Different cathode materials for lithium-ion batteries

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Abstract. Due to the increasing need for electronic products like smartphones and electric vehicles, lithium-ion battery research has long been a prominent field of study. Lithium-ion batteries are a growing battery technology that is widely used in industries such as power, electronic equipment, communication, civil aviation, and the military as an efficient, dependable, and long-lasting energy storage system. Lithium-ion batteries' cathode materials are an essential component, and how well they function has a significant impact on how well and how long the battery will survive. Based on their structural characteristics, layered rock salt, spinel, and olivine are the three major types of materials used to create cathodes. Each structure has a unique arrangement that gives the matching materials a varied performance. To serve as a guide for choosing cathode materials for the next lithium-ion batteries, this article discusses the research progress of cathode materials with various architectures based on these three structures and analyzes their benefits and drawbacks.

Keywords: Lithium-ion batteries, cathode materials, structural characteristics.

1. Introduction

The use of non-renewable resources such as oil to meet our energy demands has long been accepted [1]. However, with the increasing severity of the energy crisis, it is becoming more crucial than ever to develop new methods of energy storage that can help preserve these limited fossil fuel resources. Fortunately, significant progress has been made in the field of electrochemical energy storage, and one notable advancement is the introduction of lithium-ion batteries (LIBs).

Recent studies have showcased promising developments in the field of energy storage, thanks to LIBs. These batteries, with their high voltage and capacity, are widely utilized in various devices including phones, torches, and electric cars. Cathodes, anodes, electrolytes, and diaphragms are the typical components of LIBs. In particular, cathode materials, which are a significant component, play a crucial function in LIBs by delivering lithium ions for the electrolytes. However, the ingredients of cathodes still have shortages such as low stability and high cost. Even though there are lots of options to make up these cathodes, each active compound has its unique steric configuration and element which leads to disparate properties.

The cathodes in LIBs play a vital role in facilitating the movement of lithium ions through the electrolyte. However, cathode materials still have certain limitations, such as low stability and high cost. While there are numerous options for cathode compositions, each active compound possesses its unique structural configuration and elemental makeup, leading to distinct properties. For the lithium ions to move from the cathode to the anode, creating an electric current, there must be a potential difference between the two poles of the LIB. Various materials can be used as cathodes to provide the necessary lithium ions, including $LiNiO_2$, $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, and others. Each material exhibits slight differences in its properties, which in turn influence the performance of the LIB in various aspects.

This review aims to categorize the most commonly used cathode materials in LIBs based on their structural configurations. Potential future improvements will also be considered with the goal of enhancing LIB performance.

2. LIBs

Lithium-ion batteries (LIBs) are high-energy batteries that include integrated lithium ions that can escape into positive and negative materials. Positive, negative, electrolyte, diaphragm, housing, and electrode leads make up its five primary structural elements. Intercalated lithium compounds, such as $LiNiO_2$, $LiCoO_2$, $LiMn_2O_2$, etc., are used as the positive electrode material. $LixC_6$, a carbon-lithium interlayer complex, serves as the negative electrode material, whereas $LiClO_4$, $LiPF_6$, and other dissolved lithium salts serve as the electrolyte. Lithium ions are transferred from the positive electrode to the negative electrode via the electrolyte during the charging process. The positive electrode is in a condition where lithium is scarce, whereas the negative electrode is lithium abundant. To maintain the negative electrode's charge balance, the external circuit simultaneously sends electronic compensatory charges to the carbon negative electrode. On the other hand, lithium ions are transferred from the negative electrode to the positive electrode, which is already lithium-rich, via the electrolyte. The advantages of lithium-ion batteries are mainly manifested in large capacity, high operating voltage, long cycle life, and high safety, but at the same time, there are some disadvantages, such as high internal impedance of the battery, large changes in operating voltage, and high cost. Research has never stopped being done by scientists. Due to its superior carbon structure and thermal conductivity, graphene is increasingly being studied in lithium-ion batteries. Kuhe et al. studied the reversible intercalation of lithium in double-layer graphene, and they found that lithium ions present a tight order in the double-layer space, which means that the lithium-ion storage capacity of double-layer graphene is far more than LiC_6 [2]. Shi et al. have shown that a high-performance graphene film can be used as a fluid collector for both $LiFePO_4$ positive and $Li_4Ti_5O_{12}$ negative electrodes [3]. Graphene-based integrated lithium-ion batteries offer a high specific capacity and better cycle stability when compared to conventional metal oxides. Additionally, it was discovered that transition metal oxides are better suited to societal demands than graphene thanks to their ease of manufacture, cheap cost, and status as typical ecologically favorable materials, according to an experimental study on the application of transition metal oxides in lithium-ion batteries.

