

Development of Low Temperature Lithium Ion Batteries

Jiarun Chen *

Chemical engineering institute, Qingdao University of Science and Technology, Qingdao,
Shandong, China

* Corresponding Author Email: 1158981575@qq.com

Abstract. This article briefly introduces the history of the birth of lithium-ion batteries and discusses the necessity of studying how to make lithium-ion batteries work properly under low-temperature conditions. It also introduces the development of ternary materials, a common material for lithium-ion batteries, in the past two years, as well as the working conditions and performance advantages and disadvantages of ternary materials and another commonly used positive electrode material, lithium iron phosphate, in different environments. Finally, a comprehensive overview of the development path of lithium-ion positive electrode materials under low-temperature conditions is given.

Keywords: Lithium battery, Cathode material, Low temperature.

1. The birth of lithium-ion batteries

In 1991, Sony announced a new product lithium-ion battery (LIB), which marked a revolutionary change in battery technology. Before this, lithium battery technology encountered many challenges, especially due to safety issues. In the early days, there was a fire in a mobile phone using an Energy lithium/molybdenum disulfide battery, which caused the user to be injured, which caused concern about the safety of lithium batteries.

Sony and other companies have been trying to develop a lithium metal battery with manganese dioxide positive electrode, but this system also has safety problems. During this period, the author studied the Li/MnO₂ system in the Energizer Research Laboratory and found the safety hidden trouble of lithium batteries. The signs of dendritic lithium short circuits and accidental battery explosion observed in the test show the seriousness of these safety problems.

Despite the safety problems, interest in lithium metal technology continues because these batteries have high specific energy and energy density. Compared with previous aqueous systems, the high battery potential and low atomic weight of lithium make lithium batteries significantly improved. Besides Sony, other companies are also studying different types of lithium batteries, such as the Li/TiS₂ system of Exxon Group and the Li/NbSe₃ system of Bell Laboratories Group.

However, the Exxon system is also plagued by safety problems, especially lithium anode and electrolytes containing LiClO₄ salt are sensitive to impact and may explode under strong enough impact conditions. In addition, the cycle efficiency of lithium electrodes is poor and its cycle life is limited. Most studies use excessive lithium metal to improve efficiency, but the capacity will decrease with the number of cycles.

Although the early exploration of lithium battery technology was not successful, these studies provided us with a deep understanding of the process and material requirements. It is found that secondary batteries are more sensitive to impurities such as water in electrolytes and electrode materials, and their processing methods are different from those of primary batteries. These works provide valuable experience for pushing LIBs to the best state of the current system.

Generally speaking, the research and development of lithium metal batteries laid the foundation for the appearance and improvement of LIBs. Although LIBs have been widely used today, there are still some shortcomings, such as cycle life and safety. The improvement of the current system will determine the future performance of LIBs [1].

2. Necessity of development of low-temperature LIB

LIBs have become the main power supply for many consumer products because of their high energy density, high power density, and long life. In recent years, with the consideration of energy density and economy, LiFePO_4 , LiMn_2O_4 , LiCo_2O_4 , $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and $\text{LiNi}_{1-x-y}\text{MnyCozO}_2$ have become mature cathode materials, while graphite still dominates the anode market. The weight and energy density of LIBs has reached 250 Wh kg^{-1} , providing more than 300 kilometers of driving mileage for electric vehicles.

However, although LIBs have achieved great success in the field of consumer products, their applications in transportation and large-scale energy storage have also brought new challenges and opportunities. In addition to the requirements of energy density, power density, fast charging ability, life, and safety, the working temperature of LIBs is also an urgent problem.

According to the climate in China, in winter, the temperature in 38% of areas is below -20°C . In addition, the lowest temperature in high-latitude countries can even reach about -40°C . Therefore, LIBs used at low temperatures (LT) need to be able to work normally at extreme LT as low as -40°C .

According to the application goal of the American Advanced Battery Association (USABC) for electric vehicles, batteries need to survive for 24 hours under non-operating conditions of -40 to -66°C and provide at least 70% energy at the rate of C/3 at -20°C . The service life of the battery should exceed 15 years in the temperature range of -30 to -52°C , and the charging time should be less than 15 minutes at 80% state of charge. In addition, special batteries for military and polar exploration need to be able to work at -60°C , while low-temperature batteries for aerospace applications need to be able to work effectively at -80°C . However, the most suitable operating temperature range for LIBs is 15 to 35°C . At LT, the performance of the latest LIB will be seriously degraded, mainly due to the significant reduction of output energy and power [2].

