

# The Application of Nanomaterials in Lithium-ion Battery Separators

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**Abstract.** With the rapid development of electric vehicles and smart grids, lithium-ion batteries (LIBs), as key energy storage devices, face the demand for improved safety. The traditional polyolefin separator has problems like insufficient thermal stability and poor interfacial compatibility, which have become a technical bottleneck for the development of high-energy-density batteries. This study aims to enhance the thermal stability and electrochemical performance of LIBs separators through nanomaterial modification strategies, providing solutions for developing next-generation high-safety batteries. This paper first introduces the basic functional requirements of LIBs separators and the performance limitations of traditional materials, focusing on the key issues of the shrinking behavior of PE/PP separators at high temperatures and their electrolyte wettability. Then, it explores three types of nano-modification methods: PVDF-based materials improving interfacial properties through polar groups, ceramic nano-coatings significantly enhancing thermal stability, and metal nanomaterials optimizing ion transport kinetics (with a 4C capacity retention rate of 84.3%). Finally, it analyzes the relationship between nanostructure parameters and the macro-properties of separators and reveals the mechanism of uniform  $\text{Li}^+$  deposition through synchronous radiation techniques. This research provides theoretical guidance for the design of high-safety LIBs separators. It has essential reference significance for the development of new energy storage devices such as solid-state batteries.

**Keywords:** Lithium-ion batteries, separator, nanomaterials.

## 1. Introduction

With the rapid consumption of global fossil energy and the intensification of greenhouse gas emissions, energy crises and environmental pollution have become key issues limiting the sustainable development of human society [1]. Developing clean energy storage technologies represented by lithium-ion batteries (LIBs) has become an important way to achieve the "dual-carbon" strategic goals [2]. Compared with traditional lead-acid and nickel-metal hydride secondary batteries, LIBs have advantages such as high energy density, long cycle life, and environmental friendliness, and have shown great potential in electric vehicles and smart grids [3].

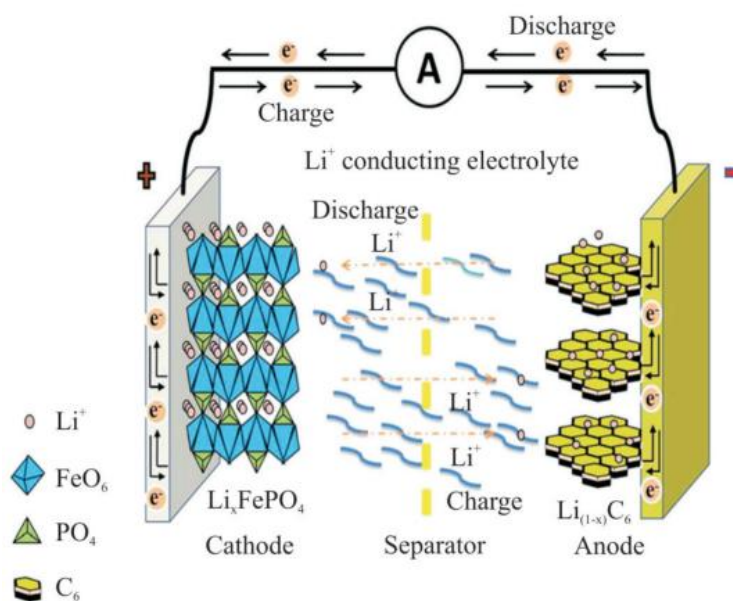
The core structure of a lithium-ion battery consists of four parts: the positive electrode, negative electrode, electrolyte, and separator. The separator needs to physically isolate the positive and negative electrodes to prevent short-circuits while providing a channel for lithium-ion transport through its microporous structure [4]. However, traditional polyolefin separators have shortcomings such as poor thermal stability and insufficient electrolyte wettability, which seriously limit the battery's high-rate performance and safety [5]. In recent years, the introduction of nanomaterials has provided new ideas for solving this problem: constructing nano-porous structures can increase the porosity of separators to over 70% [6], using ceramic nano-coatings can make separators maintain structural stability at 200°C [7], and functionalized nano-fibers have shown the ability to inhibit lithium dendrite growth [8].

This paper systematically analyzes the innovative applications of nanomaterials in LIBs separators, focusing on the mechanisms by which nanostructure design improves separators' thermal stability, ionic conductivity, and interfacial compatibility. The research results can provide theoretical guidance for developing high-safety, long-life next-generation lithium-ion batteries and have essential reference significance for the functional design of separators in new energy storage devices [9].

