Research Status of Cathode Materials for Lithium Ion Batteries

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Abstract: Thanks to the promotion of new energy vehicles, the industry of lithium-ion batteries has ushered in its booming period. The current industry of lithium ion batteries is in rapid development with great potential. Therefore, many researchers have turned to focus on lithium ion batteries to obtain better lithium ion batteries. In this paper, the literature review of cathode materials for lithium ion batteries is to be carried out from the following aspects, including the overview of lithium ion batteries, their basic performance indexes, and the classification and preparation methods of cathode materials. Besides, the present situation and modification strategies of cathode materials for lithium ion batteries will be further analyzed, so as to improve their electrochemical performance.

Keywords: Lithium Ion Battery; Cathode Material; Lithium Iron Phosphate; Lithium Cobaltate; Secondary Battery

1. Research Background of Lithium Ion Batteries

1.1 Development of Lithium Ion Batteries

During the development of social civilization, science, and technology, it is precisely the change in energy structure that has led to historic progress and improved people’s lives. Since the 1990s, with the rapid development of electronic information technology, many electronic devices need an energy supply to realize the characteristics such as small size, lightweight, high energy density, and long cycle life. Under this background, lithium ion batteries came into being, which not only promoted the upgrading of new electronic equipment, but also directed society towards intelligence and environmental friendliness.

However, the research on lithium ion batteries is not always favorable. In 1913, Gilbert N Lewis, a professor at Massachusetts Institute of Technology, published the paper The Potential of the Lithium Electrode in the Journal of the American Chemical Society, which expounded and measured the electrochemical potential of lithium metal for the first time. Thus, it was regarded as the earliest systematic study of lithium metal batteries [1]. However, due to lithium being a reactive metal, it has not attracted much attention.

In 1976, Silbernagel et al. [2] thought that lithium can be inserted into LixTiS2 with a small lattice expansion effect, while lithium ions can gradually occupy the octahedral position in the interlayer space. By demonstrating this process, they obtained a patent. The battery has harvested wide attention because of its high energy density. However, it is easy to produce lithium dendrites during the charge-discharge cycle, which leads to short circuits and potential safety hazards.

In 1980, the research group of John B. Goodenough first discovered that lithium cobaltate can be used as a cathode material. They believed that LiCoO2 has a large layer spacing in the transition metal oxide LiXO2 (X=V, Cr, Ni, Fe) with a layered structure. Besides, the low spin Co4+/Co3+ redox pair has a higher affinity for electrons, which makes oxygen polarize cobalt stronger to obtain 4V voltage and higher energy density. In the following years, LiNiO2 and LiMn2O4 were discovered one after another [4].

In 1997, Professor Goodenough [5] reported that lithium iron phosphate is a crystal with an ordered olivine structure, in which ferroxide hexahedron is connected with each other on the same side. This structure perfectly balances the redox energy of lithium iron phosphate electrodes with the mobility of lithium ions in the crystal,
and its characteristics can meet the requirements of power lithium ion batteries, with its capacity, cycle performance, and safety obviously improved. Moreover, this material is cheaper and safer than lithium cobaltate, so it has been greatly popularized in the next 20 years.

1.2 Working Mechanism of Lithium Ion Batteries
The working mechanism of a lithium ion battery is the same as other secondary batteries, that is, the chemical energy of the battery is converted into electric energy and output to the external circuit through the discharge process. Then, the lithium ion battery is restored to its original state through the reverse electrification of the external power supply during the charging. At that time, lithium ions and electrons in the cathode are separated from the lattice, while lithium ions migrate to the anode in the electrolyte, and electrons migrate to the anode through the external circuit. Finally, they are embedded in the anode material by compounding into lithium atoms or alloying there. The discharge is opposite to the charging when electrons drive electronic devices through external circuits [6].

Taking graphite/lithium cobalt oxygen battery as an example [7], lithium ions in cathode LiCoO$_2$ move out during the charging, pass through the electrolyte, and embed between carbon layers of graphite to form lithium-carbon interlayer compounds in the battery. The discharge is just the opposite, that is, lithium ions move out from the interlayer of the graphite anode, pass through the electrolyte, and enter the LiCoO$_2$ cathode.

