

Comparative analysis of ternary lithium batteries and lithium iron phosphate

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Abstract. Ternary lithium batteries (TLB) and lithium iron phosphate batteries (LIPB) are two popular battery types in the current battery market. They have their own advantages and disadvantages in performance and application areas. Through the analysis of the structure, performance and application of the two types of batteries, it can be seen that the anode of TLB is an octahedral structure with high energy density, strong fast charging ability and excellent low temperature discharge performance. The different ratios of nickel, cobalt and manganese in the anode material are suitable for a variety of unused occasions. However, the high-temperature stability of TLB is poor, and thermal runaway is easy to occur at high temperatures, and their cycle life is relatively short. LIPB are known for their high safety, long cycle life and relatively low cost. Its unique olivine crystal structure and stable P-O covalent bonds give it excellent thermal stability, even at high temperatures, the battery will not easily decompose. The disadvantages of LIPB are mainly reflected in their lower energy density and low-temperature discharge performance. Combining the advantages of the two materials to develop a new battery material with both high energy density and high safety will be an important research direction in the future.

1 Introduction

In today's society, batteries have been deeply used in all aspects of our lives, such as mobile devices, electric vehicles, energy storage systems and medical devices. This fully reflects the importance of batteries to our life. With the gradual depletion of fossil resources, energy transition is imminent, and the development of clean and sustainable energy has become a priority. Among them, solar and wind energy have been proven to be effective alternatives to fossil energy. However, due to the unstable supply of these energy sources, the stability of the power grid is seriously affected. To mitigate and solve this problem, the combination of solar or wind power generators with energy storage devices has become a viable option [1]. As a result, the battery market has been expanding year on year in recent years. The Asia-Pacific consumer battery market size is expected to reach USD 8.78 billion by 2023 and is projected to continue growing until 2032 [2]. Among the many battery types, Li-ion batteries are favored for their superior performance, making them an important energy option for electric vehicles and other sectors, and they stand out as the mainstream of the industry in terms of applications. As far as electric vehicles are concerned, 67.3% of electric vehicles loaded with TLB, 32.6% of electric vehicles loaded with LIPB, and 0.1% of electric vehicles

loaded with other batteries will be used in 2023 [3]. This paper focuses on the structural and performance characteristics of TLB and LIPB, and compares and analyses their advantages and disadvantages.

2 Ternary lithium batteries

2.1 Structural characteristics of ternary lithium batteries

Ternary lithium batteries are chemical batteries in which the positive electrode is made of a mixture of nickel, cobalt and manganese, and the negative electrode is made up of graphite in which lithium ions are inlaid and released. As for the anode structure, the anode material of TLB has a layered structure, with nickel atoms, manganese atoms, cobalt atoms, and oxygen atoms forming an octahedron, as in Figure 1 [4]. Thus, the TLB has the advantages of lithium cobaltate, lithium nickel, and lithium manganese batteries at the same time. Where lithium ions are located between the layers of the octahedron and can be released by inserting them back and forth between the layers. The presence of nickel atoms increases the capacity of the battery, the presence of cobalt atoms can help to maintain structural stability and improve electronic conductivity, and the presence of manganese atoms reduces costs and improves structural safety [5]. Thus the ratio of nickel, cobalt and manganese in the ternary material can vary according to the demand. The structure of nickel-cobalt-manganese ternary material can be expressed as $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ where $x+y+z=1$. Based on the elemental molar ratio structural types such as type 333, type 523 and type 811 can be obtained [6]. Graphite, the negative electrode material, has good electrical conductivity and stability, and is better for the storage and release of electrical energy. Electrolytes are usually found in the form of gel polymers, often formed from a mixture of polymers, organic solvents and lithium salts [4]. It has the advantages of both solid and liquid electrolytes, with good ionic conductivity and some thermal stability. For the diaphragm, it is often made of materials such as polypropylene or vinyl membranes [7].

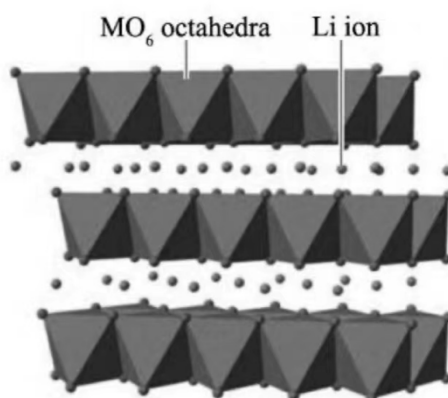


Fig. 1. Structure of TLB cathode material [4].

