Advances in the Application of Lithium-Rich Oxide Materials in Lithium-ion Battery Cathodes

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Abstract. With the rapid growth of global energy demand and the increasing awareness of environmental protection, the development of efficient, safe, and environmentally friendly energy storage systems has become one of the hotspots in today's science and technology fields. Lithium-ion batteries (LIBs) have shown great potential for application in portable electronic devices, electric vehicles, and large-scale energy storage due to their high energy density, low self-discharge rate, and long cycle life. However, with the continuous technological advancement and expanding market, the requirements for the performance of LIBs are increasing, especially in terms of energy density and cycle stability. Li-rich oxides as cathode materials for Li-ion batteries are not only capable of releasing a large amount of lithium ions during charging, providing a much higher specific capacity than traditional cathode materials, but also have less reactive oxygen involved in the reaction in their layered structure, which helps to maintain the cycling stability and average operating voltage of the materials, thus extending the service life of the batteries and improving the overall performance. In this paper, we first explore the effects of the layered and disordered structures in the crystal structure of Li-rich oxides on the performance of LIBs. Then, the paper summarizes the problems of Li-rich oxides. Finally, two methods, ion doping, and surface capping, are proposed to improve the performance of Li-rich oxides.

Keywords: Lithium-rich oxides, cathodes, crystal structure, modification.

1. Introduction

In the global energy transition and sustainable development context, efficient, clean, and renewable energy storage technology has become critical for social progress and industrial upgrading. As the core representative of modern energy storage technology, lithium-ion batteries, with their high energy density, long cycle life, low self-discharge, and environmentally friendly characteristics, have demonstrated unrivaled application advantages in many fields, such as portable electronic devices, electric vehicles, smart grids, and energy storage systems. However, with the continuous expansion of application scenarios and the increasing demand for performance, the limitations of traditional lithium-ion battery cathode materials have gradually appeared, especially in terms of energy density and cycling stability, which are challenging to meet the future demand for high-energy, long-life battery systems [1]. Therefore, developing new high-performance anode materials has become a hot and challenging issue in lithium-ion battery research.

Lithium-rich oxides, a new type of cathode material with unique chemical composition and structural properties, have attracted wide attention since their introduction. These materials usually include layered lithium-rich manganese oxides, such as $xLi_2MnO_3\cdot(1\text{-}x)LiMO_2$ (M is transition metal elements such as Ni, Co, Mn, etc.) and $Li_{1+x}M_{1-x}O_2$, etc., which are not only rich in lithium resources but also capable of releasing lithium ions far exceeding those of conventional materials during charging and discharging, thus realizing a higher specific capacity [2,3]. This characteristic is of great significance for improving the energy density of lithium-ion batteries, which is expected to provide strong support for the long-distance driving of electric vehicles and the long-time power supply of large-scale energy storage systems.

2. Structures of Lithium-Rich Oxides

2.1. Layered Structure

The layered structure is one of lithium-rich oxides' most remarkable structural features. Lithium, oxygen, and transition metal layers are arranged in alternating layers to form a stable layered framework in this structure. This unique arrangement allows lithium ions to diffuse freely between the layers, thus giving lithium-rich oxides excellent ionic conductivity and lithium storage capacity. At the same time, less reactive oxygen in the layered structure is involved in the reaction, which helps to maintain the cycling stability and average operating voltage of the materials [4].

There are some benefits to the layered structure. First, it facilitates the movement of lithium ions during electrochemical cycling, which is crucial for lithium-ion batteries. Lithium ions can travel swiftly through the channels between the layers, enabling rapid charging and discharging. Second, the layered structure has a high specific capacity due to its large capacity to hold lithium ions. These materials' capacity is raised by the layers of the structure that are rich in lithium. The layered structure does, however, also come with some difficulties. A significant problem is structural instability. Phase shifts and degradation of the layered structure can occur during cycling, eventually reducing capacity and subpar cycling performance. Various approaches are used to address these issues. Doping with additional elements, for instance, can increase structural stability and enhance electrochemical performance. Additionally, surface coatings can strengthen the material's strength and prevent deterioration.

2.2. Disordered Structure

Lithium-rich oxides often have a certain degree of structural disorder. This disorder can manifest in different ways. For instance, the crystal lattice may have a random distribution of lithium and transition metal ions. The oxygen framework may also be somewhat distorted and irregular.

A disordered structure in lithium-rich oxides can have positive and negative effects. On one hand, it can improve the electrochemical performance in some ways. The disorder can provide more places for lithium ions to go and make it easier for them to move, resulting in higher capacity and better rate capability. On the other hand, the disordered structure can also cause problems. It can make the structure less stable and make it difficult to accurately predict and control the electrochemical behavior. The irregularity in the structure can also affect the durability over multiple cycles and the reliability of the material [5].

