Cutting-Edge Nanotechnology Used in Separators of Lithium Battery

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Abstract. As extreme weather events like sandstorms and droughts become increasingly frequent, governments worldwide have acknowledged the urgent need to address ongoing environmental degradation. In response, numerous policies and proposals aimed at preserving the Earth have been rapidly introduced. Among these, the adoption of electric vehicles (EVs) has emerged as a key solution to air pollution and greenhouse gas emissions, with lithium batteries playing a central role in their functionality. To enhance the safety and extend the lifespan of these batteries, separators have been developed, and recently, nanotechnology has been applied to improve their performance. This article explores the role of nanotechnology in advancing lithium battery separators for EVs. It provides an overview of the basic classifications of separators, comparing their respective advantages and disadvantages. Further, the article explores the manufacturing processes of nanoparticles and separators, highlighting how nanotechnology is integrated into separator design. The theoretical principles behind improving the affinity between electrolytes and separators are also analyzed. Finally, the use of separators in lithium-metal batteries is discussed.

Keywords: Lithium battery; separator; nanotechnology; electric vehicle.

1. Introduction

After John Bannister Goodenough built the first chargeable modern Li-ion batteries, its great advantages, such as high energy density and longer life cycle, attracted people's attention to use it on various devices. Although many applications have been done, like mobile phones and computers, EVs are still a virgin waiting to be explored. Due to the rising awareness of protecting the environment, governments around the world give support to the innovations of EVs and high taxes to fossil energy car companies [1]. EVs and their lithium-ion batteries are under the spotlight. A lithium-ion battery consists of four parts, which are a separator, anode, cathode and electrolyte. Most people pay attention to the anode and cathode of the batteries, but separators are easy to ignore. However, a Separator plays an important role in battery, which is used to prevent the anode and cathode from contacting directly, resulting in thermal runaway [2]. For that propose, it should be a good transporter of ions and not easy to be changed under heat. For example, polypropylene (PP) and polyethylene (PE) are usually considered great raw materials to make separators, because of their great mechanical strength and significant chemical stability, but this kind of material has low thermal stability [3]. Some researchers choose ceramic coating to solve it [4]. Additionally, nano ceramic coatings can be an economical solution for improving separators' wettability. Separators have a great progress in separating cathode and anode.

On the other hand, multifunctional separators have not been applied in commercial EVs. In addition, Li-metal, which has greater energy density did not have enough stability to be installed on EVs. With the help of higher energy density batteries, the more competitiveness the EVs will have in the competition with gasoline vehicles. This article aims to help researchers know how nanotechnology can help separators make progress and give inspiration about what should be improved in the future.

2. Classification

2.1. Single-Layer and Multilayer Separator

Generally, there are three types of separators [5]. First is single-layer and multilayer separators. In the early days, woods were chosen to be the candidate for separator. However, after it was immersed in the electrolyte, wooden separators were rotten. In the 1980s, absorbent glass mat (AGM) was used in sealed lead acid batteries as the separator. It was replaced because it withstood heat over 50 ℃. By using nanotechnology, thin polyolefin separators with submicron-sized holes (30-100 nm) were made. Small nanoholes not only help the ions pass but also enable holes on separators can be closed before thermal runaway. They are usually used in commercial batteries in our cell phones and laptops. The manufacturers choose this kind of separator mostly because of its impressive mechanical strength and great chemical resistance. For lower prices, PE, which is commonly used in other products like plastic bags, becomes the raw material of separators. However, the thermal stability of it is quite a risk. People may worry about the safety of batteries. As a result, the Tri-layer separators were invented.

