion, however, if the variation tendency is contrary, it belongs to the anti-spinel type location confusion. When the sintering temperature is low, it is apt to produce the anti-spinel location confusion in LiMn_2O_4 . With the increase of sintering temperature, the confused degree with the anti-spinel type gradually reduces, however, the confused degree with 16c type increases to some extent. When the atom location confusion with the anti-spinel type appears in LiMn_2O_4 , both the initial discharging capacity and cycling properties of LiMn_2O_4 reduce. However, the atom location confusion with 16c type does not affect the charge and discharge properties of LiMn_2O_4 .

Key words: Li-ion battery; cathode; LiMn_2O_4 ; confused degree; electrochemical property

1 Introduction

Lithium ion batteries possess a series of advantages such as single high voltage, large specific capacity, long cycling life and no memory effect, which makes them have good application prospects in the fields of portable electric apparatus, electric tools and electric automobiles. The properties of cathode material determine the comprehensive properties of the lithium ion battery to a great extent[1]. So, the researches and developments become hot topics and people pay more attention to them[2–4]. In the already commercialized cathode material at present, more than 90% is LiCoO_2 . Co resources are deficient and toxicant, which makes the lithium ion batteries have high cost and produces pollution to the environment, so people have kept looking for green cathode material with low costs and good properties since the lithium ion battery comes out[5–8]. LiMn_2O_4 with low cost, abundant resources and no environmental pollution, will be considered as the ideal cathode material. However, LiMn_2O_4 with spinel structure has Jahn-Teller effect, which can cause the

capacity to decay very fast during charge and discharge [9], and the dissolution of Mn can cause further deterioration of cycling properties at high temperature ($\geq 55^\circ\text{C}$)[10–11]. For this reason, many methods, such as doping and surface coating method, have been adopted to improve the cycling properties of LiMn_2O_4 [12–13]. In the present study, the type of atom location confused degree, the confused degree and judgement method in LiMn_2O_4 were analyzed. The effect of preparation process on structure and electrochemical properties of LiMn_2O_4 was also investigated.

2 Experimental

The xerogel precursor was prepared by citric acid complexing method using lithium acetate and manganese acetate as raw materials. Then, the obtained xerogel precursor was sintered at 300°C for 6 h. After that, it was sintered at various temperatures for 6 h.

The structure of the LiMn_2O_4 was analyzed by D/max-rB X-ray diffractometer with the radiation of CuK_α , the tube voltage of 50 kV, the tube current of 50 mA and the scanning ratio of $5^\circ/\text{min}$.

LiMn₂O₄, conductive carbon black, plasticizer DBP and polymer according to mass ratio of 78:4:10.2:7.8 and dispersant acetone were mixed to prepare cathode film with a thickness of 0.2 mm on a TB-160-ZE type instrument. Cathode film, polypropylene film, graphite anode film were assembled into a battery in a vacuum glove box and electrolytic liquid was EC+DMC+1 mol/L LiPF₆.

The charge and discharge experiment was carried out on a BFGS-9256 type instrument. The charge and discharge rate was 0.3C and voltage range was from 3.0 to 4.3 V.

3 Results and discussion

3.1 Effect of sintering temperature on atom location in LiMn₂O₄

Fig.1 shows XRD patterns of LiMn₂O₄ prepared at various temperatures. It can be seen that the prepared products are mainly composed of LiMn₂O₄ with spinel structure sintered at various temperatures and a small amount of manganese oxides can be found after being sintered at 450–650 °C. When the sintering temperature changes, peak intensity ratio of LiMn₂O₄ (I_{111}/I_{311} , I_{311}/I_{400}) is different to some extent. Impurities and their contents in LiMn₂O₄ are listed in Table 1. It can be found that more Mn²⁺ exist in LiMn₂O₄ when the xerogel precursor is sintered at low temperature.

