Development trend of cathode materials commonly used in lithium batteries

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Abstract. With the profound scientific and economic advances, people's demand for electronic products is increasing daily. Lithium-ion batteries are broadly applied due to their significant advantages in weight, volume, and lifespan. The anode of a lithium-ion battery is the main component in the electronic reaction of lithium ions. The materials currently used for the anode of lithium-ion batteries are mainly $LiFePO_4$, ternary lithium batteries, and $LiMnO_2$. Sometimes lithium titanate and $LiCoO_2$ are also used. Different anode materials share their benefits and drawbacks regarding various aspects such as energy density, cost, cycle life, safety, and environmental effects. Material modification or surface coating of the positive electrode of lithium-ion batteries is currently a popular solution, which also has a significant influence on changing the market share of different positive electrode lithium-ion materials. At last, this paper discusses the modification schemes for different types of lithium-ion batteries in the future by reviewing the literature.

1 Introduction

As the scientific and economic advances are increasingly prosperous, people's demand for electronic products is increasing day by day. Lithium-ion batteries are broadly applied in a wide range of industries like consumer electronics, electric vehicles, renewable energy storage, medical equipment, drones, and robotics due to their significant advantages in terms of weight, size and service life. However, we currently still face various problems when using lithium-ion battery anode materials regarding energy density, cost, cycle life, safety and environmental influence. It is inevitable that lithium-ion battery technology will be improved in the future production development.

The basic structure of a lithium-ion battery comprises four main sections: the positive electrode material, the negative electrode material, the electrolyte and the separator. During the charging process, lithium ions in the positive electrode material are precipitated, entering the electrolyte, and passing through the separator to embed in the negative electrode. During the discharging process, lithium in the negative electrode material loses electrons, is converted into lithium ions, returns to the electrolyte and passes through the separator to return to the positive electrode [1-3]. This cyclic process ensures that lithium-ion batteries can be repeatedly used. Currently, the production technology of lithium-ion batteries has

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basically reached 300 Wh/kg. Under the development of various fields in the future, the energy amount of lithium-ion batteries may reach 500Wh/kg

In the 1990s, Japanese companies were the first to successfully produce lithium-ion batteries, and their rapid development followed. Over the past three decades, the application of lithium-ion batteries has gradually expanded, and they have become the main type of battery in consumer electronics, electric vehicles, renewable energy storage, medical equipment and other fields. In the future, with the global trend of the Internet of Everything, lithium-ion batteries will play an essential part in various fields.

At present, the main cathode materials for lithium-ion batteries on the market are mainly $LiFePO_4$, ternary lithium batteries, and $LiMnO_2$. Sometimes lithium titanate and $LiCoO_2$ are also used. The research on lithium-ion batteries significantly contributes to promoting the popularization of renewable energy storage, power interruption (solar energy storage), and the development of portable electronic devices. Moreover, its application in smart grids, energy storage systems, and microgrids has improved energy utilization efficiency and system stability.

2 Lithium iron phosphate material

Lithium iron phosphates ($LiFePO_4$) is the earliest material adopted in lithium-ion batteries and is usually called 'ferroelectric'. At present, the main methods for preparing $LiFePO_4$ anode materials include the high-temperature solid-phase method, the carbon thermal reduction method, and the hydrothermal synthesis method. LiFePO4 batteries are widely applied in solar and wind energy storage systems. They can provide stable power output and extend the cycle life, which is ideal for large-scale power storage needs. Their durability and safety make them ideal for home and industrial energy storage [7]. Moreover, $LiFePO_4$ is one of the battery materials chosen by many electric vehicle manufacturers. In 2022, the installed capacity of power batteries in China will be 302.3 GWh, of which the installed capacity of $LiFePO_4$ power batteries will be 184.5 GWh, accounting for 61%. A large number of popular models such as the entire range of BYD vehicles, the Model Y/3, the Xiaopeng P7/P5, the GAC Aion S/Y, etc. all use $LiFePO_4$ power batteries [6]. LiFePO4 batteries are also available for a wide range of portable electronic devices, whose safety and longevity make them widely used in specific portable devices. However, $LiFePO_4$ faces problems as a cathode material, like low energy density, poor low-temperature performance, poor electrical conductivity and bulky size. There are currently several solutions to these challenges.

