Research and Development on the Separators of Li-ion Batteries

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Abstract. With the rapid development of the lithium-ion batteries, the lithium-ion battery separator, as a critical component of lithium-ion batteries, had been extensively studied. In this paper, the main function and performance indicators about the separator materials, recent research and development status at home and abroad of lithium ion battery separators were reviewed. The types and existing problems of mainstream diaphragms in the existing market were described. The production methods of the separators were discussed mainly. It simply introduces the status of the separator’s modification and development of new type of battery separator. Finally, the future development trend of battery separators was forecasted.

1. Introduction
Compared with traditional rechargeable batteries, lithium-ion batteries have the characteristics of high specific energy, rapid charge and discharge, long cycle life, low self-discharge rate, no memory effect, stable discharge voltage, good safety performance and small environmental pollution [1-4]. Therefore, since the early 1990s, lithium-ion battery had become the focus of new power technology research. Lithium-ion batteries were composed by positive and negative electrodes, electrolyte and diaphragm. The separator is an important part of lithium battery, who directly determines the performance of lithium battery. It is an important determinant of battery capacity, cycle performance and safety performance, so the research on battery separators must be taken seriously [5].

Battery diaphragm refers to the polymer membrane between the positive and negative electrodes of lithium ion battery. Its main function is to isolate the positive and negative electrodes to prevent short circuit, at the same time, allow ions to pass freely between the poles and prevent the free passage of electrons [6]. Its performance determines the capacity, internal resistance and interface contact area of the battery, which can directly affect the safety and performance of lithium-ion batteries. Battery diaphragm with excellent performance is a necessary condition to improve the comprehensive performance of lithium-ion batteries.
2. Research and development status at home and abroad
From the perspective of the overall domestic lithium battery diaphragm market, the main diaphragm market is still dominated by foreign brands, including SK of South Korea, Asahi Kasei of Japan, Teijin, Cellguard of the United States, etc. Membrane technology development in China started late, the size of the diaphragm on the enterprise is less, the lack of independent intellectual property rights, in production technology in the lithium battery diaphragm production of key raw materials, formula, lack of research is often membrane is easy to do it, but the quality qualified rate is low, the poor stability and uniformity, unable to industrialization of mass production. At present, domestic diaphragms are mainly used for low-end mobile phone batteries, but the future research and development of diaphragms will focus on new energy vehicle power batteries and power system energy storage battery diaphragms. The key should be to solve the heat resistance of the diaphragm, the production of high temperature resistant composite diaphragm can maintain the integrity of the diaphragm after a large area of positive and negative electrode short circuit in the process of charge and discharge; Under the premise of not affecting the capacity, we can make thinner diaphragm which can meet the needs of small and micro products and multifunctional composite film which can meet the performance requirements of power battery. Develop a diaphragm with better liquid absorption and retention performance to improve ionic conductivity. Research the polymer electrolyte diaphragm, fiber diaphragm, ceramic diaphragm and other new products [7-9].

Lithium battery diaphragm industry has experienced a hard road of development in China, the main reason is for the stability of the technique and technology, optimize and improve exploration research is not enough, blindly copying foreign products and equipment, production of diaphragm consistency and uniformity is poorer, qualified rate is low, this also is many industry development in our country are faced with the common fault. The gap between the development of China's diaphragm and foreign countries is still huge, want to break through foreign technical barriers, need long-term exploration and research. Therefore, in a certain period of time, China's diaphragm production enterprises are still faced with the problem of how to strengthen independent research and development, really have independent intellectual property rights, improve the level of production technology, process maturity and product quality, and at the same time avoid repeated construction and vicious competition in the industry, and avoid excess capacity in the low-end diaphragm market [8-10].

3. Preparation method of lithium battery diaphragm
At present, according to different preparation processes, lithium-ion battery membranes can be divided into two categories: dry (melt stretching, MSCs) and wet (thermally induced phase separation, TIPS). Dry stretching can be further divided into unidirectional stretching and bidirectional stretching. The pore forming mechanism of membrane micropores is different.

3.1 Dry stretching
The dry method (melt stretching method) is based on the principle of melt-extruding polyolefin resin materials to form thin sheets. Due to the shear stress generated during the extrusion process, the oriented lamellae grow perpendicular to the extrusion direction. In the subsequent annealing process, the size and thickness of the lamellae can be increased, so as to obtain a hard elastic material with high orientation and high crystallinity. The hard elastic material film is subjected to thermal stretching with a certain stretching ratio and then heat-set to obtain a microporous film. In the dry stretching process, the structure of the oriented lamella depends on the process of polyolefin melt extrusion and the subsequent heat treatment process.

The dry uniaxial stretching method is to cold stretch a polyolefin film with high crystallinity in the direction of the lamella orientation along the direction of the lamellae at room temperature to form defects such as silver streaks, and then stretch at a high temperature to make the defects stretch. and then prepare the microporous film after heat setting. The membrane prepared by the dry uniaxial stretching method has an elongated microporous structure. The dry uniaxial stretching method was first seen in the patent of Celanse Company in the United States, and was used to prepare a
single-layer polypropylene microporous film. Figure 1 and Figure 2 are the SEM images of Celgard's PP2400, PP2500, PP2730 single-layer and 2325 (PP / PE / PP) three-layer porous membranes prepared by melt stretching method. It can be observed from the figure that the pores of the microporous membrane prepared by the uniaxial stretching method are elongated, and the surface pore size distribution is relatively uniform. The microporous membrane prepared by this method is only stretched in the longitudinal direction, so the strength of the porous membrane in the transverse direction is relatively poor. Many patents have introduced the preparation process of this polyolefin microporous membrane [11].

