Selection of Cathode Materials for Lithium-Ion Batteries at Different Temperatures

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Abstract. With the widespread application of lithium-ion batteries in more and more fields, selecting appropriate electrode materials in different environments has become a key issue in the research of lithium-ion batteries. In recent years, with the rapid development of science and technology, lithium-ion batteries have become a key point of development, and their applications in special fields have put forward higher requirements for the performance of lithium-ion battery cathode materials. At present, electrode materials are widely used in fields such as instrument testing equipment, vehicle-mounted equipment batteries, and vehicle-mounted canopy batteries. In these cases, precise control of the operation temperature of electrode materials is required, and it is necessary to ensure that the electrode materials used still have good performance at high or low temperatures. Therefore, it is crucial to study the selection of lithium-ion cathode materials at different temperatures. This article first introduces common positive electrode materials and the working principles of lithium-ion batteries, elaborates on the selection of lithium-ion positive electrode materials at different temperatures and the modification treatment of some positive electrode materials to adapt to corresponding temperature conditions, and discusses the reasons, principle, and significance.

Keywords: Lithium ion battery, cathode materials, high temperature, low temperature.

1. Introduction

Currently, lithium-ion batteries have become the main source of energy for a variety of electronic devices and vehicles such as automobiles. Its high energy density and long life have made it the preferred energy solution for wireless communication devices, portable electronic devices, and electric vehicles. At present, China has introduced a series of related laws such as "Management Methods of New Energy Vehicles", "Dual Carbon Policy", "Notice on Management of Lithium-ion Battery", etc. Therefore, choosing the appropriate lithium-ion battery materials in different environments has become an important issue. Therefore, the selection of suitable materials for lithium-ion batteries in different environments has become more and more important. However, in the current situation, there are numerous incidents of damage to equipment or even fire or explosion due to inappropriate selection of electrode materials, and unsuitable electrode materials may lead to the release of hazardous substances during the use of the battery, posing potential risks to the environment and human health. Therefore, the selection of suitable battery electrode materials in different environments is essential to ensure battery performance, safety, and environmental protection, and the safe use of lithium-ion batteries has become a major issue limiting the development of the technology [1]. In the current study of battery material selection, more attention is paid to the cathode electrode materials such as lithium iron phosphate, ternary materials, lithium manganate, lithium cobaltate, etc. These cathode materials have high energy density, excellent thermal stability, long cycle life, and high safety performance, and have a wide range of applications in the fields of electric vehicles, energy storage systems, and portable electronic devices. Therefore, reasonable selection of the above materials in different environments can greatly facilitate people's life, better ensure the performance of the battery and better protect the operation of the equipment, which is of great research significance and value [2].

2. Introduction to Lithium-Ion Batteries

2.1. Working Principle of Lithium-Ion Batteries

The working principle of the lithium-ion battery mainly relies on the process of embedding and detaching lithium ions and electrons between the positive and negative active substances. The essence is an electrochemical redox reaction. With the de-embedding of lithium ions and electrons, the macroscopic intrinsic parameters of the positive and negative substances change, which is manifested in the change of the battery's capacitance and voltage [3]. Lithium-ion battery consists of a positive electrode, negative electrode, electrolyte, and diaphragm. The positive electrode is usually composed of lithium salt, metal oxides, and conductive agents, while the negative electrode uses carbon materials. The electrolyte is usually an organic solvent such as carbonate or polymer gel. The diaphragm isolates the positive and negative electrodes and prevents short circuits. During the charging process, lithium-ion batteries work as follows: when an external power source applies voltage, lithium ions are released from the positive electrode and migrate to the negative electrode through the electrolyte. At the same time, the negative electrode of the carbon material will be embedded in lithium ions, the formation of lithium compounds. This process is reversible, i.e., during the discharge process, lithium ions are de-embedded from the negative electrode and migrate to the positive electrode, releasing electrical energy to be supplied to external devices.

