Overview of Preparation Process of Lithium Iron Phosphate Batteries for New Energy Vehicles

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Abstract. Lithium iron phosphate batteries have become one of the most popular batteries in the new yuan automobile industry because of their stable operating voltage, good stability and long cycle life. Lithium iron phosphate batteries are generally composed of positive collector fluid, negative collector fluid, positive material, negative material, diaphragm, electrolyte and other parts. The preparation process of lithium iron phosphate batteries include co-precipitation method, precipitation method, hydrothermal method, sol-gel method, ultrasonic chemistry method and other preparation methods. This paper introduces the preparation mechanism, battery structure and material selection, production process and performance test of lithium phosphate batteries with iron-based compounds such as ferrous phosphate trihydrate as iron source, lithium hydroxide or lithium oxide as lithium source, and single carbon source such as glucose, acetylene black, graphene, carbon nanotubes, etc. At the same time, important processes such as the batching process, wet grinding process, spray granulation process, sintering process, crushing process and finished product post-processing process are introduced in detail. Among them, spray granulation, sintering and crushing are the most critical steps in LFP production, which directly determines the performance of the LFP products produced. Finally, we look forward to the development of lithium iron phosphate batteries and provide views on future new energy vehicle batteries.

Keywords: Preparation of lithium iron phosphate batteries; technological process; natural capacity.

1. Introduction

With the increasing problem of environmental pollution and the over-development of non-renewable resources, more and more new energy vehicles have appeared in the automobile industry. The most important battery manufacturing process and battery materials in new energy vehicles have also attracted extensive discussion and attention. Among them, lithium iron phosphate (LEP) is an olivine-type cathode material, which is one of the earliest large-scale commercially commercialised cathode materials. It has attracted much attention because of its stable working voltage, good stability and long cycle life [1].

Lithium iron phosphate batteries have also become one of the most popular batteries in the new energy vehicle industry.

At the same time, the weight, energy storage, endurance, environmental impact and battery life of lithium iron phosphate batteries in new energy vehicles have also aroused widespread discussion. Various processes for preparing lithium batteries have also attracted much attention from the industry.

It was first made from iron phosphate and lithium sources and solid-phase method. After that, precipitation method, co-precipitation method, hydrothermal method, soluble gel method and other methods are mainly used to obtain nano-scale lithium iron phosphate particles. Because of their poor stability and electrochemical properties, there are many studies on their modification, mainly by carbon wrapping, metal wrapping, impurity doping, surface modification and other methods. It aims to improve the electron conductivity and specific surface area of lithium iron phosphate, shorten the ion diffusion path, and inhibit lithium ion migration to make nanomaterials and multiphase structural materials, so as to improve the stability, electrochemical properties and conductivity of lithium iron phosphate [2].

In the future, the research on lithium iron phosphate will also focus on material selection and performance development, in order to improve the life, energy storage and safety of lithium iron phosphate batteries for further large-scale production and application.

This article will introduce the main preparation process and methods of lithium iron phosphate batteries for new energy vehicles.

2. Lithium Iron Phosphate Battery Production Process

Iron phosphate and lithium iron phosphate belong to the same sorbius crystal system, which makes the structure stable during the embedding and release of lithium, and iron phosphate contains both iron source and phosphorus source [3]. In the synthesis process, lithium iron phosphate can be prepared by introducing lithium carbonate or lithium hydroxide into the lithium source [3]. As a precursor of lithium iron phosphate, the preparation process of iron phosphate is currently the focus of many cutting-edge enterprises and scientific research institutions [4-6].

The co-precipitation process is simple, easy to operate and easy to industrialise; The iron phosphate prepared by hydrothermal method has uniform particle size distribution and high crystal phase purity, but the reaction process is difficult to monitor and the reaction result is difficult to control. The sol gel method can realise the diffusion of components in the nanometer range, so the reaction temperature is low and the product uniformity is good, but the pores in the gel will escape gas or organic matter when drying, causing shrinkage; The ultrasonic chemistry method has the characteristics of short reaction time and high reaction efficiency, but it is difficult to achieve industrialisation due to the limitations of equipment [7-10].

