

Application progress of nickel-rich layered oxide positive electrode material in Lithium-ion Batteries

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Abstract. Lithium-ion batteries (LIBs) are one of the hottest batteries available today. If the technology is developed and perfected, it will be used in many facilities and battery cars for the benefit of humanity. In LIBs, the cathode material is one of the most essential aspects, and it is responsible for storing and releasing lithium ions to complete the charging and discharging process of the battery. Nickel-rich layered oxide has higher specification capacity and energy density than other cathode materials. Moreover, after many charging and discharging processes, the effect of its performance is relatively small, which can significantly improve the service life of the battery. This paper first introduces the working principle of lithium-ion batteries. Then, nickel-rich layered oxide cathode materials' essential characteristics, performance, and crystal structure are introduced. In addition, this paper presents its standard preparation methods. Finally, different modification methods of Li-rich layered oxides are discussed, including elemental doping, surface coating, and core-shell structure.

Keywords: LIBs, nickel-rich layered oxide, positive electrode materials.

1. Introduction

LIBs are widely used and the subject of substantial study and development. It is ubiquitous in everyday life, from computers and cell phones to battery-operated vehicles. Many sectors favor LIBs because of their high energy density, lightweight construction, and quick charging capabilities. The fundamental mechanism by which these batteries operate is the transfer of lithium ions between the positive and negative electrodes during lithium-ion batteries' charging and discharging cycles [1]. The lithium-ion battery consists of a positive electrode, a negative electrode, an electrolyte, a separator, and some safety devices. The positive electrode is an electrode with a relatively high potential in a battery. During the charging process, lithium ions will detach from the positive electrode and embed into the negative electrode, which is very important for the battery. Many materials can be used as positive electrodes, such as LiCoO_2 , but the disadvantage is that cobalt is a relatively scarce metal at a higher price [2]. Unstable chemical reactions may occur under high-temperature conditions, reducing safety. For example, LiFePO_4 has poor performance at low temperatures and reduced charging and discharging efficiency, which limits its application in some cold regions [3]. Also, the charging speed is relatively slow. This article chooses nickel-rich layered oxide positive electrode material, which has many advantages, such as its material structure facilitating the transport of lithium ions, high specific capacity, and environmental friendliness. This article mainly discusses the application of lithium-rich layered oxides in LIBs, which is of great significance for the future development of LIBs.

2. Working Principle of LIBs

One of the most popular rechargeable batteries on the market today, LIBs offer an innovative and effective operating concept. To put it briefly, the primary mechanism behind the charging and discharging of lithium-ion batteries is the reversible migration of lithium ions between the positive and negative electrodes, which creates a reversible redox reaction system. The term "rocking chair batteries" (LIBs) accurately depicts the operational condition of lithium ions within the battery. Lithium ions travel from the positive electrode material to the negative electrode via the electrolyte

acting as a "bridge" and become incorporated in the negative electrode material lattice throughout the charging process. Concurrently, an electric current is created when electrons move via an external circuit from the positive electrode to the negative electrode. The battery can store electrical energy thanks to this mechanism. Lithium ions are de-embed from the negative material and return to the positive electrode through the electrolyte during discharging. At the same time, electrons move from the negative electrode back to the positive electrode via the external circuit, freeing electrical energy for the device's use. Lithium-ion batteries may be repeatedly charged and drained for usage because of the reversible migration of lithium ions between the positive and negative electrodes [4].

The charging and discharging process of LIBs is the reciprocating motion of lithium ions and electrons. When charging, power is applied to the battery so that the lithium ions and electrons follow different paths to the graphite layer; when discharging, the lithium ions and electrons return to the metal oxide side along the original path by applying a load. This process enables the conversion between electrical and chemical energy. Notably, materials such as electrolytes and barrier films are insulators for electrons. In this process, electrons do not move directly between the positive and negative electrodes but participate in the chemical reaction on the electrodes, as shown in Figure 1 [4].

The superior performance of LIBs is due to their unique structure and materials. Cathode materials typically contain reducible lithium salts, such as carbon-based cathodes, metal oxide cathodes, or polymer cathodes, which have good lithium-ion embedding and detachment capabilities. The anode materials are mainly covalent lithium materials, such as carbon or metal covalent lithium, which can hold large amounts of lithium ions and maintain structural stability. On the other hand, the electrolyte is an ionic conductor and an electronic insulator, which blocks the positive and negative electrodes of the battery and simultaneously provides a channel for lithium ions to migrate.