2.2 Performance Characteristics of Ternary Lithium Batteries

TLB has a high energy density usually 200 Wh/kg, and with in-depth research, it possibly up to 300 Watt-hours/kg in the future, which is able to provide a long time of endurance and higher power output, a characteristic that allows them to be used in lightweight or devices that require a long time of power supply [4]. It also has the ability of fast charging, which

can significantly improve the convenience of the product. Moreover, lithium ternary batteries are environmentally friendly. Its constituent materials do not contain heavy metals and toxic substances, so it is less polluting to the environment and can strictly meet the environmental requirements. In addition, ternary lithium batteries have better discharge performance at low temperatures. At $-20\text{ }^{\circ}\text{C}$, the battery capacity only decreased by 70.14% of $25\text{ }^{\circ}\text{C}$. (TLB battery capacity at $25\text{ }^{\circ}\text{C}$ for 100%) [7]. But the cathode of the TLB is not resistant to high temperatures, it will be at $250\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ is to carry out internal decomposition, thermal stability is poor. The decomposed cathode encounters the combustible electrolyte and carbon materials in the battery, after which it will react rapidly to generate a large amount of heat. The safety of its positive electrode is poor, in the event of external impact, the positive electrode and the positive electrode in the TLB separator is easy to be damaged, resulting in a short-circuit battery. Short-circuit batteries are prone to thermal runaway and then rapidly warm up and finally spontaneous combustion. Secondly, the theoretical service life of lithium ternary battery is 2000 times of charging and discharging. After 3900 cycles, the battery capacity will be reduced to 66%, which shows that its cycle life is short [4].

3 Lithium iron phosphate batteries

3.1 Structural characteristics of lithium iron phosphate batteries

The negative electrode of LIPB is usually composed of graphite, which can be effectively embedded and embedded off lithium ions, and its positive electrode is usually composed of LiNiO_2 , LiMn_2O_4 , LiCoO_2 , LiFePO_4 and other materials. Among them, LIPB material (LiFePO_4) is widely studied for its abundant resources, low toxicity and high stability [4]. This material is usually a stable olivine crystal structure with orthorhombic homology to the space group Pnma , as shown in Figure 2. LiFePO_4 consists of a polyoxo anionic framework composed of FeO -octahedral, LiO -octahedral and PO -tetrahedral sites. The oxygen arrays are hexagonally close packed with octahedra sharing edges and faces as shown in Figure 3 [8]. Lithium ions are located in the edge-octahedral (LiO) chains, divalent iron ions occupy the corner-sharing octahedra (FeO_6), and phosphorus ions are located in the tetrahedral sites (PO_4). Among them, the P-O covalent bond has an important chemical bonding energy, which avoids the release of oxygen in the high charge state, and it is its anode that keeps its structure stable even in high temperature environments [9]. The three-dimensional structure presented by LIP crystals forms a one-dimensional ion transport channel, thus limiting the diffusion of lithium ions [4]. The electrolyte for LIPB is usually a mixture of organic solvents and lithium salts with good ionic conductivity and thermal stability. Diaphragm is usually one or two of polyethylene and polypropylene, and is often used as a single-layer or multi-layer composite film. There are also an inorganic ceramic film on the surface of the membrane to enhance the treatment, to a certain extent, to improve the safety of the battery [10].

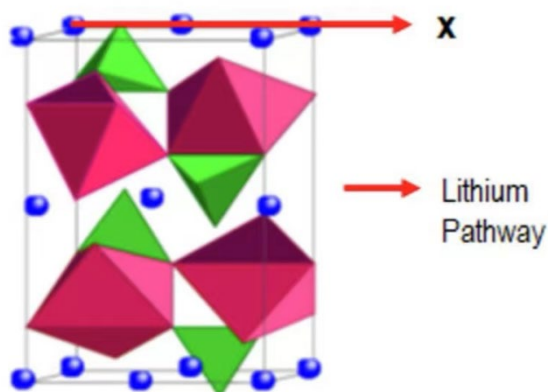


Fig. 2. LIPB cathode material structure [4].

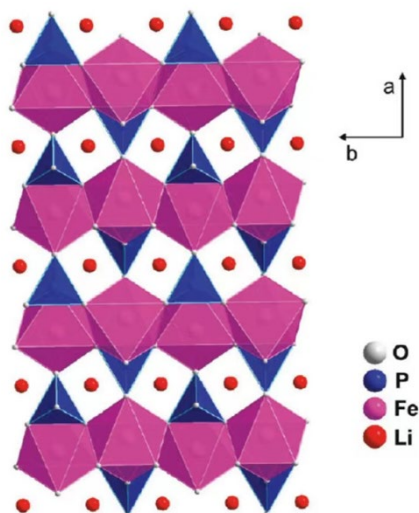


Fig. 3. Olivine structure of LIPB [9].