The following figure 1 shows the preparation mechanism of lithium iron phosphate. Iron-based compounds such as trihydrates ferrous phosphate are used as iron sources, lithium-based compounds such as lithium hydroxide or lithium oxide are used as lithium sources, and single carbon sources such as glucose, acetylene black, graphene, and carbon nanotubes are used as raw materials. They are dissolved in single solvents or mixed solvents such as ultrapure water, ethylene glycol, propylene glycol, and organic amines according to a certain ratio, and then the pH value is adjusted by adding alkaline substances such as ammonia or sodium hydroxide, so that Fe3+ reacts with phosphate to produce iron phosphate. At the same time, lithium ions began to be embedded in iron phosphate. After that, the precipitation is washed many times with an appropriate amount of solvent to remove impurities, and then the precipitation is dried to remove the residual solvent. It is calcined at 700~800 °C to make it thermal decomposition and lattice rearrangement to make lithium iron phosphate crystals. Finally, the obtained products are crushed, ground, iron removed, screened and other steps to obtain a micrometre- or nano-scale lithium iron phosphate product of uniform particle size, as shown in Figure 1[2].

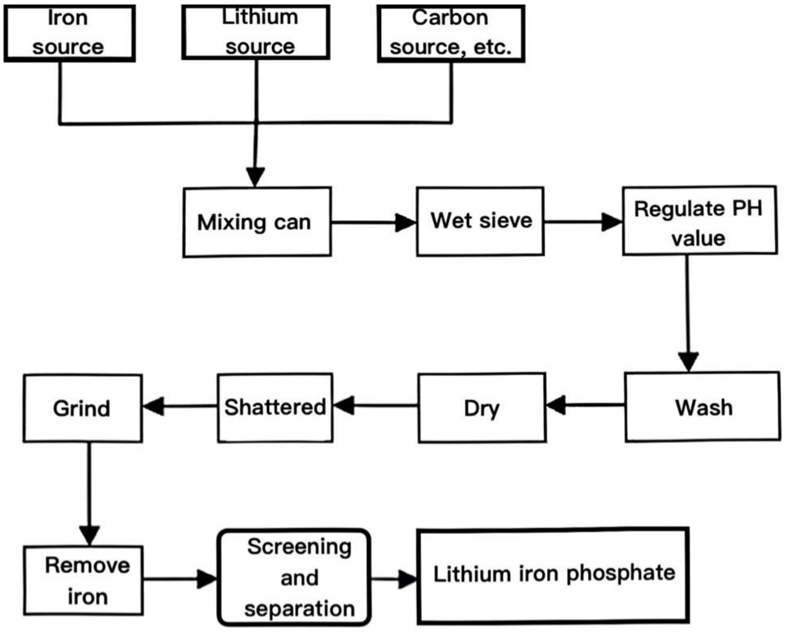


Fig 1. Preparation mechanism of lithium iron phosphate [2].

Figure 2 is a typical process flow chart of iron phosphate synthetic fibre LEP in a large-scale production line of LEP. The raw materials in this process are FePO4, Li2CO3, glucose and PEG, which are the iron phosphate process line [11]. The process can include multi-step processes of batching, wet grinding, spray granulation, sintering, crushing, and finished product post-processing (as shown in Figure 2). Spray granulation, sintering and crushing are the most critical steps in LFP production, which directly determines the performance of the LFP products produced [11].