2.2. Common Positive Electrode Materials

Cathode materials determine the performance and characteristics of the battery. In lithium-ion batteries, common cathode materials include lithium cobaltate, lithium nickelate, lithium ferrate, and lithium manganate. Lithium cobaltate has high conductivity and ion diffusion rate, which can provide high discharge performance and cycle stability. In addition, the structure of lithium cobaltate has a certain reversibility, which can maintain good structural stability during the charging and discharging process, thus prolonging the service life of the battery. Therefore, it has the advantages of high voltage, smooth discharge, high specific energy, and good cycle performance [4]. However, due to its influence by the operating voltage, due to the irreversible phase transition of lithium cobaltate material, from the hexagonal crystal phase to the monoclinic phase, which leads to a sharp decline in the performance of lithium-ion batteries, battery capacity and service life are reduced [5]. At present, the preparation of lithium cobalt is mainly chemical synthesis and solid phase method. The chemical synthesis method is the appropriate amount of cobalt salt and lithium salt reaction in solution, and then after precipitation, washing, drying, and other steps to get lithium cobaltate; the solid-phase method is the appropriate amount of cobalt oxide and lithium carbonate according to a certain molar ratio of mixing and then reacted at high temperature to get lithium cobaltate. Lithium manganate belongs to the cubic crystal system, in the structure, manganese tetraoxide provides three-dimensional diffusion channels, and in the charging and discharging process, the crystal always maintains the initial cubic structure, which allows the material to have a good multiplicity performance [6]. $LiMn_2O_4$ batteries have high specific energy and specific power, and low self-discharge rate during charging and discharging, which means that they can keep the charge for a long time without rapid loss. In addition, $LiMn_2O_4$ batteries have a long cycle life and can withstand multiple charge/discharge cycles without significant performance degradation. In addition, $LiMn_2O_4$ batteries have a faster charging speed and can be recharged in a short period of time. $LiMn_2O_4$ batteries have high safety performance and are not prone to overcharge, over-discharge, short-circuit, and other safety problems. At present, the preparation of lithium manganate battery material mainly relies on the high-temperature solid phase method, sol-gel method, hydrothermal method, chemical precipitation method, and other preparation methods [7]. Lithium iron phosphate belongs to the orthorhombic crystal system, this structure improves the volume utilization rate of the battery at the same time also ensures its stability at high temperatures, and the utilization performance of the battery is improved. Lithium iron phosphate battery thermal runaway risk is lower, and can effectively reduce the use of the process of safety hazards; secondly, lithium iron phosphate battery has a long service

life, a cycle life of up to thousands of times; lithium iron phosphate battery also has a high operating temperature range and high energy density and specific energy. At present, the preparation of lithium iron phosphate mainly includes the high-temperature solid-phase method, carbon thermal reduction method, sol-gel method, hydrothermal/solvent thermal method, co-precipitation method and so on [8]. Lithium nickelate is an oxygen atom set up square dense stacking arrangement of layered oxides, which is a weak and stable layered structure. It has the advantages of ultra-high energy density and environmental friendliness, but lithium nickelate itself has poor thermal stability, and it is difficult to meet people's demand for safety. At high temperatures, lithium nickelate gradually changes from a layered structure to a spinel structure, accompanied by the generation of oxygen; in addition, its energy storage also faces great challenges, with time, the chemical properties of the material with decline of time. In response to these problems, lithium nickel oxide ($LiNiO_4$) batteries are often modified. Commonly used modification methods include elemental doping, surface coating, design of secondary particle structure, and electrolyte modification [9]. At present, the commonly used methods for the preparation of lithium nickelate are the solution method, solid-phase method, hydrothermal method, and so on.

3. Positive Electrode Material Selection at Different Temperatures

The optimal operating temperature of lithium-ion batteries is 20-45 °C [10], however, in different environments, the optimal operating temperatures of the electrode materials need to be taken into account. The study of the effect of different temperatures on the electrode materials is an important topic, which is of great significance to improve the working performance and stability of the battery. Electrode materials are the core components of electrochemical energy storage devices, and their performance directly affects the efficiency of energy storage devices, the electrochemical properties of electrode materials, and the lifetime, among which the temperature is a key factor in determining the lifetime of the battery.

3.1. High Temperature Conditions

At present, the rapid development of science and technology, the increase in energy demand, high-temperature combustion and electrolysis, and other processes have become an important way of energy conversion, in these processes, the electrode materials need to be able to withstand high temperatures and pressures in high-temperature environments, and at the same time have a good electrical conductivity and chemical stability, in order to ensure that the efficiency of the energy conversion and the safety of the equipment. Therefore, the selection of electrode materials at high-temperature conditions is of great significance in the field of energy, material processing and manufacturing, environmental protection, and resource utilization. When selecting electrode materials, electrode materials at high temperatures environments should be considered to have good thermal stability, chemical stability, low combustibility, high conductivity, and good corrosion resistance. At high temperatures, the loss of internal electrolyte decomposition and SEI film thickness increase leads to a decline in battery performance, the number of cycle charging is reduced, and the degree of aging increases [11], which in turn causes the side reaction intensification, internal resistance increases, heat generation increases, generates a large number of gases, resulting in faster battery aging, and some even cause an explosion. Some studies have shown that in the lithium iron phosphate battery (negative electrode is columnar graphite) at 45 ℃ for the study of the cycle, when the capacity decays to 90%, for less than 500 times the number of cycles; while at room temperature, it can reach 1300 times. By analyzing the electrolyte at 45 ℃, it was found that the electrolyte salt concentration decreased from 13.19 wt% to 12.98 wt%, and the cathode porosity decreased from 46.22% to 40.11% [12]. At present, to cope with the high-temperature environment, the commonly used cathode materials for lithium ion batteries are lithium manganate (optimal temperature of 0 ation decreased from 13.19 wt% to 12.98 wt%, and t-20 ℃ -55 ℃), ternary materials (optimal temperature of -20 ℃- 60 ℃) and so on. The optimum temperature is -20 ℃-60 ℃), etc. In the high-temperature

