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The Development of High-Power LIBs Separators

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Abstract. Separators present the crucial functions of separating the positive and negative electrodes due to the free flow of lithium ions through the liquid electrolyte that fills in their open pore. Separators for liquid electrolyte Lithium-ion batteries can be classified into porous polymeric membranes, nonwoven mats, and cellulose separators. When a lithium-ion battery is being overcharged, it releases the heat and results in the inner-short. The polyethylene (PE) separators used here had shut down at around 135°C to cool the exothermal batteries. To enhance the meltdown temperature of the separator, a PE separator was coated with polymers synthesized from various ethylene glycol dimethacrylate monomers. At the same time, nonwoven mats have the potential to be low cost and thermally stable separators. Furthermore, the lithium-ion phosphate/lithium half cell using cellulose separator exhibited stable charge-discharge capability even at 120 °C. This paper presents an overview of the PE and PP membranes of lithium-ion battery separators, discusses how to solve their disadvantages, and reviews the cellulose-based materials developed for potential application in the lithium-ion battery.

1 Introduction

With the rapid development of society, the energy problem has become an important topic in the world. Because of excessive coal and oil consumption, the produced Nitrogen Oxides cause great harm to human respiration, such as pulmonary edema and tracheitis. Additionally, air pollution and acid rain also have bad impacts on human living environments. Moreover, excessive carbon emissions would lead to global warming and climate crisis. The severity and urgency to protect the environment force countries worldwide to gradually shift from high carbon fossil consumption energy to green, low carbon, and renewable energy. Therefore, researches on renewable energy such as nuclear energy, wind energy, geothermal energy will replace fossil fuels and become the mainstream trend in the world. Fossil fuels are the most important energy sources used in the automobile industry. Therefore, the development of electric vehicles is the key policy in all countries. Among all of this, the development of lithium-ion batteries is an important part of replacing the fuel vehicles' power system.

Moreover, lithium-ion batteries are an important transformation direction of electric vehicles. The efficiency of a fuel car is less than that of an electric vehicle. Only a portion of the fuel energy is converted into kinetic energy, and a portion of it is translated to heating. On the contrary, the battery doesn't have this problem. Nowadays, a lithium-ion battery is the first way to develop an energy storage battery. The lithium-ion battery has the characteristics of high energy density, small unit volume, large voltage, long cycle life, and modular integration. Usually, a lithium-ion battery includes positive& negative electrodes, a battery separator, and an electrolyte. The role of the electrode and electrolyte is to produce a redox reaction and to generate current. The battery separator is used to separate the positive and negative electrode, avoid short circuits inside the battery, and allow lithium-ion to pass through freely. The battery will release a lot of heat in the process of high-current charging and discharging, leading to a significant increase in the battery's internal temperature, and there is a risk of occurring of electrode decomposition separator damage, and thermal running. Today's lithium-ion batteries, such as Tesla ternary lithium-ion batteries, combusts and explode easily. The basic reason is that the high-temperature resistance of the separator is not enough. Due to that, the separator material plays a dominating role in the safety performance of lithium-ion batteries. A good separator can effectively help the lithium-ion movement in the electrochemical reaction and help to charge and discharge efficiently [1]. Therefore, the high-temperature-resistant separator is an important research direction of lithium-ion batteries.

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Figure 1. The cellulose separators in the LIBs.

To improve the high-temperature resistance, the existing separator materials can be modified by thermal resistant materials. On the other side, the new high-temperature-resistant materials can be directly used as the battery separator. The control of the film-forming process is also helpful to improve the heat resistance of the membrane. At present, the polyolefin microporous separators such as polyethylene (PE) and polypropylene (PP) membranes are commercially available because of their superior properties such as electrochemical stability, considerable mechanical strength, and thermal shutdown property. Nevertheless, they have some disadvantages when used in future energy storage devices and electric or hybrid-electric vehicles. One of the most serious issues is their inferior thermal stability due to their low softening and melting temperature. Therefore, it is difficult to perform the critical function of electronic isolation between cathode and anode in large-sized batteries under elevated temperature and vigorous conditions. Tremendous efforts have been made to develop high-performance separators with superior electrolyte wettability, improved thermal stability, and enhanced rate capability. One strategy was to incorporate inorganic nanoparticles into PE or PP membranes to achieve better thermal and interfacial stability; the other was to fabricate polymeric nonwovens based on heat-resistant resins. Unfortunately, the incorporation approach suffered from poorly bonded nanoparticles, and the nonwovens had a limitation of low mechanical strength [2]. And other problems are intrinsically hydrophobic characteristics, inferior dimensional stability, and low porosity. To tackle these disadvantages, extensive efforts are focused on surface modification and surface polymer coating. However, these solutions are limited in practical applications due to their high manufacturing cost, environmental problems, and inherent defects of polyolefin separators [3].