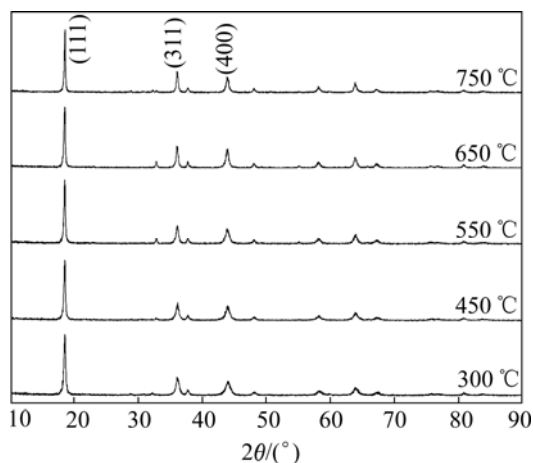


Fig.1 XRD patterns of LiMn₂O₄ sintered at various temperatures

According to the crystal X-ray diffraction principle, for powder samples, the relative intensity of crystal face (HKL), I_{HKL} , can be expressed as

$$I_{HKL} = P_{HKL} \cdot |F_{HKL}|^2 \cdot \varphi(\theta) \cdot A(\theta) \cdot \exp(-2M) \quad (1)$$

where P_{HKL} is the multiplicity factor, $|F_{HKL}|^2$ is the structure factor, $\varphi(\theta)$ is the angle factor, $A(\theta)$ is the absorbing factor and $\exp(-2M)$ is the temperature factor.

Table 1 Impurities and their contents in LiMn₂O₄ sintered at various temperatures

Temperature/°C	Impurity	Impurity content/%
300	Mn ₃ O ₄	2
450	Mn ₂ O ₃	2
550	Mn ₂ O ₃	8
650	Mn ₂ O ₃	9
750	Mn ₂ O ₃	10
300+750	Mn ₂ O ₃ + Mn ₃ O ₄	3

If the influence of the absorbing factor and temperature factor is neglected, the following formula can be obtained:

$$\frac{I_1}{I_2} = \frac{P_1 \cdot \varphi(\theta_1)}{P_2 \cdot \varphi(\theta_2)} \cdot \frac{|F_1|^2}{|F_2|^2} = C \cdot \frac{|F_1|^2}{|F_2|^2} \quad (2)$$

where C is a constant.

It is obvious that the change of peak intensity ratio is caused by the change of the structure factor. The value of structure factor $|F_{HKL}|^2$ depends on the atom kind, quantity and position in the cell. $|F_{HKL}|^2$ can be written as

$$|F_{HKL}|^2 = F_{HKL} \cdot F_{HKL}^* \quad (3)$$

where F_{HKL} is the structure amplitude.

The expression formula of F_{HKL} is

$$F_{HKL} = \sum_{j=1}^n f_j \exp[2\pi i(HX_j + KY_j + LZ_j)] \quad (4)$$

where f_j is the atom scattering factor of j atom in cell, X_j , Y_j and Z_j are the coordinate of j atom in cell.

There are 4 lattice points in the cell of face center cubic lattice and their coordinates are as follows:

$$(0,0,0), \left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \left(0, \frac{1}{2}, \frac{1}{2}\right)$$

According to Eqn.(3), $|F_{111}|^2$, $|F_{311}|^2$ and $|F_{400}|^2$ can be respectively calculated as follows:

$$\begin{aligned} |F_{111}|^2 &= 16f_{111}'^2 \\ |F_{311}|^2 &= 16f_{311}'^2 \\ |F_{400}|^2 &= 16f_{400}'^2 \end{aligned} \quad (5)$$

where f_{HKL}' is the scattering factor of face center cubic lattice.

Fig.2 shows the schematic diagram of lattice atom group of LiMn₂O₄. The structure of LiMn₂O₄ belongs to the face center cubic lattice and each lattice is made up of 2 lithium atoms, 4 manganese atoms and 8 oxygen atoms.