Researchers are investigating the disordered structure of lithium-rich oxides to understand their origin and how they affect the material. Advanced techniques such as X-ray diffraction, neutron scattering, and electron microscopy are used to examine the atomic-level details of the disorder. By understanding the disordered structure, people can find ways to improve lithium-rich oxides and utilize their potential for advanced energy storage and other applications.

3. Challenges for Lithium-Rich Oxides

3.1. Large First-Time Irreversible Capacity

The large irreversible capacity in the first cycle is a significant problem for lithium-rich oxides. When these materials go through their first charge-discharge process, they often lose a considerable amount of capacity that cannot be recovered. There are a few reasons for this. One main reason is the formation of an SEI layer. When a battery is charged for the first time, the electrolyte reacts with the surface of the electrode material and forms an SEI layer. This uses up some lithium ions and causes irreversible capacity loss. Another reason is the irreversible oxidation of oxygen in the lattice. In lithium-rich oxides, oxygen can be oxidized during the first charge, but this process is often not completely reversible, so we lose capacity. Research shows that lithium-rich oxides have a big problem with sizeable irreversible capacity in the first cycle. Their study finds that forming the SEI layer and the irreversible oxidation of oxygen contribute to this significant initial capacity loss [6].

3.2. Fast Voltage Decay

The rapid voltage decay is another major challenge for lithium-rich oxides. During the charge-discharge cycles, the voltage of lithium-rich oxides often drops quickly. This can be due to several factors. One main reason is the structural instability of lithium-rich oxides. As the battery is cycled, the crystal structure of the material can change in various ways, such as having phase transitions and the migration of transition metal ions. These structural changes can lead to a decrease in the electrochemical potential and, thus, the voltage decay. For example, research shows that lithium-rich oxides do indeed have rapid voltage decay. Their study finds that structural changes and oxygen redox reactions play important roles in the voltage decay [6].

3.3. Poor Rate Performance

The poor rate performance is also a significant problem for lithium-rich oxides. Lithium-rich oxides often have difficulty performing well at high charge and discharge rates. This is mainly because the diffusion of lithium ions is slow, and complex electrochemical reactions are occurring. The complex crystal structure of lithium-rich oxides can prevent the rapid movement of lithium ions, resulting in limited rate capabilities. For instance, research shows that lithium-rich oxides have poor rate performance. Their study finds that as the current density increases, the capacity of the material drops significantly, indicating the difficulty in achieving high-rate charging and discharging. And they also find a way to improve the rate performance [4].

4. Modification of Lithium-Rich Oxides

4.1. Ion Doping

Ion doping modification refers to introducing a small amount of other metal or non-metal ions into the lattice of lithium-rich oxides to achieve the modulation of the structure and properties of the material by replacing the original ions or occupying the lattice gap positions. Dopant ions can improve the electrochemical properties of lithium-rich oxides by affecting the lattice parameters, electronic structure, and ion transport channels of the material. Specifically, doping ions can stabilize the crystal structure of the material, inhibit the migration of transition metal ions, increase the diffusion rate of lithium ions, and enhance the redox reversibility of oxygen.

Transition metal ions such as cobalt, nickel, and manganese are often used in the doping modification of lithium-rich oxides. These ions can replace the position of the original transition metal ions and improve the conductivity and ion mobility of the material by modulating the electronic structure of the transition metal layer. Alkaline earth metal ions such as barium and magnesium are also used in the doping modification of lithium-rich oxides. These ions usually have a large ionic radius, which can stabilize the peroxide and superoxide anions in lithium-rich oxides and reduce the oxygen precipitation reaction, thus improving the first-loop Coulombic efficiency and cyclic stability of the materials. In addition, non-metallic ions such as fluorine and chlorine can replace the position of oxygen ions and improve the capacity and multiplicity performance of the material by modulating the anion redox reaction of the material.

Li et al. fabricated an Al-rich surface mixed-arrangement layer on the LMR surface using a liquid-phase method to improve the performance of the material. Al^{3+} doping resulted in the formation of Al-O covalent bonds with O near the surface to lower the oxygen oxidation potential and improve the reversibility of the involvement of surface oxygen in redox reactions. The electrochemical test results showed that the modified material could reach a discharge capacity of 305 mAh/g in the first week, and the Coulombic efficiency was increased to 91% in the first week. In addition, cyclic voltammetry curves show that Al surface doping helps to reduce the onset potential of oxygen valorization and alleviate the voltage hysteresis caused by oxygen valorization. The capacity retention after 100 weeks of cycling is 87.4% at 1C multiplicity, and the voltage decay is also much lower than that of the undoped material [7].

