Research Status of Spinel LiMn$_2$O$_4$ Cathode Materials for Lithium Ion Batteries

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Abstract. As a new type of green power system, lithium ion battery has been widely developed in the field of new energy. Lithium manganese oxide has become a hot topic due to its low price, safety and pollution-free properties. In this paper, the research progress of positive electrode material LiMn$_2$O$_4$ for lithium ion batteries in recent years is reviewed, in addition, the structural properties, synthesis methods, existing problems and modification aspects of the material are described.

Keywords: Lithium-ion batteries; Cathode materials; Spinel LiMn$_2$O$_4$; Review.

1. Introduction

Due to the problems of global environmental pollution and the shortage of fossil energy, the new energy field has attracted more and more attention. Compared to traditional chemical power supply, lithium ion batteries have the advantages of green environmental protection, high energy density, long cycle life and memory-free effect$^{[1,2]}$. It have great potential in the field of portable electronic products and power automobile industry. At present, the more mature cathode materials are mainly layered LiCoO$_2$, olivine structure of LiFePO$_4$, LiNi$_{1-x-y}$Co$_x$M$_y$O$_2$(M=Mn, Al) of ternary layered structure and spinel LiMn$_2$O$_4$, etc$^{[3-6]}$. Due to the scarcity and toxicity of cobalt resources, the cathode materials containing cobalt have the problems of high production cost and pollution of the environment. By contrast, spinel LiMn$_2$O$_4$ has higher safety performance, lower cost and friendly environment, which has a good development prospect.

2. The Structure and Problems of LiMn$_2$O$_4$

The theoretical capacity of spinel LiMn$_2$O$_4$ is 148 mAh·g$^{-1}$ and the actual capacity is about 120 mAh·g$^{-1}$. Spinel LiMn$_2$O$_4$ belongs to the cubic crystal system, and its space group belongs to the Fd3m type. The lattice parameter is 0.8245 nm, and the schematic diagram of the crystal structure was shown in Figure 1. From the figure, the oxygen atoms form cubic dense stacking, and the corresponding oxygen octahedra are connected by common edges. Lithium ions and manganese ions occupy 8a of oxygen tetrahedron and 16d of oxygen octahedron, respectively$^{[8]}$, constitute [Mn$_2$O$_4$].
That forms a three-dimensional tunnels structure that allows lithium ions to diffuse more easily, making it more suitable for use in large power batteries\cite{9-11}.

Figure 1. Crystal structure of spinel LiMn$_2$O$_4$\cite{7}.

Spinel LiMn$_2$O$_4$ cathode material has many advantages, however, its cycle stability and high rate discharge performance are not ideal enough, especially at high temperature, the attenuation of discharge specific capacity is serious, which limits its large-scale application. These problems are due to: (1) the Jahn-Teller effect of manganese ions. The asymmetric occupation of electrons in degenerate orbit results in distortion of the geometric configuration of the molecule, which reduces the symmetry and degeneracy of the molecule and further reduces the energy of the system. This is called Jahn-Teller effect\cite{12}. The manganese ions in the crystal structure are composed of Mn$^{3+}$ and Mn$^{4+}$, in addition, Mn$^{3+}$ belongs to a proton type Jahn-Teller ion with high spin and high magnetic moment\cite{13,14}. In the discharge process, with the continuous embedding of lithium ions, the valence state of Mn decreases, and Mn$^{4+}$ will also be converted to Mn$^{3+}$, resulting in the transformation of crystal structure from cubic crystal system to tetragonal crystal system with low symmetry, which will hinder the diffusion of lithium ions and electron conduction. (2) the dissolution of Mn. In the discharge process, the amount of Mn$^{3+}$ will be more and more, and the material surface will appear disproportionation reaction. Mn$^{3+}$ will become Mn$^{4+}$ and Mn$^{2+}$. The generated Mn$^{2+}$ can be dissolved in the electrolyte, resulting in loss of Mn ions. And the reaction of lithium salt LiPF$_6$ in electrolyte and trace water produces HF and other acidic substances, the equation is as follows:

\[
\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{POF}_3 + 2\text{HF} + \text{LiF}; 4\text{H}^+ + 2\text{LiMn}_2\text{O}_4 \rightarrow 3\lambda\cdot \text{MnO}_2 + \text{Mn}^{2+} + 2\text{Li}^+ + 2\text{H}_2\text{O}
\]

which causes dissolution and erosion on the material surface\cite{15}, further accelerating the production of Mn$^{2+}$. The non-electrochemical active substances generated by the relevant chemical reactions also hinder the diffusion of Li$^+$, resulting in the significant attenuation of the discharge capacity of spinel LiMn$_2$O$_4$.