The principle of operation of LIBs not only determines their charging and discharging performance but also significantly impacts their safety and stability. Due to the relatively low mobility efficiency of lithium ions, the charging rate of a battery is limited by its physical properties. However, batteries' charging speed and energy density can be significantly enhanced by improving lithium ions' migration and embedding efficiency by improving positive and negative electrode materials and electrolytes. In addition, temperature control inside the battery is crucial, as temperature variations affect not only the dissipation behavior of LIBs but also the characteristics of the battery, such as capacity, thickness, repetition rate, volume, and total resistance.

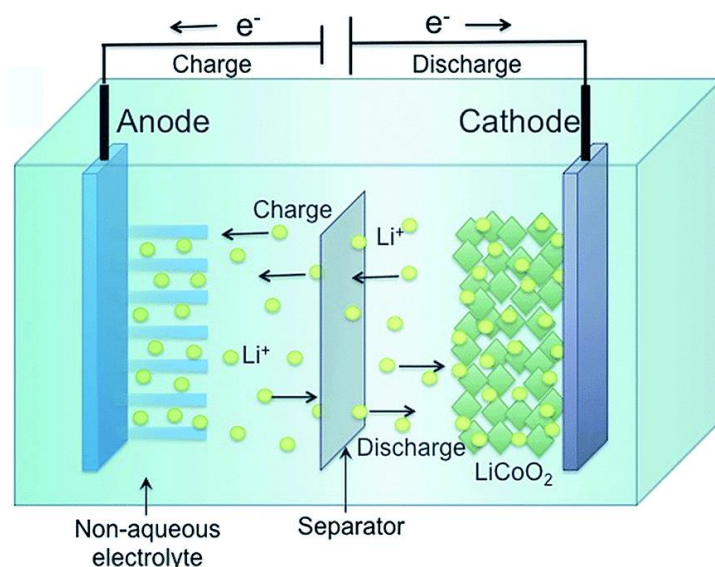


Figure 1. Working Principle of LIBs [4]

3. Structure and Properties of Nickel-Rich Layered Oxides

Figure 2 [5] illustrates the typical layered structure of the α -NaFeO₂ type for nickel-rich layered oxides, such as LiNi_xMyO₂, where x is typically more than 0.5, and M stands for additional transition metal elements like Co and Mn. This structure comprises stacks of rock salt layers that alternate between being filled by lithium ions and octahedral layers that are inhabited by oxygen and transition metal ions. Lithium ions present in the interlayers can be reversibly implanted and removed during charging and discharging. The predominant element in nickel-rich layered oxides is nickel, and adding more of it may significantly raise the battery's specific capacity. However, high nickel content also brings problems, such as poor cycling and thermal stability. Adding other transition metal (e.g., Co, Mn) elements can improve the material's cycling stability, thermal stability, and multiplicity performance. For instance, adding cobalt can increase the material's electrical conductivity, while adding manganese helps stabilize the material's structure. Scientists have created core-shell structures to improve the properties of layered oxides that are rich in nickel. A "Li-rich, Ni-rich core with high capacity and a "Li-rich, Mn-rich shell with outstanding structural stability" are the typical components of this structure. Lithium ions eventually penetrate the core-shell precursor during high-temperature lithiation processes, causing interdiffusion of elements across the interface between the nickel-rich core and the manganese-rich shell. After prolonged cycling, the layered Li-rich-Ni-rich core is guaranteed high structural reversibility because of this thermally forced interdiffusion of atoms, creating a Li-rich-Mn-rich shell of regulated thickness. The researchers enhanced the Ni-rich layered oxides' characteristics via doping, surface modification at the primary particle level, compositional gradient anode, morphological control techniques, and the core-shell structural design. These techniques successfully prevented the development of microcracks, enhanced the materials' cycle stability, and enhanced their multiple characteristics [6].

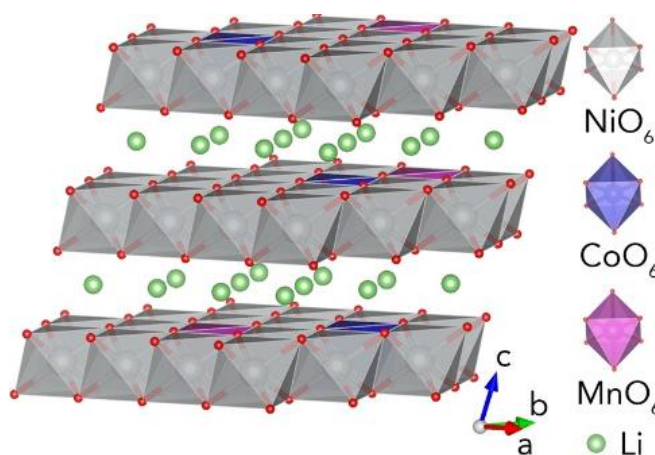


Figure 2. Structure of Nickel-Rich Layered Oxides [4]

