# Advances in Research on Positive and Negative Electrodes of Lithium-ion Batteries

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**Abstract.** In recent years, the new energy vehicle industry has boomed, and the demand for lithium-ion batteries has increased. However, the performance of lithium-ion batteries fails to meet the ultra-high demand for supplying automobiles for long-distance driving. This paper provides an in-depth discussion on the performance of lithium-ion batteries from the perspective of positive and negative electrode materials, respectively, with a detailed overview of the cell structure, material advantages and disadvantages, preparation conditions, and methods to enhance performance. Lithium manganate is inexpensive and rich in mineral resources, but its structure is unstable. Lithium iron phosphate is chemically stable, but its efficiency is low. Ternary anode material has high specific capacity, but its structure is unstable. Carbon anode is chemically stable, but its specific capacity is low. Silicon anode has excellent specific capacity, but due to its chemical properties, its battery life is extremely short. The pursuit of power supply, range, and safety in new energy vehicles is the goal of lithium-ion battery development at this stage. This paper provides a reference for understanding the structure of lithium-ion batteries and provides a macro idea for the sustainable development of the new energy industry.

**Keywords:** lithium-ion battery, anode material, cathode material, energy storage, new energy.

## 1. Introduction

In the spring of 1990, lithium-ion batteries were first successfully developed by Japan's Sony Energy Development Corporation. Its volume ratio, energy ratio, and mass ratio are high. It can be charged with no pollution or other characteristics, to a large extent in line with the needs of the development of the battery industry. Therefore, lithium-ion batteries have been fully developed. However, with the development of the battery industry, human beings have caused irreparable damage to the earth. The energy crisis continues to be serious, and the climate conditions continue to be harsh. Humans have almost exhausted the earth's fossil energy, which means human beings must develop towards clean energy. The new energy industry has emerged.

Due to the clean conditions of lithium-ion batteries, they have become the main development object of the new energy industry. The concept of lithium-ion batteries appeared in the public eye once again. In order to cater for the needs of the new energy automobile industry, lithium-ion batteries need to overcome three major problems: insufficient power supply, range, and safety of automobiles. To solve the three major problems of new energy vehicles, they can be solved by the various components of the battery. Lithium-ion batteries contain many assembly units, including a positive electrode, a negative electrode, an organic electrolyte, a diaphragm, and an organic shell. Thus, finding materials that are inexpensive, efficient, have a long service life, and have a high level of safety has become an important solution. $LiCoO_2$ is the most common anode material for lithium-ion batteries. Nevertheless, it is unfavorable to the popularization and application of the battery due to the low cobalt resources and high price. Replacing cobalt with manganese and iron is one way to reduce material costs. The negative electrode materials used are carbon or silicon. For carbon anodes, some studies show that batteries are prone to the problem of discharge capacity being larger than charging capacity. It is a phenomenon that makes the reversibility and Coulomb capacity of the battery greatly reduced. The battery capacity can be greatly improved by finding carbon materials that can hold more lithium ions. For silicon anodes, in the face of the problem of exponential growth of anode volume, carbon and silicon dopants can be developed to solve the problem.

This paper will provide an overview from two perspectives: positive electrode materials and negative electrode materials. Positive electrode materials are explained separately for lithium manganate, lithium ferrous phosphate, and ternary materials. The anode materials are explained as carbon and silicon. The entire text uses the same means of explanation for each material. The content covers the preparation method, cell structure, advantages and disadvantages, and means of performance enhancement. It provides a reference for the public to recognize lithium-ion batteries.

## 2. Cathode Material

### 2.1. Classification of Cathode Electrode Materials

The perfect cathode material in lithium-ion batteries has always been a goal pursued by researchers, and various cathode materials have different points and different shortcomings. In Table 1, the relevant data on popular anode materials in recent years is gathered. From the table, cobalt-based, manganese-based, nickel-based, iron-based, and ternary cathode materials show different advantages in terms of overpotential, specific capacity, free energy, etc. In this paper, we will emphasize manganese-based, iron-based, and ternary materials to give an overview of the cathode materials.

**Table 1.** Positive material configuration [1-4].

| Positive material | Average Voltage(V) | Gravimetric Capacity(mAh/g) | Gravimetric Energy(kWh/kg) |
|---|---|---|---|
| $LiCoO_2$ | 3.7 | 140 | 0.518 |
| $LiMn_2O_4$ | 4.0 | 100 | 0.400 |
| $LiNiO_2$ | 3.5 | 180 | 0.630 |
| $LiFePO_4$ | 3.3 | 150 | 0.495 |
| $Li_2FePO_4F$ | 3.6 | 115 | 0.414 |
| $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ | 3.6 | 160 | 0.576 |
| $Li(Li_aNi_xMn_yCo_z)O_2$ | 4.2 | 220 | 0.920 |

#### 2.1.1. Spinel type $LiMn_2O_4$

$LiMn_2O_4$ is prepared from $CH_3COOLi$ and $(CH_3COO)_3Mn$ by the high-temperature solid-phase method at 800℃ [1]. $LiMn_2O_4$ has a great advantage in occupying most of the market for anode materials because of its high voltage plateau, high electrical conductivity, high practical safety, environmental friendliness, and huge mineral reserve of Mn at a low price. The structure of spinel $LiMn_2O_4$, which is a cubic crystal cell with a Fd3m space group structure, is schematically shown in Fig. 1.