Tri-layer separators (PP/PE/PP) have a PE material in the middle, which has a lower melting point. Some people think the PE layer can be melted first to stop the electrolyte from passing through, and the PP material with a high melting point will keep both the shape and function of a separator. The shutdown temperature is in the range of 130 ℃ (which the PE starts to melt) to 160 ℃ (which the PP starts to melt). Recently, the separator, which has a larger shutdown temperature range (120-200 ℃), has been invented. They use PI (polyimide) and PE layers to reach it [6]. A wider shutdown temperature range leads to a safer battery. Lower shutdown temperature can stop ions from passing through immediately, preventing the basic structure of the separator from being destroyed. Before the polar polymers were found, neither the single-layer nor multilayer polymer separators could solve the problem that the non-polar polymers have no affinity to liquid electrolytes. It can affect ions' mobility.

2.2. Nano Ceramic Coating Separator

Nano ceramic coatings on the separator can solve this problem. Usually, the ceramic particles are mental oxides in nano size, such as SiO_2, SnO_2, or Al_2O_3 [7]. The mental oxides are polar particles. Electrolyte with ions is a polar liquid, but the usual material of separators such as PE and PP are non-polar. When a polar liquid has contact with a polar surface, the liquid particle with ions will attract electrons on the polar surface. The touch surface of the liquid will expand.

Meanwhile, the highly porous structure can increase the affinity to liquid. For these two reasons, the ceramic additive separator can help the separator surface be wet, resulting in the improvement of ions mobility. Ceramics can also stop the mental fines breaking the inter-electrode space of the separator, which has some benefits in the prevention of short circuits [8].

2.3. Multifunctional Separator

Multifunctional separators have a huge difference from the two separators above. Both ceramic coating and muti-layers are trying to improve separators, but multifunctional separators hope that the separators should solve some problems in the anode or cathode. Research shows that a separator which is made by poly[divinylbenzene-(vinylbenzyl-aza-15-crown-5)-vinylbenzylchloride] was invented. It can absorb Mn ions in batteries to reduce the capacity loss in battery lifecycle processes [9].

3. Manufacture and Cost

3.1. Dry Processes and Wet Processes

To make the ions pass through the separators, nano holes were made on polymer separators. Dry processes and wet processes are the usual methods to make nano holes on separators. In dry processes, polyolefin film was made by extruder. The film will be annealed to change the internal structure. The film will be stretched at a low temperature to make submicron-sized holes in the film [10]. In the wet processes, the low molecular weight substance was added to the polyolefin film. After the additive film was extruded, it was mixed with a chemical solvent. The low molecular weight substances were removed to make nanoholes. Compared with separators made by dry processes, that in wet processes have better overall strength [10]. However, the cost of wet-processed separators is about 3 yuan per square meter, and dry processes are half of the price. Separators account for about 20% of the total price of a battery [11]. Nanotechnology is not just about nanoholes but also nanowires.

3.2. Electrostatic Spinning

Nanowires can be made by electrospinning. When the polymer liquid is applied with high voltage static, polymer liquid will be squirted under the electric field force. The liquid thermoset is into nanowires. The nonwoven separators made in this way have higher porosity which can improve ions mobility [12].

3.3. Alkoxide Hydrolysis

Nanoparticles in the ceramic coating can extend the surface of the coating. In this way, the coating can be paved on the separator thoroughly, or the large particles can be stuck in holes. The method of making these nanoparticles is to hydrolyze alkoxide aluminum [13]. It is a general way to make high-purity alumina particles. These kinds of particles are used on Tesla batteries.

3.4. Sol-Gel Process

As it has been introduced, introducing nano ceramic particles in polymer separators can improve mechanical performance and its affinity with electrolytes. However, most of the ceramics were added less than 15 wt.%. It is because ceramic powders have low dispersity in high viscosity liquid. With the help of sol-gel processes, separators with a high proportion of ceramic can be manufactured. Sol-gel processes can form inorganic networks in hybrid structures. After metal alkoxide and organic polymer are mixed, hydrolysis and polymer matrix processes happen inside the polymer. It allows a high proportion of ceramic particles can be dispersed properly in a polymer base. In this sol-gel process, a recent article reported that 27 wt.% SiO_2 was added to the PAN separator base [14]. The process of hydrolyzing alkoxide aluminum is shown below:

$$2\mathrm{Al} + 6\mathrm{ROH} \rightarrow 2\mathrm{Al(OR)_3} + 3\mathrm{H_2} \tag{1}$$

$$2\mathrm{Al(OR)_3} + 4\mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} \cdot \mathrm{H_2O} + 6\mathrm{ROH} \tag{2}$$

$$\mathrm{Al_2O_3} \cdot \mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} + \mathrm{H_2O} \tag{3}$$