4.2. Surface Coating

Applying a surface coating has demonstrated numerous benefits in enhancing material characteristics. Currently, surface coating primarily consists of the following aspects.

Initially, applying a surface coating can greatly enhance the stability of materials. For instance, in certain electrode materials, applying a layer of stabilized oxide or polymer material on the surface can avoid the unwanted side reaction between the electrode material and the electrolyte. This aids in preserving the structural integrity of the electrode material and mitigates the deterioration of material performance caused by side reactions during charge/discharge cycles.

Second, the coating might improve the material's conductivity. By covering some active materials, which are inherently less conductive, with a coating of highly conductive carbon material, it is possible to produce an extremely effective electron transport channel. This improves the performance of the battery multiplier and enables the battery to function properly even when charging and discharging at high current levels by increasing the material's electron transfer rate throughout the charge and discharge process [8].

Additionally, surface coating has the ability to control a material's interfacial characteristics. One way to modify interfacial properties is by applying a certain functional material on the surface of particular nanomaterials. This can alter the material's wettability and surface energy. This not only makes the material easier to disperse in a particular medium but also enhances the material's interfacial compatibility with other components, enhancing the material's overall performance in real-world applications.

4.2.1. Carbon Coating

Carbon coatings are often used to modify lithium-rich oxides. Carbon coatings can enhance the conductivity and structural stability of lithium-rich oxides [9]. The carbon layer acts as a protective barrier to prevent direct interaction between the active material and the electrolyte and also reduces side reactions. This improves cycling stability and reduces voltage decay. The benefits of applying carbon coatings in lithium-ion batteries include improved electrical conductivity for increased rate capability and minimized side reactions for improved cycling stability [7]. In conclusion, carbon coating shows potential as a modification technique for lithium-rich oxides. It has the ability to address some of the hurdles encountered with these materials and enhance their functionality for potential application in lithium-ion batteries.

4.2.2. Oxide Coating

Oxide coating is a commonly used technique for lithium-rich oxides. Adding an oxide coating can improve the stability and electrochemical performance of lithium-rich oxides. An oxide coating on the surface prevents direct interaction between the active material and the electrolyte, thus reducing side reactions and improving cycling stability [10]. The efficiency of lithium-sulfur batteries can be improved by using reduced graphene oxide as a coating. This further highlights the potential of oxide coatings to enhance the electrochemical properties of different battery materials. In conclusion, the application of oxide coatings is a successful technique for the modification of lithium-rich oxides. It can address some of the obstacles encountered with these materials and increase their efficacy for potential applications in lithium-ion batteries.

5. Conclusion

Among LIBs, lithium-rich oxides have attracted much attention as cathode materials due to their advantages of high energy density and low cost. However, lithium-rich oxides still face many challenges in practical applications, such as large reversible capacity loss in the first charge/discharge, voltage and capacity decay, and poor cycling stability. To address these issues, this paper introduces two commonly used modification means, including: ion doping modification and surface coating modification.

Ion doping can regulate the lattice structure of lithium-rich oxides by introducing foreign ions to form more stable compounds. This helps to reduce changes in the lattice structure during charging and discharging, thereby improving cycling stability. However, its effect is often limited, and it is difficult to completely solve the problems existing in lithium-rich oxides. The modification mechanism of ion doping is complex, involving lattice structure, electronic structure, ion migration, and other aspects, which have not been fully elucidated yet. In the future, the mechanism of the influence of ion doping on the electrochemical performance of lithium-rich oxides should be studied in depth by means of theoretical calculations and experimental validation to provide theoretical guidance for the optimization of the doping process.

Surface coating can form a protective layer on the surface of the lithium-rich oxide particles, preventing direct contact between the active substance and the electrolyte and reducing the occurrence of side reactions, thus improving cycling stability. It can also be used as a fast channel for lithium ion transport to increase the diffusion rate of lithium ions, thus improving the multiplicity performance of the battery. However, the uniformity of the cladding layer is often difficult to ensure, resulting in inconsistent modification effects. Future research should improve the uniformity of the cladding layer and the interfacial bonding between the cladding layer and the substrate material by enhancing the cladding process to ensure the consistency of the modification effect. In addition, more kinds of capping materials should be explored, and the influence mechanism of different capping materials on the electrochemical performance of Li-rich oxides should be studied in depth to provide theoretical guidance for selecting the best capping materials.

It is believed that with the development of science and technology, the electrochemical performance of lithium-rich oxides can be further improved to promote their wide application in LIBs.

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