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Li-Rich Manganese-Based Cathodes for Lithium-Ion Batteries

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Abstract. High-energy-density lithium-ion batteries have been in high demand and this has led to a lot of research on the advanced cathode materials. Li-Rich Manganese-Based Cathodes are also a promising candidate due to their ultrahigh reversible capacity, which is attributed to the co-participation of transition-metal cations and lattice oxygen anions in charge compensation, as well as low cost and rich manganese resources. Nonetheless, there are three inherent difficulties that greatly impede their practical application: low initial Coulombic efficiency due to irreversible oxygen release during first activation, severe voltage decay caused by layered-to-spinel phase transformation during cycling, and poor interfacial stability due to electrolyte oxidative decomposition and resistive cathode electrolyte interphase formation at high operating voltages. To solve these problems, three mainstream modification approaches have been developed simultaneously: element doping targets bulk structural degradation via lattice stabilization and oxygen release suppression and transition-metal migration; surface coating with inert layers like Al_2O_3, TiO_2, phosphate, fluoride etc. operates at the electrode-electrolyte interface to physically prevent side reactions; electrolyte additives control in-situ CEI formation to stabilize interfacial layer. It is stressed here that only simultaneous inhibition of oxygen release, phase transformation and high-voltage interfacial side reactions can convert the inherent capacity advantage of Li-Rich Manganese-Based Cathodes into practical energy density. Future works should focus on coupled bulk and interfacial regulation strategies, followed by systematic full-cell validation to promote their practical application.

Keywords: lithium-ion batteries, lithium-rich manganese-based cathodes, high capacity, voltage decay, surface coating

1. Introduction

The lithium-ion battery has been under the necessity of further development with regard to its higher energy density and reduced cost due to the high speed growth of the electric vehicles and large-scale storage systems. The need to shift the world towards low-carbon energy systems has put a tremendous pressure on electrochemical power storage technologies. In the case of electric cars, batteries are needed to be longer driving distances and quicker charging, and in the case of grid scale storage solutions, renewable energy integration is required to have an affordable and long-lasting

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solution. These demands of applications have driven traditional chemistry of lithium-ion batteries to their actual limits of performance.

The existing cathode materials of the commercial sector are obvious to be blocked. Nickel based ternary cathodes are dependent on limited sources of cobalt and nickel that result in expensive manufacturing costs and the risk of supply. The price of the raw material (cobalt, nickel) is unstable and the geopolitical issues associated with its production are also a threat to the long-term development of the production of nickel-rich cathodes. Lithium iron phosphate cathodes have very good stability and safety features however they do not have high specific capacity which limits the improvement of the battery energy density. This is also due to the low voltage of lithium iron phosphate which is relatively lower to meet the energy density demand of electric vehicles of the future. Consequently, it has become a vital research topic in the battery area to produce new cathode substances that will be capable of having both high capacity and low cost as well as large reserves of elements.

Li-Rich Manganese-Based Cathodes is a promising cathode material of the next generation that has been researched with great interest as it has the potential to have high capacity and resource benefits. Unlike traditional cathode materials, which can be used only in the form of cation redox, Li-Rich Manganese-Based Cathodes are superior in terms of capacity since both transition metal cations and lattice oxygen anions take part in charge compensation [1]. The dual redox reaction allows this material to hold more than twice the amount of charge compared to the normal cathodes where the valence change of the transition-metal alone occurs. In the meantime, the manganese-based composition significantly decreases the cost of the material and enhances its sustainability. One of the most prevalent transition metals found on the Earth crust is manganese, and the availability of the element across the globe ensures that the supply chain issues that were associated with cobalt and nickel will not occur. However, their commercialization is also limited by many defects, such as low initial Coulombic efficiency, constant voltage loss over time, and electrode-electrolyte interface instability.

These issues are interconnected and will have a negative impact on the practical application of this material. The main features, shortcomings and common ways to change Li-Rich Manganese-Based Cathodes in their nature were summarized in the present paper, which is aimed at giving an insight into the current state of the art and future development of the field.

2. Basic properties of Li-Rich Manganese-Based Cathodes

2.1. Ultrahigh capacity potential

The main benefit of Li-Rich Manganese-Based Cathodes is that they have the capacity to be extremely high in their reversibility as compared with other cathode materials which are used in layers [2]. This capacity advantage is a milestone and a breakthrough in relation to the conventional chemistries of cathodes, and it is also the main reason why this area has been researched so much. The co-redox process between transition metal cations and lattice oxygen anions are unique and thus overcome the limit of capacity of the traditional single cation redox reaction system making the material capable of having good energy storage ability. In normal layered cathodes, the only charge compensation mechanism occurs via valence variation of the ions of transition metals, and hence, there is a theoretical maximum amount of lithium that can be extracted and inserted into the cathode. Li-Rich Manganese-Based Cathodes solve this problem by participating in the charge compensation reaction using the lattice oxygen and consequently, extracting more lithium and increasing the reversible capacity.