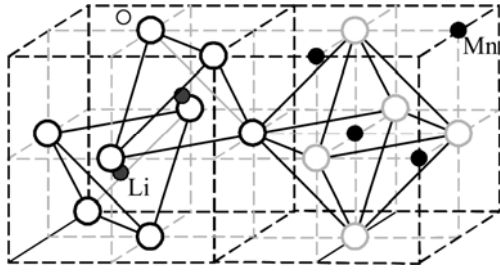


Fig.2 Schematic diagram of lattice atom group

If the coordinate origin is at the line centre of two lithium atoms, the coordinates of 8 oxygen atoms are respectively:

$$\left(-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}\right), \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right), \left(-\frac{1}{4}, 0, 0\right), \left(0, -\frac{1}{4}, 0\right), \\ \left(0, 0, -\frac{1}{4}\right), \left(\frac{1}{4}, 0, 0\right), \left(0, \frac{1}{4}, 0\right), \left(0, 0, \frac{1}{4}\right)$$

The coordinates of 4 manganese atoms are

$$\left(0, \frac{1}{2}, 0\right), \left(\frac{1}{4}, \frac{1}{2}, \frac{1}{4}\right), \left(\frac{1}{4}, \frac{3}{4}, 0\right), \left(0, \frac{3}{4}, \frac{1}{4}\right)$$

The coordinates of 2 lithium atoms are

$$\left(-\frac{1}{8}, -\frac{1}{8}, -\frac{1}{8}\right), \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right)$$

According to Eqn.(4), the following formulae can be obtained:

$$\begin{aligned} f'_{111} &= 2f_{111}(\text{Mn}) - \sqrt{2}f_{111}(\text{Li}) \\ f'_{311} &= -2f_{311}(\text{Mn}) - \sqrt{2}f_{311}(\text{Li}) \\ f'_{400} &= 8f_{400}(\text{O}) + 4f_{400}(\text{Mn}) - 2f_{400}(\text{Li}) \end{aligned} \quad (6)$$

The corresponding atom scattering factors of (111) diffraction peak of Mn and Li ($2\theta=18.6^\circ$, $\lambda=0.15406 \text{ nm}$, $\sin\theta/\lambda=1 \text{ nm}^{-1}$) is respectively

$$f_{111}(\text{Mn})=18.85, \quad f_{111}(\text{Li})=1.96$$

The corresponding atom scattering factors of (311) diffraction peak of Mn and Li ($2\theta=36^\circ$, $\lambda=0.15406 \text{ nm}$, $\sin\theta/\lambda=2 \text{ nm}^{-1}$) are respectively

$$f_{311}(\text{Mn})=15.3, \quad f_{311}(\text{Li})=1.8$$

The corresponding atom scattering factors of (400) diffraction peak of Mn and Li ($2\theta=44^\circ$, $\lambda=0.15406 \text{ nm}$, $\sin\theta/\lambda=2.4 \text{ nm}^{-1}$) are respectively

$$f_{400}(\text{O})=4.65, \quad f_{400}(\text{Mn})=13.88, \quad f_{400}(\text{Li})=1.65$$

Putting them into Eqn.(6), we can obtain:

$$f'_{111}=34.93, \quad f'_{311}=-33.15, \quad f'_{400}=89.42$$

According to Eqns.(2) and (5), the following equations can be obtained:

$$\frac{I_{111}}{I_{311}} = \frac{P_{111} \cdot \varphi(9.3^\circ)}{P_{311} \cdot \varphi(18^\circ)} \times \frac{|F_{111}|^2}{|F_{311}|^2} = 1.35 \times \frac{34.93^2}{33.15^2} = 1.50$$

$$\frac{I_{311}}{I_{400}} = \frac{P_{311} \cdot \varphi(18^\circ)}{P_{400} \cdot \varphi(22^\circ)} \times \frac{|F_{311}|^2}{|F_{400}|^2} = 6.25 \times \frac{33.15^2}{89.42^2} = 0.86$$

However, if the atom location confusion appears in LiMn_2O_4 , for example, some lithium atoms and manganese ions are exchanged to form anti-spinel structure, then the structural formula can be written as $[\text{Li}_{1-\gamma}\text{Mn}_\gamma]_{8a}[\text{Mn}_{2-\gamma}\text{Li}_\gamma]_{16d}\text{O}_4$, where γ can be regarded as the confused degree. Thus, the scattering factor of lattice f'_{HKL} in Eqn.(6) can be written as