## 2. The Structure and Principle of LIBs

A lithium-ion battery is a secondary battery whose core structure consists of four key parts: the positive electrode, negative electrode, separator, and electrolyte. The choice of positive electrode material directly affects the energy density and safety of the battery. The most widely used material currently is cobalt oxide ( $\text{LiCoO}_2$ ) with a layered structure, with a theoretical specific capacity of up to 274 mAh/g [4]. Phosphate iron lithium ( $\text{LiFePO}_4$ ) with an olivine structure is also widely used in power batteries due to its excellent thermal stability and cycling performance [10]. For negative electrode materials, graphite is widely used for its stable electrochemical performance and low cost, with a theoretical specific capacity as high as 372 mAh/g [111]. The electrolyte system usually adopts a mixture of lithium salts such as  $\text{LiPF}_6$  dissolved in organic solvents like ethylene carbonate (EC) and dimethyl carbonate (DMC), which can maintain a stable ionic conductivity over a wide temperature range [12]. This paper mainly introduces the separator, a key part of the battery. It must physically isolate the positive and negative electrodes to prevent short-circuits and have good ionic permeability. The separator's performance, such as porosity, pore size distribution, and wettability, will significantly affect the battery's overall performance.

The working principle of a lithium-ion battery is the reversible insertion and de-insertion process of lithium ions in the crystal lattice of the positive and negative electrode materials [7]. Figure 1 shows the working principle of a lithium-ion battery. During charging, lithium ions are extracted from the positive electrode material crystal lattice under an external electric field, pass through the electrolyte, and move towards the negative electrode through the separator pores. At the same time, electrons flow to the negative electrode through the external circuit. During discharging, the opposite ion and electron transfer processes occur [7]. In this reaction process, the separator plays a dual role. Its microporous structure provides a transport channel for lithium ions, and its insulating properties effectively prevent electrons from passing directly [13]. The ionic conductivity of the separator is directly related to the internal resistance of the battery, and optimizing the separator structure can improve the charge-discharge efficiency of the battery by more than 15%. The thermal stability of the separator has a decisive impact on the battery's cycle life. A separator that maintains structural integrity at high temperatures can extend the battery's cycle life by 30% [122].



**Figure 1.** Schematic illustration for the working mechanism of a typical LIBs [133]

### 3. Literature References

#### 3.1. Traditional Separator Materials

At present, commercial lithium-ion batteries mainly use microporous polyolefins as separator materials, including monolayer polyethylene (PE), monolayer polypropylene (PP), and PP/PE/PP trilayer composite structures [5]. These materials are widely used due to their low cost, high mechanical strength, and good chemical stability. The microporous structure of polyolefin separators is mainly prepared through dry-stretching (melt extrusion + stretching) or wet-stretching (thermally induced phase separation + solvent extraction) processes. The pores of dry-stretched separators are elongated, with a porosity of about 40%-50%, while the pores of wet-stretched separators are more uniformly distributed, with a porosity of 50%-60% [5].

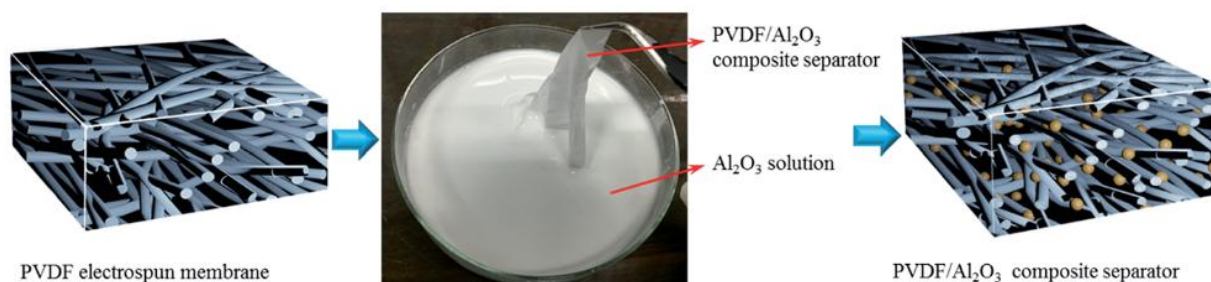
Traditional polyolefin separators have many performance defects. They have poor thermal stability. The melting points of PE and PP are 135°C and 165°C, respectively. When the temperature exceeds 120°C, the separator will shrink significantly, with a shrinkage rate of over 50%, which can easily lead to battery short-circuits [55]. The non-polar nature of polyolefin materials gives them a contact angle with polar electrolytes of over 80°, resulting in an electrolyte absorption rate of less than 60%, seriously affecting ionic transport efficiency. Traditional separators' low porosity and uneven pore size distribution also limit the battery's rate performance, causing rapid capacity decay during high-rate charging and discharging [7]. The mechanical strength of polyolefin separators also decreases significantly at high temperatures, and they may be pierced during the growth of internal battery dendrites.

