

Review

Preparation and Doping Mode of Doped LiMn_2O_4 for Li-Ion Batteries

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Abstract: Spinel LiMn_2O_4 is an appealing candidate cathode material for Li-ion rechargeable batteries, but it suffers from severe capacity fading, especially at higher temperature (55 °C) during discharging/charging. In recent years, many attempts have been made to synthesize modified LiMn_2O_4 . This paper reviews the recent research on the preparation and doping modes of doped LiMn_2O_4 for modifying the LiMn_2O_4 . We firstly compared preparation methods for doped spinel LiMn_2O_4 , such as solid state reactions and solution synthetic methods. Then we mainly discuss doping modes reported in recent years, such as bulk doping, surface doping and combined doping. A comparison of different doping modes is also provided. The research shows that the multiple-ion doping and combined doping modes of LiMn_2O_4 used in Li-ion battery are excellent for improving different aspects of the electrochemical performance which holds great promise in the future. From this paper, we also can see that spinel LiMn_2O_4 as an attractive candidate cathode material for Li-ion batteries.

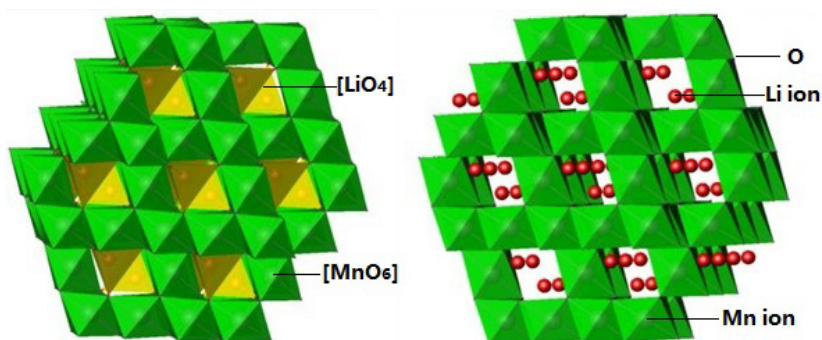
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1. Introduction

Li-ion batteries are the most suitable power supplies for many portable electronic devices, such as cellular phones, digital cameras and notebooks, because of their high energy and power density [1,2].

LiMn_2O_4 spinel is an attractive candidate cathode material for Li-ion rechargeable batteries with a three-dimensional framework because it has many advantages, such as low toxicity, cost efficiency, environmental friendliness compared to other lithiated transition metal oxides, such as lithium cobalt oxide or lithium nickel oxide [3–5]. The structure of spinel LiMn_2O_4 (space group $\text{Fd}\bar{3}\text{m}$) is shown in Figure 1. It consists of a cubic close-packing arrangement of oxygen ions at the 32e sites, the Li ions at the tetrahedral 8a sites, and the Mn^{3+} and Mn^{4+} ions at the octahedral 16d sites. This shows a cubic spinel-type structure [6].

Figure 1. The structure of spinel LiMn_2O_4 .



However, the disadvantage is that spinel LiMn_2O_4 suffers from severe capacity fading, especially at higher temperature ($55\text{ }^\circ\text{C}$) during discharging/charging. This limits its cycle ability and does not allow its commercialization [7]. The capacity fading is mainly due to four reasons [8,9]: (i) phase transition from cubic to tetragonal phase upon 3 V cycling, (ii) micro-crack formation on the surface of the cathode material after electrochemical cycling, (iii) formation of a surface dead layer (SEI layer) on the surface of the electrodes after electrochemical cycling and (iv) formation of oxygen vacancies due to the dissolution of manganese in the electrolyte.

In recent years, several attempts have been made for synthesizing modified LiMn_2O_4 doped with various elements to inhibit capacity fading and improve the electrochemical performance. For instance, the nonmetals B [10–12], F [13–15], S [16], Br [17], the general metals Mg [18], Al [19], Ti [20,21], Cr [22,23], Fe [24], Co [19,25–27], Ni [28], Cu [29], Zn [30–32], Ga [33], Zr [34], Ru [35], Ag [36,37], Sn [38], Au [39], the rare-earth metals La [40], Ce [41], Pr [42], Nd [43], Sm [44], Gd [45], and the actinide dopants Th [46], U [47]. Some researchers have also modified LiMn_2O_4 with surface coating [48–52] electrolyte modification [53], laser annealing [54], pulsed laser deposition [55], process optimization [56] or battery technology [57,58]. Among these, the doping method shows better electrochemical performance for it can weaken the Jahn-Teller effect and improve the stability of the structure. The increased stability of the structure and the weakened Jahn-Teller effect can further improve the cycle performance. The coating method can decrease the dissolution of the active material and minimize surface overpotential [59].