And then, it is well-known that the polyolefins are not renewable because of their source from the ever-decreasing fossil oil. An alternative way to solve this problem is to achieve the transition from fossil-based resources to biomass-based resources. As we all know, cellulose is one of the most abundant, renewable resources on the earth and possesses outstanding properties such as biocompatibility, desired chemical stability, and environmental benignancy. Furthermore, it was reported that the initial decomposition temperature of cellulose is above 270 °C. These abundances, renewable and superior thermal stability could qualify cellulose as a very promising material for battery application instead of fossil-based chemicals. In very recent years, a number of cellulose-based materials have been developed for potential application in lithium-ion batteries such as a binder, separator, and electrolyte additives because of their unique characteristics and providing new greater opportunities. Carboxymethyl cellulose (CMC) and natural cellulose were used as flexible, porous, low cost, and electrochemically stable separators for low power applications [4]. New materials and new technologies have been widely used in this field, but only a small number of high-temperature-resistant membranes have been industrialized [5]. This article mainly describes the advantages and disadvantages of commercial LIBs and their improvement.

2 The types of commercial LIBs separators

Lots of materials can be used for separators, like PP, PE, glass fiber, PEEK, PVDF, PI, and aramid membrane. But due to the commercial need, only a portion of them have been commercialized. The safety factor would always be the priority, then with the difficulty of the process and the cost. Several properties like permeability, heat resistance, chemical stability, wettability, dimensional stability, and strength would be considered the important factor for the commercial membrane that determines the safety of lithium-ion batteries. Thickness is beyond safety, but it is also important as it will determine the internal resistance. The most popular materials used are PP and PE or the combination PP/PE because of their excellent mechanical properties, chemical stability, and acceptable cost[6]. PE has high strength, while PP has high permeability, porosity, and mechanical property.

3 The disadvantages of the commercial LIBs separators

Although polyolefin materials are widely used in commercial lithium-ion batteries, they still have lots of disadvantages. PP and PE are known for their low melting point, which has 130 °C and 110 °C, respectively. So, their usage has been limited in certain conditions due to the melting temperature. Furthermore, there's an observation of loss in mechanical strength after exposure to different temperatures and decreased tensile strength in a certain direction, which provides the anisotropy property [6]. The most popular manufacturing method now is the dry and wet process, as illustrated in Figure 2.

