Application metal oxide cathode materials for lithium ion batteries

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Abstract. The popularity of portable electronic devices has boosted the speedy advancement of devices for storing electrical energy. At the same time, the development of electric vehicles urgently requires lithium batteries to have higher power density and performance. The strong points of lithium ion battery are environmental friendliness, also specific capacity of high level. Lithium cathode material is one of the key factors affecting battery performance. The requirements for positive electrode materials are good safety, good service life, and less self-discharge. Among all cathode materials, metal oxide cathode material is the most potential types, which comes from a wide range of sources and has rich production experience. In this paper, four kinds of lithium metal oxide cathode materials including lithium cobaltate, lithium nickelate, lithium manganate and ternary composite oxide cathode material were analyzed, and discussed the performance of lithium metal oxide cathode materials in practical applications, where further pointed out the existing problems of metal oxide cathode materials and put forward several directions for future improvement to improve the performance of lithium ion battery cathode materials in the future development and production process.

Keywords: lithium-ion battery, metal oxide cathode material, application performance.

1. Introduction

In the 1950s, lithium-ion batteries began to enter public's vision. Based on the increasing demand for clean energy for industrial development in the 21st century, as well as the popularity of portable devices for storing electrical energy and the development of new energy vehicles for the past few years, lithium-ion batteries stand out among new energy materials with their high energy density, lasting cycle life, fast charge and discharge speed, and green environmental protection. The production and use of lithium-ion batteries only produce a small amount of waste liquid, no gas emissions. Compared with the lithium-ion batteries, the burning of coal, oil, natural gas and other traditional energy sources will lead to a large amount of greenhouse gas emissions and aggravate the greenhouse effect. In the composition of lithium-ion batteries, the positive electrode is a significant component, which has an irreplaceable impact on the overall indicators of the battery, which requires the materials used in the positive electrode to have high specific capacity and excellent cycle performance [1].

The basic characteristics of the cathode material are the composition of LixMyOz, through the redox release of the transition metal element M and to obtain Li^+, which is air sensitive. What's more, its electrochemical performance is closely with respect with the crystal structure, the properties of transition metals can greatly affect the electrochemical properties of cathode materials. Lithium ion battery oxide cathode materials mainly include lithium cobalt, lithium nickel, nickel cobalt manganese ternary material and lithium manganese. Lithium manganate and lithium iron phosphate are expected to have a further development for power batteries area. Compared with lithium cobalt oxide, these two materials have a superiority of saving cost, and have excellent thermal stability and safety. While in the field of communication batteries, three-element composite materials and lithium nickelate are ideal alternatives to take over lithium cobaltate cathode materials. Compared with lithium cobaltate, the three elements have a comparative price advantage and higher safety, and lithium nickelate has a higher capacity.

Metal oxide cathode material has the advantages of high operating voltage, stable discharge, friendly environment and high specific capacity. Meanwhile, the disadvantage includes high cost, poor safety, general cycle life, and poor material stability. The physical properties of cathode materials mainly include particle size distribution, vibrational density, specific surface area, crystal structure and appearance quality. These properties will directly affect the electrochemical performance [2]. It will indirectly affect the safety of battery. The electrochemical properties of cathode materials for lithium-ion batteries mainly include the specific capacity of the first discharge, the efficiency of the first charge and discharge, the capacity ratio of the discharge platform, the rate performance and the cycle life. Also, the cathode material of lithium-ion battery should meet three characteristics. In the process of charge and discharge, the material and the electrolyte should have good electrochemical compatibility [3-5]. Material has good electrode process dynamic performance. And the deem-bedding of lithium ion should cause less loss to the cathode material.

In this paper, the research progress of metal oxide cathode materials such as lithium cobalt oxide, lithium nickelate, lithium manganate, and nickel-cobalt-manganese terpolymer materials at home and abroad is reviewed, and the advantages and disadvantages of these cathode materials are analyzed and summarized, and the existing research is prospected, hoping to promote the development of high energy density, lasting cycle life also inexpensive lithium ion battery positive electrode and its application in high-end fields.

Table 1. Performance comparison of several main cathode materials [4].