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The two-phase redox nature of Li-Rich Manganese-Based Cathodes is also shown by the charging process, in which transition-metal cations are oxidized first and then lattice oxygen is activated at higher voltages. The dual nature of the cathode is a high charge capacity as it has anion and cationic oxidation reactions. As both cationic and anionic redox centres can be used to store more charges per unit mass than those cathodes that use only one redox centre, the Li-Rich Manganese-Based Cathodes have the potential of storing more charge per unit mass. This property of dual redox is the basis of application of the Li-Rich Manganese-Based Cathodes to lithium-ion batteries with a high energy density and thus it is considered as one of the most promising technologies in the field of battery systems of the future.These can be seen in Figure 1.

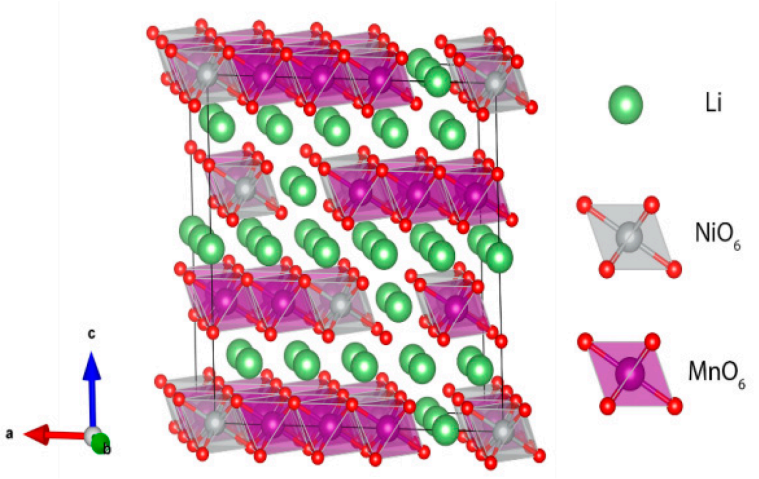


Figure 1. Li-Rich Manganese Cathodes of the crystal structure, where the atoms are arranged in layers and they are Li, transition metal and oxygen [3]

2.2. Abundant manganese resources and low cost

The Manganese-Based Cathodes of Li-Rich are a manganese-based system, low in cobalt and nickel. This is an economic as well as strategic benefit of the composition. The element of manganese has been found to be easily found in nature with high reserves and low cost that can be used to prevent the threat of price increase and shortage of resources caused by the precious metals [1]. Manganese deposits are not located within few countries as in the case of cobalt but rather spread across several continents and can be mined under relatively cheap conditions. Due to the stability of supply and predictable prices of manganese, it is suitable to be used as a base material of large battery production.

Li-Rich Manganese-Based Cathodes have an excellent price and environmental performance in comparison to nickel-rich ternary materials. The fact that the amount of cobalt and nickel is not so much needed directly affects the cost of raw material per unit battery capacity, which is a critical issue in mass production of electric vehicles and storage systems of energy in a stationary form. In addition, manganese chemistry has lower toxicity as well as higher environmental compatibility than cobalt-based chemistry, and this can be seen as being more environmentally friendly with the current focus on sustainable battery production and recycling. Li-Rich Manganese-Based Cathodes are promising due to their low-cost, high-capacity, and manganese-rich nature, but only if the limitations of its performance can be mitigated in order to achieve a high-energy application. The advantage of these resources also enables the sustainability of supply chains of batteries over the long-term,

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because the geopolitical risks associated with the supply chain of the electric vehicle industry are currently very high.

3. Main inherent problems

3.1. Low initial Coulombic efficiency

Low initial Coulombic efficiency is a common failure of Li-Rich Manganese-Based Cathodes and one of the greatest impediments to its practical use. The first Coulombic efficiency indicates the percentage of charge removed in the first charge that can be reversibly retrieved in the next discharge. In the case of Li-Rich Manganese-Based Cathodes, this efficiency is much lower than that of conventional layered cathodes, i.e., most of the lithium extracted during the initial cycle cannot be reinserted. Partial lattice oxygen is irreversibly oxidized and lost as oxygen gas during the initial high-voltage activation process, leading to irreversible capacity loss [4]. Most of the oxygen release takes place during the high-voltage part of the first charge and is directly related to the activation of the lithium-rich component in the material.

