 https://doi.org/10.1051/e3sconf/202130801008

The High-performance Separators in the Power Lithium-ion Batteries

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Abstract. In order to tackle different challenges related to the conventional energy consumptions in the near future, people need to dig more into the different types of green new energies, and the use of lithium-ion battery plays a very important role. It is necessary to enhance the performance of lithium-ion batteries via the improvement of separators. Lithium-ion batteries are now widely used in the electrical vehicles industries for their high power, long life circle, small weight and volume, large operating temperature range, and no memory effects. Separators are one of the important components of lithium-ion batteries since they can isolate the electrodes and prevent electrical short-circuits. The separator is a key element in all lithium-ion battery systems since it allows the control over the movement of ions between the anode and the cathode during the charge and discharge processes. Nowadays, to meet the safety demands of batteries, thermo-tolerant separators have become increasingly important for battery design and performances. As a result, some potential developments of the separators such as the inorganic coating and heat-resisting polymer methods are explained in this article. At the same time, the developments of those methods will also be discussed.

1 Introduction

The world's energy supply and demand balance has been broken for a long time, and the energy consumption is growing far more quickly than the provided energy. As is known to all, the fossil energy dominates the world's energy consumption. The storage of oil becomes less with the increase of refining capacity and consumption. Meanwhile, the instability in West Asia and North Africa is affecting the oil price and dragging down the global economy. The pollutants produced in the oil consumption process include solid, liquid, gas and so on, which affects the atmosphere, water bodies, soil, and vegetation in the human living environment [1]. Currently, the most concerned environmental issues are: global climate change, acid rain, ozone layer thinning, ocean pollution, water shortage, and so on.

The development of Electric Vehicle has received many attentions from the world for reducing our dependence on oil. Therefore, accelerating the development of EV has also become a worldwide consensus. From the general trend, the lightweight materials, the intelligent technologies , and the new battery packs have been applied in the EV. The performance of the battery has also been improved, and it has become cheaper and more popular. Most governments around the world are now strongly promoting the development of EV by providing many convenient and helpful policies.

The high-power lithium-ion batteries (Figure 1) used in the electric cars today has the following characteristics.

Long cycle life: The lithium-ion battery for charging and discharging cycle life at 1C multiplier is more than or equal to 800 times, the 800th time's electrical capacity is more than 70%, which is much better than other kinds of batteries.

Small weight, small volume and long range: The lithium-ion batteries are 2/3 the size of the lead-acid batteries and about 1/3 the weight of the lead-acid batteries. In addition, the capacity of the lithium-ion batteries is higher than that of lead-acid batteries with the same volume. It also has a greater battery life than others.

Large operating temperature range: Lithium batteries can work normally between -25 and 40 ℃, while the performance of lead-acid batteries and other batteries will deteriorate in winter.

No memory effect: Lithium batteries does not have memory effect. For example, if nickel-cadmium batteries are not thoroughly charged or discharged for a long time, it will leave traces in the battery, whereas lithium batteries do not have this phenomenon.

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https://doi.org/10.1051/e3sconf/202130801008

Figure1. The lithium-ion battery.

However, there are some safety risks associated with the lithium batteries. The main cause of spontaneous combustion of power lithium-ion batteries is thermal runaway, and the main causes of it are collision and short circuit. When a violent collision causes severe deformation of the battery, an internal short circuit will occur, resulting in a localized heating of the battery as the energy is released from the short circuit. The next is the short circuit inside the battery. The anode, cathode, separator and electrolyte of the lithium-ion batteries all have safety issues[2]. The decomposition of the anode material and oxidation of the electrolyte will happen at high temperature, releasing a lot of heat and causing the explosion[2]. Moreover, there will be lithium dendrites after many times charging and discharging, which will cause a short circuit by puncturing the separator. The lithium-ion battery electrolyte is a mixture of lithium salt and organic solvent. The thermal decomposition of this material is easy to happen and can be easily decomposed at high temperatures, which causes the reduction of the thermal stability of the electrolyte[3]. The mechanical strength, porosity, thickness uniformity, and blocking/rupture temperature of separators are important determinants for the LIBs safety. The application of ceramic coating in the separators can increase the mechanical strength of the original film and give them excellent performances in terms of high temperature resistance, puncture resistance, and thickness reduction.[4] At the same time, to ensure the safety of the core, the general separators porosity should be less than 50% and the thickness should be above 20 μm. The temperature at which the micro-porous structure closes is too high or too low will affect the performance of the cell, so the composition of the polymer used for separator and the optimal configuration of the porous structure need to be considered, while the rupture temperature should be higher than the blocking temperature.[4] There are some safety concerns with lithium-ion battery separators, but there will be countermeasures. This paper will focus on the disadvantages, improvements, types, characteristics, and the development of lithium-ion battery separators.

