Research on the Technological Development of Lithium Ion Battery Industry in China

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Abstract: Combined with the background of the rapid development of new energy automobile industry and the power battery gradually becoming the absolute main force of the market in recent years, this paper illustrates the current development status of global and Chinese lithium ion battery industry and analyzes the future development trend of the industry. Focusing on ternary lithium ion battery, all-solid-state lithium ion battery, anode material, lithium hexafluorophosphate electrolyte and diaphragm materials, this paper describes the research and development of different key materials and technologies of lithium ion battery, and gives the prospect of future technology development direction. Based on Chinese lithium ion battery industry background, reasonable industrialization suggestions are put forward.

1. 1 Introduction
Lithium ion batteries have the advantages of high discharge voltage, high energy density, long cycle life and no pollution. Because it relies on the transfer of lithium ions between the cathode and the anode to complete the battery charge and discharge work, it is also figuratively known as "rocking chair battery"[1]. The battery is mainly composed of cathode and anode, electrolyte, membrane and other key material, and the electrochemical properties of the battery are determined by the properties of the materials. Now, lithium iron phosphate battery as a representative of the previous generation of lithium batteries will soon become a thing of the past; Ternary material lithium ion battery has become the main technology due to its good ternary synergy and low temperature performance; All-solid-state lithium batteries combine the advantages of high energy density and safety, which is an important development direction of lithium battery technology in the future, expected to be the next generation lithium battery.

2. The Development Status of Lithium Ion Battery Industry
Globally, Japan has the earliest and most sophisticated lithium-ion battery manufacturing industry. Therefore, Japanese lithium ion battery manufacturing industry has occupied a very important position in the world for a long time. With the technological progress of other countries, especially South Korea and China, the global lithium battery industry continues to make technological breakthroughs. Their market position has been rapidly improved and the market share has been increasing. Currently, the global lithium battery market dominated by China, Japan and South Korea has basically taken shape.

In recent years, with the rapid growth of lithium ion batteries in electric vehicles, 3C and other fields, the overall production and market scale of lithium ion batteries in the world have been rapidly increased. In 2018, Total global production of lithium ion batteries reached 170.5GWh, with year-on-year growth of 15.12%. From 2005 to 2018, The global lithium battery market grew from $5.6 billion to $35 billion, and the annual compound growth rate is as high as 15.1%. In 2017, the main application market growth of lithium ion battery slowed down, but the global lithium battery growth is expected to be...
stable in the future, driven by the boom of the new energy automobile industry, and the global lithium battery market is expected to reach $40 billion by 2020 [2].

Currently, the development of global lithium ion battery industry presents four characteristics: The first is the emergence of power battery drive effect; The second is the focus of industrial development is further shifting to China; The third is the pace of technological innovation is accelerating; The last is industrial integration has continued to strengthen.

Domestically, China has become the most active lithium battery development region in the world. In terms of production, in 2017, China produces about 88.7GWh lithium ion batteries, with the Year-on-year growth of 29.3%. The output of power battery was 44.5GWh, making it the largest consumer end over 3C products, and consumption of new-energy vehicles accounted for 50% of total production [3]. Power batteries are becoming the largest driving engine in China's lithium-ion battery industry, driven by growing sales of new-energy vehicles, battery upgrades, the replacement of lead-acid by lithium batteries and the expansion of the export market. The market focus will further transfer to the power application, the domestic power lithium ion battery production enterprises ushered in a rare opportunity for development.

From the perspective of domestic lithium battery application field, the rapid development of power, 3C and energy storage industry has become the main driving force driving the development of lithium ion battery industry. Among them, 3C lithium ion battery growth is slow, resulting in a declining market share; The lithium ion battery for power is increasing rapidly due to the increase of electric vehicle production, and the steady increase of lithium ion battery penetration rate in electric bicycle makes its market share increase rapidly; The accelerated pace of energy storage power station construction and the gradual promotion of lithium ion battery in the field of mobile communication base station energy storage battery make the market share of energy storage lithium ion battery start from scratch.
3. The Development Status of Lithium Ion Battery Technology

With the rapid development of new energy vehicles, 3C and other industries, the performance of single lithium ion batteries has been unable to meet the specific needs of various applications, so people began to develop batteries with special performance for different applications. Specifically, current researches on lithium ion batteries mainly include high energy density, high power density and long life etc. [4,5].

