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Status and Development of Power Lithium-Ion Battery and Its Key Materials

1.1 Market Status of Power Lithium-Ion Battery

Lithium-ion batteries (LIBs) were invented by Sony in 1990 and brought to the market for commercialization in 1991, which kicked off the rapid development of LIBs. Initially (before 2000), most of the world's lithium batteries were produced in Japan [1–3]. However, by the year of 1997, South Korea's lithium secondary battery market began to rise, and it once surpassed Japan in the field of portable mobile electronics. In 1996, China Electronics Technology Group successfully developed 18650 batteries that can be mass-produced, marking the start of China's lithium batteries industry. At present, as an advanced energy storage technology, power LIBs have been widely used in new energy electric vehicles, providing critical support for the current greenhouse gas emission reduction.

According to the International Energy Agency (IEA), there was 16.5 million electric vehicles in the world by the end of 2021. The electric car registrations and sales share in major countries and regions in the world from 2016 to 2021 were shown in Figure 1.1. It is estimated that the total number of electric vehicles in the world will reach about 200 million by 2030, accounting for 20% of the total number of vehicles worldwide. The booming development of electric vehicles will lead to an exponential increase in the demand for power LIBs.

According to SNE Research data, the global installed capacity of power LIBs will be approximately 296.8 GWh in 2021 with a yearly increase of 115%. In view of the huge market prospects of the lithium-ion power battery industry [4], the relevant companies from different countries have deployed the power battery industry development plans. Among the world's top 10 battery companies (Figure 1.2), five of them are from China, namely Contemporary Amperex Technology Co., Ltd. (CATL), Build Your Dreams (BYD), China Aviation Lithium Battery (CALB), Guoxuan High-tech (GOTION), and Envision AESC with a total market share of 47.6%; LG Chem (LGC), Samsung SDI, and SKI, located in Korea, have a total market share of 30.4%; and Panasonic's (Japan) global market share is 12.2%.

Based on the ground of national level, the current lithium-ion power battery industry has basically developed into “three-legged (China, Japan, and South Korea)

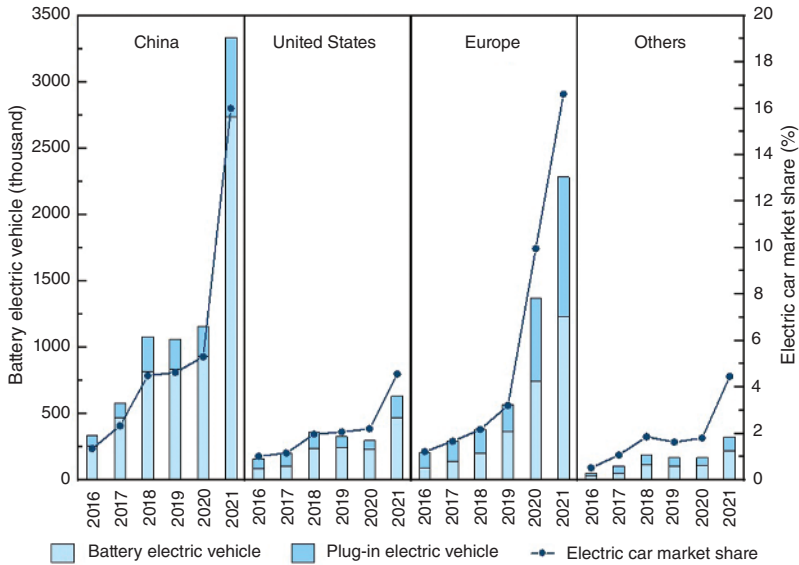


Figure 1.1 Registration volume and market share of electric cars in major countries and regions in the world, 2016-2021. *Source:* IEA.

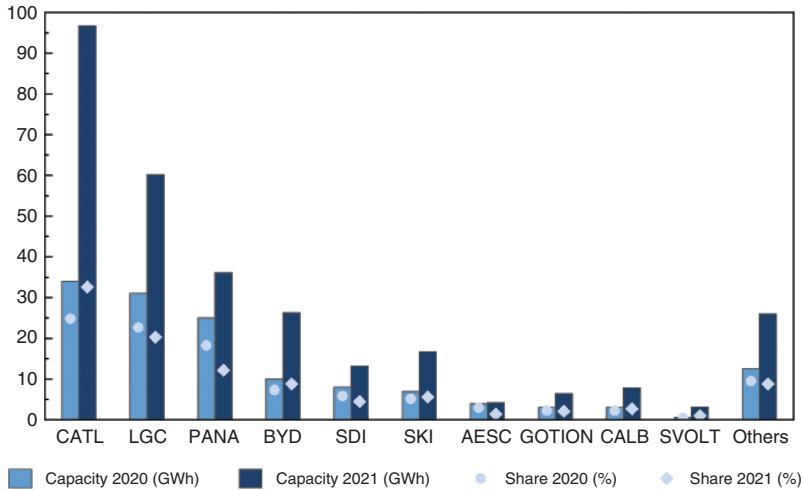


Figure 1.2 Top 10 global lithium-ion power battery companies and their installed capacity.

stand-up” pattern, and each of them has a leading enterprise in the industry. The Chinese company CATL has become not only the leader of China’s lithium battery industry but also the world’s largest supplier of power LIBs since 2017 [5] and was the first company to realize the mass production of NCM811 square batteries, which were successfully selected by GAC and BMW. From the technical route point of view, CATL also successfully realized the transition from NCM523 to NCM811.

Table 1.1 The main material production capacity of the world's major producers of lithium batteries.

	Cathode material	Anode material	Electrolyte	Separator
Country	3000 kilotons	1200 kilotons	339 kilotons	1987 million m²
China	42%	65%	65%	43%
Japan	33%	19%	12%	21%
Korea	15%	6%	4%	28%
US	—	10%	2%	6%
Other	10%	—	17%	2%

Source: Data from Eddy et al. [7].