3. Cathodes materials in LIBs

Three categories may be used to categorize the primary cathode material types: layered rock salt structure, spinel structure, and olivine structure [4]. Each has benefits and disadvantages. Each form of structure will be discussed as a mechanism and illustrative example in the sub-points that follow. This paper will give a thorough understanding of the many cathode types used in LIBs, supported by comparisons and statistics.

3.1. Layered rock salt structure

Figure 1 depicts the $LiCoO_2$ (LCO) crystal structure. It can be seen that the interlayer distance only slightly increases when lithium ions are inserted between layers of CoO_2, but the crystal structure remains the same. This structure is stable as a result. It continues to be the most investigated cathode material due to its high theoretical capacity ($274\ mA\cdot h\cdot g^{-1}$) and high bulk energy density (up to $4.2\ g\cdot cm^{-3}$) [5]. However, cobalt in this active compound containing lithium is of very high expense due to its rarity. Therefore, Ni, a substitute to replace cobalt, is used to lower the cost [6,7]. $LiNiO_2$ has the same high theoretical capacity as Co. Also, a property of high mean discharge voltage (3.7 V vs Li^+/Li) is present in $LiNiO_2$. Still, with some Ni incorporated into the Li layer, due to the similar size of the two atoms, there would be some capacity loss, and this would finally lead to a decrease in voltage [8]. Recently, some ways to modify $LiNiO_2$ were developed to overcome low stability. By doing it with copper and another metal, such as Ti or Mn, this method, known as dual incorporation, was devoted to producing the most efficient cobalt-free cathode. By now, the most efficient combination of dual incorporation includes Cu and Mg. $LiNiO_2$'s structural stability might be improved by doping Mg into $LiNiO_2$. However, it is unknown what part Cu played in the incorporation, and the truth is that simply doping Cu significantly reduces the discharge capacity [7].

Even so, the prospect of dual incorporation to support cobalt-free cathodes is still promising. After finding out the mechanism behind this, more pairs of combinations could be applied to raise the efficiency of cathodes of LIBs.

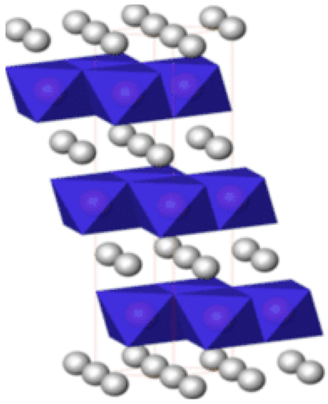

Figure 1. The two-dimensional structure of $LiCoO_2$: The silver-white spheres represent the octahedrally coordinated lithium ions, and the blue octahedra represent CoO_2 [4]

3.2. Spinel structure

At present, the widespread application of LIBs requires efficient positive electrode active materials with excellent performance. One of these positive electrode materials is spinel lithium manganese oxide $LiMn_2O_4$ (LMO), which can replace $LiCoO_2$ and is cheaper, more obtainable, non-toxic, and pollution-free [9,10]. From Figure 2, it can be seen that it has a three-dimensional ion channel that allows for lithium-ion embedding and de-embedding, with high energy density and thermal stability. In the spinel structure of $LiMn_2O_4$, Li, and Mn are situated in the 8a tetrahedral and 16d octahedral locations of cubic close-packed oxygen ions, respectively. Lithium-ion embedding and de-embedding occur at about 8 V while preserving the cubic spinel's original symmetry. But even in the 4 V area, especially at high temperatures, it can show capacity decline. Besides, due to the reaction: $2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$, Low stability and short cycle life are drawbacks of $LiMn_2O_4$ made via the solid-state technique. Its widespread applicability is also constrained by weak conductivity and magnification. According to research findings, ZnO-coated $LiMO_4$ material may enhance $LiMn_2O_4$'s electrochemical performance. Compared to LMO, LMO@Z has superior electrochemical characteristics. The initial discharge capability of LMO@Z at 0.2 C rate was 103.4 $mA \cdot h \cdot g^{-1}$. LMO@Z had specific capacities of 89.7 $mA \cdot h \cdot g^{-1}$ with a capacity retention of 87.1% after 100 cycles, in contrast to LMO, which had specific capacities of just 60.6 mA·h·g-1 with a capacity retention of 62.3%. By concurrently extracting enough lithium from brines with a high Mg/Li mass ratio using a porous $LiMn_2O_4$ electrode, the time required for lithium recovery was significantly reduced. As a result, the Mg/Li mass ratio of the solution was low. Additionally, by coating the spinel $LiMn_2O_4$ positive electrode with La_2O_3, the structural stability, high reversible capacity, and electrochemical performance of LIBs in high-temperature environments may all be improved [9].