$$\begin{aligned} f'_{111} &= 2\left[\left(1-\frac{\gamma}{2}\right)f_{111}(\text{Mn}) + \frac{\gamma}{2}f_{111}(\text{Li})\right] - \\ &\quad \sqrt{2}[(1-\gamma)f_{111}(\text{Li}) + \gamma f_{111}(\text{Mn})] = 34.93 - 40.77\gamma \\ f'_{311} &= -2\left[\left(1-\frac{\gamma}{2}\right)f_{311}(\text{Mn}) + \frac{\gamma}{2}f_{311}(\text{Li})\right] - \\ &\quad \sqrt{2}[(1-\gamma)f_{311}(\text{Li}) + \gamma f_{311}(\text{Mn})] = -(33.15 + 5.59\gamma) \\ f'_{400} &= 8f_{400}(\text{O}) + 4\left[\left(1-\frac{\gamma}{2}\right)f_{400}(\text{Mn}) + \frac{\gamma}{2}f_{400}(\text{Li})\right] - \\ &\quad 2[(1-\gamma)f_{400}(\text{Li}) + \gamma f_{400}(\text{Mn})] = 89.42 - 48.92\gamma \end{aligned} \quad (7)$$

Fig.3 shows the relationship of I_{111}/I_{311} , I_{311}/I_{400} and γ value obtained from Eqns.(2), (5) and (7). It can be found that I_{311}/I_{400} value increases, but I_{111}/I_{311} value reduces with the increase of γ value. Therefore, the characteristic of the curves is that I_{311}/I_{400} value increases, and I_{111}/I_{311} value reduces with increasing confused degree γ value when lithium ion and manganese ion exchange to form atom location confusion with the anti-spinel structure in LiMn_2O_4 .

If the exchange between lithium and manganese atoms does not appear in atom location confusion, the most possibility is that the lithium ion occupies idle 16c position because tetrahedron interval of 48f position is relatively less and the distance to high spin manganese ion is relatively short. At this moment, the coordinates of the lithium ion that occupies 16c position are

$$(0, 0, 0), \left(\frac{1}{4}, \frac{1}{4}, 0\right), \left(\frac{1}{4}, 0, \frac{1}{4}\right), \left(0, \frac{1}{4}, \frac{1}{4}\right)$$

Supposing the lithium ion amount occupying 16c position is γ ($0 < \gamma < 1$), the following equation can be obtained according to Eqn.(4):

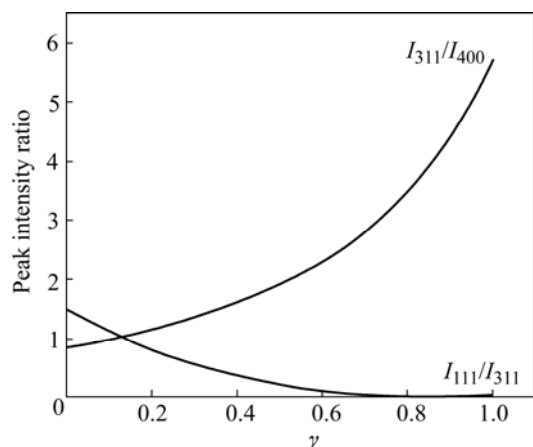


Fig.3 Relationship between peak intensity ratio and γ value with atom location confusion by anti-spinel type

$$\begin{aligned} f'_{111} &= 2f_{111}(\text{Mn}) - (\sqrt{2} + \gamma + \sqrt{2}\gamma)f_{111}(\text{Li}) \\ f'_{311} &= -2f_{311}(\text{Mn}) - (\sqrt{2} - \sqrt{2}\gamma - \gamma)f_{311}(\text{Li}) \\ f'_{400} &= 8f_{400}(\text{O}) + 4f_{400}(\text{Mn}) - (2 - 4\gamma)f_{400}(\text{Li}) \end{aligned} \quad (8)$$

Similarly, From Eqns.(2), (5) and (8) the relationship between I_{311}/I_{400} , I_{111}/I_{311} and γ value can be respectively obtained, as shown in Fig.4. It can be found that both I_{311}/I_{400} and I_{111}/I_{311} values reduce with the increase of γ value, however, the change trend is little. Therefore, the characteristic of the curves is that both I_{311}/I_{400} and I_{111}/I_{311} values reduce with increasing confused degree γ when 16c atom location confusion appears in LiMn_2O_4 .