In this paper, we summarize and analyze the preparation of doped LiMn_2O_4 , and compare doped LiMn_2O_4 preparation methods. Then we discuss bulk doping, surface doping and combined doping, and also provide comparisons of the different doping modes.

2. Preparation

The quality of LiMn_2O_4 powder used for lithium-ion batteries depends strongly on the synthetic method used. Doped LiMn_2O_4 is generally synthesized by solid state reaction and solution synthetic method.

2.1. Solid State Reaction

Solid state reactions [60–63] dope the atom in the lattice of the main structure, but all the products remain in the standard spinel structure. The products, for example, the reported $\text{Li}(\text{Mn}_{2-x}\text{Co}_x)\text{O}_4$ ($0 \leq x \leq 0.5$) [64], $\text{Li}_{1.02}\text{Ga}_x\text{Mn}_{1.98-x}\text{O}_4$ [65] and $\text{Li}_{1.2}\text{Mn}_{1.6}\text{Fe}_{0.4}\text{O}_4$ [66] just had small cell parameter changes in the lattice, and these were good for the stability of the structure and the improvement of the cycle life. Solid state reactions can be classified as dry-solid state reactions and wet-milling methods according to the differences of the pretreatment. The main difference between the dry process method and wet-milling method is whether an auxiliary liquid agent is added to the mixture before mixing. The auxiliary liquid agent is good to ensure uniform mixing. Kakuda *et al.* [59] obtained $\text{Li}_{1.10}\text{Mn}_{1.90}\text{Al}_{0.10}\text{O}_4$, using both a dry-solid state reaction and a wet-milling method. The results showed that the precursor obtained by the wet-milling method had better electrochemical performance, for the reasons that the particle was finely ground, relatively homogeneous and had good crystallinity.

The solid state reaction synthetic process is quite simple and the product obtained may meet the requirements to some extent. However, in general, solid state reactions have several disadvantages compared to the solution synthetic methods, such as the fact the product obtained is non-uniform and has irregular morphology, large particle size and a broad particle size distribution. Moreover, this method needs long heating times followed by several grinding and annealing processes. Another problem is that solid-state reactions need an extended grinding or extensive mechanical mixing. This is detrimental to the quality of the final product due to possible contamination with impurities. Solution synthetic methods are another kind of widely used method that can overcome the disadvantages of solid state reactions.

2.2. Solution Synthetic Method

The usually used solution synthetic methods are the sol-gel method, precipitation method and hydrothermal method. Compared with the conventional solid-state reactions, the sol-gel method is believed to offer many advantages such as lower temperature processing, better control of material morphology [67,68], smaller and more uniform particles. The sol-gel method is also one of the most cost-saving and time-effective ways to produce doped metal oxides in large quantities [69]. The precipitation method can make the product smaller in size, and thus higher in specific surface, but unstable in electrochemical performance. Compared with the solid-state method, the stoichiometry of lithium manganese oxide can be controlled more exactly by the co-precipitation method [70]. The hydrothermal method [8] needs high temperature and high pressure. Through this method, the particles obtained are superfine powders, and this method can produce a lot of nano-scaled metal oxides and metal composite oxide ceramic powders. The particle sizes obtained vary from several nanometers to hundreds of nanometers, which are not easy to achieve normally. Therefore, we can get more ideal products by solution synthetic methods. The sol-gel method is cost-saving and time-effective and the product shows

better control of morphology and size. The precipitation method can make the product higher in specific surface, and finally, the nano-scaled material is more easily prepared by hydrothermal methods.

2.3. Other Methods

Other methods, such as the freeze-drying method [4], polyaspartic-acid-pyrolysis method [71], melt-impregnation method [72,73], Pechini method [74,75], liquid source misted chemical deposition (LSMCD) [76], spray-drying method [28], rheological phase reaction [77] are also used to prepare doped LiMn_2O_4 .