Name	Lithium manganese oxide type A	Lithium iron phosphate	Lithium cobalt oxide	Lithium nickelate	Nickel cobalt manganese ternary material	Lithium manganese oxide type B
Main components	$LiMn_2O_4$	$LiFeO_4$	$LiCoO_2$	$LiNiO_2$	$LiNiCoMnO_2$	$LiMnO_2$
Threotical energy density (mAh/g)	148	170	274	274	278	286
Actual energy density (mAh/g)	100-120	130-140	135-140	190-210	155-165	200
Voltage platform (V)	3.8-3.9	3.2-3.7	3.6	2.5-4.1	3.0-4.5	3.4-4.3
Cycle index	>500	>2000	>300	Poor	>800	Poor
Transition metal	Rich	Very rich	Poor	Rich	Poor	Rich
Environmental performance	Non-toxic	Non-toxic	Cobalt is radioactive	Nickel is toxic	Cobalt Nickel is toxic	Non-toxic
Safety performance	Good	Excellent	Bad	Bad	Average	Good
Applicable temperature	>50fast decay	-20-75	-20-55	N/A	-20-55	High temperature instability
Compacted density	3	2.2	4.2	3.6	3.6	3

2. Different metal oxide cathode materials for lithium ion batteries

Since the successful progression and application of lithium cobalt in the 1990s, lithium cobalt oxides have been in the dominant position of positive electrode materials, among which the most widely used is lithium cobalt oxide with a layered structure [2]. The research on lithium nickel oxide in the field is also relatively early, and the current more mature representative is lithium nickelate. Lithium manganese oxide is one of the most promising lithium ion cathode materials. Nowadays, the most widely used lithium manganese anode material is lithium manganate, whose crystal structure is spinel structure. Here, this research will discuss different types of metal oxide cathode materials for lithium ion batteries. As shown in Table 1, these metal oxide cathode materials show different performance in lithium ion batteries.

2.1. Features of metal cathode materials

2.1.1 Lithium cobaltate

The two-dimensional layered structure of lithium cobaltate belongs to α-$NaFeO_2$ type, which is suitable for lithium ions when go through the process of insertion and extraction [3]. The two-dimensional layered structure of lithium cobalt oxide makes it have the advantages of high specific energy, good cycle performance, stable discharge and high operating voltage, but at the same time, lithium cobalt oxide also has problems such as high cost, poor use process safety and short cycle life.

Surface coating and bulk phase doping are common methods to improve the structure and cycle stability of lithium cobaltate [6]. The purpose of surface coating is to avoid direct contact between the surface of lithium cobaltate and the electrolyte, and to alleviate the problem of poor cycle stability caused by cobalt dissolution and oxygen precipitation. At present, the main methods for preparing lithium cobaltate are high temperature solid phase synthesis, low temperature co-precipitation method and gel method.

The cathode material of the battery in the charging state is usually a strong oxidizing compound, which is extremely unstable and easy to decompose and release oxygen. The released oxygen reacts with the electrolyte to produce a large amount of heat and gas. If the heat generated exceeds a certain limit value, it will further accelerate the decomposition of the positive electrode, produce more oxygen, promote the exothermic reaction, and then cause the temperature of the battery to go up quickly and thermal runaway occurs, lithium cobaltate materials generally exceed 200 °C will occur thermal runaway [7]. Thus, more research on improving safety and high voltage performance of lithium cobaltate materials should be focused in the future.

2.1.2 Lithium nickelate

Lithium nickelate also belongs to the α-$NaFeO_2$ structure. Lithium nickelate has the same high theoretical energy density as lithium cobaltate, the theoretical capacity of lithium nickel oxide is 274 mAh/g, and the actual capacity can reach 190~210 mAh/g. Its self-discharge rate is low, there is no environmental pollution, and the requirements for electrolyte are low. Lithium nickelate has good cyclic performance.

In terms of cost, Ni is abundant and low-cost. Furthermore, compared with cobalt, the potential of nickel REDOX process is delayed, it makes the voltage stability window of its electrolytic solution more accessible [4]. Although the lithium nickelate cathode material has a high theoretical capacity, it has been criticized for poor thermal stability and poor cycle stability during use, which is also the main reason for limiting the application of lithium nickelate cathode materials in more lithium-ion batteries. And stable lithium nickelate is not suitable for synthesis.