Table 1. Contact angle from the electrolyte on commercial separator materials [10]

	Celgard 2320 and 2325 (PP/PE/PP)	Celgard 2500 (monolayer PP)	FS2190 (PP nonwoven monolayer)	Separation (Ceramic Al_2O_3, SiO_2)
Electrolyte	P14TFSI + 10 mol% LiTFSI	P14TFSI + 10 mol% LiTFSI	P14TFSI + 10 mol% LiTFSI	P14TFSI + 10 mol% LiTFSI
Contact angle	66	65	46	44

Table 1 shows that the contact angle of separators with ceramic coating and the nonwoven method is smaller than that without these two methods. It shows that these two methods can help the separators combine with electrolytes much better.

4. Li-Metal Battery

Compared with Li-ion batteries, Lithium metal batteries can achieve high energy density. The Li-metal anode has a significant capacity at 3860 mAh g^{-1} theoretically. However, after many circulations of charging and discharging processes, Li dendrites are formed. It will break the separators and solid electrolyte interphase (SEI). The inactive Lithium, which is broken from Li dendrites, may lead to short circuits inside batteries. To prevent Li dendrites from growing and enhance the lifecycle of batteries, many kinds of separators were invented. In recent studies, two main solutions were discovered, which are defensive coating and ion-conductive coating. Both solutions used nanoparticles.

4.1. Nano Shield

Separators with nano SiO_2 coating were designed to protect the separator from Li dendrites. Sharp dendrites cannot break the curved surface of the coating. A small crack of coating was added to the pathway of Li dendrites. So, the lifecycle of the battery was expanded more than five times [15].

4.2. Ion-Conductive Separator

Compared with nano shields use nano ceramic coating to stop Li dendrites from breaking the separators, an ion-conductive separator improves the mobility of Li-ions to suppress the growth of dendrites. Recently, a PAN, LiTFSI and LLZWO composite film has been reported. It has great ionic conductivity. It has 100% coulombic efficiency after 100 charging and discharging cycles [16].

5. Conclusion

EVs are more common in people’s lives. Cars with Li batteries are becoming the final answer to reducing global carbon emissions. With people having more and more contact with modern EVs, they hope EVs could have more similarities with gasoline cars such as driving distances and charging time. With the development of battery technology, EVs with Li-ion batteries have enough mileage after the battery is charged. However, the driving distance of cars is enslaved to the energy density of the Li-ion battery. With the aid of nanotechnology, Li-ion batteries are reaching their theoretical energy density. Nanotechnology is used in battery separators. Nano holes help the ions pass through and stop the anode and cathode contact with each other. Nanowires are used to make separators with high porosity. Nanoparticles can be heat-resistant and hydrophilic coating on separators, which can improve ions mobility. The nano technology can help a non-polar polymer has its polar surface.

However, Li-ion can only be improved under its theoretical energy density ceiling. To overcome its limitation, Li-metal batteries should be developed. However, safety concerns must be the first thing to be considered. Nanotechnology in separators is economical and easy to be applied. In this article, two main methods were introduced. One is using nanoparticles to protect separators from breaking, and the other is slowing down the growth of Li dendrites initiatively by nanoparticles.

All in all, while EVs are becoming the mainstream choice of commuters, the demand for longer driving distances and longer car lifecycles will be mentioned by consumers eventually. Nano technology on separators is an economical choice for companies. Governments should increase research funding for institutes and companies. Advanced technology can attract consumers for real.

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