The reaction of each battery electrode and the battery itself is as follows:

Anode: 6C+xLi$^+$ +xe$^-$ = Li$_x$C$_6$

Cathode: LiCoO$_2$ =xLi$^+$ +Li$_{1-x}$CoO$_2$ +xe$^-$

Total Battery Reaction: LiCoO$_2$ + 6C = Li$_{1-x}$CoO$_2$ + Li$_x$C$_6$

2. Basic Performance Indicators of Lithium Ion Batteries

2.1 Capacity

2.1.1 Concepts
The battery capacity represents the amount of electricity discharged by the battery under certain conditions, which is equal to discharge current × discharge time, usually in Ah. As for batteries with different voltages, Wh is their unit. Battery capacity is divided into actual capacity and theoretical capacity. Actual capacity refers to the amount of electricity that can be given under a certain discharge system, while theoretical capacitance refers to the amount of electricity given by all active substances participating in battery reactions.

2.1.2 Influencing Factors
The discharge capacity decreases with the increasing discharge depth [9]. The larger the discharge rate, the faster the battery capacity declines. When the battery discharge rate is 1.5 ~ 3.0, the discharge capacity begins to show signs of recovery. Meanwhile, an excessive discharge rate will lead to battery damage and the degradation of battery performance is affected by temperature. The best working temperature of an ion battery is 20 °C-40 °C, with low or high temperatures affecting the battery life [10].

2.2 Specific Capacity

2.2.1 Concepts
Specific capacity has two types. One is the mass-specific capacity, which is what a unit mass battery emits, equal to capacity/mass, with mAꞏh/g as its unit. The other is volume-specific capacity, which is the amount of electricity that can be released per unit volume of the battery, equal to capacity/volume, with mAꞏh/L as its unit.

2.2.2 Influencing Factors
With the increasing cycle times and discharge rate, the specific capacity decreases. The specific surface area and porosity of electrode materials will directly affect the mass and diffusion rate of active substances in the electrode, thus affecting the specific capacity of the battery. Moreover, it can be affected by the selection and matching degree of cathode and anode pairs. For example, the combination of cathode and anode with high energy density can improve the specific capacity. The type, concentration, and stability of electrolytes will change the
specific capacity by affecting the ion transport rate and electrochemical reaction.

![Fig. 4. Cycle Performance of LMO-750, LMO-800, LMO-850 and LMO-900 at 0.3 C Rate Performance Diagram of LMO-750, LMO-800, LMO-850 and LMO-900 [11]](image)

2.3 Self-Discharge Rate

2.3.1 Concepts

The self-discharge rate refers to the holding ability of the battery’s stored electricity under certain conditions when the battery is in an open circuit state. There are always impurities in materials, which inevitably leads to self-discharge.

2.3.2 Influencing Factors

The higher the ambient temperature, the higher the activity of electrochemical materials, the more intense the side reaction, and the more obvious the chemical self-discharge. Ion batteries are easily affected by air pollution and air humidity. High air humidity and conductive particles will lead to an increase in conductivity. The general trend is that the higher the charge of the ion battery, the greater the potential difference, the more intense the side reaction, and the higher the self-discharge rate. Meanwhile, the cycle will cause an internal micro-short circuit and reduce physical self-discharge. Different impurities will affect the self-discharge rate of battery formation. After the battery is charged, Li⁺ in the cathode material comes out and is embedded in the anode graphite through the electrolyte. Metal impurities located between the cathode and the separator are oxidized and dissolved into the electrolyte by the cathode to generate metal ions, which are continuously reduced and deposited on the anode surface. Slowly deposited metal dendrites pierce the separator and contact the cathode, forming micro short circuit points and resulting in large self-discharge [12].

![Fig. 5 Principle of Battery Self-Discharge Caused by Metal Impurities Between Cathode and Separator [12]](image)

2.4 Energy Density

2.4.1 Concepts

Energy density refers to the ratio of the energy that can be charged to the mass or volume of the energy storage medium for a given electrochemical energy storage device. Mass energy density is equal to battery capacity × discharge platform/battery weight, with Wh/kg as its unit. Volume energy density is equal to battery capacity × discharge platform/volume, with Wh/L as its unit.

2.4.2 Influencing Factors

The discharge rate of a lithium ion battery refers to the current value required when the battery releases its rated capacity within the specified time. Different discharge platforms have various energy densities. In addition, battery size affects energy density. Increasing the proportion of positive active materials will improve the energy density. More negative active materials are needed to accommodate the swimming lithium ions and store energy. Up against the constant total amount of positive active material, only when as many lithium ions as possible are deintercalated from the cathode, that is, the specific capacity is increased, can the energy density be improved.

2.5 Power Density

2.5.1 Concepts

Power density refers to the ratio of the output power of the battery to its weight, which is usually expressed in W/kg.