First, the nano treatment of this material can extend specific surface areas, shorten the lithium-ion diffusion path, and effectively control both the shape and size of the $LiFePO_4$ particles, thereby improving conductivity and energy density. Second, doping modification, which involves introducing appropriate metal or non-metal elements into $LiFePO_4$, can improve the lithium-ion diffusion performance at low temperatures, enhance its low-temperature discharge capacity, and optimise the crystal structure to improve the lithium-ion diffusion rate and electronic conductivity. In addition, the addition of highly conductive additives can improve the overall conductivity of the electrode, or it can be compounded with high energy density materials to balance safety and energy density. In addition to optimizing the cathode material, the recycling of cathode materials also needs to be considered in order to achieve the goal of sustainable development. At present, direct regeneration has more advantages in terms of economy and environmental protection, but this technology is still in the preliminary research stage, while indirect regeneration is suitable for situations where the raw materials are highly complex or where high-value resource reserves are required[5].

Although the above solutions are highly feasible, nanoprocessing is difficult and costly to implement on a large scale. Currently, the market demand for LiFePO4 batteries is continuing to expand, providing market space and economic incentives for the industrial development of LiFePO4 battery recycling. However, the raw materials of LiFePO4 batteries are not highly valuable, and the economic benefits of recycling them are limited. The costs and benefits of the entire life cycle of LiFePO4 batteries need to be comprehensively considered in order to clarify the economics of industrialisation and enhance the driving force for sustainable development[5].

3 Ternary lithium battery material

Ternary lithium batteries refer to a series of oxides composed of nickel, cobalt and manganese, and the ratio of each element directly affects the performance of the battery. Studies have shown that increasing the nickel content significantly improves the energy density, indicating that nickel plays a key capacity maintenance part in ternary lithium-ion batteries [4]. As a ternary cathode material for lithium-ion batteries, NCM combines the high specific capacity of lithium nickelate ($LiNiO_2$), the profound thermal stability and the lower price of lithium manganese oxide ($LiMnO_2$), and the advantages of lithium cobalt oxide ($LiCoO_2$) with stable electrochemical properties, it has demonstrated excellent electrochemical performance. It has long been the main cathode material used in power batteries due to its high energy density [8,9]. However, its disadvantages should not be ignored, which mainly include high cost (scarce and expensive cobalt resources), low cycle life, and the risk of oxygen molecules being released during charging and discharging, which may lead to combustion or deflagration under high-temperature conditions [8]. Therefore, corresponding control and early warning measures must be taken when using ternary lithium-ion batteries to prevent extreme situations [2]. To solve these problems, high-nickel ternary cathode materials have been optimised in recent years by means of ion doping, surface coating, co-modification, concentration gradients, electrolyte modification and structural regulation.

Ion-doped cathode materials can expand the interlayer spacing of the material, increase the diffusion rate of Li, reduce the Li/Ni mixed row, and stabilize the lattice structure. Furthermore, ion doping forms higher energy TM-O bonds, which inhibit structural distortion and the generation of microcracks, thereby stabilising the material structure and improving the battery's lifespan. Coating the NCA cathode material with different substances hinders direct contact between the electrolyte and the material, inhibiting the erosion of the electrolyte and thereby improving the battery's electrochemical performance. Copolymerization combines the advantages of different modified components to more effectively enhance the electrochemical properties of the material. Modification of the microstructure of the concentration gradient can enhance the stability of the outer layer of the material, and keep the original electrochemical characteristics of the cathode material at the same time. Electrolyte modification can improve the chemical stability of the electrolyte to inhibit decomposition and form a reactive protective film on the cathode material surface, extending the cycle life of the battery. Structural regulation improves the electrochemical performance of high-nickel ternary cathode materials by adjusting the lattice structure and particle morphology, thereby enhancing mechanical stability and Li^+ diffusion performance [8]. The above optimisation solutions are currently mainly being studied in laboratories. In terms of industrialization, some of these technologies have matured and are highly feasible, promoting the future development of ternary lithium batteries.