Specifically, due to the slowdown of reaction kinetics, the output energy and power of LIBs will be significantly affected at LT. In the process of low-temperature charging, the Li^+ embedding potential of graphite anode is close to 0V, which may lead to a competitive "lithium plating" or "lithium deposition" reaction. In addition, the electroplating morphology of lithium metal in conventional electrolytes is dendritic, which may lead to side reactions and internal short circuits.

3. Development of ternary materials for low-temperature LIBs

3.1. Definition of ternary materials

Ternary material is a composite material designed for the field of new energy pure electric passenger cars, which is prepared from metal salts through multiple processes. Its advantages lie in its specific capacity, cycle life, energy density, safety, and cost compared with other materials (such as lithium cobaltate, lithium manganate, and ferrous lithium phosphate). This makes it widely used in the field of electric vehicles.

Its general molecular formula is $\text{Li}(\text{Ni}_a\text{Co}_b\text{X}_c)\text{O}_2$, where $a+b+c=1$. The main classification method is based on different specific materials X, such as aluminum and manganese. When X is aluminum, it represents a ternary material of nickel, cobalt, and aluminum (NCA); When X is manganese, it represents a ternary material of nickel, cobalt, and manganese (NCM). According to the relative content of nickel, NCM can be subdivided into different models, such as NCM111, NCM523, NCM622, NCM811, and so on. Among them, the model with higher nickel content usually has stronger comprehensive performance, but the technical threshold is also higher.

Both NCM and NCA are designed to solve the stability problem of lithium cobaltate or lithium nickelate layered structure. Among them, the doping of manganese and aluminum plays a key role. The addition of manganese helps to guide the mixing between lithium and nickel layers, thus improving the high-temperature properties of materials. The doping of aluminum can improve the lattice structure of the material to some extent, reduce the collapse, and then improve its cyclic stability [3].

3.2. Technical route of ternary materials

The two main technical routes of ternary cathode materials are the NCM route with lithium NCM as the cathode and the NCA route with lithium NCA as the cathode. In the NCM route, NCM can be divided into two main series according to its components: low cobalt symmetric ternary materials and high nickel ternary materials. Typical examples of low cobalt symmetric ternary materials are 333 and 442, in which the molar ratio of Ni/Mn is fixed at 1. This kind of material has the potential to develop in the direction of high pressure because of its low Ni content, high Mn content, and relatively complete crystal structure. However, the ternary material with high nickel content adopts a hydroxide coprecipitation process, which makes the three elements of Ni, Co, and Mn uniformly distributed in the precursor at atomic scale. At present, the representative high nickel ternary components include 622, 701515, and 811. The physical properties of 811 and NCA are very similar, and the actual gram capacity in the whole battery can exceed 190 mAh g^{-1} . However, increasing the nickel content will increase the capacity, but it will also obviously increase the negative impact. With the increase of nickel content, the mixing effect of Ni in the Li layer is more obvious, which will directly deteriorate the cycle performance and rate performance. In addition, increasing the nickel content will also lead to the deterioration of crystal structure stability and the increase of surface residual alkali content, which will lead to outstanding safety problems, especially the generation of serious gas under high-temperature test conditions.

The industrialization technical difficulties of high nickel ternary materials mainly focus on the production of precursors, the sintering of products, and the surface treatment process. Among them, the precursor preparation process accounts for 60% of the technical content. The preparation of the precursor must strictly control the atmosphere and the concentration of the complexing agent, otherwise, the nickel content will deviate from the stoichiometric ratio, which will further affect the quality of the precursor and ultimately affect the physical and chemical indexes of sintered products. The sintering process mainly involves the selection of dopants and the control of the sintering temperature and atmosphere.