For South Korea's companies, LGC began to study lithium batteries in 1996 [6], and in 2020, it became the sole supplier of GM Chevrolet Volt electric vehicles. LGC's advantage is its advanced theoretical technology on soft pack batteries. It is also the first company in the world to be proficient in laminated-stacked soft packs. However, in the application of NCM811, it is behind the CATL. The Japanese company Panasonic began to develop the lithium batteries as early as 1994 and was supported by the Sumitomo Consortium. In 2008, it began to cooperate with Tesla, the world's largest electric vehicle company and built a super battery factory in 2014. Panasonic is the first company worldwide to realize the mass production of NCA18650 + silicon carbon anode cylindrical batteries, and it is also in a leading position in terms of the electrochemical system, production yield, and consistency.

In addition, China has already set up a strong leading position in the manufacturing of key materials for power LIBs (Table 1.1). According to the report "The metal mining constraints on the electric mobility horizon," China's production capacity in cathode materials, anode materials, electrolytes, and separators is 42%, 65%, 65%, and 43% of the world's total production capacity, respectively, far ahead of other countries and regions. Japan, by contrast, has a minor advantage in manufacturing cathode materials, whereas South Korea has an advantage in manufacturing diaphragms. In addition, other countries and regions such as the United States and the European Union have a relatively small market share in the production and manufacturing of materials for powered lithium batteries. The report shows that the market space for battery production and manufacturing in Western countries still has the great potential.

1.2 Key Materials and Development of Power Battery

Power LIBs are mainly composed of cathode materials, anode materials, separators, electrolyte binders, and current collectors. The cathode materials account for more than 40% of the total cost of lithium batteries, whose properties directly affect a variety of performance indicators of lithium batteries. Therefore, the cathode

materials take a core position in lithium batteries industry [7, 8]. Currently, commercialized cathode materials for lithium batteries include lithium cobalt oxide (LCO), lithium manganese oxide (LMO), lithium iron phosphate (LFP), and ternary materials. The proportion of LFP and ternary materials is as high as 90% in all the cathode materials.

1.2.1 Dominant Cathode Materials

1.2.1.1 Lithium Nickel Cobalt Manganese Oxide

The molecular formula of the lithium nickel cobalt manganese oxide (NCM) oxide ternary cathode material is $\text{LiNi}_a\text{Co}_b\text{Mn}_c\text{O}_2$, where $a + b + c = 1$. The naming rule of specific materials is usually based on the relative content of the three elements, for example, $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ is referred to as NCM811 for short. The different proportions of the three elements endow the NCM cathode material with different properties, which can meet the needs of diversified applications. NCM material combines the advantages of three types of materials as follows: LCO, lithium nickel oxide (LNO), and LMO. By adjusting the ratio of transition metal elements, the performance of the cathode material can be effectively regulated, and the cost of the cathode material can be reduced. Among them, the Ni element is beneficial to the increase of the specific capacity of the cathode material, which, however, is harmful to its thermal stability [9]; the Co element is beneficial to improve the electrical conductivity and rate performance of the material, but it is expensive; the presence of Mn plays a role in stabilizing the crystal structure of the polycrystalline, but it will also reduce the specific capacity of the cathode material when an excessive content was used.

The main preparation methods of NCM cathode materials include high-temperature solid-phase, sol-gel, co-precipitation, hydrothermal synthesis, and other methods. At present, commercial NCM materials were generally prepared with NCM hydroxide by precipitation method. The NCM precursor is mixed with a lithium source and calcined to prepare a finished NCM cathode material. The production of NCM precursor generally adopts the hydroxide co-precipitation method, that is, the mixed salt solution of nickel, cobalt, and manganese, precipitating agent, complexing agent, etc., are added to the reactor at the same time, and the NCM precursor is synthesized under specific conditions. The internal structure of the reactor and the control of the synthesis process are very demanding. Therefore, it takes an important position in the industry chain and has a high technical barrier. However, it has an important impact on the quality of the NCM cathode material. From the practical application point of view, the characteristics of the material particles, such as the morphology, particle size distribution, specific surface area, and tap density, have a great influence on the processing performance of battery electrode and the core electrochemical performance of lithium battery, such as energy density, rate performance, and cycle life. Therefore, the spherical NCM cathode material with high density and uniform particle size distribution has become the current pursuit goal of industry.

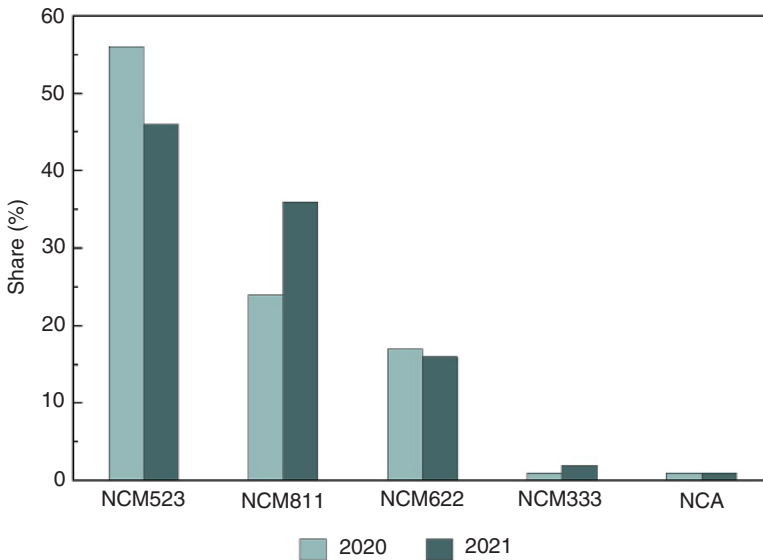


Figure 1.3 Comparison of the product structure of China's NCM materials in 2020 and 2021. *Source: SMM.*

Shanghai Metals Market (SMM) analysis of the results based on the output structure shows that, although the NCM material is still mainly NCM523, the trend of using low cobalt and high nickel is very clear. The proportion of NCM811 increased from 24% to 36% in 2021 (Figure 1.3). According to China Powder Network, GEM has developed an NCM precursor material with a molar ratio of nickel metal higher than 90% and has built an NCM precursor production capacity of 100 000 tons/yr. Sales volume of the high nickel and single crystals account for more than 80% of total sales. SKI, another power battery giant in South Korea, is earlier in the layout of ultra-high-nickel batteries and plans to launch a new NCM battery before the end of 2021. The battery has a nickel content of 88% and a cobalt content of 6%. Another South Korean company, LGC, plans to release lithium nickel cobalt manganese aluminum oxide (NCMA) batteries in 2022, with the 90% nickel content, 5% cobalt, and 1–2% manganese and aluminum.