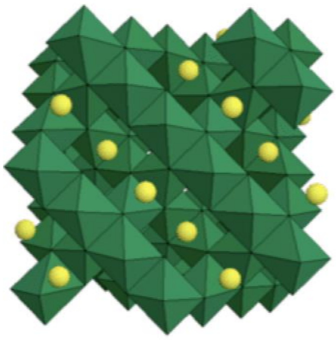

Figure 2. The three-dimensional structure of $LiMn_2O_4$.: Yellow spheres represent the tetrahedrally coordinated lithium ions and green octahedrons represent MnO_6 [4]

3.3. Olivine structure

Due to its low cost, abundance of components, and environmental friendliness, lithium iron phosphate, often known as LFP, has emerged as one of the most popular positive electrode materials for batteries. Figure 3 depicts its structure. It has a one-dimensional ion channel that allows for lithium-ion embedding and de-embedding, while the tetrahedral coordination structure allows each metal ion to be surrounded by four oxygen atoms, ensuring its high stability. This structure as a cathode material can enable LIBs to have low voltage and low conductivity. However, as the atomic size decreases, carbon coatings can improve this problem by promoting electron motion and reducing transmission distance. After hundreds of cycles, the battery built by LFP has a discharge voltage of 3.4 volts and shows no discernible attenuation. The battery's performance is superior to that of lithium cobalt and lithium nickel oxide, and it has high stability when charging and discharging. Its capacity also exceeds 170 $mA \cdot h \cdot g^{-1}$. Due to its structure, lithium iron phosphate has a very low electronic conductivity, a low rate of lithium-ion diffusion, and poor electrochemical performance in low-temperature environments. These drawbacks prevent the further use of LFP materials, so it is necessary to modify LFP to further enhance its performance. At present, the improvement research on LFP mainly includes the following aspects: The first is surface coating. coating the surface of LFP with excellent conductive properties, to improve the migration rate of ions. At present, the coating materials used are mainly carbon materials, metals and metal oxides, conductive polymers, and the like. Doping in elements is the second. The Li location is doped with additional elements, which exacerbates the flaw in the LFP crystal mechanism and speeds up the movement of lithium ions during charge and discharge [11]. The third involves increasing the amount of lithium in the LFP battery by using a particular supply of lithium and reducing the loss of lithium ions in the cathode material. This will improve the electrochemical performance and cycle efficiency of the LFP battery, but will eventually lead to a decrease in the load energy of the cathode active material [12].

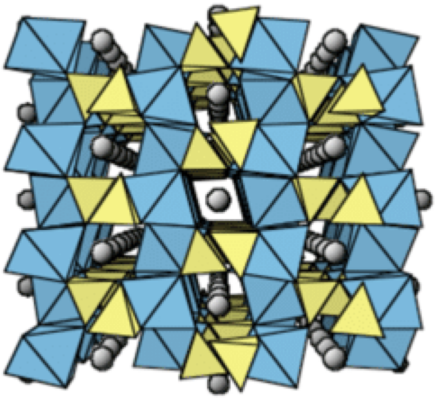

Figure 3. The one-dimensional structure of $LiFePO_4$: The silver-white spheres represent the octahedrally coordinated lithium ions, the blue octahedra represent FeO_6, and the yellow tetrahedra represent PO_4 [4]

4. Summary

The development of electrochemical energy storage has the potential to alleviate the reliance on non-renewable energy sources. By examining each of the three structures in detail, it becomes evident that they possess distinct properties. In the case of the layered rock salt structure, $LiCoO_2$ and $LiNiO_2$ are typical examples. The strong forces between each layer allow for the intercalation of lithium ions without damaging the overall structure. Additionally, any excess lithium ions intercalated between the layers only result in a slight increase in unit cell volume. This characteristic explains the high theoretical capacity of this material. Moreover, considering the scarcity of cobalt, nickel can be used as a substitute without compromising the performance of lithium-ion batteries (LIBs) while reducing production costs.

$LiMn_2O_4$ serves as a representative of the spinel structure. As a substitute for cobalt-based cathode materials in LIBs, $LiMn_2O_4$ possesses advantageous characteristics such as low cost, easy availability, and environmental friendliness, which has attracted increasing attention from the market. However, its specific capacity is relatively low compared to other materials, necessitating further research in this area.

The olivine structure, exemplified by $LiFePO_4$, offers cathodes with high specific capacity, excellent safety, and long cycle life. However, its practical application is hindered by its low electronic conductivity and limited lithium-ion mobility, resulting from its unique structural configuration. While certain measures, like carbon coating, ion doping, and lithium supplementation, have been explored to improve its performance, more advancements are required to facilitate large-scale applications of lithium-iron phosphate batteries.

As mentioned earlier, dual doping of Cu and Mg in layered rock salt structures can significantly enhance cathode performance in LIBs. However, the underlying mechanism behind this improvement remains unknown. The perplexing observation that doping Cu alone into the layered structure worsens LIB performance raises questions. Further studies could investigate the effects of dual doping in other structures (spinels and olivines) to identify potential patterns and finally unravel the mystery of dual doping. Moreover, this research may provide insights for researchers to enhance LIB performance to an even greater extent.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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