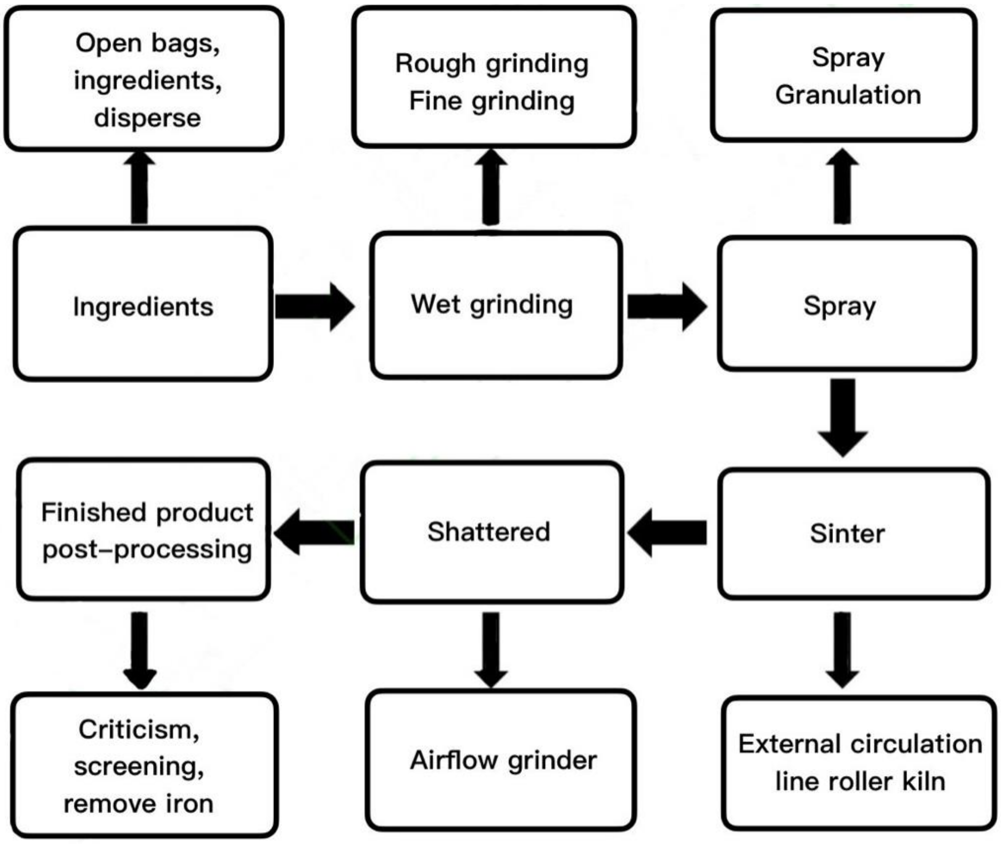


Fig 2. Process diagram of producing lithium iron phosphate [11].

3. Structure and Material Selection of Lithium Iron Carbonate Battery

3.1. Structure of Lithium Iron Phosphate Battery

The charging process is divided into five major processes: initial state, charging preparation, ion embedding and deembedding, electronic conduction and absorption of electric energy. The lithium ions embedded in the lithium iron phosphate crystal will be moved from the electrolyte to the surface of the lithium iron phosphate particles under the action of external voltage. In this process, lithium ions are embedded in lithium iron phosphate crystals and filled into the dynamic equilibrium of lithium ion concentration. The flowing electrons store electrical energy in lithium ions under the action of external voltage;

The discharging process is divided into four processes: initial state, ion embedding and deembedding, electron conduction and release of electrical energy. The lithium ion embedded in the lithium iron phosphate crystal is moved to the surface of the lithium iron phosphate crystal through the ionic conductive medium. Then the lithium ion is detached from the surface of the lithium iron phosphate crystal and enters the electrolyte. The new lithium ion is embedded in the lithium iron phosphate to achieve the dynamic equilibrium of the internal lithium ion concentration of lithium iron phosphate. With the embedding and de-embedding of lithium ions, electrons are conducted inside lithium iron phosphate, causing charge imbalance, resulting in free charge. In this dynamic process, the current and potential difference are generated, thus releasing electrical energy [2].