4 Lithium manganese oxide material

In the domestic market and research field, the share of $LiMnO_2$ batteries compared to $LiFePO_4$ batteries and ternary lithium batteries is extremely limited, and their production and research and development are mainly concentrated in Japan. $LiMnO_2$ batteries have good safety performance, good low-temperature performance, resistance to overcharging or over-discharging, and are very inexpensive. They are seen as one of the most prosperous cathode materials, and their main application area is plug-in hybrid vehicles. It is also important to note that there are 36 pure electric buses with $LiMnO_2$ as the main application, accounting for as high as 17% [10]. However, there are still significant problems with its high-temperature performance and cycle stability.

Several improvement schemes have been proposed to address these deficiencies. First, by coating the surface of the material, a layer of inert elements or compounds can be coated on the surface of the lithium nickel manganese oxide material, which can effectively decrease the contacted area between the electrolyte and the lithium nickel manganese oxide, thereby reducing the occurrence of side reactions and protecting the active material. Alternatively, a layer of fast ion conductors can be coated on the surface of the lithium nickel manganese oxide material, which can protect the positive electrode material while enhancing the lithium-ion transport rate, thereby improving the electrochemical performance [11]. Secondly, replacing the nickel-manganese ions with cations with stronger chemical bonds replacing the oxygen ions with anions, or filling the oxygen defects can make the material structure more stable, so that it can withstand more stress without collapsing [11]. Finally, structural optimisation, such as nanotreatment or porous structure design, can improve battery performance. At present, these modification methods are already being used in production and laboratories, but the technical aspects of surface coating are still widely under-explored and need further studies.

5 Lithium cobalt oxide material

In addition to the three common lithium-ion batteries mentioned above, types such as LiCoO2 batteries are still reasonable in specific application fields, although they are rare in production and research. Due to their ease of processing, unseen volumetric energy density and high working potential, lithium cobalt oxide (LCO)-based battery materials are dominant in lithium-ion batteries (LIBs) based on 3C (computers, communications and consumer electronics) [12]. However, despite their superior energy density, their other performance indicators are still inferior to those of other types of batteries. Therefore, the main solutions currently focus on surface coating technology, and the following coating methods are commonly used. (1) Carbon itself is an electronic conductor material. Some foreign scholars used the low-temperature liquid phase method to coat carbon on the surface of Li_2CO_3 material and found that carbon can enhance the cycle rate as well as high-temperature storage performance of the material. (2) Ionic conductor coating: LATP is an excellent ionic conductor material. Coating it on Li2CO3 can improve the rate and cycle performance of the material at 4.5V. (3) Electronic-ionic double conductor coating: The electrode itself is a good electronic-ionic conductor. Existing research has confirmed that AlWxFy is an excellent electronic-ionic conductor. Coating it on Li_2CO_3 can make it exhibit good electrochemical properties at 4.5V. (4) Double electronic and ionic insulation coating: oxides such as Ti, Mg, Al and Zr are often used. The research found that mechanised coating of Li_2CO_3 material with TiO helps to enhance its stability at high voltages and significantly improves its chemical and electrical properties [13]. Surface coating using these methods can solve most problems, but due to the scarcity of cobalt in the raw material of $LiCoO_2$, $LiCoO_2$ materials still cannot become a relatively large proportion of lithium-ion materials on the market. Finding suitable metal ions and a suitable ratio to replace them is also the main development direction of $LiCoO_2$ materials at present.