3. Preparation Method of Spinel LiMn$_2$O$_4$

There are many methods to synthesize spinel LiMn$_2$O$_4$, which can be divided into two main categories: one is solid phase reaction method, the other is liquid phase reaction method. Solid phase reaction method includes high temperature solid-state method, melt impregnation method, microwave synthesis method, etc. Liquid phase reaction method includes sol-gel method, hydrothermal method, etc.

3.1. High-temperature Solid-state Method

The high temperature solid phase method is a traditional method for the synthesis of spinel type lithium manganate, which is to mix and grind the lithium salt and manganese oxide in a certain proportion and calcination under high temperature for a certain time to get the final product. The synthesis process is simple and easy to operate. During the preparation by high temperature solid phase method, the calcination temperature, cooling rate and the properties of the reaction raw materials have great influence on the electrochemical properties of the final product.

3.2. Melt Impregnation Method

The melt impregnation method is similar to the high-temperature solid phase synthesis method, which is to heat the lithium salt (LiOH or LiF) with a low melting point to the melting point. The melted lithium salt is fully mixed with manganese oxide and infiltrated into the oxide pores, and then calcines...
at high temperature to obtain spinel LiMn$_2$O$_4$. This method increases the contact area between the precursors, improves the phase inhomogeneity, reduces the lithium diffusion time and thus accelerates the solid-state reaction. Zhao et al.\cite{16} used MnCO$_3$, Li$_2$CO$_3$, NaCl and KCl to prepare Spinel LiMn$_2$O$_4$ by melting impregnation method. The samples synthesized at 800°C had uniform particle size distribution and the best electrochemical properties. When the voltage range was 3.5-4.3V and the charge-discharge rate was 0.25 C, the discharge specific capacity of the material can reach 124 mAh·g$^{-1}$ and capacity retention rate up to 96% after 50 cycles. But this method is more complex and it is not easy to control the experimental parameters.

3.3. Microwave Synthesis

Microwave sintering uses the direct coupling between microwave and material to cause overall heating to reach the required temperature. This heating method has the characteristics of immediacy, fast heating rate and high energy efficiency. Liang et al.\cite{17} proposed the ultra-fast synthesis of spinel type LiMn$_2$O$_4$ by microwave induced solution flameless combustion method. The results showed that the microwave method was beneficial to the formation of polyhedral morphology of LiMn$_2$O$_4$, and the crystallization was very good, and the polyhedral crystals has grown together due to the rapid growth rate. However, this method is difficult to implement large-scale commercial production due to its high requirements for equipment material and temperature control device and the purity of raw materials.

3.4. Hydrothermal Method

Hydrothermal method usually mixes manganese oxide with lithium salt or lithium hydroxide solution, and then reacts under high temperature and high pressure to produce LiMn$_2$O$_4$. The synthesis temperature of spinel LiMn$_2$O$_4$ prepared by hydrothermal method is low, and the morphology is more controllable. The researchers synthesized spinel LiMn$_2$O$_4$ with various morphologies. Yang et al.\cite{18} obtained irregular blocks with particle size of 50~100 nm after water heating for 10 h at 200°C in accordance with the 1:2 molar ratio of α-MnO$_2$ and LiOH, and assembled them into a hybrid capacitor with a power density of 595 W·Kg and an energy density of 44.3 Wh·Kg, showing a large capacitance. LiMn$_2$O$_4$ synthesized by this method has better multiplier performance, smaller particle size and larger surface area, which is reported to be beneficial to the electrochemical performance of spinel lithium manganate, especially its cycling performance\cite{19,20}. However, the crystal shape of the synthesized product is poor, and the product is usually dried for heat treatment, and it is easy to be accompanied by Mn$_2$O$_3$ residue, which will affect the electrochemical properties of the material.