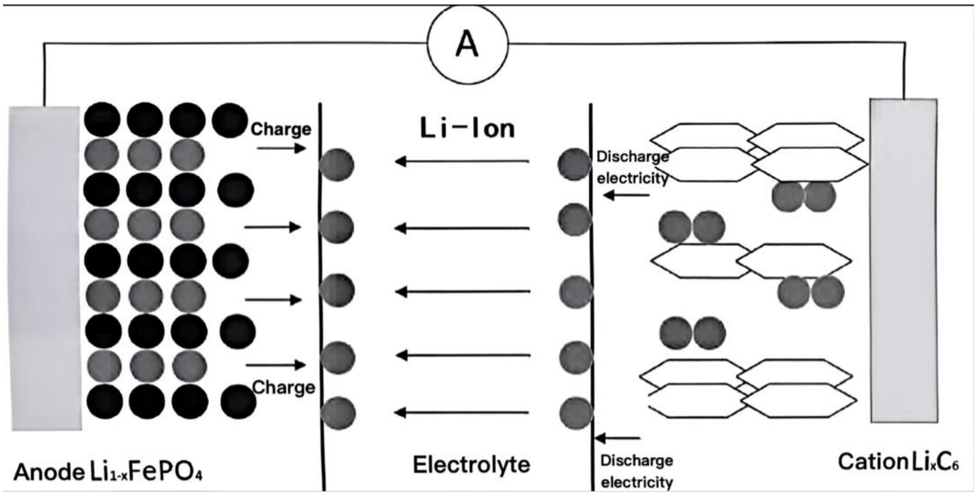


Fig 3. Working mechanism diagram of lithium iron phosphate battery [2].

3.2. Selection of Materials

Lithium-ion batteries are composed of positive electrode, negative electrode, diaphragm, electrolyte and other parts, among which the positive material has the most important impact on the energy density and cycle life of the battery [11]. At present, there are two types of mainstream cathode materials in the lithium-ion battery market, namely, layered cathode materials represented by nickel-cobalt manganese (NCM) and nickel-cobalt aluminum (NCA) ternary materials, and olivine structural materials represented by lithium iron phosphate (LFP) [11].

Commercial square lithium iron phosphate batteries are generally composed of positive collector fluid (aluminum foil), negative collector fluid (copper foil), positive material (nickel-cobalt aluminum), negative material (graphite), diaphragm, electrolyte, safety valve, positive cover, washer, shell, etc[12].

4. Production Process of Lithium Iron Phosphate Battery

4.1. Batching Process

The four ingredients required are PEG, FePO4, Li2CO3 and glucose, which are put into their respective special ingredients lines into the dispersion kettle. Glucose must use dry and cold gas in the ingredient stage, otherwise it is easy to cause glucose to absorb water and seriously reduce fluidity. After dispersion, the solid content of the slurry can generally reach 35~40%, the density is 1.1~1.2 g·cm-3, the viscosity is 700~2000 cp, and the temperature is controlled below 40 ℃ [11].

4.2. Wet Grinding Process

The dispersed material in the dispersion kettle is filtered by a 5 mesh bag filter and transported to the coarse grinding tank with a non-metallic diaphragm pump. The slurry entering the coarse grinding tank will be ground in the coarse grinding circulation line, and the slurry can be further mixed evenly. The slurry in the coarse grinding tank is pumped from the diaphragm pump to the rod sanding mill for grinding, and then returned to the coarse grinding tank after being cooled by the plate heat exchanger. The interior of the rod grinding machine includes a rotating stirring rod and a ZrO2 ball for grinding. The grinding principle is similar to that of a ball mill that is, using a high-hardness grinding ball to hit the material particles to achieve the purpose of grinding. The fine grinding tank and its supporting rod grinding machine and other equipment are exactly the same as the rough grinding process. The only difference is that the smaller diameter ZrO2 grinding ball is used, which further grind the slurry until it can can pass the 100 mesh filter. The material after wet grinding will go through the stirring and electromagnetic iron removal process to prepare for subsequent spray granulation, as shown in Figure 4[11].