performance test of $LiMn_2O_4$, it is found that the capacity of the battery is easy to decay, and the crystal structure changes from cubic to tetragonal, which leads to a decrease of conductivity. The main reason is that the trivalent manganese ions are unstable and easily disproportionate to divalent and tetravalent. Usually, the modification method of lithium manganate is to dope or parcel other metal ions, non-metal ions, rare earth elements, etc., so that they can replace part of the trivalent manganese ions, and raise the average valence of lithium manganate battery [13]. The usual modification method for lithium cobaltate electrode materials is the encapsulation or doping method. In general, lithium cobalt oxide is wrapped by divalent metal oxides to effectively improve ion transport efficiency, reduce internal resistance, improve battery life, etc. In addition, magnesium and other metals or P-type semiconductor materials are often used to dope it, which can better improve the stability of the battery [14]. The high nickel ternary materials at high temperatures, there are poor structural stability, and electrolyte interface side reactions serious problems. At present, the high-nickel ternary batteries are mainly improved by the coating method, such as wrapping tungsten with a mass fraction of 0.3%, which can best enhance the stability of high-nickel ternary electrode materials [15].

3.2. Low Temperature Conditions

Under low-temperature conditions, lithium-ion batteries are mainly used in the fields of polar scientific research, cold zone emergency response, power communication, and public safety. In this research, electrode materials need to have high conductivity, low resistance, and high charge/discharge capacity to maintain the required object operation. The selection of electrode materials at low temperatures is important in promoting the development of energy storage and conversion technologies in both scientific research and daily life, as well as in improving research in the field of energy. Under low-temperature conditions, electrode materials can improve the efficiency of the power system and the stability of the overall system, which can better promote the development of new energy technologies. At present, with the increasing demand for renewable energy, new energy technologies are also emerging. However, the performance of some new energy technologies in the low-temperature environment is not ideal, in this state, the battery shows that the electrode material is constantly deactivated, the battery capacity loss increases, and the charging rate slows down [10]. According to the existing experimental research, by comparing the lithium titanate and ternary materials in -10 ℃ cycle times and discharge capacity relationship, found that ternary batteries in the low-temperature cycling discharge capacity first increased and then slowed down in two phases, and from the experiments concluded that the lithium ions in the negative end of the precipitation of the battery in the low-temperature conditions is a key factor that affects the battery in low-temperature conditions function functionally stable or not, the battery safety performance degradation or not [16]. Therefore, it is necessary to find more suitable electrode materials for use in low-temperature environments to promote the development and application of new energy technologies. Under low-temperature conditions, the electrode materials mainly cause low-temperature aging of the battery due to the growth of negative electrode dendrites. At present, to cope with the low-temperature environment, the commonly used cathode lithium-ion electrode materials are lithium cobaltate and lithium iron phosphate. Among them, lithium cobalt oxide shows a hexagonal layered structure, with a better lithium ion transport rate, high energy, and chemical stability. However, when the temperature is less than -10 ℃, it is difficult to ensure the phase structure and interfacial stability of the electrode. According to research, the low-temperature performance is mainly limited by the lithium ion transport rate at the interface between the electrolyte and cathode. At present, the commonly used performance improvement methods include the coating method and adding lithium salt additives (e.g., lithium bis(borate)) or organic additives in the electrolyte [17]. $LiFePO_4$ batteries can show good operational performance between -20-45 ℃, but their performance is not stable when operating in very cold conditions (e.g., Antarctic and Arctic exploration missions). For the very low-temperature modification of $LiFePO_4$ batteries, a common method is to optimize the performance by using carbon layers (e.g., carbon black, carbon nanotubes, graphene, etc.) [18].

4. Conclusion

In different temperatures, the choice of lithium-ion battery electrode materials is of great significance, which directly affects the performance and service life of the battery, and even affects the safety of human life. This paper mainly starts with a basic introduction to the battery and electrode materials, and how to lithium-ion battery electrode material selection at different temperatures. Under different conditions, the energy density of the cathode material, lithium storage capacity, cycle life, and safety, as well as the conductivity, stability, and safety of the electrolyte and other factors need to be considered. In the current research, lithium-ion battery electrode materials can basically meet the single simple use of the environment, but the more complex working conditions or some extreme environmental areas cannot be better met. In addition, the existing research on the use of lithium-ion battery electrode materials is mainly based on laboratory tests, and there is a big difference between the laboratory tests and the actual use of the situation. Therefore, it is necessary to strengthen the relevant research, improve the systematicity, reliability, foresight, and data sharing, and suggest carrying out more research on electrode materials at different temperatures, current densities, cycle times, and other working conditions, in order to comprehensively understand their performance characteristics and life characteristics, and gradually put them into production and use to verify their feasibility.

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