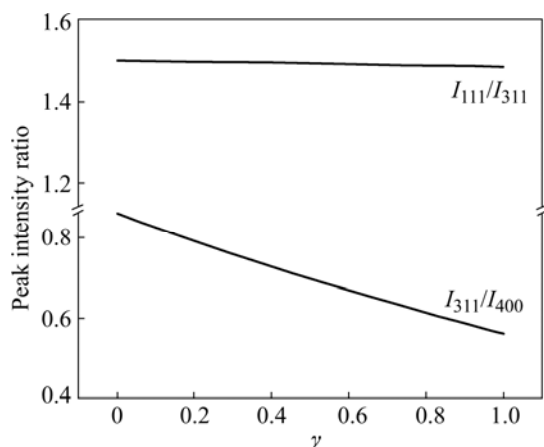


Fig.4 Relationship between peak intensity ratio and γ value with atom location confusion by 16c type

Table 2 lists the effect of sintering temperatures on peak intensity ratios I_{111}/I_{311} and I_{311}/I_{400} according to the experimental result in Fig.1. It can be found that the confused degree with anti-spinel type decreases, but that with 16c type increases with the increase of sintering temperatures.

Table 2 Effect of sintering temperature on peak intensity ratio

Sintering temperature/°C	I_{311}/I_{400}	I_{111}/I_{311}
300	1.20	2.61
450	1.19	2.59
550	1.18	2.67
650	1.14	2.66
750	1.09	2.60

Local structure of LiMn_2O_4 was studied by YAN et al[14] by adopting synchronous radiation XAFS. The results indicate that the coordinate number of the second-story of Mn—Mn is smaller than 6 in LiMn_2O_4 when the sintering temperature is low (400 °C), while the coordinate number of the second-story of Mn—Mn equals 6 in LiMn_2O_4 when the sintering temperature is high (700 °C). This conclusion is identical with our above- mentioned results. When the atom location confusion with anti-spinel type appears in LiMn_2O_4 , some manganese ions occupy the 8a location far away from the 16d location. At this time, the coordinate number of the second-story of Mn—Mn will decline.

It can be found from Tables 1 and 2, Mn^{2+} exists in LiMn_2O_4 and it is apt to produce atom location confusion with anti-spinel type when LiMn_2O_4 is sintered at the low temperature. According to the crystal field theory, manganese ion and oxygen ion whether to form coordinate tetrahedron or coordinate octahedra depends on the crystal field steady energy(CFSE) of manganese ion in these two coordinate polyhedrons. For Mn^{3+} ion, its CFSE is 136.08 J/mol[15] and 40.32 J/mol when it forms coordinate octahedra and tetrahedron with oxygen, respectively. Namely, the selection location energy of Mn^{3+} to form octahedra is 95.76 J/mol. So Mn^{3+} is easy to form coordinate octahedra with oxygen. For Mn^{2+} , its CFSE equals zero when it forms the coordinate tetrahedron or octahedra with oxygen, so Mn^{2+} can enter either octahedra or tetrahedron interval. When LiMn_2O_4 is prepared at the low temperature, Mn^{2+} resolved out from the precursor may enter the tetrahedron interval position in LiMn_2O_4 , meanwhile, Li^+ is forced to enter other positions, which produces atom location confusion with anti-spinel type. The result of TREUIL et al[16] indicates that it helps to produce Mn^{3+} with high content when sintering Li-Mn-O compound at the high temperature, which supports the above-mentioned viewpoint.

3.2 Effect of atom location on electrochemical properties of LiMn_2O_4

It can be found from Table 2 that the value of

I_{311}/I_{400} prepared at 450 °C is relatively large but the value of I_{111}/I_{311} is relatively small in LiMn_2O_4 compared with those of LiMn_2O_4 prepared at 750 °C, which indicates that LiMn_2O_4 prepared at 450 °C has bigger atom location confusion with anti-spinel type. Two kinds of samples are prepared into the test battery to carry out the charge and discharge test and the test results are shown in Fig.5. It can be seen that the initial discharge capacity of LiMn_2O_4 prepared at 450 °C is relatively lower and the capacity fading is faster during discharge.