From the current dynamic point of view, the traditional lithium manganese oxide battery, lithium cobalt oxide battery [6] and other technical routes have long fallen behind, lithium iron phosphate battery [7] technology route is being replaced, ternary lithium battery technology route gradually become the mainstream. Ternary lithium battery products are becoming more and more mature. The American Tesla Model series has achieved a breakthrough. The large-scale production and sales of Model 3 further demonstrate the feasibility of ternary lithium battery [8]. Model 3 uses a new 21700 battery, which is longer and thicker in appearance than the 18650 battery and has a 20% higher energy density. The capacity of single battery can reach 3–4.8Ah, which was greatly increased by 35%. Meanwhile, European and American companies have begun to place more of their hopes on next-generation lithium-ion batteries with higher energy densities (such as all-solid-state lithium-ion batteries) or next-generation secondary lithium ion batteries (Such as lithium-sulfur battery and lithium-air battery, which have extremely high theoretical energy density, but are not lithium ion batteries in essence). They are expecting to see big changes in these battery technologies in the automotive and energy-storage industries. General Motors and Volkswagen, for example, have made LG Chem their battery partners and invested in all-solid-state lithium ion battery technology development companies. General Motors invested in Sakti3, and Volkswagen invested in QuantumScape.

3.1. Ternary Lithium Ion Battery

Ternary lithium ion battery is a kind of lithium ion battery takes ternary material as cathode, which has high development value and market prospect because of its excellent low temperature performance. Ternary materials commonly use LiNi_{x}Co_{y}Mn_{1-x-y}O_{2}(NCM) and LiNi_{x}Co_{y}Al_{1-x-y}O_{2}(NCA). Ternary materials have obvious ternary synergistic effect, which integrates the advantages of lithium cobalt oxide, lithium nickel oxide, lithium manganese oxide and other materials, with high energy density, high capacity, low cost and good cycle stability. More importantly, ternary materials have abundant composition systems, which can be used to select the modulation level of the material system according to the performance requirements. While the disadvantage of ternary materials is that their safety needs to be improved.

At present, the research of ternary materials focuses on the following points:

3.1.1. High Nickel Ternary Materials

High nickel ternary material [9] means that the mole fraction of nickel in the material is greater than 0.6. Such ternary materials have the characteristics of high specific capacity and low cost, but there are also defects such as low capacity retention rate and poor thermal stability.

Coprecipitation combined with high-temperature solid phase method [10] is the mainstream preparation method for now. Firstly coprecipitate to obtain the precursor with uniform raw materials and uniform particle size. Then, by high temperature calcinations, ternary materials with regular surface morphology and easy control process are obtained. The spray drying method [11] is simpler and faster than the coprecipitation method, and the morphology of the obtained materials is no less than that of the coprecipitation method, which has the potential for further research. The defects of high nickel anode materials, such as cation mixing and phase change during charging and discharging, can be effectively improved by doping modification [17] and coating modification [18].

3.1.2. Lithium-Rich Ternary Materials

Due to its special structure [12] of lithium-rich ternary material xLi_{2}MnO_{3}·(1-x)LiMn_{1/3}Ni_{1/3}Co_{1/3}O_{2} (0.1≤x≤0.5), more lithium can be released, which has the advantages of wide voltage window and high specific volume, and has been favored by researchers in recent years.
Solid phase method, sol-gel method, hydrothermal method, spray pyrolysis method and coprecipitation method can be used to prepare lithium-rich ternary cathode materials with different structures. Each method has its own advantages and disadvantages, and coprecipitation is more widely used for now.