1.2.1.2 Lithium Nickel Cobalt Aluminum Oxide

The lithium nickel cobalt aluminum oxide (NCA) material is composed of three main elements of nickel, cobalt, and aluminum, and the molar ratio is usually 8 : 1.5 : 0.5. By combining LiNiO_2 and LiCoO_2 , not only the reversible capacity becomes high, but the cost also becomes low. Currently, doping Al into metal oxide and replacing manganese with Al (transition metal) are one of the most popular directions in commercial cathode materials. At present, high-nickel materials can be divided into two categories: NCM811 and NCA materials. The reversible capacity of both materials can reach about 190–200 mAh/g. However, because Al is an

amphoteric metal, it is not easy to precipitate, and the conventional precipitation method cannot be used to prepare the NCA precursor. The NCA sintering process requires a pure oxygen atmosphere, which requires not only high tightness of the production equipment but also the oxidation resistance of the internal components of the kiln equipment. Due to the above-mentioned requirements of mass production, there are certain thresholds in the manufacturing process of NCA materials. In terms of route selection, Japan is mainly based on NCA routes, while South Korea tries to let NCM and NCA routes go hand in hand. China's current NCA output is relatively small, and NCM routes are the mainstay.

At present, the most mainstream preparation method is as follows: the precipitation of nickel, cobalt, and aluminum hydroxide is first prepared with metal sulfate as the raw material and sodium hydroxide or a complexing agent as the precipitation agent. The precipitate formed is then mixed with lithium hydroxide and then calcined into an oxide product. The advantages of this process are low production cost, simple process, and suitable for large-scale production. For example, Japan's Sumitomo and Japan's Toda have entered the mass production stage. Internationally, the upstream and downstream of NCA have formed a complementary industrial chain and a relatively stable and mature supply chain. However, China's domestic market is still at the initial stage of development.

1.2.1.3 Lithium Iron Phosphate

The chemical formula of LFP is LiFePO_4 , and its theoretical specific capacity is 170 mAh/g. The actual specific capacity of the product can exceed 160 mAh/g (0.2 C, about 25 °C, the voltage platform is 3.2–3.5 V, and the tap density is 1.2 g/cm³). In the LiFePO_4 structure, there is a strong covalent bond between O and P to form a tetrahedral $(\text{PO}_4)^{3-}$ polyanion; hence, O is difficult to deintercalated, and no oxygen escapes after overcharge. When LiFePO_4 is used as a cathode electrode material, battery safety can be promised.

Solid-phase synthesis is the most widely used and most mature synthetic method for LFP production. The iron source used in this method is generally ferrous oxalate, iron oxide, iron phosphate, etc.; the lithium source is generally lithium carbonate, lithium hydroxide, lithium acetate, etc.; and the phosphorus source is generally ammonium dihydrogen phosphate and diammonium hydrogen phosphate. The disadvantage of the solid-phase synthesis method is that it is easy to produce ammonia that pollutes the environment. Representative manufacturers include A123 systems, Tianjin Strand, Hunan Rui Xiang, Peking University First, Defang Nano, etc. At present, most of the synthesis method in our country adopts the ferrophosphorus process. This process generally uses iron phosphate as the iron source, which is first mixed with the lithium source at the nanoscale. After that, the particles can be converted into high-quality LFP materials with controllable particle size by spray drying and calcination in nitrogen atmosphere. Representative manufacturers include Phostech in Canada, Shandong Feng Yuan Lineng Technology Co., Ltd., and Sichuan Yuneng New Energy Battery Materials Co., Ltd.

The emergence of LFP is a breakthrough in LIB cathode materials. The following advantages of LFP, such as low price, environmental friendliness, high

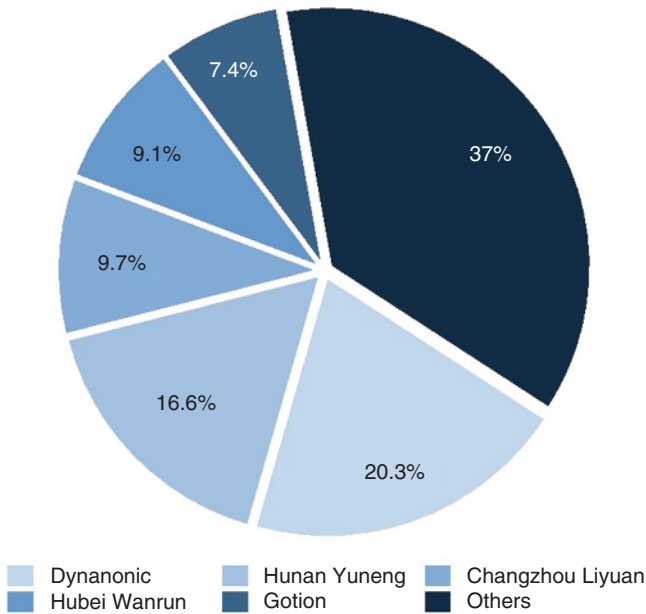


Figure 1.4 Market share of LFP manufacturers in 2021. *Source:* GGII.

safety performance, better structural stability, and cycle performance, have prompted it to have a wider market application field: Energy storage equipment, power tools, light electric vehicles, large electric vehicles, small equipment, and mobile power sources, among which, the LFP for new energy electric vehicles accounts for about 45% of its total production. The market share of LFP in China is displayed in Figure 1.4. Due to the structural reorganization of LFP batteries, the increase in energy density, the decline of new energy vehicle subsidies, the popularization of charging piles, the price advantage, and high safety advantages of LFP batteries, the installed capacity of LFP batteries in China has rapidly increased. Thus, the shipment of LFP cathode materials in China has been 470 000 tons by 2021, accounting for a year-on-year increase of 277%, according to the survey data of the Advanced Industrial Research Institute of Lithium Battery Research (hereinafter referred to as GGII).