The preparation methods discussed above showed that to improve the cycle performance and decrease capacity fading, a better target product which is uniform, appropriate in size, stable and pure in spinel structure is needed, so we should choose the appropriate method according to the demands. Sometimes, the method is not used alone, but rather more than one method [44] is used in a preparation.

The common raw materials used are carbonates [22,78], acetates [79], nitrates [44,71], sulfates [80], hydroxides [73], oxides [81] of Li, Mn and the doped-ion. The preparation processes are various. Some [78–80] first synthesized a precursor, then reacted it with other raw materials to obtain the target product. Some [62,81] mixed all the raw materials at once and then reacted them together. The differences of the process may influence the morphology, particle size, and therefore the electrochemical performance to a great extent [80].

3. Doping Mode

Doping, based on the modification in the bulk or on the surface, can be classified as bulk doping or surface doping.

3.1. Bulk Doping

Bulk doping can change the crystal lattice parameters. This may lead to volume shrinkage which is beneficial for stabilizing the main structure and improving the cycling performance. Bulk doping can be classified as single-ion doping and multiple-ion doping depending on whether one or more ions are doped.

3.1.1. Single-Ion Doping

Single-ion doping may have single effects on the electrochemical performance and the structure, and sometimes may have no influence on the electrochemical performance. Some examples of single-ion doping increased cycle performance, but reduced the first discharge capacity. Some single-ion doping examples gave higher capacity, but not so good cycle performance. Others obtained no high capacity and no perfect cycle performance. The following examples of single-ion doping obtained good cycle performance, but low discharge capacity.

Cathode films of Al-doped LiMn_2O_4 ($\text{LiMn}_{1.8}\text{Al}_{0.2}\text{O}_4$) were synthesized by a liquid source misted chemical deposition technique for a lithium micro-battery [76]. The $\text{LiMn}_{1.8}\text{Al}_{0.2}\text{O}_4$ exhibited more improved electrochemical recharge abilities than pure spinel LiMn_2O_4 film, because the substitution of

Al^{3+} for Mn^{3+} increased Mn-O bonding strength in the spinel framework and suppressed the two-phase behavior of the unsubstituted spinel during the intercalation/deintercalation. It had no capacity fading over 100 cycles and showed an initial discharge capacity of $52 \mu\text{Ah}/\text{cm}^2$. However, the $\text{LiMn}_{1.8}\text{Al}_{0.2}\text{O}_4$ suffered from large initial capacity losses.

Yang, *et al.* [82] synthesized Al-doped LiMn_2O_4 nanorods. The experiments showed that Al dopants reduced the dissolution of Mn^{3+} ions significantly. The $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ nanorods were much more stable than LiMn_2O_4 against electrolyte etching, and this was reflected by the magnification of both size shrinkage and a conductance decrease. $\text{LiAl}_{0.1}\text{Mn}_{1.9}\text{O}_4$ nanorods achieve 96% capacity retention after 100 cycles at 1 C rate at room temperature, and 80% at 60 °C, whereas LiMn_2O_4 showed worse retention of 91% at room temperature, and 69% at 60 °C. Moreover, Al-doped LiMn_2O_4 nanorods had good battery performance at low temperature, but the initial capacity at 1 C rate of the doped sample was around 100 mAh/g, or a bit lower compared to the nearly 120 mAh/g of the sample without doping.

Some researchers [83–88] showed that single-ion doping can improve the cycling stability of the spinel with reduced capacity because the dopants are not electrochemically active and do not contribute to the capacity, but this is inconsistent with the following example which gave higher capacity, but not so good cycle performance.

Singhal *et al.* [9] obtained powders of $\text{LiMn}_{1.99}\text{Nd}_{0.01}\text{O}_4$ spinel by a sol-gel method. Charge-discharge characteristics for $\text{LiMn}_{1.99}\text{Nd}_{0.01}\text{O}_4$ cathode materials in 3.4–4.3 V voltage range were obtained, and the initial discharge capacity of this material was found to be about 149 mAh/g. The results showed that by doping with small concentrations of rare-earth element Nd, the capacity fading was considerably reduced compared to the pure LiMn_2O_4 cathodes. The reduced capacity fading was suitable for Li-ion battery applications, but we can clearly see that the capacity retention was about 91% after 25 charge-discharge cycles, which was not as good as the Al-doped LiMn_2O_4 discussed above.