On the other hand, as a ternary material, the research and development of NCA started earlier in foreign countries, while it started relatively late in China. There are more than 15 domestic enterprises engaged in NCA production, but most of them are in the initial stage of construction and development or the stage of sample submission and testing in small batch production. Compared with Japan and South Korea, there is an obvious gap in the field of NCA materials in China. The NCA battery used by Tesla comes from Matsushita, Japan, which drives the global NCA production boom. At present, the domestic NCA production is about several hundred tons. The technical difficulty of industrial production of NCA materials lies in the need to master the coprecipitation process of precursors and the unique Al doping technology. In addition, the control of sintering temperature and atmosphere is also the key. In addition to material challenges, the battery production process also needs to match NCA materials. NCA materials are easy to absorb moisture because of the high content of alkaline substances on the surface, so it is necessary to strictly control the moisture in the homogenization and coating workshop to prevent the slurry from coagulating into jelly during homogenization, which will affect the coating effect. In addition, special measures such as adding a small amount of oxalic acid to improve the coagulation of slurry or adding cosolvent to NMP to improve the agglomeration during pulping are taken. In addition, the compatibility with NCA for electrolytes also has high requirements, otherwise, the battery cell will be seriously inflated, and it is difficult to pass the high-temperature cycle and storage test.

Generally speaking, the development trend of ternary materials in the future is to develop towards high nickel. High nickel content can improve the material capacity, but at the same time, it also puts forward higher requirements for the structural stability, thermal stability, and cycle performance of products, which tests the ability of enterprises to control products [3].

3.3. Comparison between ternary lithium battery and lithium iron phosphate battery at low temperature

At present, the types of power batteries for new energy vehicles are mainly divided into Ferrous lithium phosphate and ternary lithium batteries, which divide the share of power batteries in the new energy market. Therefore, it is particularly important to compare their working conditions in low-temperature environments.



Figure 1. New energy vehicles in cold weather.

3.1.1. Performance

Ternary lithium battery: Ternary lithium battery usually performs well at LT, and its performance attenuation is less than that of lithium iron phosphate battery. This is because ternary materials (such as lithium nickel manganese cobalt oxide, NMC for short) have higher specific energy and better low-temperature characteristics.

Lithium iron phosphate battery: the performance of lithium iron phosphate battery at LT may be affected to some extent, and its capacity and power may decrease, resulting in the battery performance is not as good as that at room temperature.

3.1.2. Battery capacity

Ternary lithium battery: The capacity of ternary lithium battery remains relatively good at LT because its chemical reaction can usually be carried out more effectively at lower temperatures.

Lithium ion phosphate battery: The capacity of lithium iron phosphate battery may decrease at LT, which is mainly due to the material characteristics and the limitation of chemical reaction.

3.1.3. Power output

Ternary lithium batteries: Ternary lithium batteries can usually provide better power output at LT, which makes them more suitable for applications requiring high power output at LT, such as electric vehicles.

Lithium iron phosphate battery: The power output of lithium iron phosphate battery at LT may be limited to some extent, and its performance may not be as good as that at normal temperatures.

3.1.4. Security

Ternary lithium battery: Ternary lithium battery is relatively safe at LT, and its chemical reaction is usually stable.

Lithium iron phosphate battery: Lithium iron phosphate battery also has good safety at LT, but some problems may occur at extreme LT, which requires appropriate measures for management and prevention.

To sum up, although ternary lithium batteries and lithium iron phosphate batteries can work at LT, ternary lithium batteries usually perform better and have higher performance and stability. This makes them more popular in low-temperature environments, especially in applications that require high performance and safety.

4. Breakthrough of sub-zero temperature

As a battery component, the anode plays a key role in maintaining the stable operation of batteries. From the electrochemical point of view, the electrode performance under LT conditions is affected by multiple challenges, mainly including increased charge transfer resistance and kinetic limitations that limit the transport of Li^+ ions. In addition, the formation of a solid electrolyte interface (SEI) on the anode side also has a great influence on the performance of the battery. Therefore, the key to improving the performance of anode-side LT batteries is to optimize the electrode structure and reaction interface to reduce the resistance and maintain the stability of SEI.

As the first commercial anode material for LIBs, graphite has attracted extensive attention in the past decades. However, in a low-temperature environment, graphite electrode faces many challenges. According to the data of ARL, when the temperature dropped from $-30\text{ }^{\circ}\text{C}$ to $-40\text{ }^{\circ}\text{C}$, the electrolyte resistance, SEI resistance and charge transfer resistance of the graphite electrode increased significantly, which harmed the battery performance. In addition, the diffusion coefficient of Li^+ in graphite also decreases sharply in the state of complete lithiation and lithium removal [4].