2 Development of LIB separator

2.1 Types of Commercial LIB separator

Currently, the commercial LIB is used in various applications, such as power source of EV and 3C product like mobile phone, camera, etc. Different standards are required for various situations. The separators applied in the LIBs are commonly the polyolefin like Polyethylene, Polypropylene, and their compositions (two sheets, PP/PE/PP three sheets). There are dry and wet methods to produce the separator. Both methods contain a stretch step to produce the pores in the separator. The dry method with stretch is used for producing PP porous membrane [5][6]. Olefin resin is melted and squeezed into the membrane during the process. The annealing process can increase the size and number of zones with high crystallinity. the mechanical stretch would be performed to break the zone with low crystallinity. This method with high production efficiency and yield is quite simple and almost without any pollution.

The wet method is usually used for producing PE membrane with micropores. After mixing the PE with a substance like paraffin oil, we can build the membrane by stretching it in longitude and latitude directions. The pores can be formed after extracting the paraffin oil. PP membrane and PP/PE/PP composite membrane are usually used for high-power lithium-ion batteries. The composite membrane can fuse the porous tunnel at about 135°C, which can be used as a stopper of the batteries in inaptitude working temperature. There is a gap between the stopping temperature and the temperature at which the separator will be totally broken. Because the melting temperature of PE is 135°C and that of PP is 165°C.

2.2 The disadvantages of the commercial LIBs separators

As mentioned above, separators on the market typically consist of PP/PE bilayer or PP/PE/PP trilayer as a safety device in commercial LIB. In an ideal situation, when the internal temperature in LIB is higher than the melting temperature of PE under harsh conditions, the PE layers are softened and melted, closing the pores on the separator and preventing the continuity of reaction. Nevertheless, in real cases, this type of separator always loses control to thermal runaway. There is only 30℃ between the melting temperature of PE and PP. The fact is that the temperature would keep increasing onto the melting temperature of PP due to thermal inertia, causing the shrinkage of the separator as shown in Figure 2 followed by internal short-circuiting of the LIB.

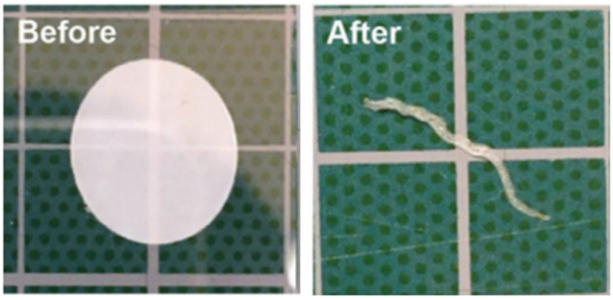

Figure 2. Thermal shrinkage of a PP separator over temperature ranges from 150°C to 200°C [7].

2.3 The improvement to the commercial separators

Considering the requirements of production and further meeting the requirements of processing and manufacturing, a good separator should have chemical stability (no reaction with electrolyte and electrode materials), wettability (easy permeability without elongation and contraction), thermal stability (good high-temperature isolation), mechanical strength (not easily punctured), ionic conductivity (high porosity making ions pass freely) and performance of automatic shutdown (in cases of overheating or short circuit). In general, there are two main ways to improve present separators.

Aiming at the previous defects, the polyolefin separators' surfaces are mainly modified by inorganic coating, heat-resisting polymer, or the combination of both [8], which make the membrane could maintain its shape after softening to keep the battery safe. Al_2O_3 particles can coat the PE membrane by using acrylic acid as a binder [9]. The separator got from this process has a contact angle with electrolyte only 9.73°. The wettability will improve from 85% to 165%. The most important property is that the shrinkage is less than 3% at high temperatures. Figure 3 shows the morphology of the modified PE separator after heat treatment.