The reason why lithium nickelate is difficult to synthesize, in fact, refers to the ideal stoichiometric ratio of lithium nickelate is not easy to synthesize, the main reasons are the following aspects. First, there is a large potential barrier in the process of Ni^{2+} oxidation to Ni^{3+}, which makes it difficult to completely oxidized, and the position of Li^{+} will be occupied by the remaining Ni^{2+}, resulting in the formation of non-stoichiometric compounds. Second, at high temperature, lithium nickelate is easy to undergo irreversible phase transition, and because of its own instability, easy to decompose. Third, when the temperature is high, the lithium salt will volatilize, resulting in a lack of lithium.

Doping is one of the most effective lithium nickelate modification, through the electrode preparation process in the lithium, nickel or oxygen site to introduce new ions to promote the electrochemical performance of the material [8]. Doping is generally divided into three categories: cationic doping, anionic doping and co-doping. Among them, non-transition metal cations doped Ni based cathode materials are representative, for example, magnesium doping can significantly improve the cycle performance of lithium nickelate batteries. Aluminum doping can improve the REDOX potential of the battery.

Surface coating modification is another effective way to improve lithium nickelate cathode materials [5]. Phosphates, fluorides, lithium salts and conductive materials are all used as coating materials for lithium nickelate layered positive electrodes. Surface coating can inhibit oxygen escape and oxygen defects in the lattice, so that the stoichiometric ratio of the material can be maintained, this will lead to a firm structure, and the cycle performance is even better.

2.1.3 Lithium manganate

Lithium manganate material has layered structure and spinel structure. The theoretical specific capacity of layered lithium manganate is 285 mAh/g. The theoretical specific capacity of spinel lithium manganate is 148 mAh/g, and the actual specific capacity is 90~120 mAh/g. The preparation technology of spinel lithium manganate mainly includes high temperature solid phase method, hydrothermal method and chemical precipitation method [9, 10].

The outstanding advantages of lithium manganate are good stability, no pollution, high operating voltage and low cost, lithium manganate electrode has some significant disadvantages. First, in the electrolyte will gradually dissolve, disproportionation reaction. Second, during deep discharge, when the average valence of manganese is 3.5, Jahn-Teller distortion occurs, causing changes in the lattice volume of spinel and loss of electrode composition. Third, the electrolyte is unstable during high voltage charging [3].

Surface coating is an effective modification method for lithium manganese oxide. At present, lithium fluoride coating is a development direction with great potential [11]. Aimed to realize the widespread market application of lithium manganate cathode materials for lithium-ion batteries, the critical step is to explore and study the inherent shortcomings of lithium manganate materials from the aspects of regulating structure and morphology, reducing the dissolution of manganese ions, inhibiting Jahn-Teller effect, and improving electrical conductivity. In the field of power batteries, lithium manganate is the most promising cathode material [1].

2.1.4 Nickel-cobalt-manganese ternary cathode materials

In nickel-cobalt-manganese ternary cathode materials, nickel participates in REDOX reaction and determines material capacity. The outermost layer of cobalt atoms contains two electrons, which makes cobalt doped materials have good conductivity, additionally arise the conductivity of ionic, improve the magnification performance, and reduce the Li/Ni mixing degree to a certain extent [12]. Manganese has few influences on the REDOX reaction, but can make the structure less susceptible to be damaged [13]. Nickel-cobalt-manganese ternary cathode material combines the stability of lithium cobalt, the high capacity of lithium nickel and the low cost of lithium manganate and other characteristics, by controlling the proportion of three metal elements, the use of synergistic effect to obtain a material with good comprehensive performance. However, there are also obvious shortcomings in the use of ternary materials: such as relatively low platform, low first charge and discharge efficiency [13].

High temperature solid phase method is always used to synthesis NCM. Other ways include solvothermal method, sol-gel method and co-precipitation method. At present, the more suitable method is co-precipitation method, which is simple to operate, and the prepared product has uniform morphology and high vibration density. The factors affecting the properties of different ternary anode materials are also different. For nickel-manganese equivalent ternary anode materials, the content of nickel will obviously affect the capacity of the battery, while the content of manganese will affect the stability of the battery during operation. For nickel-rich ternary cathode materials, the content of Co significantly affects the ionic conductivity, the higher the content of Co, the better the conductivity, the better the charge and discharge ratio. Shape is another factor affecting the ternary cathode material, spherical or spheroid ternary cathode material, long cycle life, high rate discharge performance, excellent electrochemical performance and better safety performance of $LiCoO_2$, is an ideal cathode material to replace $LiCoO_2$. Reversible gram capacity, safety performance and cycle performance are higher/better than $LiMn_2O_4$.