4. Preparation of Nickel-Rich Layered Oxides

Lithium-ion batteries, as necessary energy conversion and storage devices, have demonstrated enormous promise for application in energy storage systems, electric cars, and other industries with the fast development of new energy technologies. Nickel-rich layered oxides have been a hot topic in contemporary study because of their excellent energy density and high specific capacity.

Co-precipitation is one of the most popular techniques for creating layered oxides that are rich in nickel. Transition metal ions such as nickel, cobalt, and manganese can precipitate simultaneously to produce a homogenous hydroxide or carbonate precursor by carefully regulating the reaction conditions and the ratio of metal salt solution to precipitant. Subsequently, the precursor is mixed with a lithium source and calcined at high temperatures to obtain the final nickel-rich layered oxide. The advantage of the co-precipitation method is that it can accurately regulate the composition and microstructure of the material, but the process is relatively complex and requires high equipment [7].

The sol-gel method is a preparation method based on forming metal alcohol salts or metal salts in organic solvents and then gelation, drying, and calcination to obtain the target product. In the preparation of nickel-rich layered oxides, metal salts such as nickel, cobalt, manganese, and lithium salts are usually dissolved in a suitable solvent, a complexing agent is added to form a sol, and then a gel is formed by evaporating the solvent by heating. Finally, the product is obtained by high-temperature calcination. The sol-gel method has the advantages of uniform mixing of raw materials, low reaction temperature, product purity, etc. Still, the process cycle is longer, and the cost is relatively high [8].

The hydrothermal synthesis method is used in high-temperature and high-pressure water solutions by reacting metal salts and alkali, which directly synthesizes nickel-rich layered oxide. This method has the characteristics of fast reaction speed, high crystallinity of the product, and can avoid the impurities that may be introduced in the traditional method. However, the hydrothermal synthesis method requires high equipment, and the reaction conditions are difficult to control accurately, so it is somewhat limited in practical application [8].

The spray drying method is a metal salt solution through the spray device atomization, in the high-temperature airflow rapid drying to get the precursor powder, and then mixed with the lithium source calcination preparation of nickel-rich layered oxide method. This method has the advantages of a simple process, high production efficiency, and uniform product particle size distribution. However, in the spray drying process, the droplets' drying speed and temperature significantly impact the product's performance, and the process parameters need to be controlled strictly.

In addition to several primary methods above, there are other methods for preparing nickel-rich layered oxides, such as solid-phase reaction, electrochemical deposition, and template methods. Each method has its characteristics, according to different application requirements, to prepare nickel-rich layered oxides with specific properties and structures.

5. Modification of Nickel-Rich Layered Oxides in LIBs

5.1. Ion Doping

Ion doping is a standard modification method that can improve the material's lattice energy to stabilize the crystal structure. Suitable ion doping can help to reduce the degree of cation mixing in the material, suppress the Jahn-Teller effect, maintain the structural stability of the material, and effectively improve the electrochemical properties of the material [9]. Ion doping comes in three primary forms: multi-element co-doping, anion doping, and cation doping. Figure 3 illustrates how F-doped anode materials were created by Kim et al. [10] via a solid phase process. It was discovered that changing the oxygen location from F to F could strengthen the link between F and the transition metal, improve structural stability, and prevent phase transition. Furthermore, replacing F⁻ at the oxygen position reduces a portion of the transition metal, raising the ionic radius and increasing lithium ions' diffusion coefficient, leading to better cycling performance at high current densities.