3.5. Sol-gel Method

Sol-gel method is the final product obtained by dissolving manganese salt and lithium salt by complexing agent, solidifying sol and gel, and calcination at a relatively low temperature. In this process, Mn ions and Li ions can be more uniformly dispersed in the solution, the reaction is more complete, the reaction time is shortened, and the particle size of LiMn$_2$O$_4$ obtained is smaller. H.Liu et al.\cite{21} took manganese acetate and lithium acetate as raw materials, citric acid and glucose as chelating agent to synthesize LiMn$_2$O$_4$, which had a high discharge specific capacity. At the rate of 0.1c, the first discharge specific capacity was 146.3mAh ·g$^{-1}$, which was higher than the discharge specific capacity of commercial LiMn$_2$O$_4$. However, a large number of organic solvents are used in the sol-gel process, which will cause certain pollution to the environment and is difficult to recycle, so it is difficult to make large-scale commercial production.

4. Modification of Spinel LiMn$_2$O$_4$

LiMn$_2$O$_4$ materials started to be commercialized very early. They are mostly used in small portable electronic devices and have a small market share, mainly due to poor cycling performance at high temperatures and severe capacity degradation. In order to obtain LiMn$_2$O$_4$ materials with better performance, researchers at home and abroad have done a lot of research.

4.1. Doping

The implementation of doping is to introduce a certain amount of other elements into the lattice of the
material in order to improve the electrochemical performance of the material. The doping modification of 
spinel LiMn$_2$O$_4$ can be roughly divided into metal element doping, non-metal element doping, rare 
earth element doping and composite ion doping.

The metal cation doping can improve the stability of spinel structure and the cycling performance of 
the material. Liu et al.\cite{22} prepared spinel LiMn$_2$O$_4$ doped with Co, Fe and Al by supercritical 
hydrothermal method respectively. Among them, the sample material doped with Co had better 
crystallinity, more stable structure and dispersed grains, while the sample doped with Fe and Al had 
smaller grains. The spinel structure after doping metal ions was more stable, which improved the 
cycling performance of the material to some extent. However, the doping ions replace the Mn$^{3+}$ 
involved in the Mn$^{3+}$ — Mn$^{4+}$ reaction. Increasing the doping amount would reduce the content of 
active Li, which would lead to a decrease in the first discharge capacity of the material.

Compared with cations, there are fewer types of non-metallic anion elements, and the most studied 
one s are F-, Cl$^-$ and S$^{2-}$. Doping anions can significantly increase the primary grain size of LiMn$_2$O$_4$ 
and reduce the specific surface area. However, anion doping can produce oxygen defects, so the 
modification effect of anion doping alone on the cycling performance is not very obvious.

The doping of rare earth elements can reduce the cell volume of the material to some extent, and the 
larger ion radius is conducive to the de-embedding of lithium ions in the spinel cubic structure. 
However, the relative molecular weight of rare earth elements is relatively high, and the introduction 
of excessive rare earth elements is not conducive to the electrochemical properties of lithium 
permanganate. S.Bhuvaneswar\cite{23} used the solid phase synthesis method to obtain LiSc$_{0.06}$Mn$_{1.94}$O$_4$, the 
initial discharge capacity of pure LiMn$_2$O$_4$ at 1 C was 117 mAh·g$^{-1}$ and the capacity still kept at a rate 
of 74% after 500 cycles. At the same conditions, the initial specific capacity of LiSc$_{0.06}$Mn$_{1.94}$O$_4$ was 
114 mAh·g$^{-1}$ and the capacity still kept at a rate of 90% after 500 cycles. The structure and 
morphology of the recycled materials remained intact without lithium-rich agglomeration. The results 
showed that the Sc doped lithium manganate had high diffusion coefficient, low charge transfer 
resistance and good rate performance.