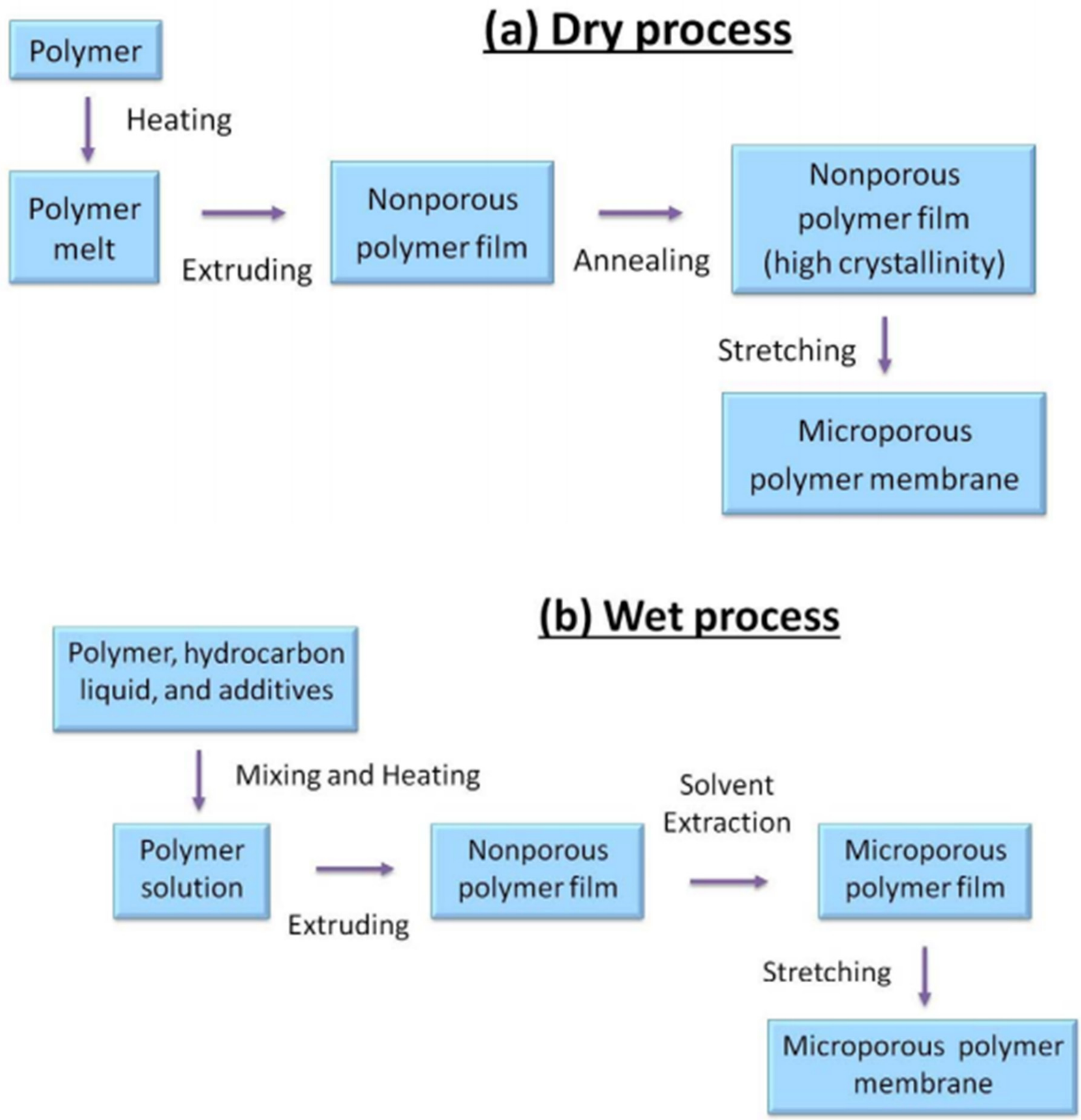

Figure 2. Two traditional membranes making process: (a) Dry process and (b) Wet process

3.1 Disadvantages in dry process

Figure 2a shows the process of dry process, which has been used the most since it is usually processed by mechanical stretch the most, with no solvent involved. Two stretching methods in the dry process are uniaxial stretch and biaxial stretch. The uniaxial stretch involves stretching in one direction while experiencing a compressive force in a perpendicular direction. This stretching method will result in a structure shown as Figure 3. The strength in the membrane is isotopic, with lower strength in the lateral direction, the direction parallel to force applied, while higher strength in perpendicular direction. The membrane produced by uniaxial stretch is usually thicker than that of biaxial stretch, affecting the permeability. On the other hand, Biaxial stretch provides mostly circular pores instead of the slit-like pores from the uniaxial stretch. Still, it only guarantees limited success compares to uniaxial stretch, which is more successful to date. The β nucleated polypropylene stretched membrane usually has a wide pore size distribution, which can cause current uneven transfer [7].

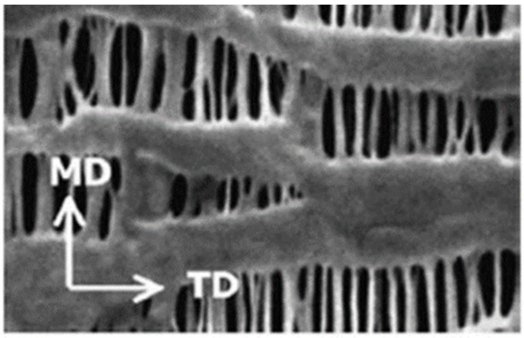

Figure 3. Microstructure of membrane from uniaxial stretch [8].