1.2.1.4 Lithium Nickel Manganese Oxide

The molecular formula of lithium nickel manganese oxide (LNM) is $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which belongs to the spinel structure. The voltage platform is about 4.7 V, the theoretical specific capacity is 146.7 mAh/g, and the actual specific capacity is about 130 mAh/g; LNM has a high working voltage, high energy density, and low production cost. It combines the advantages of NCM materials and LFP materials, which is the goal of a new generation of cathode materials.

There are many preparation methods for LNM, including solid phase, co-precipitation, sol-gel, solution combustion synthesis, hydrothermal, solvothermal, and spray deposition methods. Public information shows that Honeycomb Energy mainly improves the performance of LNM through three methods: cation doping, single crystal technology, and nano-network coating. Doping technology involves the use of cations with high chemical bond energy with oxygen to dope into the crystal structure, which is conducive to the stability of the structure after de-lithiation under high voltage. Single crystal technology has a higher particle strength than traditional spherical polycrystalline particles, which is beneficial to improve safety and cycling performance. The use of a nano-network coating can make the material more uniform and reduce the side reaction with the electrolyte to improve the cycle life.

Reducing the cobalt content has become the primary measure for reducing the cost of NCA or NCM cathode materials, and the development of high-nickel and cobalt-free materials has become an inevitable trend. Tesla has always used the ternary battery (NCA) provided by Panasonic, in which the Co content is less than 3%, and the next generation of products can reduce the content of Co to zero. Since then, cobalt-free batteries and cobalt-free materials were born. According to Gaogong Lithium Grid, Honeycomb Energy's Changzhou plant has officially mass-produced cobalt-free materials, with an annual output of up to 5000 tons. Mine Road Network speculates that, by 2025, the global production of LNM oxide materials will reach 85 000 tons, and the demand will reach 100 000 tons. If LNM solves the problems of large-scale production and high-potential electrolyte tolerance, it will surely become the next generation of mainstream cathode materials.

1.2.2 Anode Materials

The negative electrode material is the main body that stores lithium when the power battery is charged, accounting for about 10% of the battery cost. Anode materials can generally be divided into two categories: carbon materials and noncarbon materials. Carbon materials include artificial graphite, natural graphite, mesophase carbon microspheres, petroleum coke, carbon fiber, and pyrolytic resin carbon. Noncarbon materials include titanium-based materials, silicon-based materials, tin-based materials, and nitrides.

1.2.2.1 Graphite

Since graphite materials have the advantages of high electronic conductivity, high specific capacity, stable structure, and low cost, they have become the most widely used and mature anode materials, and they are the absolute mainstream route in the anode industry, accounting for 95% of the total amount. Graphite can be divided into natural graphite and artificial graphite. Due to raw material and process characteristics, the internal structure of artificial graphite anode materials is more stable than natural graphite products.

Artificial graphite is generally divided into four major processes, namely crushing, granulation, graphitization, and sieving. Among them, the technical threshold

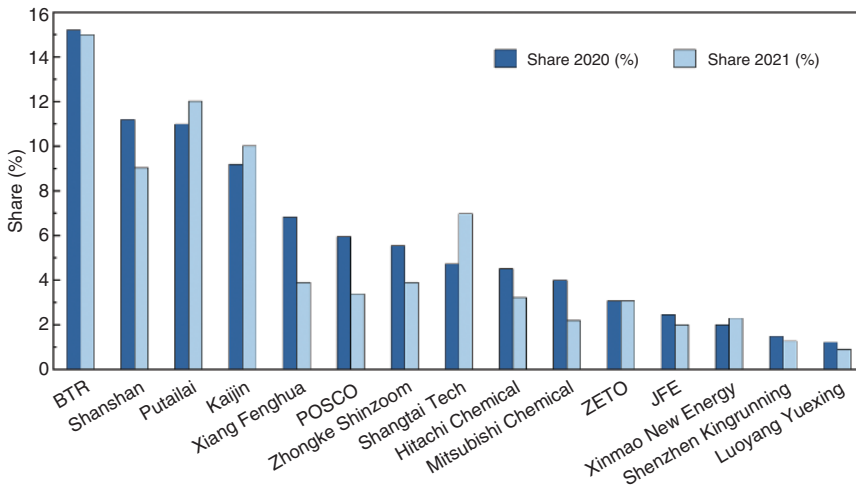


Figure 1.5 Market share of global anode material manufacturers in 2020–2021.
Source: White Paper on global lithium-ion battery industry, Starting Point Research.

and production level of the negative electrode industry are mainly reflected in the two links of granulation and graphitization. Granulation needs to control the particle size, particle size distribution, and morphology of graphite, and these physical parameters directly affect the performance indicators of the anode material. For example, the smaller the particles, the better are the rate performance and cycle life, but the worse are the first-time efficiency and compaction density; therefore, a reasonable particle size distribution is required.

From a global perspective, companies from Japan and China have always dominated the market of anode materials (Figure 1.5). The top five Chinese companies, including Berterry (BTR), Shanshan, Putailai (Jiangxi Zichen), Kaijin, and Xiang Fenghua, account for more than half of the global market. According to the data from EVTank, due to the significant increase in demand for LIBs in various fields around the world, global shipments of anode materials reached 905 000 tons in 2021 with a year-on-year increase of 68.2%. From the perspective of negative electrode product structure, the proportion of artificial graphite products will further increase (Figure 1.6). Other anode materials represented by silicon-based anodes failed to achieve the expected growth due to the switch of the main shipment models of Chinese cylindrical battery products and the delay in the upgrade of the high-nickel system of square power LIBs, and their market share declined dramatically.