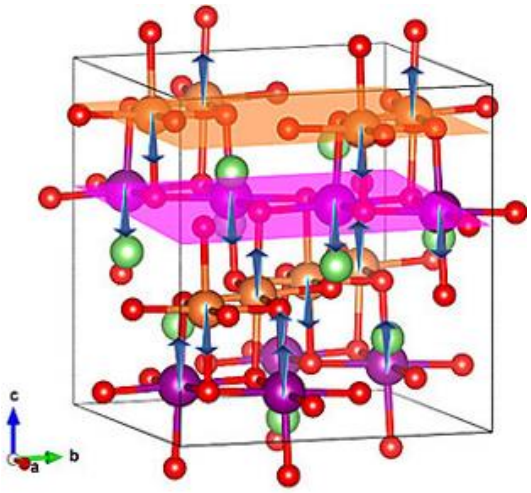


**Figure 1.** Structure of $LiMn_2O_4$. https://pubs.acs.org/doi/full/10.1021/acsomega.1c01162

$Li^+$ is located at position 8a, and manganese ions and $O^{2-}$ are according to 16d and 32e [2]. Combined with the crystal structure of $LiMn_2O_4$, it can be concluded that $Li^+$ is continuously detached

from the lattice during charging. Eventually, $LiMn_2O_4$ changes to $Mn_2O_4$. This change results in a change of manganese ions from +3 to +4 valence. During the subsequent discharge process, $Li^+$ was re-embedded back into the $LiMn_2O_4$ lattice, and the +4 valent manganese ion was reduced to +3-valent. Throughout the discharge process, two voltage plateaus appeared, and the large amount of $Mn^{3+}$ made the capacity of the material decay problematic: (i) the Jahn-Teller effect of $Mn^{3+}$ [3]. The high degree of spin and magnetic moments of $Mn^{3+}$ caused the oxygen octahedron to change from a cubic phase to a tetragonal phase. This structural change leads to changes in the lithium-ion de-embedding sites and migration channels, so that its transportation path receives obstruction and reduces the cycling performance of $LiMn_2O_4$. (ii) Disproportionation of $Mn^{3+}$. During the charging and discharging process, some manganese ions existed as $Mn^{2+}$ in the electrolyte, which was detached from the battery cycle. The reduced number of manganese ions that could be utilized for benefits led to the collapse of the $LiMn_2O_4$ structure, which seriously reduced the cycling efficiency. So far, in order to solve the problem of manganese ions, researchers are using morphological control, elemental doping, and surface coating to improve the performance of $LiMn_2O_4$. The latest study found that the conductivity of aluminum and cobalt doped $LiMn_2O_4$ was greatly improved, and no spurious peaks appeared [4].

### 2.1.2. Olivine $LiFePO_4$

Due to the scarcity of resources and the toxicity of cobalt-based lithium-ion battery cathode materials, iron-based cathode materials have become one of the research directions for researchers. The high-temperature solid-phase method is the most widely used and technologically mature method to produce $LiFePO_4$. The raw materials are $Li_2CO_3$, $e(CH_3COO)_2$, and $NH_4H_2PO_4$, which are calcined at a high temperature of 500~800°C under the protection of inert gas (helium, argon).

$LiFePO_4$ belongs to the olivine-type cubic crystal system with the space group Pmnb. It is arranged in a slightly distorted hexagonal, close-packed manner and has a very stable structure [5]. Due to the structural advantages of $LiFePO_4$, it has the following three characteristics: (i) The oxygen ions in $(PO_4)^{3-}$ are linked to the phosphorus ions through strong covalent bonds, which makes the oxygen ions present very firmly in $LiFePO_4$ and difficult to be detached during high temperature calcination. This property enhances the safety of $LiFePO_4$ to a great extent [6]. (ii) $Li^+$ is in the middle of the spatial mesh octahedron in the $LiFePO_4$ lattice. During the battery working process, the structure of $LiFePO_4$ does not change when the $Li^+$ is exfoliating and embedding. This property gives $LiFePO_4$ very good stability and high cycling efficiency. (iii) Theoretically, $LiFePO_4$ is able to hold 170 mAh per gram. Actually, it can hold 140mAh per gram. Compared with $LiCoO_2$, the capacity is comparable [7]. However, the structure of $LiFePO_4$ makes it too stable chemically, which also leads to the blockage of $Li^+$ migration channels, reducing the electronic conductivity and ion diffusion coefficient of $LiFePO_4$. This problem greatly limits the chemical performance of $LiFePO_4$. In order to improve this difficulty, it has been solved in three main ways [8]. (i) Surface capping using carbon or other metals (ii) metal doping. At the position of Li and Fe, other metal ions are doped to enhance the diffusion coefficient of Li. (iii) Synthesis of $LiFePO_4$ using nanotechnology.