The following research obtained no high capacity, and not so good cycle performance: Malyovanyi *et al.* [66] obtained the over-stoichiometric spinel structure Fe-doped $\text{Li}_{1.2}\text{Mn}_{1.6}\text{Fe}_{0.4}\text{O}_4$. This oxide showed good reversibility in the first several cycles, and the capacity was near 105 mAh/g, but the capacity was not so high, and the cycle performance was not so good due to its low capacity retention rate.

B-doped LiMn_2O_4 , $\text{LiB}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.01, 0.02, 0.05, 0.10, 0.20$) [11] was homogeneous in size, had a high degree of crystallinity, and had better electrochemical performance. The results showed that the B^{3+} doped ($\text{LiB}_x\text{Mn}_{2-x}\text{O}_4$) spinel was an apt candidate with good electrochemical performance and use in lithium-ion batteries. $\text{LiB}_{0.01}\text{Mn}_{1.9}\text{O}_4$ had the best discharge capacity of 120 mAh/g for substituted LiMn_2O_4 . At the 30th cycle, the discharge capacity was found to be 90 mAh/g. The result is better than that of the Fe-doped LiMn_2O_4 above, but it is not satisfactory because of the fast capacity fading. Single-ion doping may have single effects on the electrochemical performance and the structure, and some may have no good outcome, but can be perfected by multiple-ion doping.

3.1.2. Multiple-Ion Doping

Multiple-ion doping can help the doped LiMn_2O_4 acquire strong comprehensive features of different elements. Xiao *et al.* [89] synthesized $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_{3.95}\text{F}_{0.05}$ ($M = \text{Al}, \text{Co}, \text{Cr}$ and Mg , separately). $\text{LiMn}_{1.95}\text{M}_{0.05}\text{O}_{3.95}\text{F}_{0.05}$ ($M = \text{Al}, \text{Mg}$) showed an integrated crystal structure and favorable

cycle performance at 800 °C. The initial discharge capacities of the $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_{3.95}\text{F}_{0.05}$ and $\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_{3.95}\text{F}_{0.05}$ were 118.07 mAh/g and 123.95 mAh/g respectively and the capacity was hardly faded. The efficiencies of the $\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_{3.95}\text{F}_{0.05}$ and $\text{LiMn}_{1.95}\text{Mg}_{0.05}\text{O}_{3.95}\text{F}_{0.05}$ during the 20th charge and discharge processes were 94.77% and 99.04%, respectively. These results are better than that of the single-ion doping.

Aiming at obtaining an improved charge/discharge cycling performance, doped and milled spinel $\text{Li}_{1.05}\text{M}_{0.02}\text{Mn}_{1.98}\text{O}_{3.98}\text{N}_{0.02}$ ($\text{M} = \text{Ga}^{3+}$, Al^{3+} or Co^{3+} , $\text{N} = \text{S}^{2-}$ or F^-) were synthesized by Eftekhari *et al.* [90]. The doped spinel presented higher initial specific discharge capacity (117–126 mAh/g) and had an excellent electrochemical performance. It also had a low capacity loss even after the 300th charge and discharge cycles (from 120 to 115 mAh/g or 4%). It is clear that the multiple-ion doped product had high initial specific discharge capacity and long cycle performance.

S-Y multiple-ion doped LiMn_2O_4 [91] also had a pure spinel structure and good electrochemical performance. The first discharge capacity of S-doped LiMn_2O_4 reached 196.1 mAh/g, but its capacity decreased more than half of the capacity after 20 cycles. The Y-doped LiMn_2O_4 , at the charge and discharge rate of 0.2 C, and cycled 26 times, had a capacity retention rate of 98.6%, but the first discharge capacity was low. The surprise was that the obtained S-Y multiple-ion doped LiMn_2O_4 had a better electrochemical performance than the single-ion doped LiMn_2O_4 . Cycled 26 times, the capacity remained at 142 mAh/g. No better evidence than this could prove that the multiple-ion doping can help the doped LiMn_2O_4 present comprehensive strong features of different elements. Multiple-ion doped products have high discharge capacity and long cycle performance, so multiple-ion doping is promising for using LiMn_2O_4 as the cathode material for Li-ion batteries.