2.2. Future development

With in-depth research on positive electrode materials, it can be found that positive electrode materials composed of metal oxides have greater development potential, and their electrochemical performance still has great room for development. It is necessary to design modifications in order to expand the application range of metal oxides. Currently, the best way is to carry out multi-element doping modification, utilizing the synergistic effect between different elements to maximize the electrochemical performance of lithium cobalt oxide materials. However, the relevant research is not in-depth enough, and the mechanism of the synergistic effect of elements in multi-element doping is still relatively lacking. Further research is needed to further explore.

3. Conclusion

This research analyzed the application performance of four common metal cathode materials in lithium ion batteries. In lithium ion batteries, conductivity, specific capacity, and cycle life are highly concerned indicators, and these two points should also be paid attention to in actual production and application processes. Comprehensive analysis of lithium cobalt oxide, lithium nickel oxide, lithium manganese oxide, and nickel cobalt manganese ternary oxides shows that surface coating and doping modification are effective ways to upgrading the behaviour of the two metal oxide cathode materials. This is closely related to the properties of the metal itself. In future development and application, attention should be paid to the improvement of various metal oxide cathode materials.

References

[1] Zhang Zhiyong, Bao Shengjun, Xie Shengzhong. Current Situation and Suggestions for Standardization Construction of Composition Analysis and Performance Testing of Positive Electrode Materials for Lithium Ion Batteries. Chemical Minerals and Processing, 2023, 1-16.

[2] Wang Chongguo, Liu Guanglong, Jin Xiaorong. Research progress on positive electrode materials for lithium-ion batteries. Contemporary Chemical Research, 2023, (9): 12-14.

[3] Lu Xiaoting. Research progress on positive electrode materials for high-capacity lithium-ion batteries. Aging and Application of Synthetic Materials, 2022, 51 (4): 121-123.

[4] Wang Lei. Analysis of the Development Trend of Positive Electrode Materials for Lithium Ion Batteries. Journal of Changji University, 2020, (4): 118-122.

[5] Wang Huan, Qiao Qingdong, Li Qi. Research on the Current Situation of Cathode Materials for Lithium Ion Batteries. Power Supply Technology, 2019, 43(11): 1887-1890.

[6] Liu Qiaoyun, Qi Xiuxiu, Hao Weiqiang. Research progress on modification of lithium cobalt oxide cathode material for lithium batteries. Power Supply Technology, 2022, 46(12): 1357-1359.

[7] Ye Bin. Study on the surface modification of lithium cobalt oxide cathode and its characteristics of low-temperature and high-voltage energy storage. University of Chinese Academy of Sciences (Chinese Academy of Sciences Shanghai Institute of Silicate), 2023.

[8] Liu Jinyu, Jiao Liansheng, Wang Yan, et al. Research status of positive electrode materials for lithium-ion batteries. Journal of Hebei Normal University for Nationalities, 2020, 40(2): 121-128.

[9] Tang Xiaohu Preparation and surface modification of spinel lithium manganese oxide cathode material. Shenyang University of Technology, 2023.

[10] Yuan Dong Research on the synthesis, preparation, and modification of lithium manganese oxide cathode materials. Guizhou University, 2022.

[11] Wei Jingbin, Liang Weiqiang. Modification of cycling performance of lithium manganese oxide cathode materials for new energy vehicle power lithium-ion batteries. Powder Metallurgy Industry, 2023, 33(5): 106-112.

[12] Huang Guoxin Research on Niobium Doping Modification of Lithium Nickelate as a Positive Electrode Material for Lithium Ion Batteries. Guangxi University, 2023.

[13] Wu Caiyun, Feng Chuanqi, Zhang Chaofeng, et al. Research progress on layered nickel cobalt lithium manganese oxide ternary cathode materials. Battery, 2022, 52(1): 3-7.