To meet the challenge of low-temperature environments, researchers have carried out extensive exploration and experiments, mainly focusing on improving anode materials and treatment methods. For example, the mixture of partially oxidized graphite and metal nanoparticles, as well as the Sn-graphite composite anode, show that it can still maintain a relatively high capacity at extreme LT (such as $30\text{ }^{\circ}\text{C}$). In addition, pre-lithiation treatment and the use of composite electrodes have been proven to be effective methods to improve the electrochemical properties of graphite at LT. For example, by pre-lithiating the hard carbon anode, a high capacity retention rate of over 67% can be achieved at $-40\text{ }^{\circ}\text{C}$, which is far superior to the traditional LIB.

In addition, the development of novel graphene electrodes with structure control (such as free-standing 3D folded graphene) also provides new possibilities for improving LT performance. These structurally controlled electrodes significantly improve the performance of the battery by optimizing the charge storage kinetics of Li^+ and maintaining the stability of the anode structure. For example, some studies show that at $40\text{ }^{\circ}\text{C}$, the graphene electrode with structure control can maintain excellent capacity, such as the charge capacity of 154 mAh g^{-1} .

To sum up, by optimizing material selection, structural design, and treatment methods, the electrochemical performance of anode at LT can be significantly improved, which provides important support and potential for the application and expansion of LT batteries [5].

Compared with graphite, lithium titanium titanate (LTO) performs better at LT because of its superior lithium-ion intercalation behavior. Although LTO has low electronic conductivity, which will affect its electrochemical performance at LT, these problems can be effectively alleviated by reducing particle size and optimizing structural design. For example, the pod-like LTO structure prepared by researchers through hydrothermal reaction and solid-state process protects the internal nanoparticles and prevents them from being broken during the redox process, thus maintaining high cycle stability and electrochemical performance.

5. Conclusion

In addition, the preparation of graded porous LTO-titanium dioxide (HP LTO-TO) microspheres also showed significant performance advantages. This structure is composed of ultra-thin nanosheets with a large specific surface area, which greatly shortens the ion diffusion path and improves the low-temperature discharge performance of the battery. Through the analysis of a high-resolution transmission electron microscope, the researchers confirmed the coexistence of LTO and titanium dioxide, which enhanced the cation transmission efficiency and further improved the performance of the battery.

To sum up, the key to LTO's superiority over graphite in low-temperature environments lies in its excellent ion diffusion characteristics and structural stability, which makes it more and more popular in electric vehicles and other applications.

References

- [1] Marco-Tulio F. Rodrigues, Ganguli Babu, Hemtej Gullapalli, Kaushik Kalaga, Farheen N. Sayed, Keiko Kato, Jarin Joyner and Pulickel M. Ajayan. A materials perspective on Li-ion batteries at extreme temperatures[J]. *Nature Energy*, 2017, :1-16.
- [2] Fanbo Meng, Xingyu Xiong, Liang Tan, Bin Yuan, Renzong Hu. *Energy Storage Materials*[J]. *ELSEVIER*, 2022, 44:390-407.
- [3] Nan Piao , Xuning Gao, Huicong Yang , Zhenqiang Guo, Guangjian Hu, Hui-Ming Cheng , Feng Li. *Etransportation* [J]. *ELSEVIER*, 2022:1-18.
- [4] Suihan Cui , Yi Wei , Tongchao Liu , Wenjun Deng , Zongxiang Hu , Yantao Su , Hao Li , Maofan Li , Hua Guo , Yandong Duan , Weidong Wang , Mumin Rao , Jiaxin Zheng , Xinwei Wang , and Feng Pan. Optimized Temperature Effect of Li-Ion Diffusion with Layer Distance in Li (Ni x Mn y Co z) O 2 Cathode Materials for High Performance Li-Ion Battery [J]. *Materialsviews*, 2016:1-14.
- [5] George E. Blomgren. The Development and Future of Lithium Ion Batteries [J]. *The Electrochemical Society*, 2017, 164:1-12.