To achieve the maximum energy density of Li-Rich Manganese-Based Cathodes, it is necessary to increase the initial Coulombic efficiency.

3.2. Severe voltage decay during cycling

The long-term cycling of Li-Rich Manganese-Based Cathodes is also associated with severe voltage decay behavior that directly undermines the energy density benefit of the material [5-7]. Voltage decay is a phenomenon in which the average discharge voltage reduces gradually with the increase in number of cycles and it is especially strong in Li-Rich Manganese-Based Cathodes as compared to conventional cathode materials. Since the capacity and voltage are both factors contributing to the energy density of a battery, the constant reduction in operating voltage will reduce the energy-density advantage despite the relative stability of the discharge capacity. This renders voltage decay among the most harmful failure modes in practical applications.

The root cause of the voltage degradation is that the spontaneous irreversible phase transition of the layered structure to spinel and rock-salt structures occurs. The process of deintercalation of lithium ions in a repeated manner causes an unceasing movement of the transition metal ions, which ruins the stable lattice structure of the original layer [5]. The local stresses and structural distortions are created as the result of the removal and insertion of the lithium ions during each charge-discharge cycle, and these stresses and distortions serve as the driving force of the migration of transition-metal ions. With time passing, the ions migrate and then restructure the crystal structure locally, forming gradually the initial layered form into spinel like and ultimately rock salt like regions. Such change of structure tends to begin at the particle surface and grain boundaries where the defects in the structure and stress are localized, and later on it spreads towards the interior of the particle. This electrochemical reaction mechanism is altered by the gradual degradation of the structure leading to the loss of the voltage platform and constant decline in the average discharge voltage.

The spinel and rock-salt phases have different redox potentials and Li^+ transport properties compared to the original layered phase, and thus directly contribute to the observed voltage decay.

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3.3. Poor interfacial stability

Li-rich manganese-based cathodes operate at high cutoff voltages that readily induce severe oxidative decomposition of carbonate electrolytes [8]. The high operating voltage necessary for activating the anionic redox process generates a highly oxidizing condition at the cathode surface well beyond the electrochemical stability window of typical carbonate based electrolytes. In such conditions, electrolyte solvents are constantly oxidized to give a wide range of decomposition products that build up on the material surface. Continuous side reactions yield a thick and highly resistive cathode electrolyte interphase (CEI) on the material surface. In contrast to the solid electrolyte interphase on graphite anodes that is typically thought to be beneficial to protect the anode, the CEI formed on high-voltage cathodes is often unstable, electronically insulating and ionically resistive.

The unstable CEI film enhances charge transfer impedance and uses active lithium, which leads to constant capacity fading when cycling [8, 9]. The thicker the CEI layer becomes as a result of cycling, the harder it is for lithium ions to pass through, increasing the interfacial resistance and decreasing the rate capability of the electrode. The ongoing expansion of the CEI also depletes the finite amount of lithium inventory in the electrolyte and cathode, which further exhausts the active lithium that can be reversibly cycled. Besides, the decomposition of the electrolyte forms acidic products that corrode the surface of the cathode, promote transition metal dissolution, and further enhance interfacial and structural degradation. The dissolved transition-metal ions may diffuse into the electrolyte and deposit on the anode leading to more side reactions and loss of capacity at the negative electrode. Indirectly, sluggish diffusion kinetics of lithium-ions in the material also affects the overall electrochemical performance since slow transport of ions in the bulk material enhances concentration polarization and reduces the rate capability.

These interface issues in addition to the bulk structural problems form a complicated degradation network that can only be solved by comprehensive modification plans.

4. Common modification strategies

Three mainstream modification methods are widely adopted to solve the above problems of Li-Rich Manganese-Based Cathodes. These methods include element doping, surface coating, and electrolyte additive engineering. Each strategy targets a different aspect of the degradation process. Their mechanisms of action are complementary rather than mutually exclusive. Element doping operates at the bulk lattice level to improve structural stability. Surface coating provides physical protection at the particle surface. Electrolyte additives regulate the chemical environment at the electrode–electrolyte interface. The specific advantages and limitations of each method are summarized in Table 1.