3.2 Performance Characteristics of Lithium Iron Phosphate Batteries

LIPB has high safety, due to its stable olivine structure, the battery cathode has excellent chemical properties and high temperature resistance. Due to its P-O covalent bond, the battery will not release oxygen in the face of impact, pinprick and short-circuit, which makes him even if the damage will not burn, only to reach 700 °C to 800 °C between the internal decomposition. LIPB has a high cyclability, after 5000 cycles of use still has 84% of the battery capacity. This is due to the high stability of the LIP lattice, which makes lithium ion embedding and embedding out of the lattice have less effect on the lattice and good reversibility [4]. And because the raw materials of the battery are iron and phosphorus this kind of rich materials, make the LIPB has a low cost, is conducive to large-scale production and application. In addition, LIPB does not produce toxic substances, in line with the requirements of green environmental protection. However, under low temperature conditions, the discharge performance of LIPB is poor. At -20 °C, the battery capacity drops to only 54.94% at 25 °C. (The capacity of LiFePO_4 battery is 100% at 25°C) and so far, the energy

density of LiFePO_4 battery is usually 105Wh/kg, and a few of them can reach 130~150 Wh/kg. It is also challenging to break through 200Wh/kg in the future [11].

4 Comparison between lithium ternary batteries and lithium iron phosphate batteries

Nowadays, both LTB and LIPB are widely used in the field of electric vehicles and have become the two most popular types of electric vehicle batteries. This section will compare them in seven aspects: environmental friendliness, energy density, safety, cost and price, charging efficiency, low temperature discharge and cycle life.

Lithium ternary batteries and LIPB are environmentally friendly, and none of the constituent materials are toxic, and they do not produce toxic substances.

In terms of energy density, TLB has a higher energy density, usually 200 Wh/kg, and there is room for improvement in the future. In contrast, only a few LIPB can reach 130-150 Wh/kg, with less room for future improvement. This makes TLB smaller and more convenient to use while providing the same amount of energy [11].

In terms of safety, LIPB has high safety. It will not spontaneously combust after being subjected to external forces, and will only decompose internally when it reaches 700 °C to 800 °C. In contrast, lithium ternary batteries will decompose at 250 °C to 300 °C, which is less thermally stable. In contrast, lithium ternary batteries will decompose at 250 °C to 300 °C, with poor thermal stability. And it is easy to cause a short-circuit under the action of external force, and the temperature rises to reach the spontaneous combustion temperature and spontaneous combustion [4].

In terms of cost price, LIPB has a lower cost. Because the current iron and phosphorus resource reserves are sufficient, the price is low. In contrast, nickel, cobalt and manganese cost price is relatively high.

In terms of charging efficiency, the TLB is much more efficient. When charging at ten times the constant charging current, there is little difference in the charging efficiency of the two batteries. When charging at 20 times the constant charging current, the charging efficiency of TLB is significantly better than that of LIPB [12].

In terms of low-temperature discharge, TLB has better low-temperature discharge. At 25 °C, both TLB and LIPB have 100% battery capacity. However, at -20 °C, the battery capacity of Li-ion ternary battery drops to 70.14% of that at 25 °C. The LIPB decreased even more, down to 54.94% [7].

In terms of cycle life, LIPB has better cyclability. Lithium ternary batteries in the cycle after 3900 times the battery capacity will be reduced to 66%. And LIPB in the cycle after 5000 times and 84% of the battery capacity [4].

From the comparison of seven aspects, Li-ion ternary battery has environmental friendliness, while Li- FePO_4 battery has environmental friendliness, lower cost price, higher safety and longer cycle life. The two battery structures are different, both have their own respective advantages and disadvantages, and are widely used by customers in different needs and scenarios. But for now, neither battery is the optimal choice. In the future, our research on these two types of batteries should be continued and deepened. Continuously improve their performance, or try to combine their superior performance in the direction of research, to create a new combination of the advantages of the two new cathode materials to replace ternary materials and LIPB. At the same time, the research on new alternative energy sources is also developing rapidly. It is believed that a perfect solution will be applied to the automotive industry in the near future.

5 Conclusion

Lithium ternary batteries and LIP batteries have their own advantages and disadvantages in terms of performance and application areas. By analyzing the structure, performance and application of the two batteries, the octahedral structure of the anode of Li-ion ternary battery, with its high energy density, fast charging ability and excellent low temperature discharge performance, has been widely used in the occasions requiring high energy output, such as electric vehicles. The different ratios of nickel, cobalt and manganese in the cathode material allow it to be applied to different needs. However, TLB has poor high-temperature stability, are prone to thermal runaway at high temperatures, and have a relatively short cycle life. Therefore, the applicability of TLB is limited in high temperature and long life applications. LIPB are known for their high safety, long cycle life and relatively low cost. Its unique olivine crystal structure and stable P-O covalent bonds give it excellent thermal stability, even at high temperatures, the battery will not easily decompose. The disadvantages of LIPB are mainly reflected in their low energy density and low temperature discharge performance, which limits their application in some high energy demand and low temperature environments. However, due to its low cost and environmental friendliness, LIPB has been widely used in price-sensitive markets such as energy storage devices and economical electric vehicles.

Lithium ternary batteries and LIPB have their own advantages and limitations, future research should continue to focus on improving the energy density, safety and cycle life of the two, in order to achieve a comprehensive improvement in performance.

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