1.2.2.2 Lithium Titanate

The chemical formula of lithium titanate is $\text{Li}_4\text{Ti}_5\text{O}_{12}$, referred to as LTO, which has been studied by many energy workers because of its “zero strain” advantage. “Zero strain” means that the volume and lattice constant of the lithium titanate material change very little during the phase change. Therefore, the main advantages of lithium titanate are good cycle performance. The cycle life of lithium titanate energy storage batteries is more than 15 000 times, with the good charging rate in the range

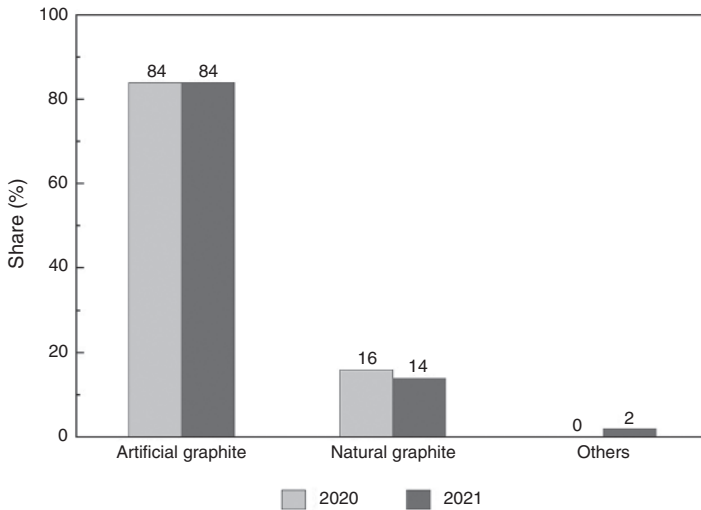


Figure 1.6 In 2020–2021, anode material industry structure. *Source:* GGII.

of 10–20°C. Lithium titanate also has a good low-temperature performance and still has 70% capacity in the extremely cold environment of -50°C . Lithium titanate material has a low energy density, and its theoretical capacity is 175 mAh/g. At present, commercial lithium titanate has been developed to 170 mAh/g, and the first effect can be as high as 99.5%.

The industrial production method of lithium titanate still adopts the high-temperature solid-phase method. Usually, battery-grade TiO_2 and lithium salt $\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2CO_3 are dispersed in water or organic solvent according to a specific stoichiometric ratio and mixed uniformly. After high-energy ball milling to nano-scale, spray-drying granulation, and high-temperature calcination, the final product lithium titanate is obtained.

In terms of industrialization, the leading companies include the American Ao Titanium Nano Technology Company (now acquired by Yinlong New Energy), Japan's Ishihara Industry Co., Ltd., and the British Johnson Matthey Corporation. There are Sichuan Xingneng New Material Co., Ltd. and Huzhou Weihong Power Co., Ltd. in China. Dong Mingzhu's perseverance to "Yinlong Titanium" made Yinlong's lithium titanate battery famous within a short period. With its fast-charging, low-temperature properties and safety characteristics, lithium titanate is widely used in public transportation buses and logistics vehicles that do not require high mileage. The market size of lithium titanate batteries is worth the wait.

1.2.2.3 Silicon Carbon

Silicon is the anode material with the highest theoretical capacity found so far. The theoretical specific capacity is 4200 mAh/g, which is 10 times more than that of graphite. Mixing silicon and graphite to form a silicon-carbon-based composite

anode material not only combines the characteristics of good carbon conductivity and high silicon specific capacity but also can effectively buffer the expansion of silicon, which can significantly improve the overall electrochemical cycle performance of the material. From the commercialization path, the silicon-carbon material can be divided into silicon-carbon anode and oxygen-silicon-carbon anode materials.

The silicon-carbon anode material is first prepared by forming a precursor of nano-silicon and the matrix-graphite material through a granulation process, and the precursor is then prepared by surface treatment, sintering, pulverization, screening, demagnetization, and other processes. At present, the commercial application capacity of the silicon-carbon anode is about 450 mAh/g.

The silicon-oxygen negative electrode material is made by synthesizing pure silicon and silicon dioxide into silicon monoxide to form a silicon-oxygen negative electrode material precursor, and the precursor is then prepared into a modified SiO_x/C through the processes of pulverization, classification, surface treatment, sintering, sieving, demagnetization, etc. The modified SiO_x/C is then mixed with graphite according to the required capacity of the negative electrode, and a new type of oxygen-silicon graphite negative electrode material can be obtained; the capacities of the new oxygen-silicon graphite anode materials are mainly concentrated in two types: 420 and 450 mAh/g, with a small amount of 500 and 600 mAh/g. According to the China Powder Network, BTR's silicon-based anode products are at the leading position in the industry. It has made new breakthroughs in the development of silicon-carbon anode materials, and its specific capacity has been increased to 1500 mAh/g; BTR has completed a variety of technical development and mass production of sub-silicon products, and the specific capacity of some products reaches more than 1600 mAh/g. Snow's SiO product has a gram capacity of more than 500 mAh/g and the first coulombic efficiency is more than 89%, and it can achieve an 800-week cycle retention rate of more than 80%. It has completed the small-scale development and is in the stage of preparing for the pilot and mass production.

The industrialization of silicon-based anode batteries by global battery manufacturers is steadily advancing. As early as 2012, Japan's Panasonic has applied silicon carbon anodes to lithium batteries, while Hitachi Chemical is the largest supplier of silicon-carbon materials in the world as well as Japan's Shin-Etsu, Wu Yu Chemical, and American Ampris, all of which have deployed silicon carbon anode materials. The industrial application of silicon carbon anodes in our country is still at the initial stage. At present, CATL, BYD, GOTION, BAK, and Tianjin Lishen are all making efforts in the field of silicon-carbon materials, and BTR has achieved mass production. The high-tech lithium power grid predicts that the market demand for silicon-based anodes will exceed 30 000 tons in 2022, and the market size is expected to exceed 3.5 billion in the future.

1.2.3 Electrolyte

The electrolyte plays a role in transferring charge between the cathode and anode electrodes. According to the physical form of the electrolyte, it can be divided into

liquid electrolyte, solid electrolyte, and solid–liquid composite electrolyte. Batteries that use solid electrolytes are called solid-state batteries.