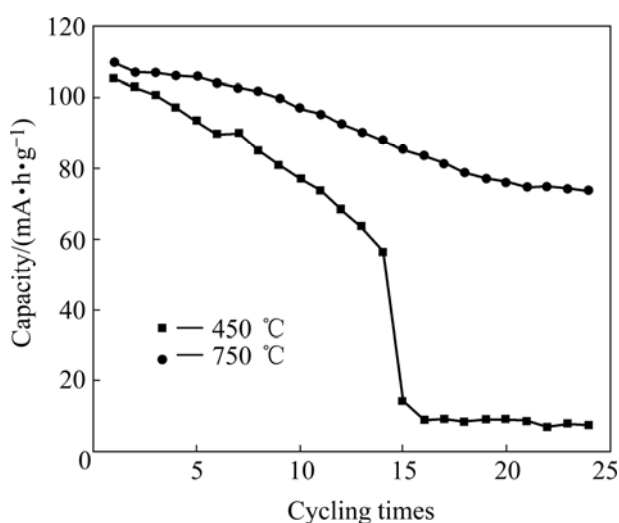


Fig.5 Curves of capacity vs cycling times of LiMn_2O_4 sintered at different temperatures

In LiMn_2O_4 with spinel structure, the oxygen ion occupies the 32e location of face centre cubic, the lithium ion lies in the 8a location of its tetrahedron interval and the manganese ion lies in the 16d location of its octahedra interval. In addition, there are idle tetrahedron interval 48f location and octahedra interval 16c location. Octahedra in 16c location and tetrahedron in 8a location are on the same face to form the three-dimensional path of the lithium ion, that is, 8a-16c-8a, as shown in Fig.6[17].

When the atom location confusion appears in LiMn_2O_4 , the manganese ion occupies 8a position and the lithium ion enters 16d position. It locally forms the anti-spinel structure. Then, the lithium in 16d position can not be moved without the diffusion path, so the capacity reduces. Meanwhile, the diffusion path of the manganese ion occupying 8a position will stop the diffusion of the lithium ion and reduce diffusion rate of the lithium ion, which increases the density of the lithium ion on the particle surface of LiMn_2O_4 , aggravates Jahn-Teller effect and accelerates capacity fading. So, LiMn_2O_4 prepared at 750 °C has relatively high initial capacity and cycling properties.

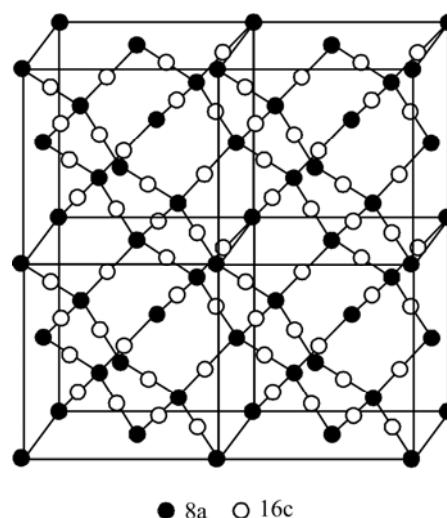


Fig.6 Diffusion pathway of lithium ion in spinel structure

4 Conclusions

1) The atom location confused degree increases with the decrease of the X-ray diffraction peak intensity ratio of I_{111}/I_{311} in LiMn_2O_4 . The type of confused degree depends on the variation tendencies of I_{311}/I_{400} and I_{111}/I_{311} . If their variation tendency is the same, it belongs to the 16c type and if the variation tendency is contrary, it belongs to the anti-spinel type.

2) When sintering temperature is low, it is apt to produce the atom location confusion with anti-spinel type in LiMn_2O_4 . With the increase of sintering temperature, the atom location confused degree with anti-spinel type gradually reduces, however, the atom location confused degree with 16c type increases to some extent.

3) Initial discharge capacity reduces and cycling properties drop when there occurs atom location confusion with anti-spinel type in LiMn_2O_4 . However, the atom location confusion with 16c type does not affect the charge and discharge properties of LiMn_2O_4 .

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