Figure 1. SEM photos of single layer Celgard separators used in lithium batteries: (a) PP 2400, (b) PP 2500, (c) PE 2730

Figure 2. SEM of Celgard (PP / PE / PP) separators used in lithium batteries

Figure 3. SEM of microporous membrane by biaxial drawing

The Institute of Chemistry, Chinese Academy of Sciences has developed a dry biaxial stretching process with independent intellectual property rights. The β-polypropylene film with high β crystal content is prepared by adding heterogeneous nucleation. During the stretching process, the difference in density between the phases leads to the transition from low density to high density, and the β crystal form to α crystal form is transformed into micro pores, and then heat-set to make a microporous membrane. The polypropylene microporous membrane prepared by the dry biaxial stretching method has a microporous structure different from that of the membrane made by the uniaxial stretching process (Figure 3).

In the process of preparing polyolefin microporous film by melt stretching method, a number of
factors affect the structure of the microporous film, such as tensile temperature, tensile ratio, heat setting temperature, wafer morphology of melt extrusion, annealing temperature and so on. The microporous membrane prepared by the dry biaxial drawing method has different microporous structure from that of the membrane prepared by the uniaxial drawing process. Due to the bidirectional stretching, the pore size distribution of the microporous membrane is more uniform, and the transverse mechanical strength of the membrane is also improved, so the performance is higher when applied to the lithium ion battery. The dry drawing process is simple and pollut-free, easy to operate and industrialize, and does not need solvents. Therefore, most companies at home and abroad use this method to prepare lithium battery diaphragm, such as Celgard and UBE. The polypropylene microporous membrane prepared by S. W. Lee et al. by this method, has an average pore size of 0.05 m and an average porosity of 30%-40%, and has good mechanical properties and permeability [10-13].

3.2 Wet stretching

The wet method, also known as thermally induced phase separation (TIPS), was a method for preparing battery separators that has only been developed in recent years. The preparation process is to mix polyolefin resin with hydrocarbon liquid or some compounds with low molecular weight and high boiling point, and then heat the polymer to dissolve in it to form a uniform system. Phase separation occurs in the cooling and cooling process, and then unidirectional or bidirectional stretching of the samples after phase separation can be carried out to produce porous microfilms with pore diameter connected.

The wet method was applicable to a wide range of materials for preparing porous membranes. Currently, companies used this method including Entek, Asahi Kasei, Mitsui Chemicals, Tonen and UBE from Japan. The pore size of microporous membrane prepared by thermally induced phase separation is relatively small and the pore size distribution is relatively uniform. For the microporous membrane prepared by bidirectional stretching, due to the bidirectional stretching, the longitudinal and transverse strength of the microporous membrane is relatively large, and the puncture resistance strength is correspondingly good. Moreover, compared with the microporous membrane prepared by dry stretching, the thickness of the microporous membrane can be made thinner, thus improving the energy, contact area and current density of the battery. The wet stretching preparation process was complicated and not easy to industrialize. Moreover, a large amount of solvents need to be used, which is easy to cause environmental pollution. Figure 4 shows the SEM image of the surface of the microporous membrane prepared by the thermally induced phase separation method [6]. It can be found that the microporous structure of the membrane prepared by this method is different from that of the microporous membrane prepared by the melt stretching method.

![Figure 4. SEM of lithium battery separators by wet stretching (a) Setela (Tonen), (b) Hipore-2 (Asahi)](image-url)

In the process of preparing microporous membranes by thermally induced phase separation, there are many factors that affect the membrane structure, such as: cooling rate, polymer molecular weight, initial concentration of polymer solution, solvent molecule movement and nucleating agent, crystallization ability, etc. The cooling rate plays an important role in the phase separation and the time taken for the degree of subcooling, and may change the phase separation mechanism of the
polymer system, thereby having an important impact on the membrane structure. The molecular weight of the polymer has an effect on the phase diagram of the polymer-solvent system, thereby affecting the phase separation time and the membrane structure. The initial polymer concentration affects the mechanism of phase separation. The effect of solvent molecules on the polymer affects the phase separation, thereby affecting the structure of the microporous membrane. The addition of nucleating agent can better control the pore size and uniform distribution of the microporous membrane. In addition, the crystallinity and fluidity of the solvent also have a certain influence on the structure of the microporous membrane [13].

4. Prospects for Lithium Ion Battery Separator
Due to the contradictions in demand for performance improvement, balancing or even simultaneously improving the performance and safety of the separator is an important research direction for power lithium battery separators. At present, the method of grafting functional groups and adding hydrophilic substances can improve the wettability of the membrane; the composite of polymers with different melting points and the use of high crystallinity polymers can improve the thermal shutdown temperature and thermal melting temperature of the membrane. For porosity, strength and thermal dimensional stability, a porous matrix material, such as non-woven fabric or electrospun fiber, is used as the reinforcing matrix to ensure the strength, dimensional stability and thermal melting temperature of the film; Using other polymers as pore-forming materials can improve the porosity and wettability of the membrane, and is an effective means to improve the performance and safety of the membrane at the same time. More research should be based on the reinforced composite structure to improve the performance and safety of the separator at the same time, thereby promoting the large-scale application of power lithium-ion batteries.

5. Conclusion
High-power and high-energy battery systems require high-safety and high-quality diaphragm materials. In the field of technological development, diaphragms have developed from a single polyolefin material to a variety of materials and conform to the direction of materials, from simple structures to complex mechanisms. This requires us to conduct a more in-depth study on the modification and function of the porosity, pore size distribution, safety and mechanical strength of the lithium battery separator to ensure the performance of the battery power performance and the development of the lithium battery to a higher specific energy system.

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