3.1.3. Single Crystal Ternary Materials
Single-crystal high-voltage ternary materials can improve the transfer efficiency of lithium ions and reduce the side reactions between materials and electrolyte, so as to improve the cycling performance of materials under high voltage. First prepare the ternary material precursor by coprecipititates. Then, under the action of high temperature solid phase, the single crystal LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 could be obtained. This material has a good layered structure and high energy density. After 1,300 cycles, the discharge specific capacity of the whole battery is still 98% of the initial discharge capacity, and it is a ternary cathode material with excellent electrochemical performance [13].

3.1.4. Doping Modification with Graphene
Graphene has a single atom-thick two-dimensional structure with stable structure and conductivity up to 1×10^6 S/m. Graphene has the following advantages: 1) Good conductivity and heat conduction are helpful to improve the multiplier performance and safety of the battery; 2) More storage space for lithium, which can improve the energy density of batteries; 3) Particle size is extremely small, and lithium ion diffusion path is short, which is conducive to improving the power performance of the battery [14].

Graphene-doped ternary cathode materials were prepared by ultrasonic combined with wet chemical method, which not only ensured the uniform mixing of graphene and ternary materials, but also protected the microstructure of the materials from being damaged. The SEM results showed that the mixed particles are secondary grains formed by the aggregation of well-crystallized primary grains, and graphene-doped modified ternary materials fill more and more gaps between particles with increasing graphene content, which is the main reason for the improvement of its electrochemical performance, and the particles were not damaged in the process of modification. The electrochemical performance test results showed that when the doping amount of graphene was 1%, the material showed the best electrochemical performance.

3.1.5. High Voltage Electrolyte
Currently, ionic liquid, dinitrile organic matter and sulfone organic solvent are used as electrolyte of high-voltage ternary material. Ionic liquids with low melting point, incombustible, low vapor pressure and high ionic conductivity show excellent electrochemical stability and are widely studied.

The oxidation stability of electrolytes and the safety performance of batteries can be effectively improved by replacing all or part of the new solvent with high pressure stability. However, most of the new solvents have poor reduction stability and high viscosity, which results in reduced cycle stability of battery cathode materials and battery multiplier performance. Film forming additives are also essential in high voltage electrolytes. The addition of a small amount(<5%) of film forming additive can lead to its oxidation before solvent molecules. The common film forming additives include tetraphenyl-phosphine ammoniate, LiBOB, lithium difluorodioxalate borate, tetramethoxy titanium, succinyl anhydride, trimethoxyphosphorus, etc. [15].

3.1.6. Assisted Synthesis of Surfactants
Adopt coprecipitation, with the synergistic effects of surfactant, ultrasonic vibration and mechanical stirring, and finally the prepared flake precursor and lithium carbonate are grown into ternary layered structure through high temperature annealing. This is a new synthesis technology of ternary anode material.

The surfactant has a good shape control effect on the precursor. OA and PVP can be used as surfactants to prepare the progenitors with excellent morphology, and the size distribution of the
nanocrystals was uniform which is about 400nm. The specific capacity of the first discharge of the battery assembled at the rate of 1C is $157.093 \text{mAh} \cdot \text{g}^{-1}$. After 50 cycles of 1C, 2C, 5C and 10C, the capacity retention rate was more than 92% [16], indicating good electrochemical performance.

3.1.7. Other Methods of Synthesis of Ternary Materials
Among the main methods for preparing ternary anode materials, solid phase method, coprecipitation method and sol-gel method all require several hours of high-temperature sintering, with large energy consumption and complex preparation process. By adopting other synthesis methods, the process and material properties can be effectively improved, which including microwave synthesis [17], infrared synthesis [18] and plasma synthesis [19].