Table 1. A comparison of three popular modification strategies

Modification Method	Core Advantages	Main Limitations
Element Doping	Doping of cations (Mg^{2+} and Zr^{4+}) will stabilize the lattice and prevent phase transition and migration of transition metals [10]. F^- is anionic doping, which takes the place of oxygen in the lattice to minimize the release of irreversible oxygen; P^{5+} -cation doping maximizes the bonding of lattices and structural stability. Successfully relieves low efficiency at the start as well as voltage degradation.	Over doping lowers active sites and specific capacity. Non-uniform doping causes unstable modification effects.

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Table 1. (continued)

Surface Coating	To physically isolate electrolyte contact, inert protective layers of Al_2O_3, TiO_2, phosphate and fluoride are applied on the material surface [11, 12]. It prevents interfacial side reactions and dissolution of transition metals, maximizes CEI film state, and enhances cycling stability.	Too thick coating enhances the lithium-ion diffusion resistance and degrades rate performance, while too thin or uneven coating cannot provide long-term protection.
Electrolyte Additives	Functional additives selectively oxidize to produce dense and conductive CEI film in situ, which stabilizes the cathode interface and inhibits further electrolyte decomposition [8]. It is a low-cost strategy and it can be used in industrial production.	Only improves interfacial properties and cannot fundamentally solve bulk structural degradation. Overuse of additives enhances the viscosity of electrolytes and decreases ionic conductivity.

As shown in Table 1, the three modification strategies target different failure mechanisms of Li-Rich Manganese-Based Cathodes. Element doping primarily addresses bulk structural issues. It effectively improves low initial Coulombic efficiency by suppressing irreversible oxygen release. It also mitigates voltage decay by inhibiting transition metal migration and layered-to-spinel phase transition. Foreign atoms are introduced into the lattice through doping. These atoms strengthen the metal–oxygen bonds and reduce the mobility of transition-metal ions. The layered structure is thereby stabilized against degradation processes that occur during cycling. Surface coating and electrolyte additives, in contrast, mainly focus on interfacial stability. Surface coating provides a physical barrier to isolate the active material from the electrolyte. Electrolyte additives regulate the in situ formation of a stable CEI film. Both approaches reduce interfacial side reactions, transition metal dissolution, and CEI-related impedance growth. They thereby enhance cycling performance.

The selection of an appropriate modification strategy depends on the specific performance limitation that needs to be addressed. Element doping is often the most effective approach for materials suffering primarily from low initial Coulombic efficiency and severe voltage decay. This is because it directly targets the bulk structural origins of these problems. Surface coating or electrolyte additives may be more suitable for materials with good bulk stability but poor interfacial performance. These approaches protect the surface without altering the favorable bulk properties. The degradation of Li-Rich Manganese-Based Cathodes involves coupled bulk and interfacial processes. Given this coupling, the combination of element doping with surface coating or electrolyte engineering represents a rational direction. This direction can achieve comprehensive performance optimization [7, 11]. Such synergistic approaches simultaneously address multiple degradation pathways. They are increasingly recognized as the most promising route toward practical application.

5. Conclusion

Li-Rich Manganese-Based Cathodes are highly promising next-generation cathode materials for high-energy-density lithium-ion batteries. They deliver ultrahigh reversible capacity. This capacity comes from the co-participation of transition-metal cations and lattice oxygen anions in charge compensation. They also offer low cost and abundant manganese reserves.

However, three inherent challenges hinder their practical deployment. First, low initial Coulombic efficiency arises from irreversible oxygen release during the first activation. Second, severe voltage decay originates from layered-to-spinel phase transformation during cycling. Third,

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poor interfacial stability results from electrolyte oxidative decomposition and resistive CEI formation at high operating voltages.

Three mainstream modification strategies have been developed to address these issues, each targeting a specific problem at a distinct location. Element doping addresses bulk structural degradation. It stabilizes the lattice and suppresses oxygen release and transition-metal migration. Surface coating targets interfacial side reactions at the electrode–electrolyte boundary. It uses inert layers such as Al_2O_3, TiO_2, phosphate, and fluoride to physically isolate the active material. Electrolyte additives regulate CEI formation at the interface. They promote a dense, ion-conductive interfacial film in situ.

Only by simultaneously inhibiting oxygen release, phase transformation, and high-voltage interfacial side reactions can the intrinsic capacity advantage of Li-Rich Manganese-Based Cathodes be translated into usable energy density. Future efforts should focus on the rational combination of these strategies. In-depth mechanistic studies and full-cell validation are also needed. These advances will accelerate the commercialization of Li-Rich Manganese-Based Cathodes.

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