### 2.1.3. High-nickel ternary cathode materials

One of the high-nickel ternary materials is NCM811. The precursor of NCM811 was first prepared by the co-precipitation method in a continuous stirred kettle reactor (CSTR, 5R). The prepared precursor was homogeneously ground with excess $LiOH-H_2O$. Subsequently, NCM811 was obtained by the high-temperature solid-phase method by sintering at 720°C under a pure oxygen atmosphere for 15 h. NCM811 has an $\alpha$-$NaFeO_2$ layered structure and belongs to the hexagonal crystalline system with the space group (166, R-3m) [9]. In the crystal structure of NCM811, oxygen ions occupy position 6c, presenting cubic dense stacking; lithium ions and transition metal ions (Ni, Co, Mn) are located at positions 3a and 3b, respectively, alternately occupying the octahedral voids with oxygen ions as the skeleton to form a two-dimensional alternate layer, which in the c-axis direction becomes presenting ABCABC... Layer arrangement.

The higher specific capacity of the NCM811 provides great help in improving battery performance, but it also brings many problems. (i) a mixed arrangement of lithium and nickel ions. The ionic radii of nickel and lithium are close to each other, and some nickel ions at position 3b tend to occupy the lithium ions at position 3a, leading to ion mixing, which in turn leads to the collapse of the lattice structure during batteries working process. (ii) Surface instability: NCM811 can be corroded with a great possibility by $CO_2$ and $H_2O$ in the atmosphere. (iii) Poor thermal stability. Ni and oxygen ion energy bands overlap at high charge, which will activate the redox reaction of oxygen ions to produce electron exchange and release a large amount of heat, leading batteries out of control in thermal problems. At present, A popular research direction is to improve electrochemical performance by surface coating modification. A large number of studies show the use of metal oxides such as MgO, $ZrO_2$, and $Al_2O_3$ to coat NCM811 [10]. The co-precipitation method is a mature technology for capping Mg-Al-layered double oxides on the surface of NCM811 material. It can not only prevent the surface-side reaction to inhibit the HF corrosion but also decrease the $Li^+$ and $Ni^+$ mixing and discharging potential. As a result, the capacity retention of 100 cycles at 0.5c in 2.75~4.3V was increased by 18% compared with the original sample.

## 3. Anode Material

### 3.1. Classification of Anode Materials

In Table 2, the popular anode materials in recent years and their various data are assembled. Carbon, due to its excellent stability, and silicon, due to its excellent specific capacity, have succeeded in capturing more than 90% of the market share.

**Table 2.** Negative material configuration [11, 12].

| Negative materials | Gravimetric capacity (mAh/g) | Volumetric capacity ($mAh/cm^3$) | Volume change (%) | Voltage vs Li | Lithiated phase |
|---|---|---|---|---|---|
| Graphite | 372 | 818 | 114 | 0.05 | $LiC_6$ |
| Sn | 994 | 7266 | 358 | 0.6 | $Li_{4.4}Sn$ |
| Si | 4197 | 9780 | 413 | 0.4 | $Li_{4.4}Si$ |
| $Li_4Ti_5O_{12}$ | 175 | 613 | 100 | 1.6 | $Li_7Ti_5O_{12}$ |

#### 3.1.1. Carbon anode materials

Usually, the anode plays the role of embedding and detaching $Li^+$ in batteries. This requires structure of carbon to provide a good insertion channel for lithium ions. At the same time, it also needs to be structurally stable and not easy to disproportionately react, leading to structural collapse. During battery charging and discharging, the chemical formula of the product of the lithium insertion compound is $Li_xC_6$ ($0<x\leq1$). Ideally, perfect crystalline graphite can bring the x value to 1, the maximum value. At this point, the carbon-negative electrode can reach a theoretical capacity of up to 372mAh/g, and its volumetric capacity is 833 $mAh/cm^3$ [11]. In reality, the x-value for reversible lithium insertion in most carbon materials is between 0 and 0.5. If the battery efficiency is to be improved, it can be done by increasing the magnitude of x. The x-value is related to the carbon structure, electrode geometry, electrolyte composition, insertion reaction rate, and other factors. Researchers have conducted a lot of studies on carbon with different structures and have come up with data as shown in Table 3. Carbon is classified according to its material structure into: graphite, carbon fiber, petroleum coke, disordered carbon, and petroleum cracked carbon. It was shown that almost all C/Li batteries showed a discharge plateau of 0.8 V at the first discharge. Due to the irreversible nature of the plateau, the batteries showed poor performance, in which the discharge capacity was greater than the charge capacity. The voltage plateau needs to disappear only after several charge and discharge completions, and the coulombic efficiency is close to 100%. In order to solve this challenge, researchers have developed methods such as cladding modification, surface modification, and doping modification.