3.2. All-Solid-State Lithium Ion Battery
Traditional lithium ion batteries use organic electrolyte, of which the volatility, flammability and other issues are the key factors causing the safety of lithium ion batteries. Using solid electrolyte to replace organic electrolyte is an important way to solve the safety problem of large-capacity lithium ion battery. In 1973, Fenton [20] and others found that electrolytes with ionic conductivity could be formed by complexing polyoxyethylene(PEO) with alkali metal sodium salt; In 1979, Armand [21] formally proposed the application of polymer electrolyte in solid electrolyte of lithium ion battery. Since then, the all-solid-state polymer electrolyte used in lithium batteries has triggered extensive research at home and abroad. Currently, all-solid-state lithium battery can provide energy density up to 300~400Wh/kg, and also has a longer service life. Toyota has successfully trialled a small, all-solid-state battery, which it plans to commercialise by 2020. All-solid-state lithium battery becoming a new generation of lithium ion battery has been the consensus of academia and industry. Electrolyte materials are the core of all-solid-state lithium batteries, mainly including polymer electrolyte and inorganic solid electrolyte.

3.2.1. Polymer Electrolyte Battery (Polymer electrolytes of polyoxyethylene and its derivatives are)
The composition of polymer electrolyte is similar to that of organic electrolyte, which is composed of lithium electrolyte and "solvent", except that the solvent of polymer electrolyte exists in solid form. Polymer electrolyte batteries are generally prepared by printing, coating and roll-to-roll technology. The cathode and anode plates are coated with polymer electrolyte respectively, and then cured by ultraviolet radiation. Then the cathode and anode plates are pressed together tightly, and finally the battery unit is made by cutting and lamination. Compared with liquid electrolyte batteries, polymer electrolyte batteries have two major advantages: 1) Better thermal stability and high safety performance which support the battery to work at 60~120°C for a long time, and not easy to occur combustion explosion; 2) Lighter weight, good viscoelasticity and excellent machining performance.

However, due to the high crystallinity of PEO, its ionic conductivity at room temperature is low, only $10^{-7} \sim 10^{-6} \text{s/cm}$, which seriously affects the conductivity of the battery. Therefore, it is necessary to modify PEO. PEO transports lithium ions in chains, which have a low capacity in the crystalline zone. Increasing the ratio of amorphous zone in PEO is a way to improve the ionic conductivity. In the aspect of reducing crystallinity, people have carried on extensive research, which can be divided into two categories based on different modification methods: PEO derivatives system and organic-inorganic hybrid system.

PEO derivatives system crosslinks or copolymerizes PEO or groups containing PEO structural units with other polymers PEO, Perturbs the arrangement order of PEO chain or form branched structure, thus inhibiting PEO crystallization. Grafting PEO structural unit groups on polysiloxane chains to form comb polymers is a good modification method, and the conductivity can be improved to $10^{-4} \text{S/cm}$ [22].

In the organic-inorganic hybrid system, inorganic fillers are added into PEO matrix to disrupt the order of polymer chain in the matrix and reduce the crystallinity; At the same time, the interaction between the packing surface and the polymer chain as well as the lithium ion promotes the formation of multiple fast lithium ion channels on the surface, thus improving the conductivity, generally up to $10^{-5}$
The fillers widely studied now mainly include metal oxides such as MgO, Al₂O₃, SiO₂, zeolite, montmorillonite, nanomaterials, porous or layered structural materials, etc. [23].

3.2.2. Inorganic solid electrolyte battery (LiPON electrolyte and sulphide glassy electrolyte)

LiPON is an ideal electrolyte material for lithium ion battery. The battery multiplier performance and recycling performance prepared by it are excellent, and it can work at 50 °C. After 45,000 cycles, the capacity retention rate reaches above 95%. Although the conductivity of this electrolyte is not high (10⁻⁶ S/cm), due to the preparation of sputtering technology [23], the electrolyte layer is very thin and has good contact with the electrode interface, and the overall resistance of the battery is small.