2.5.2 Influencing Factors

Energy density refers to the power that a unit mass of a battery can hold. The higher the energy density, the higher the power density. Increasing the proportion of lithium elements and letting many lithium ions carry energy repeatedly is a main measure. For example, lithium hexafluorophosphate has good electrochemical stability and conductivity, but poor thermal stability. With moderate conductivity, lithium perchlorate has battery safety problems as a strong oxidant [13].

Lithium
tetrafluoroborate has good low-temperature performance, high conductivity, wide electrochemical window, and good thermal stability. However, it is difficult to form a stable SEI film on the anode surface [14]. Compared with LiPF6, LiFSI has better thermal stability, hydrolysis stability, and higher ionic conductivity, which does not corrode the positive aluminum foil [15].

3. Classification of Cathode Materials for Lithium Ion Batteries

3.1 Layered Oxide LiMO2

3.1.1 LiCoO2 Cathode Material

At present, LiCoO2 with the α-NaFeO2 layered structure is the main cathode material for lithium ion batteries, belonging to the hexagonal system and R-3m space group. LiCoO2 is composed of LiO6 and CoO6 octahedrons, in which Li and Co occupy 3b and 3a alternately and respectively, and O occupies 6c, arranged in cubic dense packing [16]. It has the advantages of high voltage, stable discharge, suitable for large current discharge, high specific energy, good cycle performance, and a simple preparation process.

However, as a cathode material for large-scale batteries, LiCoO2 has many problems. With the increasing cycle times, the battery capacity decays greatly, with its poor overcharge resistance and thermal stability. Ohzuku et al. [18] found that when the charging voltage reaches 4.5V, the hexagonal phase begins to change into the monoclinic phase, which is related to the Jahn-Teller distortion of the CoO6 octahedron. Therefore, in order to reduce irreversible capacity loss and maintain a stable voltage platform, the charging cut-off voltage is usually limited below 4.2V. Aiming to overcome the shortcomings of LiCoO2, the doping coating is used to increase its capacity, improve cycle performance, and promote structure stability.

3.1.2 Layered Structure of LiMnO2

The Mn reserves in China are abundant and the application of LiMnO2 can greatly reduce the cost of commercial lithium ion batteries. Therefore, it has become a research hotspot now. The crystal structure of layered LiMnO2 can be divided into a monoclinic phase and an orthorhombic phase. The orthorhombic phase is β-NaMnO2 structured and belongs to the Pmmn space group, with a=0. 2805nm, b=0. 5757nm, c=0. 4572nm, and Z=2 as its lattice parameters. LiO6 and MnO6 octahedrons are aligned alternately in the lattice. The MnO6 octahedron skeleton is elongated by 14% due to the Jahn-Teller effect caused by the migration of Mn to the lithium layer. The monoclinic phase is a-NaFeO2 structured, which is similar to that of LiCoO2. Besides, it belongs to the C2/m space group, with a=0. 5439nm, b=0. 2809nm, c=0. 5395nm, and Z=2 as its lattice parameters. MnO6 octahedron forms an ordered transition metal layer, and the Li layer is distributed in turn. However, the monoclinic phase has poor thermal stability compared with the orthorhombic phase, which cannot be synthesized by the traditional method of solid-state reaction, so it is generally prepared by ion exchange with NaMnO2 [20]. LiMnO2 has the following advantages such as high theoretical capacity, overcharge, over-discharge resistance, good thermal stability, abundant resources, no pollution, and low price [21].

However, Mn3+ produced during charging and discharging leads to Jahn-Teller distortion [23], which distorts the layered structure into the rhombic structure, seriously damaging the electrochemical performance of layered LiMnO2 material that is uniform orthogonal. Moreover, its preparation conditions are harsh, so it cannot be commercialized up to now.

3.2 Spinel Oxide LiMn2O4

The crystal structure of LiMn2O4 belongs to the Fd-3m space group. The oxygen skeleton of LiMn2O4 is the same as that of LiMO2. O is located at 32e to form a face-centered cubic structure, and Mn occupies 50% of the oxygen octahedron at 16d, in which trivalent and tetravalent Mn ions account for half each, with Li located at 8a in the oxygen tetrahedron. In this structure, the Mn2O4 array is formed by a MnO6 octahedron with shared edges, and the empty octahedron at 16c provides a
diffusion network for lithium ions. Moreover, the rapid migration of lithium ions in this channel makes LiMn$_2$O$_4$ show excellent rate performance [24].