**Table 3.** Structural data of several carbon materials and their Coulomb capacities [11].

| Carbon | Structural parameters (d/A)(L/A) | Coolum capacity (C/mAh·g$^{-1}$) |
|---|---|---|
| PPCA | amorphous | 145 |
| benzene cracking carbon | 3.49 100 | 300 |
| M-46 carbon fiber | 3.42 | 80 |
| Petroleum coke fiber | 3.39 237 | 180 |
| Sugar alcohol resin cracked carbon | 3.80 | 320 |
| graphitic | 3.354 >1000 | 0 |

### 3.1.2. Silicon anode materials

At present, carbon material occupies more than 90% of the market share among the anode materials used in lithium-ion batteries. However, due to its low specific capacity and easy reaction with organic electrolyte, human have to find a new material to solve these problems. It has been found that silicon can make the specific capacity of the battery reach 3000mAh/g, which greatly improves the battery performance. Lithium and silicon can form $Li_{12}Si_7$, $Li_7Si_3$, $Li_{22}Si_5$, and $Li_{13}Si_4$ [11]. These compounds hold a theoretical capacity up of to 4200mAh/g. At the same time, when lithium is embedded in silicon, the over-voltage is lower than 0.5V, and organic solvent molecules will not be embedded in the silicon anode. These two advantages make silicon an excellent negative electrode material and help put it into practical applications. However, the volume of silicon changes significantly when it is embedded in delithium, causing the anode material to crumble and shatter, reducing the battery cycle performance. Moreover, the volume effect of silicon causes the SEI membrane to re-rupture and generate, resulting in a large amount of active lithium-ion loss, which causes the battery capacity to drop by leaps and bounds. Converting monolithic silicon into nanocrystalline silicon can effectively alleviate this phenomenon. The study of vacuum-deposited amorphous silicon film shows that 50nm silicon film not only has an amazing discharge capacity in the electrolyte solution with PC as solvent but also has perfect high-rate discharge output [12]. It can discharge 3600 mAh per gram when the environment is 2C. Its reversible capacity is more than 3000 mAh/g at 12C, which can be maintained unchanged in 1000 cycles. Besides, its discharge capacity of 3000 times after discharge cycles at 30C maintains an ultra-high rate of 30C. The capacity is still more than 2000 mAh per gram after 3000 discharge cycles.

### 3.2. Performance Enhancement

Carbon has high cycling efficiency, but it can only contain 372 mAh per gram. Meanwhile, silicon has an ability to hold 3000mAh, even more, per gram. However, silicon has a high-volume expansion rate and poor cycling performance. If you want to make your lithium-ion batteries work even better, it is a good idea to study materials that combine the advantages of carbon and silicon. There are three main methods for the preparation of silicon-carbon anode materials: the hydrothermal method, the mechanical ball milling method, and the chemical vapor deposition method. The anode material prepared by the hydrothermal method will form a silicon oxide compound between the carbon shell and silicon core to make its grain distribution uniform and shape controllable, but this method requires too much equipment, which hinders its practical application. Mechanical ball milling method solves the problem of silicon volume expansion to a great extent, and reduce the energy required for the reaction to happen. What's more, the process is simple and can be mass produced. The composites synthesized by chemical vapor deposition (CVD) have good cycling performance and do not require high equipment, which is suitable for mass production.

## 4. Conclution

Lithium-ion batteries have occupied a major position in human life. At the same time, they also bring new development opportunities for the new energy industry. This paper starts with the cell structure and describes the preparation methods, such as the high-temperature solid phase method

and the co-precipitation method. For the positive electrode material specific capacity, safety and other conditions cannot be satisfied at the same time. Surface coating, metal ion doping, and the use of nanotechnology can solve the problem. For the negative electrode material specific capacity, service life cannot be taken into account. The problem can be used to enhance the performance of the binder, change the structure, and create multi-element hybrid materials. As the energy crisis continues to be serious, the climate conditions continue to be harsh, and the new energy industry must be the main direction of development in the future. Lithium-ion battery demand will certainly be higher. This paper provides a reference for recognizing lithium-ion batteries and provides ideas for the further development of high-efficiency and long-life lithium-ion batteries.

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