1.2.3.1 Liquid Electrolyte

The function of the electrolyte is to transfer lithium ions between the anode and the cathodes, and the electrons are not transferred, which ensures the smooth progress of charging and discharging. Electrolyte is very important to the performance of lithium batteries and is known as the “blood” of LIBs. According to statistics from the Huajing Industrial Research Institute, electrolytes generally account for about 7–12% of battery costs. The general composition is a solvent, lithium salt, and additives. The most frequently used lithium salt is lithium hexafluorophosphate. The solvents are mainly carbonates, ethers, and carboxylates. According to their functions, additives can be divided into film additives, conductive additives, and flame retardant additives.

The preparation of the electrolyte is mainly divided into three sections: solvent synthesis, material mixing, and post-processing. Among them, the technical barrier is the composition of the formula at the material mixing stage. The electrolyte composition of different battery types is slightly different. The formula is basically dominated by downstream lithium battery companies, while the electrolytes of some subdivided into high-end consumer products or high-nickel power products are generally jointly developed by lithium battery companies and electrolyte companies. As the core key material of the electrolyte, lithium hexafluorophosphate is very deliquescent and needs to be synthesized in nonaqueous solvents such as anhydrous hydrogen fluoride and low alkyl ether, and the production conditions are extremely harsh.

Before 2010, the production capacity of lithium hexafluorophosphate was mainly concentrated in Japanese companies such as Stella, Kanto Denka, and Morita Chemical and the South Korean company Hosei. In 2011, Chinese companies’ hexafluoro carbon production capacity accounted for less than 15%. After 2011, companies such as Tianci High-tech (TINCI), Xinzhoubang, and other companies have achieved technological breakthroughs and began to expand their production significantly. In 2021, the market share of Chinese enterprises increased to more than 80% (Figure 1.7). According to the “White Paper on the Development of China’s Lithium-ion Battery Electrolyte Industry (2022)” released by EVTank, China’s electrolyte market will ship 507000 tons in 2021 with a year-on-year increase of 88.5%. According to the forecast of Guohai Securities, the global demand for lithium batteries will reach about 1200 GWh by 2025, corresponding to an electrolyte demand of about 1.32 million tons, with a compound annual growth rate of 35% during this period. The electrolyte market has a huge space.

1.2.3.2 Solid Electrolyte

Liquid electrolyte has hidden dangers such as volatile organic solvents and high-temperature flammability, and its development in the field of lithium batteries is very limited. The solid electrolyte is not only difficult to decompose at high temperatures, but it can also inhibit the generation of lithium dendrites, effectively alleviating the safety and durability of lithium batteries. Solid-state electrolyte is the core component

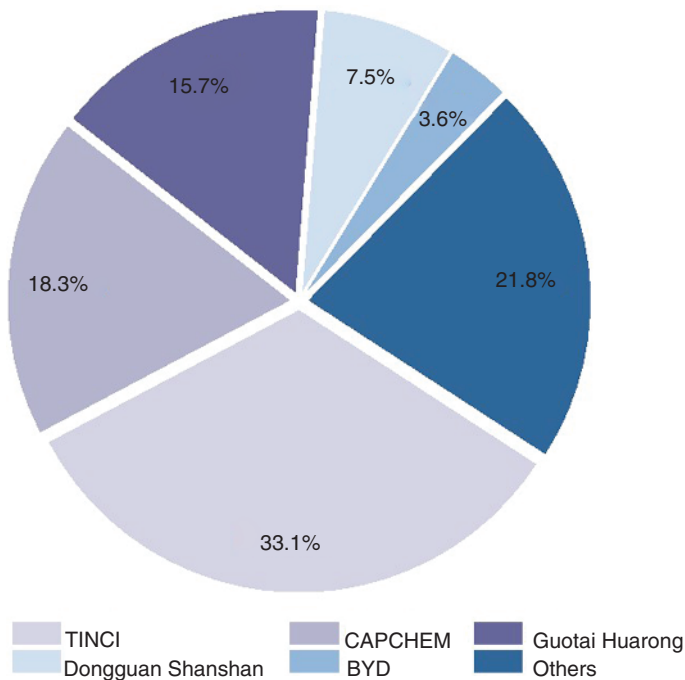


Figure 1.7 Market share of electrolyte in China in 2021. *Source:* Xinzhu Information, Huajing Industry Research Institute.

of solid-state lithium batteries and the technical focus of solid-state battery development. At present, solid electrolytes are mainly divided into three categories: polymer solid electrolytes, oxide solid electrolytes, and sulfide solid electrolytes.

The polymer solid electrolyte is complexed by a polymer matrix and a lithium salt. Commonly used lithium salts include LiPF_6 , LiClO_4 , and LiAsF_6 . The matrix includes polypropylene oxide (PPO), polyvinylidene chloride (PVDC), polyethylene oxide (PEO), polyacrylonitrile (PAN), and polyvinylidene fluoride (PVDF). Representative types of oxide electrolytes include lithium lanthanum zirconium oxide (LLZO), lithium aluminum germanium phosphate (LAGP), and lithium aluminum titanium phosphate (LATP). The general process is to mix the desired oxidizing material with lithium source ball milling, press into tablets, and then calcine to increase the density. The sulfide solid electrolyte evolved on the basis of the oxide electrolyte, but the sulfide is really easy to react with water that generates the toxic H_2S gas. The production conditions are also harsh. At present, methods such as halide doping or introduction of new elements are used to improve its chemical stability in water (Table 1.2).

From the perspective of technology route of enterprise, Japanese and Korean enterprises mostly adopt sulfide solid electrolyte technology [10], Chinese enterprises mostly use oxide electrolytes, while European and American enterprises choose polymer, oxide, and sulfide routes. Solid electrolytes still have problems such

Table 1.2 Comparison of three solid electrolytes.