#### 3.2. PVDF-Based Separators

Polyvinylidene fluoride (PVDF) and its copolymer PVDF-HFP stand out as new-generation separator materials. PVDF materials have excellent chemical stability and are almost resistant to swelling or degradation in conventional organic electrolytes, enabling them to withstand long-term electrolyte corrosion. PVDF has a melting point of about 170°C and a low glass transition temperature, allowing it to maintain good mechanical properties over a wide temperature range [13]. The strong polar C-F bonds in PVDF molecules give it a contact angle with electrolytes of less than 50°, with an absorption rate of over 300%, far higher than that of polyolefin materials [6]. By introducing hexafluoropropylene (HFP) monomers for copolymer modification, the crystallinity of PVDF can be significantly reduced, forming a richer pore structure within the material. The porosity of PVDF-HFP separators can reach over 70%, and their ionic conductivity is 2-3 times higher than that of traditional PP separators [14]. PVDF materials also have a unique self-shutdown characteristic. The pores gradually close when the temperature approaches the melting point, preventing thermal runaway [12].

#### 3.3. Ceramic Composite Separators

Ceramic composite separators, combining inorganic ceramic particles with organic polymer matrices, can achieve flexibility and high-temperature resistance. After thermal stability testing, these separators show no significant shrinkage at 200°C, while traditional PP separators have a shrinkage rate of over 50% under the same conditions [7]. The high surface of ceramic particles allows for a contact angle of less than 30°, with an absorption rate over 50% higher than that of pure polymer separators [6]. Their unique "ceramic skeleton" structure maintains mechanical integrity at high temperatures. Even if the polymer matrix melts, the ceramic network can isolate the electrodes effectively and prevent battery short-circuits. Ceramic particles can also neutralize trace acidic substances like HF in the electrolyte, improving the long-term cycling stability of the battery. Batteries using Al<sub>2</sub>O<sub>3</sub>/PVDF composite separators have a capacity retention rate of 90% after 500 cycles at a 1C rate, a 15% improvement over traditional separators, as shown in Figure 2. Another advantage of ceramic composite separators is their ability to suppress lithium dendrite growth effectively. Their high-hardness surfaces prevent dendrite penetration [7].



**Figure 2.** Preparation of Al<sub>2</sub>O<sub>3</sub>/PVDF composite separators [7]

## 4. Progress in the Application of Nanomaterials in Lithium-ion Battery Separators

### 4.1. Inorganic Nanomaterials

#### 4.1.1. Aluminum oxide nanomaterials

Alumina (Al<sub>2</sub>O<sub>3</sub>) nanoparticles have significant advantages as separator modification materials. With a high melting point of 2054°C and excellent thermal stability, they are ideal for enhancing the high-temperature performance of separators. Through sol-gel methods or atomic layer deposition technologies, a functional layer of Al<sub>2</sub>O<sub>3</sub> with a thickness of 5–20 μm can be formed on the surface of a polyolefin substrate. This modification significantly improves separator performance. At 200°C, the shrinkage rate of Al<sub>2</sub>O<sub>3</sub>/PP composite separators can be controlled within 5%, much lower than the 50% shrinkage rate of traditional PP separators. This is mainly due to the high thermal stability of Al<sub>2</sub>O<sub>3</sub> nanoparticles and strong interaction with the substrate. Additionally, the abundant hydroxyl groups on the surface of Al<sub>2</sub>O<sub>3</sub> give it excellent electrolyte affinity, reducing the contact angle to below 15° and increasing the absorption rate to 300% [12]. The α-Al<sub>2</sub>O<sub>3</sub> purification technology developed by the Zhengzhou Research Institute of China Aluminum Corporation (with impurity content ≤50 ppm) further enhances material performance. Its coated separator remains structurally intact under a high-current discharge of 150 A, increasing the battery's cycle life by 40% [122].