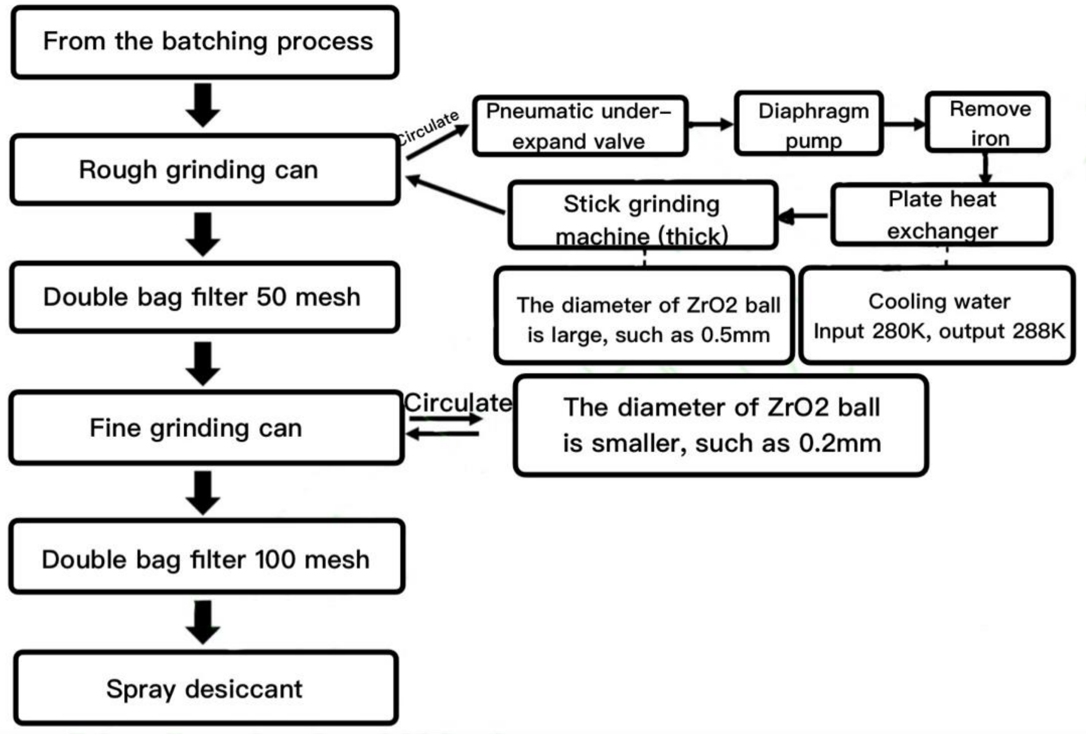


Fig 4. Process diagram of wet grinding and spray drying, omitting conveying devices, temporary storage de-vices, iron separator devices and valves [11].

4.3. Spray Granulation Process

In the process of spray granulation, the high-speed rotating centrifugal nozzle at the top of the spray drying tower disperses the slurry into small droplets, during the process of falling in the tower, the droplets will be dried into small powders by the hot air flow ejected below, the prepared dry powder is sucked into the gas-solid separation tank, so as to achieve the uniform distribution of the material on the surface of LFP primary particles. The spray-granulated material needs to fall into the cooling temporary storage warehouse for cooling due to high temperature. The cooling temporary storage warehouse has a water-cooled warehouse wall, and N2 protection is included to prevent glucose oxidation. Subsequently, the vacuum cavity is used to cooperate with the Roots pump that pumps air downstream, and the material is transported to the corresponding temporary storage warehouse after the end of the spray granulation process by negative pressure conveying, and the material will be further cooled in the process of negative pressure conveying. In the subsequent sintering process, PEG and glucose form carbon inclusions on the surface of the particles at high temperature, thus achieving uniform carbon coating [11].

4.4. Sintering Process

The materials obtained from spray granulation are loaded into a box bowl and transported to the kiln by the outer circulation line for sintering, so that various raw materials undergo a solid reaction and form LFP particles with uniform carbon coating. After the powder after spray granulation is sent to the temporary storage warehouse, it will be added to the bowling machine for bowling. The outer circulation line has equipment to shake, stack, cover and arrange the box bowl in turn, so that the box bowl enters the kiln in the form of six columns and two layers and top caps, that is, a single kiln section contains 12 box bowls. The sintering of LFP needs to be protected by N2 atmosphere, so the box bowl needs to go through the atmosphere replacement room when entering and leaving the kiln to prevent external oxygen from entering the kiln. The kiln can be divided into heating section, insulation section and cooling section from beginning to end. The box bowl will slowly pass through each temperature zone in turn in the kiln and reach the corresponding temperature in the temperature zone, so that the material can be sintered according to the set temperature curve [11].