3.2 Disadvantages in wet process

The wet processing is shown in Figure 2b, which usually involves mixing the polyolefin resin with some lightweight liquid or substance, melting to form the sheet, and extracting the liquid out by using some volatile solvent after uniaxial or biaxially stretch. The liquid the process used is not environmentally friendly and costly compares to the uniaxial stretch method. Furthermore, the membrane also tends to experience a shrinkage in the transverse direction. The low wettability and poor electrolyte retention properties are also the limitations of polyolefin materials [8]. Wettability and electrolyte retention are important properties since they determine ion transport. The internal resistance is lower, and the conduction can be faster if the membrane can absorb more electrolyte and retain it.

4 The improvements to the commercial separators

Several methods improve the membrane based on the polyolefin materials, both from processing and membrane modifications.

4.1 Optimize the membrane from the production process

Membranes produced by Celgard is the "best-characterized battery separator in literature" so far since they have been widely used in numerous battery systems. The PP/PE/PP trilayer structure in CelgardTM microporous membranes provides exceptional puncture strength [9] and the additional strength due to composing structure. Furthermore, the difference in melting point will also allow it to have a cutoff function when PE melts while PP still maintains. Nitto Denko has a type of membrane designed by mixing polyolefin resin with the high molecular weight rubber through oxidation in the air during the wet process. This method can increase the melting point to 200 °C [10]. During the biaxial stretch, the uniform polypropylene film with a high β-crystal structure can be processed by biaxial stretching and heat setting under tension to get larger porosity and higher thermal stability [11]. A highly permeable microporous polyolefin membrane can be produced according to patent [12]. The microporous structure can be formed by first preparing the polyolefin solution in a certain ratio, cooling the extruded and stretched the molten state solution into a gel-like sheet, then heat-set in a certain temperature after removing the residual solvent from the sheet.

4.2 Membrane modification methods

The electron-beam irradiation is an effective way to decrease thermal shrinkage, according to the experiments by Kim.[13]. Furthermore, an increase in ionic conductivity and rate capability is also observed due to the presence of the carbonyl group after the irradiation. By applying the polydopamine, the wettability and ionic conductivity can be increased because of the hydrophilic surface of the membrane [14]. The hydrophilic surface can also "increase the liquid electrolyte uptake", results in a longer life cycle of the membrane. The porous polyacrylate coating improves the meltdown temperature of the PE membrane to 188°C with the same shutdown temperature [15], providing a safer property after the shutdown happens. Inorganic particles inserted into the membrane can result in ionic conductivity, thermal stability improvement [16]. And inorganic particle coating can increase the wettability due to the large surface area in contact with the electrolyte [17].

5 The new high-temperature-resistant LIBs separators

5.1 Separator prepared with inorganic material

The representatives of inorganic separator materials are glass fiber and ceramic. Glass fiber is an ideal separator material with excellent performance. It has good high-temperature resistance, which can work at 400 ℃, much higher than the melting temperature of PP and PE. It also has the characteristics of good corrosion resistance, low potential loss, and high ion transmittance. The glass microfiber can be produced industrially now, but it can't be popularized in batteries used daily due to the high cost. The glass microfiber is mainly used for battery performance testing and special high-temperature resistance batteries for rockets and missiles that do not care about cost [18].

Ceramic materials are also commonly used as high-temperature resistant separator materials, and it already has practical applications as coating materials of traditional separators to improve their thermal stability. There are also entirely ceramic separators. However, the mechanical strength and structure of ceramic separators still need to be optimized. One solution is to use the mixture of ceramic and organic materials to make separators, such as the separator made of the mixture of SiO_2 and polyamide, which not only have a sponge structure and good high-temperature resistance but also has a much higher porosity and liquid absorption than commercial polypropylene membrane. Although the separator made with a mixture of ceramic and organic has excellent performance, organic and ceramic proportions still need more research. Furthermore, it is difficult to fabricate large-area ceramic separators with uniform thickness in the industry.

5.2 Separators prepared with heat-resistant polymeric materials

Another way to improve the heat resistance of separators is to use heat-resistant polymeric materials. Aramid fiber is one of the heat-resistant polymeric materials used for separators. The aromatic groups in aramid molecular structures provide good heat resistance. Besides, the polar amide groups in aramid have good compatibility with the polar solvent in the electrolyte of lithium-ion battery. Another heat-resistant polymeric material is polyimides

(PI). PI not only has amide groups but also has a higher heat resistance and corrosion resistance than aramid. Compared with glass fibers, these polymers have better application scenarios at high temperatures and have better processability. Besides, aramid fiber and PI can be made into nanoscale fibers to enhance mechanical performance and gain other properties [19-20].