Classification	Subdivision	Representative enterprise	Advantages	Shortcomings
Organic electrolyte	Polymer	Bolloré, Solid Energy	Low-density, good viscoelasticity, and the most mature technology, taking the lead in small-scale mass production	Room temperature ionic conductivity is low Low theoretical energy density upper limit
Inorganic electrolyte	Oxide	Sakti3, ProLogium, QingTao Development, Beijing WeLion, Ganfeng Lithium Group	Excellent battery rate and cycle performance, commercial products are already available	Mechanically hard, the solid–solid interface is not in good contact, and the mass production cost is high
	Sulfide	Toyota, Samsung, Panasonic, CALT	The highest ionic conductivity, most likely to be used in batteries on a large scale	Unstable, high requirements on the production environment, difficult to develop

Source: Adapted from Evergrande Research Institute and Zhongqi Consulting.

as low interface stability, large-scale grain boundaries, vacancies, and local electronic conductance. Solid-state batteries have not yet formed an industrial chain. The “New Energy Automobile Industry Development Plan (2021–2035)” puts forward the requirements for strengthening the R&D and industrialization of solid-state batteries. For the first time, solid-state batteries have been raised to the national level, and solid electrolytes and solid-state batteries are expected to improve dramatically. According to industry chain research, solid-state batteries will be gradually commercialized in 2025 and become the main technical route for power batteries in 2030. According to Bank of China International Securities, the global demand for solid-state lithium batteries is expected to reach 494.9 GWh by 2030, with a market space of more than 150 billion yuan.

1.2.4 Separator

Separator is a key material to ensure the safety of battery system and affect its performance. It is placed between the cathode and anode as a device to isolate the electrodes. Therefore, the separator must have good insulation to prevent short circuiting of the cathode and anode electrodes or short circuits caused by burrs, particles, and dendrites. In addition, separator is a microporous channel with charging and discharging functions and rate performance. Therefore, the separator needs to have a certain tensile strength, puncture strength, high porosity, and uniform distribution.

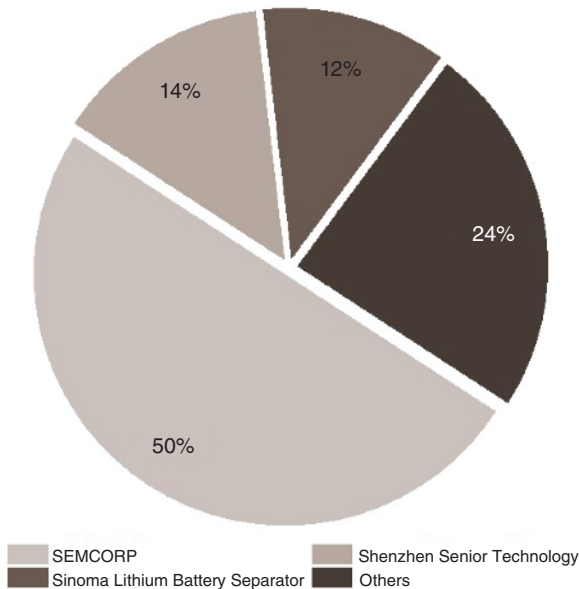


Figure 1.8 Pattern of separator for wet process in 2021. *Source:* Intelligence Research Group.

The pore size of separator is generally 0.03–0.05 or 0.09–0.12 μm ; the thickness is generally less than 25 μm . By ensuring the mechanical strength, the thinner the separator, the better is the performance of the battery. The current mainstream wet base film products in the power market are mainly concentrated in the 9 and 12 μm fields. The 5 μm separator is mainly used in the field of consumer batteries. The mainstream materials for the separator are polypropylene (PP) microporous film and polyethylene (PE) microporous film. Separator is the material with the highest technical barrier among lithium battery materials. Microporous preparation technology is the core of the separator preparation process. Therefore, the separator process can be divided into dry and wet methods. The raw material of the dry process is generally PP; the process is simple, and the cost is low. The raw material of the wet process is generally PE, which has more advantages in high-power batteries and has relatively higher strength.

In recent years, the output and performance of Chinese wet process separator manufacturers have come closer to those of foreign companies; the production of separator has basically achieved localization, and their market share has continued to rise (Figure 1.8). However, there are still gaps in indicators, production technology, and equipment technology when compared with Japanese and American companies such as Asahi Kasei and Tonen. The separator company W-Scope estimates that the global lithium battery market will have 20 billion square meters of separator demand by 2025 and close to 32 billion square meters by 2030, which is 5.3 times that of 2020.

1.2.5 Binder

Binders are indispensable in LIBs, and their amount is very small, accounting for about 1–10% of the active material components. The main function of the binder is

to bind the various components of the pole piece (active material and conductive agent) and the current collector together to form a stable pole piece structure, relieve the volume change of the electrode material during the charging and discharging process, and regulate dispersion effect of the slurry. Therefore, the binder must be able to withstand the swelling and corrosion of the electrolyte and the electrochemical effects of the charge and discharge process.

The current commercial binders include oil-based binder systems: mainly PVDF and PAN; aqueous binder system: sodium carboxymethyl cellulose (CMC), styrene butadiene rubber (SBR), sodium alginate (ALG), polyacrylic acid (PAA), and polyvinyl alcohol (PVA). At present, the cathode electrode of the battery is mainly PVDF binder, and *N*-methylpyrrolidone (NMP) is used as the solvent, accounting for up to 90%. The negative electrode material usually uses SBR as the binder, CMC as the thickener, and water as the solvent.

Solvay Group in Belgium, Kureha Co., Ltd. in Japan, Arkema Group in France, and Shanghai Sanaifu New Materials, Shandong Huaxia Shenzhou New Materials, Sinochem Lantian, etc., in China share the global lithium battery cathode binder PVDF market. Japan's Zeon Co., Ltd., Japan Paper, and China's Blue Ocean Blackstone Technology occupy the field of water-based adhesives. According to the statistical data, the output of lithium battery binders in China has increased annually in the past five years. As of 2021, it has reached 48 000 tons with a yearly increase of 34.5%. Benefiting from the rising demand for lithium batteries, China's lithium battery binders will also maintain rapid growth in the next five years. It is estimated that by 2025, China's lithium battery binder market is expected to approach 10 billion yuan.

1.2.6 Current Collector

The current collector is a component that is bonded to the outside of the cathode and anode electrodes in the battery and collects the current generated by the active material of the battery. It is one of the indispensable components in LIBs. Materials that can be used as current collectors for lithium batteries are metal conductor materials such as aluminum, copper, nickel, and stainless steel. With the continuous development of lithium battery technology, the trend of current collectors is to reduce the thickness and weight by ensuring new energy.