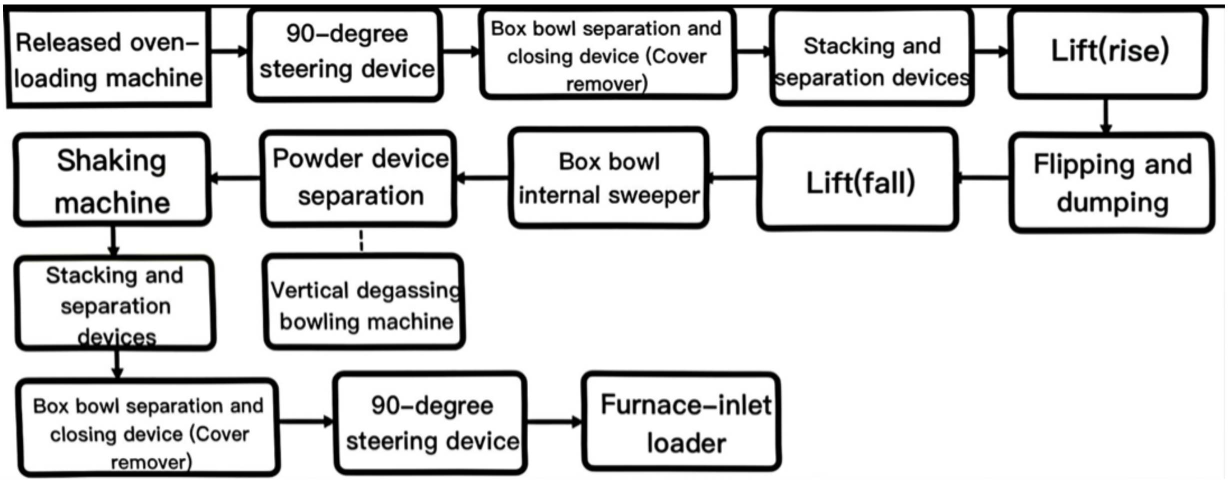


Fig 5. External circulation line of kiln for sintering lithium iron phosphate [11].

4.5. Crushing Process

The key equipment of the crushing process uses airflow grinding, the main principle is to use the Laval nozzle in the lower part of the airflow grinding mainframe to accelerate the compressed air to supersonic speed and converge at a point, the material falling from the top of the airflow grinding mainframe is impacted by high-speed airflow, causing the collision, friction and shearing of particles and particles, particles and warehouse walls, thus crushing the particles. The crushed particles will be screened by the grading wheel at the top. The particles with large particle size that cannot pass through the grading wheel will fall back to the airflow grinding host and continue to be crushed. The particle size can be controlled by adjusting the speed of the grading wheel. The qualified particles through the classification wheel will be collected by the cyclone separator and the gas-solid separation tank, and the discharged compressed gas will be filtered and dusted. Here, the compressed air can be filtered into the compressed air main pipeline or discharged as exhaust gas [11].

4.6. Finished Product Post-Processing Process

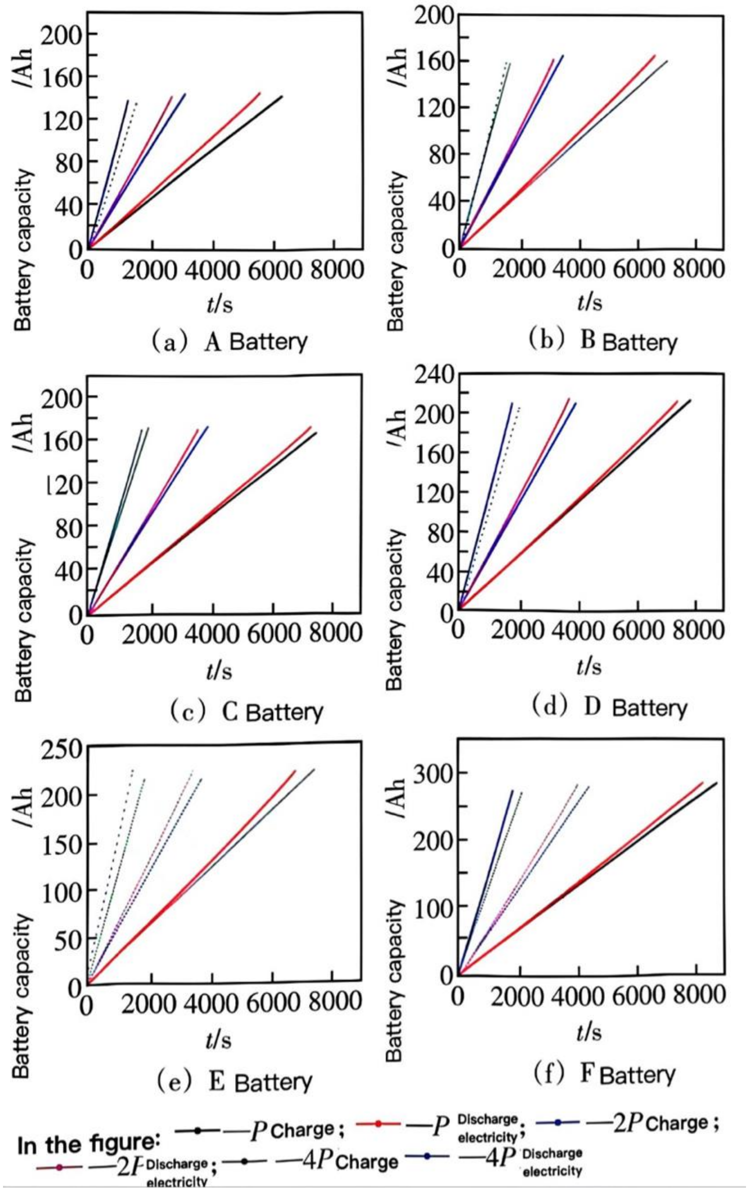
The main purpose of the finished product post-processing is to mix different batches of materials in batches, so that the performance of several consecutive batches of products is consistent, and the final screening and iron removal steps of the material is carried out, and the particle size and magnetic foreign matter content of the product are finally checked.