Fig. 8 Space Group Structure of Spinel Lithium Manganese Oxide [25]

It is found that LiNi$_{0.5}$Mn$_{1.5}$O$_4$ obtained by replacing part of Mn in LiMn$_2$O$_4$ doped with Ni has good high voltage stability, and the actual discharge specific capacity even reaches 146 mAꞏh/g [26] [27]. As for LiNi$_{0.5}$Mn$_{1.5}$O$_4$, its three-dimensional lithium ion transmission channel and high operating voltage ensure the high energy density and power density of lithium ion batteries.

3.3 Olivine Phosphate LiMPO$_4$

3.3.1 LiFePO$_4$ Cathode Material

The crystal of lithium iron phosphate has olivine ordered structure and belongs to the orthorhombic crystal system in the Pnmb space group. Concerning the crystal structure of lithium iron phosphate, iron and phosphorus react with oxygen to form FeO$_6$ octahedron and PO$_4$ hexahedron respectively. FeO$_6$ octahedrons and PO$_4$ tetrahedrons alternately link to form a space skeleton, and Li atoms fill the voids of the skeleton to form LiO$_6$ octahedrons. P-O covalent bond energy is strong, which makes it high in thermal stability and dynamic stability. Macroscopically, the battery has high safety [28]. In addition, LiFePO$_4$ has a high theoretical capacity, a stable discharge platform, stable structure. It also has the advantages of other cathode materials, such as abundant resource reserves, low prices, and environmental protection [29]. Therefore, the cathode material of lithium iron phosphate has become one of the most potential ones for power lithium ion batteries, which has become a hot topic studied by many researchers [30].

However, LiFePO$_4$ also has some problems. Because there is no continuous octahedral network of LiFePO$_4$, its electronic conductivity is only $10^{-3}$-$10^{-5}$ S·cm$^{-1}$ at room temperature, which becomes the bottleneck restricting its large-scale utilization. In order to solve these shortcomings, the commonly used methods mainly include nanocrystallization of particles, carbon coating, and ion doping. Nanocrystallization can shorten the transport distance of Li$^+$ in LiFePO$_4$ particles, and make Li$^+$ deintercalation faster and more complete, thus improving the electrochemical performance of materials [31].

Fig. 9 Schematic Diagram of Crystal Structure of Olivine LiFePO$_4$ [32]

3.3.2 LiMnPO$_4$ Cathode Material

The crystal structure of LiMnPO$_4$ is olivine and belongs to the orthorhombic system, with $a=0.0611$ nm, $b=0.1045$ nm, and $c=0.0475$ nm as its unit cell parameters. O is a slightly twisted hexagonal compact packing, while Li and Mn occupy the octahedral O. Meanwhile, Li is in 4a and forms LiO$_6$ octahedral with O, Mn is at 4c and forms MnO$_6$ octahedron with O. P and O form PO$_4$ tetrahedron. In this structure, two LiO$_6$ octahedrons including one MnO$_6$ octahedron and one PO$_4$ tetrahedron share the same side. This alternating structure also makes the material stable in lithium ion migration channels. At the same time, in the tetrahedral structure of PO$_4$, the P-O bond has strong covalence, which enhances the structural stability of LiMnPO$_4$. During the charging and discharging, O in the lattice is not easy to escape, which makes the material extremely safe [33]. However, problems also occur in LiMnPO$_4$ for the 2eV band gap leading to low electronic conductivity. The disproportionation reaction of Mn$^{3+}$ and the side reaction of electrolytes are also shortcomings [34]. Martha et al. [35] used carbon black as the carbon source to prepare carbon-coated LiMnPO$_4$/C as the cathode material. The synthesized cathode material showed excellent electrochemical performance, and the charge-discharge capacity reached 140 mAh g$^{-1}$ at 0.10 times.

Carbon material, as the coating material of electrode material, shows electrochemical activity to electrolyte at low potential and does not oxidize at high voltage [36] with good chemical stability, which can be used as a good protective layer to delay the degradation of material and slow down the capacity attenuation during battery charge/discharge cycle.
4. Preparation Method of Cathode Material for Lithium Ion Battery

4.1 Sol-gel Method

The preparation of the sol-gel method is to put the precursor in a specific solvent system and mix it uniformly so that it undergoes hydrolysis and condensation chemical reaction to form a transparent and uniform colloidal system. For example, Zhang et al. [39] prepared Li₃V₂(PO₄)₃ materials by methods of sol-gel and solid-phase. The LVP materials prepared by the solid-phase method have a large and uneven particle size, while those prepared by the sol-gel method have good particle uniformity and small particle size.