However, when LiPON material is used as electrolyte, cathode and anode materials of its battery must be prepared into thin film electrode by magnetron sputtering, pulsed laser deposition, chemical vapor deposition, electron beam evaporation and other methods. Therefore, the preparation of membrane anode and cathode materials matching LiPON electrolyte is the key of this kind of batteries. Meanwhile, due to the preparation process of cathode and anode films, conductive materials cannot be added into the electrodes like ordinary lithium ion batteries, and the electrolyte cannot infiltrate the electrode, so the lithium ion and electron migration ability of the electrode are poor. Therefore, the resistance of the battery can be reduced only if the cathode and anode layers are ultra-thin. Making ultra-thin batteries has always been the advantage of LiPON's all-solid-state electrolyte battery. In today's era of multifunctional and miniaturized electronic devices, new concept products designed with the advantages of ultra-thin batteries will bring more convenience to people's lives.

Sulfide electrolyte has the advantages of high thermal stability, good safety performance, wide electrochemical window and high conductivity, which can reach 10⁻⁴~10⁻³ S/cm at 0°C, and has prominent advantages in high power and high and low temperature batteries. However, the sulfide itself is an inorganic powder with high hardness and poor interface compatibility with the electrode, which makes the battery interface mass transfer resistance larger and has a great impact on the multiplier performance of the battery. Meanwhile, powder gaps in electrode materials need to be filled with electrolytes to speed up the conduction of lithium ions, which is difficult to achieve with sulfide. In addition, during the battery charging and discharging process, the electrode material will have volume changes, which will worsen the contact between electrolyte and electrode, and possibly break the structure of inorganic electrolyte.

The film-forming technology of sulfide electrolyte is the focus of this kind of electrolyte battery. There are three common methods of film formation for sulfide electrolytes [24]: 1) High pressure pressing method. The film obtained by this method is brittle and thick. It is usually used in battery test; 2) Laser pulse deposition method, which is suitable for the application of thin film battery; 3) Using polymer electrolyte or other polymer materials to assist sulfide electrolyte film formation. The film materials with good machining properties can be obtained by this method, which has a good application prospect.

4. Conclusion and Suggestions

China has become the world's largest producer of lithium-ion batteries, and the market demand is still expanding. At present, the rapid development of global lithium ion battery industry is mainly due to the unprecedented rise of electric vehicle industry. Meanwhile, steady consumption of 3C products and increasing demand for energy storage base stations and equipment strongly support the continuous expansion of domestic and even global lithium ion battery market. The key to the development of lithium ion battery industry lies in the technological progress of key battery materials. Suggestions for promoting the industrialization of lithium ion batteries are as follows:

1. Improve ternary materials properties and strengthen all-solid-state lithium ion battery materials research. Focus on the core issues such as high nicklization, lithium enrichment and optimization of preparation methods of ternary materials, and constantly improve the performance and safety of ternary materials, so as to develop more mature ternary lithium ion battery; Focus on the research on the
performance of solid electrolyte materials and solve the core problems of materials, so as to realize the industrialization of all-solid-state lithium battery.

2. Strengthen upstream and downstream links and improve the industrial chain to form an industrial advantage. Rely on the technology, market and capital between upstream and downstream enterprises to carry out in-depth cooperation. On the one hand, the development of new materials drives the improvement of battery performance and quality of new-energy vehicles; On the other hand, through the research and development of new energy vehicles to react on the battery, new materials industry, to guide the battery, new materials industry technology development direction, form a virtuous cycle and complementary resources, establish the industry advantages.

3. Accelerate the development and application of safety technologies, and establish and improve the safety evaluation system for lithium ion batteries. Strengthen the research on battery model, process method, test method, data traceability, risk assessment, technical standard and other common problems; Set up multi-level safety technology system and database from material, battery, module to system, and propose new risk level standard, then provide systematic solution for battery risk assessment.