The polymeric materials can also be composited with inorganic materials. The polyethylene terephthalate (PET) has a heat deflection temperature of 60-200℃ [21], and it can be further improved by compounding inorganic layers on the surface PET separators. For example, the PET separator compounded with ceramic materials can keep its electric property at 200℃ for a long time and has little shrinkage [22]. In addition, PET can be processed easily, making it possible to popularize in daily used batteries, such as in electric vehicle batteries.

5.3 Separator with hierarchical structure

The ideal material of LIBs separator should possess properties like high chemical and electrochemical stability, high thermal stability, highly porous feature, and so on. However, no material can possess all these properties. Therefore, the separator with a hierarchical structure that can make use of the characteristics of different materials attracts much attention.

The hydroxyapatite nanowire (HAP NW) networks with excellent thermal stability [23], fire resistance, and superior electrolyte wettability, but their mechanical strength is poor.Combininge the HAP NW with cellulose fibers (CFs,) which have high mechanical strength, form a hierarchical cross-linked network structur. Thee as-prepared HAP/CF separator shows superior electrolyte wettability, mechanical robustness, high thermal stability, and fire resistance.

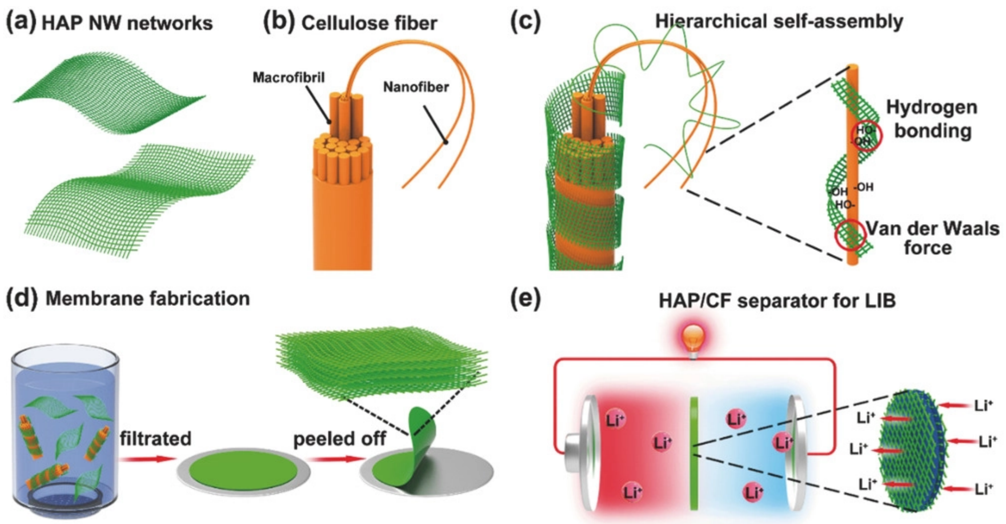

Figure 4. Schematic illustration of the new kind of highly flexible and porous separator based on HAP NW networks with excellent thermal stability, fire resistance, and superior electrolyte wettability. a) HAP NW networks. b) CFs. c) Hierarchical assembly of HAP NW networks and CFs. d) Suction filtration process for fabricating the layered and highly porous HAP/CF separator. e) The application of the HAP/CF separator in the LIB [23].

6 Conclusion and outlook

In general, with the development of lithium-ion batteries, ensuring their safety is a problem that cannot be ignored. The heat resistance of the lithium-ion battery separator determines its performance and safety at high temperatures. Here we summarize the development of power lithium-ion battery and their corresponding energy problems, the types of commercial lithium-ion battery separators and their shortcomings, and the improvement scheme of commercial separators. The development trend and type of high-temperature-resistant separators are also summarized in the review.

The most popular materials used are PP and PE or the combination PP/PE, but both have a low melting point, limiting their usage under high temperatures. Several methods improve the membrane based on the polyolefin materials, both from processing and membrane modifications. For example, the polypropylene film with a high β-crystal structure and the PP/PE/PP trilayer structure.

Using high-temperature-resistant materials to make new type separators can effectively improve the heat resistance, such as inorganic materials and heat-resistant polymeric materials. Combining various materials can complement each other's shortcomings to create a multilayer structure film with good performance at high temperatures.

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