4.2. Surface Modification

Surface modification is the physical or chemical means of wrapping a layer of other materials on the 
surface of the active material, which can effectively isolate the contact between the active material and 
the electrolyte and reduce the interaction between them. Researchers explored a variety of coated 
materials, such as oxides, phosphate, solid electrolyte, lithium compounds. These cladding materials 
have good stability, well coat on the surface of LiMn$_2$O$_4$ materials, and reduce the lithium ionic lattice 
changes caused by embedded, inhibit Jahn-Teller effect in the process of inhibition of circulation and 
Mn dissolution, so as to make the composite has more excellent cycle performance\cite{24}. C.Mu et al.\cite{25} 
used catalytic chemical vapor phase precipitation to modify a layer of carbon protective layer on the 
surface of nanometer rod LiMn$_2$O$_4$ to form a capsule-like structure (CCs). This carbon film not only 
provided physical and chemical protection for the material, insulated the contact reaction between 
electrolyte and LiMn$_2$O$_4$, but also improved the electrical conductivity of the material. Studies showed 
that the specific capacitance of LiMn$_2$O$_4$/CCs as electrode material was 451 F/g in 0.5 M Li$_2$SO$_4$ 
aqueous solution with current density of 0.5 A/g, which is much better than that of LiMn$_2$O$_4$(304 F/g).
Even if the current density was 8 A/g, the specific capacitance can reach 380 F/g. In addition, its cycle 
performance was also very good, in 1500 times of charge and discharge cycles, the capacity retention 
rate was 95%. On the other hand, the surface coating is not widely used in the industrialization of 
modified anode materials, and the surface coating technology needs to be continuously optimized in 
order to achieve large-scale application.

5. Concluding

Lithium-ion batteries represent the mainstream of on-board power for electric cars around the world, 
and its performance development has been highly concerned by all circles. As one of the positive 
electrode materials with great development potential, spinel LiMn$_2$O$_4$ has become a research direction 
for researchers to improve its electrochemical performance by various means. This paper summarized 
the performance attenuation, preparation and modification of spinel LiMn$_2$O$_4$ materials, and the
advantages and disadvantages of different methods of lithium manganate materials are analyzed, which providing reference for further improving its electrochemical performance.