4. Develop industrial automation and intelligence to improve the efficiency of industrial manufacturing. With the steady improvement of automation level in China, robot automation enterprises are also constantly expanding the layout of lithium ion battery manufacturing industry. Under the background of Intelligent Manufacturing and Industry 4.0, following industrial rules and vigorously developing automatic and intelligent production lines will effectively improve the consistency of lithium ion batteries, improve product qualification rate and reduce labor costs.

5. Focus on sustainable development and create a lithium battery recycling system. About 70 to 80 per cent of the electricity used in the batteries of new energy vehicles is still available, and many basic metals can be extracted and reused if properly treated. Enterprises should make it clear that before the industrialization of lithium battery, they should fully consider how to recycle, dismantle and reduce pollution. In addition, equipment used in the recovery process should be equipped with more advanced technologies and introduced into the form of automation. Establish a stricter management system to improve the recycling, storage, transportation and classification standards of lithium battery reuse. At the same time, it also relies on the improvement of national policies, laws and regulations to provide policy guarantee for the power battery recycling system.

Only in this way, enterprises can occupy a place in the increasingly competitive lithium battery market, and lithium ion battery industry can develop healthily.

References

[1] Armstrong A R and Bruce P G 1996 Nature 381 499
[2] 2017 China Lithium Battery Industry Market Demand Forecast and Investment Strategy Planning Analysis Report Forward Looking Research Institute 2018
[3] Liu Y L 2019 Power Technology 42(2) 181
[4] Guo Y G, Hu J S and Wan L J 2008 Nanostructured materials for electrochemical energy conversion and storage devices Advanced Materials 20 2878
[5] Li H, Wang Z X, Chen L Q and Huang X J 2009 Research on advanced materials for Li-ion batteries Advanced Materials 21 4593
[6] Chen J, Tao Z L and Gou X L 2006 Chemical Power - Principle, Technology and Application Chemical Industry Press 302
[7] Lou S J and Li C 2013 Progress in Research on Battery Cathode Materials for New Energy Vehicles Powered by Iron Phosphate The 10th henan automobile engineering technology seminar 328
[8] Gao Fen 2019 Hebei Enterprises 5 91
[9] Hu G X 2009 Power Battery Technology and Applications Beijing: Chemical Industry Press 140
[10] Kim M G, Shin H J, Kim J H, et al. 2005 Electrochem. Soc. 152(7) A1320
[11] Zhang Z G, Ma X H, Lu C H, et al. 2015 Chinese Ceramic 8 19
[12] Wang L Y 2019 New Chemical Materials 03 73-76,81
[13] Ye Z K 2018 Guangdong Chemical Industry 8 88,117
[14] Yu J L 2018 Preparation and Modification of NCA for Lithium Ion Battery China Excellent Master's Thesis Database 12 1-88.
[15] Shuang-Jie Tan, Junpei Yue and Xin-Cheng Hu 2019 Angewandte Chemie 23 7884
[16] Wu T Y 2017 Rare Metals 10 48
[17] Zhai X J, Yu Y L, Fu Y and Wang Y X 2009 Materials Science and Technology 1 101
[18] Ding C X, Meng Q S, Wang L, Chen C H 2009 Mater Res Bull 44 492
[19] Zheng J 2016 Proceedings of The Seventh National Conference on Physical and Inorganic Chemistry 4
[20] Fenton D E; Parker J M and Wright P V 1973 Polymer 14 589
[21] Armand M 1980 Materials For Advanced Batteries New York: Plenum Press 145
[22] Zhang Z, Jin J, Bautista F, Lyons L, Shariatzadeh N, Sherlock D, Amine K and West R 2004 Solid State Ionics 170 233
[23] Moreno M, Quijada R, Santa Ana M A, Benavente E, Gomez-Romero P, González G 2011 Electrochim. Acta 58 112
[24] Kamaya N, Homma K, Yamakawa, Hirayama M, Kanno R, Yonemura M, Kamiyama T, Kato Y, Hama S, Kawamoto K, Mitsui A 2011 Nat. Mater. 10 682