#### 4.1.2. Silicon Dioxide Nanomaterials

Silica (SiO<sub>2</sub>) nanomaterials excel in separator modification with their unique three-dimensional porous network structure. SiO<sub>2</sub> nanoparticles have a high specific surface area and abundant surface silanol groups, significantly improving separators' electrolyte wettability and ionic transport performance. A team from Fudan University used the sol-gel method to coat SiO<sub>2</sub> nanoparticles onto cellulose nanofibers (CNF), successfully preparing a CNF-SiO<sub>2</sub> composite separator. This material shows excellent comprehensive performance: a porosity of 75%, an ionic conductivity of up to 1.2 mS/cm, 2.3 times higher than traditional PE separators [13]. Notably, this composite separator maintains a stable pore structure at 300°C, and the difference between the pore-closing temperature and the melting-breaking temperature is expanded to 80°C, significantly reducing the risk of battery thermal runaway [13]. These characteristics make SiO<sub>2</sub> nanomaterials an important choice for developing high-safety lithium-ion battery separators.

### 4.2. Metal Nanomaterials

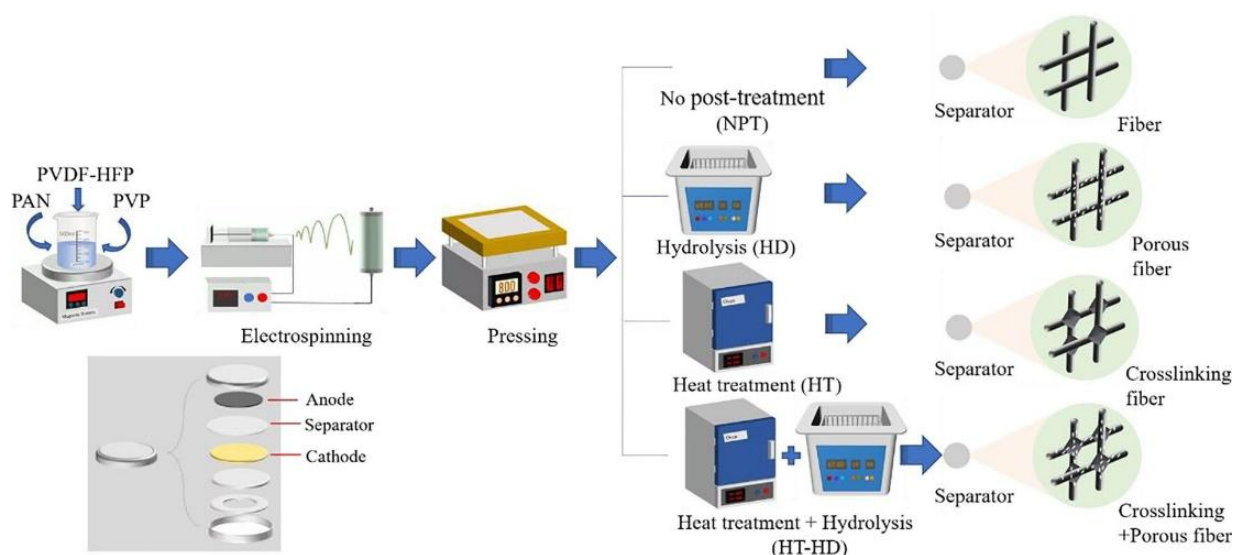
Silver nanowires, with a diameter of 20–50 nm, form a three-dimensional conductive network, increasing the electronic conductivity of PVDF separators to 10<sup>-4</sup> S/cm. Experiments show that adding 1.5 wt% AgNWs to the separator can enhance the capacity retention rate of LiFePO<sub>4</sub> batteries to 84% at a 4C rate. This is attributed to the alloying reaction of Ag with Li<sup>+</sup>, which forms a dense SEI film on the negative electrode surface [12]. Aluminum nanoparticles (AlNPs) generate a LiAlO<sub>2</sub> interfacial layer through in-situ reactions, extending the battery's cycle life by over 40% under 4.5 V high-voltage conditions. A team in Jiangsu developed Al@SiO<sub>2</sub> composite particles to produce a PP-

based separator via dry-stretching. The melting-breaking temperature is increased to 180°C, with an instantaneous discharge current endurance of 150 A [13].