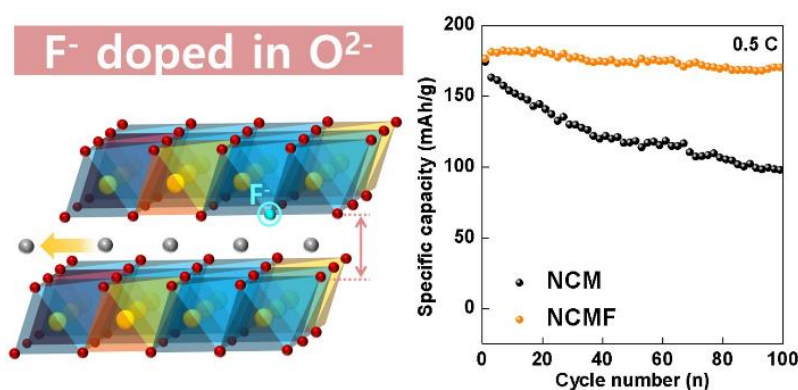


Figure 3. Structure of fluorine-doped $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ [9]

5.2. Surface Capping

To provide a physical barrier that prevents direct contact between the cathode material and electrolyte and efficiently inhibits side reactions, surface capping refers to the uniform capping of a layer of thick inert material on the surface of the cathode material. One may categorize the capping materials into oxides, fluorides, phosphates, lithium, etc. Materials for oxide capping are the most often used. Oxide capping materials are the most common, and they can significantly improve cycling performance and thermal stability. In contrast, fluoride capping materials can resist HF corrosion and avoid the destruction of cathode materials, and the capping layer can also effectively mitigate the deterioration of the structure [11]. Liu et al. [12] prepared $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cathode materials capped with SnO_2 and Li_2SnO_3 by sol-gel and solvothermal methods. It was concluded that both SnO_2 and Li_2SnO_3 coatings could effectively inhibit the side reactions at the cathode/electrolyte interface, reduce the interfacial resistance, and enhance the migration of lithium ions at the cathode/electrolyte interface.

5.3. Core-Shell Structure and Concentration Gradient

Recently, concentration gradients and core-shell structures have become popular study subjects. In general, the core-shell structure refers to coating the surface of nickel-rich materials with materials that have high electrochemical characteristics to increase the durability of cathode materials. It is discovered that the electrochemical performance is significantly impacted by the poorly combined core-shell structure, which leads to fractures appearing soon after several cycles. The steady rise in Mn content from the inside to the outside of the cathode material and the gradual reduction in Ni content from the inside to the outside of the cathode particles are called concentration gradients. The rise of Mn ion content on the surface can improve the stability of the material, and the performance of the material prepared by core-shell structure and concentration gradient is better. Still, the process is more complicated and less efficient. Wu et al. [13] prepared $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ with a core-shell structure using $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$, which has a high nickel content in the core and a high manganese content on the surface. It was found that the cathode material prepared with the ratio of $\text{C}_4\text{H}_8\text{N}_2\text{O}_2$ to Ni of 0.03:1 maintained a discharge capacity of 100 mAh/g after 500 cycles at 5 C and a voltage range of 3.0–4.5 V, which was much higher than that of the original $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode material of 60 mAh/g, and the core-shell structure had a better performance under the conditions of high diversity and high temperature. The core-shell structure also performed better under high diversity and temperature conditions. At the same time, the core-shell structure also has better electrochemical performance at high diversity and temperature.

6. Conclusion

Because of their high specific capacity and energy density, nickel-rich layered oxides have garnered significant interest as cathode materials. However, such materials have certain intrinsic drawbacks, such as structural instability and cycle capacity degradation. This work summarizes many approaches to these problems through modification, such as surface coating, elemental doping, and core-shell structure.

To improve LIBs' electrochemical performance, elemental doping can alter the materials' chemical stability, electrical structure, and crystal structure. Nonetheless, the doping impact of distinct elements differs and can have intricate consequences on the electrical and crystal structures of the materials, making precise predictions challenging. To provide a scientific foundation for choosing doping elements and regulating doping concentration, we should further our understanding of how doping elements affect material qualities in the future by theoretical computations and experimental confirmation.

A small coating layer may not sufficiently insulate the active material from direct contact with the electrolyte, leading to a poor modification effect; a thick coating layer may impede the transfer of lithium ions and lower the multiplicity performance of the material. To accurately manage the

thickness of the coating layer while balancing the demands for interfacial protection and lithium-ion transport, researchers must improve the coating process parameters. Chemical bonding and interfacial reactions are simultaneously introduced to strengthen the bonding between the cladding layer and the base material to increase the stability of the cladding layer.

The design of the core-shell structure is further complicated by the need to carefully consider the morphology, structure, composition, and other characteristics of the core-shell material. Furthermore, the core-shell contact may alter throughout the cycling process, which might impact the material's long-term stability. To accomplish the accurate design of the core-shell structure, future research should primarily focus on optimizing the core-shell materials' composition, structure, and morphology. With the continuous progress of science and technology and in-depth research, it is believed that the application of nickel-rich layered oxides in LIBs will have a broader prospect.

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