3.2. Surface Doping or Coating

Surface doping and coating are not the same, but the similarity is that they both can modify the surface of the material. Surface doping and coating can save dopant by doping into or only coating the surface. This can decrease the manganese dissolution by reducing the apparent contact area with the electrolyte. Some researchers [25,34] decreased the initial discharge capacity or specific capacity, but some [68,92] did not.

A nano- Al_2O_3 [73] particle coating improved the capacity retention of spinel LiMn_2O_4 efficiently at both room temperature (25 °C) and 55 °C. The mechanism of improvement for surface modified LiMn_2O_4 can be attributed to the inhibition of a surface Jahn-Teller distortion, the decreasing of Mn^{3+} dissolution and good electric contact among particles. Compared with as-prepared LiMn_2O_4 , the specific capacity of $\text{LiMn}_2\text{O}_4/\text{Al}_2\text{O}_3$ was a little lower.

If Ag contents are too high, the coated layer may form a barrier for the movement of Li ions, which hinders lithium ion movement of the spinel and results in bad initial specific capacity [75]. Son *et al.* synthesized Ag nanoparticle coated LiMn_2O_4 . The coated LiMn_2O_4 showed excellent cycle ability at 2 C galvanostatic condition. In his work, 3.2 wt % Ag coated LiMn_2O_4 cathode did not show any lowering of initial capacity.

In the research of Guo *et al.* [93], surface Co-doped (2%, mole percent) spherical LiMn_2O_4 showed improved specific capacity and the electrochemical performance during cycling. Even at the temperature

of 55 °C, the Co-doped (2%, mole percent) spherical LiMn_2O_4 had a higher capacity of 119.1 mAh/g than the pure LiMn_2O_4 whose capacity was 112.6 mAh/g.

Modifying the surface of the material and blocking the manganese dissolution, can reduce the apparent contact area with the electrolyte and hinder the surface Jahn-Teller distortion. These are key points in the surface doping and coating methods that improve the cycle performance and reduce the capacity losses.

3.3. Combined Doping

Surface doping and coating can reduce the apparent contact area with the electrolyte, so they can decrease the manganese dissolution. This modifying can hinder the surface Jahn-Teller distortion. Some bulk doping methods can improve the cycling performance and enhance the activity of manganese in spinel LiMn_2O_4 . Combining the surface doping and bulk doping can achieve better results.

He *et al.* [94] combined cobalt doping on the surface and yttrium doping in the bulk to improve the cycle stability of spherical spinel LiMn_2O_4 at elevated temperature (55 °C). The cobalt surface doping was more effective than cobalt bulk doping at the same doping level, because the surface cobalt doping was more effective in preventing manganese from dissolving into the electrolyte. Doped yttrium enhanced the activity of manganese in spinel LiMn_2O_4 and increased the specific capacity, but the cycle ability was decreased, because the active manganese can be easily dissolved into the electrolyte during cycling. Manganese dissolution could be effectively inhibited by co-surface doping of 0.5% yttrium and 0.5% cobalt. The surface co-doped spherical spinel LiMn_2O_4 had excellent performance combining the advantages of the surface cobalt doping and bulk yttrium doping. Combined doping methods can integrate the advantages of different doping modes, so it is an attractive option for modifying the spinel LiMn_2O_4 . This combined doping mode is also promisingly used in other batteries and industries.

4. Conclusions and Prospects

The quality of LiMn_2O_4 powder used for lithium-ion battery strongly depends on the synthetic method used. The simplest method, the solid state reaction, obtains non-uniform, irregular and large particles with impurities. Solution synthetic methods are more complex but can make the product more uniform, small in size and have better electrochemical performance. The various doping modes influence different aspects of the electrochemical performance. Based on the recent research, we found that the multiple-ion doping can help the doped LiMn_2O_4 have comprehensive strong features of different elements. Some bulk doping methods can improve the cycling performance and enhance the activity of manganese in spinel LiMn_2O_4 . Surface doping and coating can decrease the manganese dissolution by reducing the apparent contact area with the electrolyte and inhibiting the surface Jahn-Teller distortion. We can draw two conclusions: one is that we can get relatively special required products from the solution synthetic methods, such as better control of morphology and nano-scaled materials. The other is that multiple-ion doping and combination doping modes are effective ways to achieve better results.

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