4.2 Method of High-Temperature Solid State

At present, a high-temperature solid state is still the mainstream method to prepare cathode materials. Generally, it refers to ball milling and mixing powders evenly. Meanwhile, a large number of composite oxides are generated through contact, reaction, nucleation, and crystal growth reactions between solid interfaces [41]. The main technological processes are as follows. 1. The raw materials of each element are fully physically mixed. The common methods are agate mortar hand grinding and machine ball milling. Compared with the former, the latter is more uniform and smaller in granularity to obtain a powder with a larger specific surface area, which is beneficial to crystal growth during sintering. 2. Put the uniformly mixed powder in the corresponding atmosphere, and adjust the sintering time, temperature, batching ratio, etc. before calcining it. This method is simple to operate and control with short process procedures and easy industrial production. However, it takes a long calcination time with high energy consumption and low efficiency. Besides, it’s poor in the uniformity of target materials and electrochemical performance of prepared target products, apart from its difficult formula control [42] [43].

4.3 Coprecipitation Method

The coprecipitation method means that two or more cations exist in the solution in a homogeneous phase. After the precipitation reaction, uniform precipitation of various components can be obtained. It is an important method to prepare ultrafine powder of composite oxide containing two or more metal elements [44] [45]. For example, Lin Zhicheng et al. [46] prepared the black precursor by using methanol as solvent and adding a lithium source at 450 °C for 8h. The lithium, lithium carbonate, and lithium hydroxide are uniformly mixed with lithium acetate as lithium sources. Then, they sintered the red-brown powder after lithium mixing at 800 °C to synthesize different lithium-rich cathode materials. Because of the same morphology of precursors, the lithium-rich cathode materials synthesized by sintering at 800 °C with different lithium sources keep similar morphology to the precursors before sintering, all in elliptical long blocks. It is found that the length of the three samples is from 3.5 μm to 5 μm with relatively uniform size, but Li₂CO₃-800 are more seriously agglomerated, and the morphology of CH₃COOLi-800 and Li₂CO₃-800 remains more complete with dense nanoparticles on the surface. The nanoparticles on the CH₃COOLi-800 surface are smaller with more micropores. However, LiOH-800 is incomplete with a smoother surface.

4.4 Hydrothermal Method

The hydrothermal method is one that dissolves the required raw materials into water (or solvent) and seals them in a container with certain pressure. Then, the powder is dissolved and recrystallized to obtain cathode material powder due to hydrothermal reaction. In order to realize good electrochemical performance, it is necessary to select appropriate reaction conditions, including raw material particle size, water or solvent temperature, pressure, time, pH, heating, stirring rate, solvents, adjuvants, and dispersants, etc [47][48].

The hydrothermal method can be used to prepare materials with fine grains in a simple preparation method, which takes a short time. However, the preparation of materials by hydrothermal method requires higher instruments, which is also the main factor affecting the industrialization of the hydrothermal method [49].

5. Conclusion and Prospect

With the development of science and technology, several technical barriers to lithium ion batteries have been solved and lithium-ion batteries have stepped onto the stage with a large-scale application. Due to the emergence of new energy vehicles and the support of relevant policies, the industry of lithium ion batteries has developed rapidly, with more and more people beginning to pay attention to it. Cathode materials, as the bottleneck and focus of lithium ion battery research in recent years, are a necessary step for researchers to pursue their higher performance. There are two ways to clear the barriers in the research of cathode materials. One is to explore...
materials and constantly find new elements, organic or inorganic, layered or 3D. The second is the modification, which can also significantly improve the electrochemical performance of the original cathode material by doping metal ions and conductive agents as well as controlling the particle size. From the recent literature, new topics appear in the cathode materials of lithium ion batteries. Presumably, in the next few years, cathode materials with high energy density, high conductivity, and good recycling will emerge to improve the existing energy structure.

References

29. Zu, Z. H. (2022). First principle study on modification of LiFePO₄ cathode material for lithium-ion battery. Xi’an: Master Dissertation of Xi’an University of Architecture and Technology, DOI:10.27393/d.cnki.gxazu.2022.000295.


39. Dong, P., Xia, S. B., Zhang, Y. J. et al. (2016). Effect of complexing agent on electrochemical performance of LiNi(0.8)Co(0.15)Al(0.05)O₂ cathode materials prepared by sol-gel method. Journal of the Chinese Ceramic Society, 44(10), 1415-1420.


41. Cheng, B. (2012). Doped LiMn₂O₄ and LiMn₂O₄/graphene composites as high power and energy cathode materials for lithium-ion batteries. Jinan: Master Dissertation of Shandong University, 14-15.