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References
[1] Arai J, Yamaki T, Yamauchi S, et al. 2005 Development of a high power lithium secondary battery for hybrid electric vehicles (Journal of Power Sources) vol 146 p 788-792
[2] Kandler S, Wang C Y 2006 Power and thermal characterization of a lithium-ion battery pack for hybrid-electric vehicles (Journal of Power Sources) vol 160 p 662-673
[3] D. K. Kim, P. Muralidharan, H. W. Lee, et al. 2008 Spinel LiMn2O4 nanorods as lithium ion battery cathodes(Nano Letters) vol 8(11) p 3948-3952
[4] H. Wang, Y. I. Jang, B. Huang, et al. 1999 TEM study of electrochemical cycling - induced damage and disorder in LiCoO2 cathodes for rechargeable lithium batteries (Journal of The Electrochemical Society) vol 146(2) p 473-480
[5] W. S. Kim, K. i. Chung, Y. K. Choi, et al. 2003 Synthesis and charge-discharge properties of LiNi1-x,Co,M2O4(M=Al, Ga) compounds (Journal of Power Sources) vol 115(1) p101-109
[6] A. Yamada, S. C. Chung, K. Hinokuma 2001 Optimized LiFePO4 for lithium battery cathodes (Journal of The Electrochemical Society) vol 148(3) p A224-A229
[7] O. K. Park, Y. Cho, S. Lee, et al. 2011 Who will drive electric vehicles, olivine or spinel? (Energy & Environmental Science) vol 4(5) p 1621-1631
[8] X. Xie, D. Su, B. Sun, et al. 2014 Synthesis of single-crystalline spinel LiMn2O4 Nanorods for lithium-ion batteries with high rate capability and long cycle life (Chemistry) vol 20(51) p 17125-17131
[9] Hart R. W., White H. S., Dunn B., et al. 2003 3-D Microbatteries (Electrochemistry Communications) vol 5 (2) p 120-123
[10] Das S., Fachini I. R., Majumder S., et al. 2006 Structural and electrochemical properties of nanocrystalline Li,Mn0.5 thin film cathodes (1.0 ≤ x ≤ 1.4) (Journal of Power Sources) vol 158 (1) p 518-523
[11] Patil A., Patil V., Wook Shin D., et al. 2008 Issue and challenges facing rechargeable thin film lithium batteries (Materials research bulletin) vol 43 (8) p 1913-1942
[12] Ragavendran K, Xia H., Mandal P., Arof A K. 2017 Jahn-Teller effect in LiMn2O4: influence on charge ordering, magnetoresistance and battery performance (Physical Chemistry Chemical Physics) vol 19(9) p 6481–6486
[13] K. Y. Chung, H. S. Lee, W. S. Yoon, et al. 2006 Studies of LiMn2O4 capacity fading at elevated temperature using in situ synchrotron X-ray diffraction (Journal of The Electrochemical Society) vol 153(4) p A774–A780
[14] K. Y. Chung, C. W. Ryu, K. B. Kim 2005 Onset mechanism of Jahn-Teller distortion in 4 V LiMn2O4 and its suppression by LiM0.05Mn1.95O4(M=Co, Ni) coating (Journal of The Electrochemical Society) vol 152(4) p A791–A795
[15] Zheng H H, Sun Q N, Liu G, et al. 2012 Correlation between dissolution behavior and electrochemical cycling performance for LiNi1/3Co1/3Mn1/3O2-based cells (Journal of Power Sources) vol 207 p 134–140
[16] X. Zhao, M.V. Reddy, H. Liu, et al. 2012 Nano LiMn2O4 with spherical morphology synthesized by a molten salt method as cathodes for lithium ion batteries (RSC Advances) vol 2(19) p 7462
[17] Liang Tian, Changwei Su, Yan Wang, Bixia Wen, Wei Bai, Junming Guo 2019 Electrochemical properties of spinel LiMn2O4 cathode material prepared by a microwave-induced solution flameless combustion method (Vacuum) vol 164 p 153–157
[18] Yang X, Qu F, Niu H, et al. 2015 *High-performance aqueous asymmetric supercapacitor based on spinel LiMn$_2$O$_4$ and nitrogen-doped graphene/porous carbon composite* (*Electrochimica Acta*) vol 180 p 287–294

[19] J.S. Kim, K. Kim, W. Cho, W.H. Shin, R. Kanno, J.W. Choi 2012 *A truncated manganese spinel cathode for excellent power and lifetime in lithium-ion batteries* (*Nano Lett*) vol 12 p 6358

[20] N. Laszczynski, J. von Zamory, N. Loeffler, G.B. Cho, G.-T. Kim, S. Passerini 2014 *Synthesis of LiMn$_2$O$_4$ with outstanding lithium-insertion kinetics and longterm stability* (*ChemElectroChem*) vol 1 p 1537

[21] Haiqiang Liu, Ruiyuan Tian, Yi Jiang, et al. 2015 *On the drastically improved performance of Fe - doped LiMn$_2$O$_4$ nanoparticles prepared by a facile solution-gelation route* (*Electrochimica Acta*) vol 180 p 138–146

[22] Liu Xuewu, Wang Xiaojuan, Chen Shuhua, Tang Jie 2016 *Supercritical hydrothermal synthesis and electrochemical performance analysis of LiM$_x$Mn$_{2-x}$O$_4$* (*Materials Today: Proceedings*) vol 3 p 672–680

[23] Subramani Bhuvaneswari, U.V. Varadaraju, R. Gopalan, Raju Prakash 2019 *Structural stability and superior electrochemical performance of Sc-doped LiMn$_2$O$_4$ spinel as cathode for lithium ion batteries* (*Electrochimica Acta*) vol 301 p 342–351

[24] Chen Zi, Jiang Qu, Li Huan, et al. 2017 *Research progress in the mechanism of surface coating of spinel lithium manganate modified material* (*Functional Materials*) vol 11(48) p 11060-11065

[25] Chunhong Mu, Shuai Lou, Rashad Ali, et al. 2019 *Carbon-decorated LiMn$_2$O$_4$ nanorods with enhanced performance for supercapacitors* (*Journal of Alloys and Compounds*) vol 805 p 624-630