Screw belt mixer is a kind of large mixing equipment. The material is mixed evenly through the rotation of the internal spiral ribbon blade. The mixed materials will pass through the 200-purpose ultrasonic vibrating screen. Finally, use an electromagnetic iron breaker to remove the material for the last time. After completion, use the ton bag packaging machine to fill the finished product into a customised packaging bag and vacuum to prevent LFP oxidation [11].

5. Performance Test

Six types of lithium iron phosphate batteries are used as test subjects. Using the American Abin 20 V-300 A-2CH specification battery test system, the test samples are all commercial square lithium iron phosphate batteries composed of positive collector fluid (aluminum foil), negative collector fluid (copper foil), positive electrode material (nickel-cobalt aluminum), negative electrode material (graphite), diaphragm, electrolyte, safety valve, positive electrode cover, washer, shell, etc[12].

The battery capacity is distributed at 170~280 Ah. The use of A, B, C, D, E and F in the article represents 6 different battery brands. The rated capacity of the battery is 180 Ah, 180 Ah, 170 Ah, 206 Ah, 230 Ah and 280 Ah respectively, using the constant power of 1, 2 and 3 generation table P, 2P and 4P[12].



(a) A Battery (b) B Battery (c) C Battery (d) D Battery (e) E Battery (f) F Battery

Fig 6. Relationship among charging, discharging capacity and time of batteries with Different constant power and brands relationship [12].

Figure 6 shows the charging, discharge capacity and time relationship of batteries of different brands with different constant power. It can be seen from Figure 6 that the capacity of the battery under high-power cycle conditions is seriously attenuated,the time for all kinds of batteries to complete a charge and discharge cycle under different power is 4P>2P>P, and the useable battery capacity obtained by completing a charge and discharge cycle is P>2P>4P[12]. The test results also show that the high-power charging and discharging test time is less, but the charging and discharging capacity of the battery is relatively reduced; low-power charging and discharging make the battery obtain greater useable capacity[12].

6. Conclusion

At present, lithium iron phosphate batteries are the most common battery choice in the new energy vehicle market. Its high stability makes it one of the most popular new energy batteries. Lithium iron phosphate battery technology is relatively mature, and there is also a relatively complete industrial chain in the new energy vehicle industry, but there is still a lot of room for progress. At the same time, its weight, energy storage, battery life and battery life have become obstacles to its future development.

Nowadays, all-solid-state batteries have become the most concerned batteries in the new energy vehicle industry. All-solid-state batteries have great development prospects, and at the same time, they can also solve many problems of today's lithium batteries. The all-solid-state battery has the characteristics of light weight, long battery life, long battery life, fast charging speed, high safety and high energy density, etc. It is these characteristics that make all-solid-state batteries the most potential battery technology in the new energy battery industry, but they are still in the stage of research and development.

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