1.2.6.1 Copper Foil

Copper has many advantages such as excellent electrical conductivity, good ductility, and abundant resources. It is easily oxidized at a higher potential and is often used as a current collector for negative electrode active materials such as graphite, silicon, tin, and cobalt-tin alloy. The quality and cost of a copper foil account for about 13% and 8% of the total mass and total cost of a typical lithium battery, respectively [11]. There are mainly two types of copper foil: rolled and electrolytic ones. Rolled copper foil is an original foil made by repeatedly rolling a copper plate several times, and roughening treatment is carried out according to the requirements. Electrolytic copper foil is made by electrodepositing copper solution in a special

dissolving vessel under the action of direct current with copper sulfate electrolyte and then undergoing a series of surface treatments to obtain copper foil with smooth and rough surfaces. When copper foil is used as a current collector, the thickness is reduced from 12 to 10 μm and then to 8 μm . Up to now, most battery manufacturers use 6 μm for mass production.

According to the statistics of the Huajing Industry Research Institute, the global lithium battery copper foil production capacity will be a total of 435 000 tons in 2020. China and South Korea are the main lithium battery copper foil production countries; the top three companies in terms of production capacity are Nordisk, Lingbao Huaxin, and Jiujiang De Blessing. Affected by the increase in demand for upstream power batteries, copper foil companies of lithium battery have actively expanded their production. According to Gaogong Lithium battery, the global demand of copper foil for lithium batteries in 2021 is 380 000 tons with a yearly increase of 52%, of which the demand for power batteries is 240 000 tons (an annual increase of 75%); the total global demand of copper foil for lithium batteries is expected to be 10 000 tons in 2025, and the demand of copper foil for lithium battery will expand three times in the next five years.

1.2.6.2 Aluminum Foil

Aluminum foil is currently the main cathode current collector for LIBs. It has the advantage of good conductivity, light weight, and low cost, and the passivation layer on its surface can avoid electrolyte corrosion during the charging and discharging process. According to the composition and impurities, aluminum foil can be divided into 1 series, 3 series, and 8 series, corresponding to pure aluminum, aluminum manganese series, and other aluminum alloy series, respectively. Aluminum foil has been reduced from 16 to 14 μm and then to 12 μm in past years. Presently, many battery manufacturers have mass-produced aluminum foil of 10 μm and even 8 μm . The production of aluminum foil is to roll the aluminum foil blanks to the required thickness through multiple rolling and heat treatments. After two processes of rough rolling and finishing rolling, the aluminum foil is surface-treated, and finally, the aluminum foil is slit into the width and length required by the lithium battery manufacturer. Recently, more studies have been done on carbon-coated aluminum foil, where a thin layer of conductive carbon is coated on the surface of a normal aluminum foil to optimize the performance of battery.

Aluminum foil of lithium batteries can be divided into power battery foil, consumer battery foil, and energy storage battery foil. Among them, power battery foil is currently in the largest demand, accounting for more than 50%. Foreign suppliers of aluminum foil for lithium batteries are mainly concentrated in Japan, such as Toyo Aluminum and Hitachi Metals. Domestically, there are Dingsheng New Materials, Wanshun New Materials, Huaxi Aluminum, Nannan Aluminum, Sifangda, etc. Benefiting from the high growth in demand for power batteries and energy storage batteries, leading lithium batteries have expanded their production. According to Huan Securities, based on the consumption of 400–600 tons of aluminum foil per GWh lithium battery, it is estimated that the global lithium battery

aluminum foil is expected to reach 454–681 000 tons in 2025. The Na-ion press conference of CATL is expected to realize the industrial chain in 2023. The anode and cathode of sodium-ion batteries are made of aluminum foil. By then, the market space of lithium-ion aluminum foil will expand.

1.2.6.3 Others

Nickel is relatively inexpensive, has a good electrical conductivity, and is relatively stable in acid and alkaline solutions. Nickel can be used as both a cathode electrode current collector and a negative electrode current collector. Nickel is matched with both cathode active material LFP and negative active materials such as nickel oxide, sulfur, and carbon–silicon composite materials. The shape of the nickel current collector usually has two types: foamed nickel and nickel foil. Due to the well-developed pores of the foamed nickel, the contact area with the active material is large, thereby reducing the contact resistance between the active material and the current collector. However, when nickel foil is used as an electrode current collector, as the number of charging/discharging process increases, the active material is likely to fall off, which greatly affects the performance of the battery.

Stainless steel refers to alloy steel containing nickel, molybdenum, titanium, silver, copper, iron, and other elements, which also has good electrical conductivity. It is stable enough to resistant to corrosive media such as air, steam, water, acid, alkali, and salt. The surface of stainless steel is also easy to form a passive film, which can protect its surface from corrosion. At the same time, stainless steel can be processed thinner than copper, which has the advantages of low cost, simple process, and large-scale production.

Carbon nanotubes (CNTs) are a new type of one-dimensional nanomaterials. The unique graphitized structure and ultra-high aspect ratio of CNTs result in its excellent electrical properties; at the same time, the density of CNTs is extremely low compared to that of metals. Therefore, the thin film prepared with CNTs is expected to replace aluminum and copper foil and become a new-generation LIB collector.

1.3 Development and Trends in Power Lithium-Ion Battery

1.3.1 The Layout of Lithium-Ion Battery Production Capacity

In 2025, the global power battery demand will exceed 1 TWh. Driven by the high demand, power battery companies are vigorously expanding their production capacity. According to incomplete statistics of the starting point lithium battery, as of August 2021, 20 Asian companies including CATL, LG New Energy, CALB, Yiwei Lithium, SKI, and BYD, have a planned production capacity of more than 3000 GWh. In the past two years, European and American companies are accelerating the deployment of power LIBs. A report published in June by EU NGO Transport and Environment (T&E) put the total number of Gigafactory's built or under construction in existing projects in Europe to 38, with a combined expected annual output of