Current research is trending towards the collaborative optimization of diverse composite systems. For instance, core-shell structured CNF-SiO<sub>2</sub> nanofibers integrate the thermal stability of cellulose with the mechanical strength of SiO<sub>2</sub>, resulting in a 30% extension of battery cycle life. Bionically designed PVDF-HFP/SiO<sub>2</sub> nanowire separators, modeled after a bird's nest structure, achieve a tensile strength of 154 MPa while maintaining an ultra-thin thickness of 1.6 μm. In green processes, the electrospun in-situ hydrolysis method for preparing polyimide-SiO<sub>2</sub> composite membranes has enhanced the 5C discharge capacity retention rate by 22% compared to traditional Celgard separators [14]. These innovations have broken through the performance limitations of traditional separators and provided theoretical support for developing high-energy-density, high-safety batteries.

### 4.3. Composite Materials

Composite materials, known for their superior comprehensive performance, show significant potential in lithium-ion battery separators. Recently, researchers have developed various high-performance composite separators by combining different materials. For example, using electrospinning combined with heat treatment technology, a dual-layer multifunctional lithium-sulfur battery separator (PAN/CB/VOOH-PAN/PVDF-HFP), named HPCVPP separator, has been synthesized, as shown in Figure 3. This separator boasts up to 70.7% porosity, an absorption rate of 510.4%, and an ionic conductivity of 2.81 mS/cm. Its tensile strength increases to 20.8 MPa after heat treatment, twice that of polyolefin separators. Additionally, a rigid-flexible composite separator has been prepared by growing zeolitic imidazolate framework-8 (ZIF-8) in situ on a flexible polymer gel membrane, significantly improving the separator's porous structure and overall performance [15]. Composite material separators can effectively enhance the mechanical properties and thermal stability of separators while optimizing ionic transport efficiency, supporting the development of high-performance lithium-ion batteries.



**Figure 3.** Preparation of PAN/CB/VOOH-PAN/PVDF-HFP composite separators [15]

## 5. Conclusion

This paper systematically studies the application of nano-materials in lithium-ion battery separators. Analyzing the modification mechanisms of different types of nano-materials reveals their significant role in enhancing the thermal stability, ionic conductivity, and interfacial compatibility of separators. It was found that PVDF-based materials improve interfacial properties through polar groups, ceramic nano-coatings significantly enhance thermal stability, and metal nanomaterials optimize ionic transport kinetics, enabling a 4C capacity retention rate of up to 84.3%. Additionally,

the mechanism of uniform Li<sup>+</sup> deposition was revealed through techniques such as synchrotron radiation, providing theoretical guidance for the design of high-safety lithium-ion battery separators. These research findings not only enhance the performance and safety of lithium-ion batteries but also offer essential references for the development of new energy storage devices such as solid-state batteries.

However, there are still some limitations to applying nano-materials to separators. Introducing nano-materials may increase the production cost and process complexity of separators. For example, preparing ceramic nano-coatings requires precise coating process control to ensure uniformity and stability. Some nano-materials may undergo physical or chemical changes during long-term use, affecting their performance stability. The stability of metal nanoparticles in the electrolyte still needs further optimization to prevent aggregation or dissolution during the battery cycling process. Moreover, lithium-ion batteries themselves still face challenges such as lithium dendrite growth. Although nano-materials can somewhat suppress dendrite penetration, dendrite growth may still cause battery short-circuits under high-rate and long-cycle conditions.

In the future, applying nano-materials in lithium-ion battery separators should focus on reducing costs, improving performance stability, and optimizing production processes. On the one hand, the production cost can be reduced and their stability in the battery environment can be improved by developing new nano-materials or optimizing the synthesis processes of existing materials. For instance, research on new ceramic nano-composites can achieve high thermal stability while reducing material hardness and cost. On the other hand, nano-materials' multifunctionality should be further explored, such as designing self-healing nano-coatings to address issues like lithium dendrite growth. With new energy storage devices like solid-state batteries, applying nano-materials in separators must also adapt to new technological requirements. In solid-state batteries, nano-materials can be used to construct high-performance solid electrolyte interfaces to enhance ionic transport efficiency and interfacial stability. Future research should also focus on the environmental friendliness and sustainability of nano-materials, developing green synthesis processes to reduce environmental impact and promote the sustainable development of lithium-ion battery technology.

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