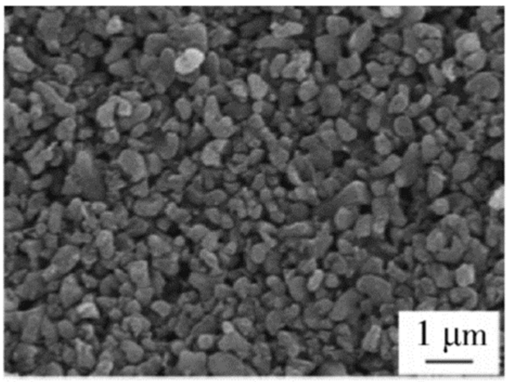

Figure 3. Coated PE separator after being treated at 150 °C.

The thermal-resistant nanofiber can be coated on polyolefin membranes. The capacity, heat resistance, and discharging efficiency are all significantly increased by coating aramid fibers and fluoride. The thickness of the membrane is around 12 μm. The porosity is around 50% to 60%. The shrinkage is around 20% to 30%. The PE separator with polymer coating has been used in Tesla Model S. This kind of separator is composed of aramid fiber and inorganic ceramic layer, which increase the temperature of pores failure, preventing the separator from melting from high temperature. The thickness can be controlled between 6 and 35 μm [10]. The porosity is between 35 to 80%. The size maintenance at pores failure is around 97%.

The introduction of an inorganic particle layer will greatly improve the wettability of the polyolefin separator, and improve the heat resistance and thermal stability of the separator. However, the inorganic coating also has its shortcomings. This modification does not change the nature of the polyolefin separator, and its heat resistance is not comparable to that of other polymer membranes with excellent high-temperature resistance. At the same time, the thickness of the separator increases significantly after the inorganic layer loading, which increases the internal resistance of the separator and the battery accordingly, and the active material is forced to decrease, and the battery capacity decreases obviously. In addition, the stripping and shedding of inorganic particles in the separator layer is also a common problem. Although the use of adhesives will alleviate the shedding problem, it can not be completely solved. The falling inorganic particles may puncture the separator and cause an internal short circuit, bringing safety hazards to the battery.

3 New battery separator materials

3.1 Aromatic polyamide separator

Aromatic polyamide fiber can be prepared into the fiber membrane by filtration and hot pressing. In addition, the amide group contained in the molecular structure of aromatic polyamide has sufficient heat resistance and has good compatibility with the polar solvent in the electrolyte of lithium-ion battery. Therefore, the prepared battery separator has excellent mechanical properties, heat resistance, and electrolyte wetting properties, which makes lithium-ion batteries obtain higher discharge efficiency, heat resistance temperature, and service life.

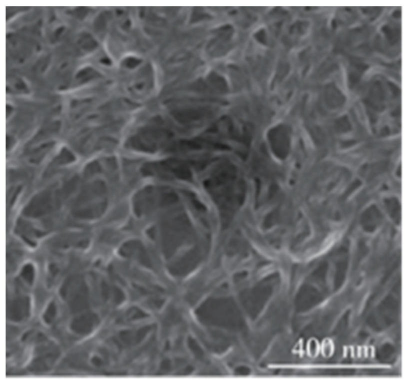

Figure 4. SEM image of aramid nanofiber.

3.2 Polyimide separator

With excellent thermal stability and heat resistance, the thermal decomposition temperature of polyimide (PI) is up to 600℃. And it also has excellent mechanical properties and high-temperature mechanical properties retention rate. In addition to the good electrolyte solution wettability, the material also has higher heat resistance temperature, corrosion resistance, and mechanical properties than aromatic polyamide.

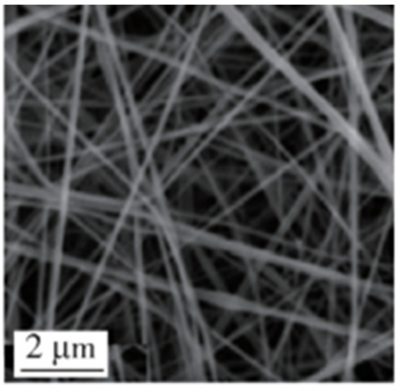

Figure 5. SEM image of PI nanofiber.