6 Conclusion

The main battery types on the market today are $LiFePO_4$ batteries and ternary lithium batteries, while $LiMnO_2$ batteries and $LiCoO_2$ batteries are mainly used in specific fields. Different battery types have different advantages and are suitable for different applications. $LiFePO_4$ batteries can be applied in various fields such as electric vehicles (EVs) and grid energy storage that require high safety and long life and lower energy density, due to their profound performance in these aspects. Ternary lithium batteries with high energy density are ideal components for these high-performance electric vehicles and portable electronic devices, but are relatively expensive and have relatively poor thermal stability. $LiMnO_2$ is low-cost and safe, and is suitable for small and medium-sized devices with short-term use, such as electric bicycles and power tools. $LiCoO_2$ is widely used in consumer electronics like cellphones and laptops, owing to its high energy density, but it is expensive and relatively unsafe. There are some commonalities in the ways in which different materials enhance the cathode materials performance. The main technologies that have been put into production are surface coating, structural optimization and doping modification, but the materials used in the modification process are quite different. Some materials have not yet been mass-produced due to high technical barriers or costs.

In the future, if the relevant technical problems can be solved, the performance of various types of batteries will be significantly improved. At the same time, the doping modification solutions under research also have the potential to bring about significant changes in market share.

References

1. L. Wang, Analysis of the Development Trend of Positive Electrode Materials for Lithium-ion Batteries. J. Changji Univ. **04**, 118-122 (2020).
2. Y. Dong, Y. Liu, Y. Hu, et al., Research on the Reaction Dynamics and Reversibility Enhancement Mechanism of Lithium Storage Based on VS_2/MoS_2 Schottky Heterojunction. Sci. Bull. **65**, 1470-1478 (2020).
3. P. Zhu, Experimental Analysis of Charging and Discharging Characteristics of Lithium-ion Power Batteries. Sci. Technol. Innov. **19**, 24-25 (2020).
4. S. Liu, H. He, C. Chang, Discussing the Past, Present, and Future of Lithium Batteries from the 2019 Nobel Prize in Chemistry. J. Appl. Technol. **20**, 135-139 (2020).
5. Y. Wang, X. Zheng, D. Ruan, et al., Recycling of Lithium Iron Phosphate Batteries: From Basic Research to Industrialization. Chin. Eng. Sci. 1-14 (2022).
6. D. Liu, F. Xiao, The Current Status of Patent Technology for Lithium Iron Phosphate Power Batteries. China Sci. Technol. Inf. **17**, 15-17 (2024).
7. L.-X. Yuan, Z.-H. Wang, W.-X. Zhang, X.-L. Hu, J.-T. Chen, Y.-H. Huang, J.B. Goodenough, Energy Environ. Sci. **4**, 269-284 (2011).
8. L. Zhao, J. Wang, Y. Zhang, et al., Research Progress on Modification of High Nickel Ternary Cathode Materials for Lithium-ion Batteries. Funct. Mater. **55**, 9064-9070 (2024).
9. P. Li, W. Li, C. Xu, et al., Research Progress on Doping Modification of Ternary Positive Electrode Materials for Lithium-ion Batteries. J. Zhengzhou Univ. (Sci. Ed.) **56**, 80-87 (2024).
10. S. Zeng, Y. Chen, J. Tang, et al., Comparison of Electrochemical Performance Based on Ternary, Lithium Iron Phosphate, and Lithium Manganese Oxide Cathodes. J. Guangdong Norm. Univ. Technol. **44**, 53-58 (2023).

11. J. Yan, Preparation and Modification of Lithium Nickel Manganese Oxide Cathode Material. Central South Univ. (2023).
12. J. Gu, J. Ji, W. Zhou, et al., Research Progress on Lithium Cobalt Oxide as Cathode Material for Lithium-ion Batteries. Appl. Chem. 1-4 (2022).
13. J. Xie, On the Development of High Voltage Lithium Cobalt Oxide Cathode Materials. Technol. News **21**, 44-47 (2023).