3.3 Polyethylene terephthalate separator

The melting temperature of polyethylene terephthalate (PET) is 255~260℃, which has good mechanical properties and excellent electrical insulation properties. It can be prepared into the battery separator and coated with inorganic nonmetallic particles, which can further improve its wettability and heat resistance, and still have mechanical stability in high-temperature environment.

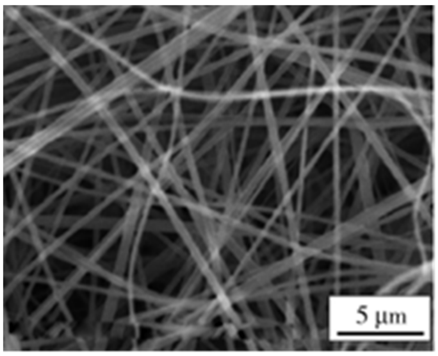

Figure 6. SEM image of PET fiber.

3.4 Poly ether ether ketone separator

Poly ether ether ketone (PEEK) separator has high thermal stability (glass transition temperature Tg>150℃, melting point Tm at 350℃, thermal degradation temperature at 600℃) along with excellent chemical resistance, and excellent mechanical properties.

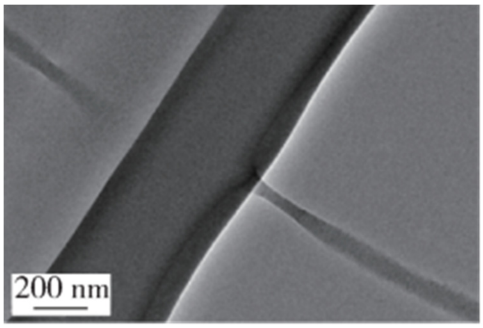

Figure 7. TEM image of PEEK fiber.

3.5 Cellulose separator materials

The battery performance of the cellulose separator is similar to that of the polyolefin separator, but it is renewable and rich in resources. Besides, the initial decomposition temperature of cellulose material is higher (>270℃), and the thermal stability is obviously better than that of polyolefin materials. The early use of cellulose materials has excellent rapid charge and discharge performance, but there is a self-discharge phenomenon, the cycle performance is not stable enough, and the voltage resistance is not good enough. Zhang used non-woven cellulose as substrate and P(VDF-HFP) as a coating to prepare cellulose/PVDF composite separator. Compared with the traditional PP membrane, the wettability is obviously enhanced and the thermal stability was greatly improved [11].

3.6 Fluorine-containing polymer separator

Fluorine-containing polymer mainly refers to PVDF materials. From the material point of view, it can be divided into three categories: single polymer, poly polymer, and organic/inorganic complex. The most commonly used single polymers include PVDF, P(VDF-HFP), and P (VDF-TrFE). Compared with polyolefin separator materials, fluorine-containing polymer separator has stronger polarity and higher dielectric constant, which greatly improves the wettability of the separator and contributes to the ionization of lithium salts. In addition, the forming methods of this kind of materials are various, such as casting, electrospun, hot pressing, and so on, which are beneficial to the regulation of porosity[12].

3.7 Inorganic separator materials

Inorganic materials are represented by ceramic fiber and glass fiber, which are ideal materials for making high-performance battery separators. With excellent high-temperature resistance, they can work continuously at 400℃. In addition, they have high breakdown voltage and low polarizability. At present, glass fiber battery membrane has been industrialized. But because of high price, it is mainly used as the thermally activated battery separator of missile and rocket in the field of special high-temperature resistant battery. Glass fiber lithium-ion battery separators are mainly produced by the British Whatman Company, which are generally used as high-performance battery separators in the lithium-ion battery electrode performance-testing platform for the characterization and research of battery electrode performance [13].

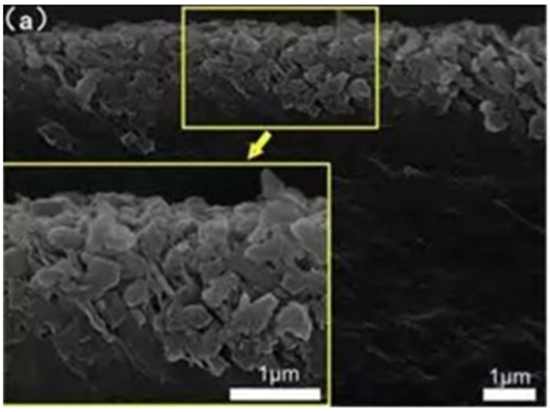

Figure 8. SEM image of ceramic fiber.

4 Conclusion

All in all, in recent years, because of the enormous challenges on the environment and energy crisis, the applications of the lithium-ion batteries have been increased obviously. Lithium-ion batteries are widely used in the electrical vehicles, laptops, and phones. Lithium-ion battery outperforms other types of batteries on long life circle, high energy densities, small weight, large operating temperature ranges, and many other factors. However, some safety issues are also needed to be concerned. The decomposition of the anode material and oxidation of the electrolyte will happen at high temperature, giving off a lot of heat and causing the explosion. At the same time, there will be lithium dendrites after charging and discharging for long cycles, which will cause the short circuit by puncturing the separator. As a result, the use of the separators in the lithium-ion battery becomes very important. The most used separators are PP and PE membrane separators. Both dry and wet methods are used to produce them. Dry method with stretch is used for producing PP porous membrane, and wet method is usually used for producing PE membrane with micropores. These separators, however, have some defects. For example, thermal runaway and internal short circuiting often occur because of the small melting gap, which is about thirty degrees, between PP and PE. A great separator should have chemical stabilities, thermal stability, mechanical strength, ionic conductivity, and the performance of automatic shutdowns. Considering the important role of the separators in the lithium-ion batteries, scientists are now developing various new scientific breakthroughs. They developed the modified polyolefin membrane via surface coating. The inorganic particles like SiO_2, Al_2O_3, TiO_2, and ZrO_2 are often used as the coating materials for the improving of the heat resistance and wettability. Other types of thermal resistant materials like aromatic polyamide, polyimide, polyethylene terephthalate (PET), Poly ether ether ketone (PEEK), cellulose, as well as fluorine-containing polymer also have their huge advantages when used as the separators for improving the safety of high power batteries.

References

1. He, Y. Luo, G., (2018) Analysis on the Impact of Oil Exploitation on the Environment. China Academic Journal Electronic Publishing House,1:160-164.
2. Wang, H., He, J., Wang, L., (2012) Safety issues of lithium-ion batteries. Advanced Materials Industry,9:88-94.
3. Xie, X., Wang, L., He, X., (2017) Factors influencing the safety issues of lithium-ion power batteries. Energy Storage Science and Technology,6:43-51.
4. Liu, Z., Jiang, Y., Hu, Q., Hu, X., (2020) Safer Lithium-ion Batteries from the Separator Aspect: Development and Future Perspectives. Energy& Enviromental Materials,1:1-27.
5. Bierenbaum, H.S., Isaacson, R.B., Drui, M.L., (1974) Industrial & Engineering Chemistry Product Research and Development. Microporous polymeric films, 13:2-9.
6. Kamei, E., Shimomura. Y., (1986) Process of producing porous thermoplastic resin article：US4563317[P].
7. Byun, S., Lee, S.H., Song, D., (2019) A crosslinked nonwoven separator based on an organosoluble polyimide for high-performance lithium-ion batteries. Journal of Industrial and Engineering Chemistry, 2019,72: 390-399
8. Wen, M., Wu, X.X., Zeng, F., (2013) Preparation and Performance of Cross□linking HDPE as Masterbatch for Lithium Battery Separator. China Plastics Industry, 41:118□121.
9. Xu, J., He, L.L., Jing, X.W., (2019) Preparation and Properties of Al_2O_3/Acrylate Emulsion Modified Polyethylene Separators. Fine Chemicals, 7:1321-1325.
10. Liu. C.N, (2015) Development Trend of Lithium Battery Separator Industry. Chinese Journal of Power Sources, 4: 657□658.
11. Zhang J., Liu Z., Kong Q., (2012) Renewable and superior thermal-resistant cellulose-based composite nonwoven as lithium-ion battery separator. ACS Applied Materials&Interfaces, 5: 128-134.
12. Wang C., Wu D.Y., (2016) LIB separators and the recent technical progress. Energy Storage Science and Technology, 5: 120-128.
13. Zhu W.Y., Shao W.G., Wang X.H., Li H., Ye H.M., Cai L.H., (2021) Application Status and Development of Heat Temperature□Resistant Separator Materials for Lithium-ion Batteries. China Plastics, 35: 151-160.