

Research Progress on Application of Nanocomposite Materials in Lithium-Ion Battery Separators

Quan Yu

*Academy of materials science and engineering, Taiyuan University of Technology, Taiyuan, China,
1811974816@qq.com*

Abstract. With the rapid growth of global energy needs, new energy technologies are experiencing vigorous development. As an advanced technology for green energy storage, Lithium-ion battery depends on its significant theoretical volume advantage and remarkable energy density, exhibiting a wide range of application values in new energy electric vehicles, large energy storage devices and various unmanned machinery. Currently, the graphite material is one of the most imperative sources of Lithium-ion battery anode materials and separator materials. However, graphite has a fatal deficiency--low electrochemical specific capacity with only 372 mAh g⁻¹, which cannot satisfy the rising demands for enhanced energy and power density. To cope with these problems, researchers try to use nanophase materials in separators. This essay will summarize the types, application scope, and merits of using nanophase materials in separators. Ultimately, this article will explicate the advantages of nanocomposites in lithium-ion battery separators and identify key areas for further improvement in their development.

Keywords: Nanocomposite material, Lithium-ion battery, separator, anode

1. Introduction

Confronting the global energy scarcity and environmental deterioration, governments worldwide have focused on developing efficient and environmentally sustainable renewable energy. As traditional fossil energy--being unsustainable--has significantly decreased and caused severe environmental damage. Therefore, as the dominant new green energy sources, photovoltaic and wind power have received tremendous attention and have achieved a great breakthrough. However, this kind of energy has some inherent defects, such as elevated supply volatility, poor controllability. Hence, to ensure the stability and optimized utilization, it's really urgent to research the advanced energy conversion and storage systems. Lithium-ion battery is an extraordinary choice; it possesses a stable and cyclic secondary battery operating system, and demonstrates excellent complementarity and compatibility with other energy sources like solar, wind and geothermal power. Thus, it can quickly and effectively store intermittent energy [1]. As an imperative part of battery, separator not only plays an important role in realizing physics insulation between positive and negative electrodes to prevent internal short circuits, but it also plays a key role in the efficient transport of lithium ions [2]. At present, polypropylene (PP) separators are widely used commercially due to their excellent electrical insulation and low ion migration resistance [3]. Nevertheless, polypropylene separators

have drawbacks such as poor electrolyte affinity, inferior thermal stability and unsatisfactory mechanical properties. Thus, this conventional material cannot satisfy the requirements of high-performance lithium-ion batteries.

Recently, designing the composites of micro-nano structure and heterogeneous materials has been verified as a valid method for solving those problems, because the separator constructed from nanomaterials possesses high ionic conductivity, good thermal stability, high electrolyte absorption rate and excellent compatibility. These outstanding performance characteristics effectively mitigate the most critical thermal runaway challenges in lithium-ion batteries, and significantly improve their performance. Nevertheless, some problems, for example, the low production efficiency, high manufacturing and raw material costs, still need to be resolved. This article will introduce the classification of nanomaterials, make comparison of different types of nanomaterials, and illuminate how nanomaterials improve the properties of separators. Generally, this article will review exemplary nanocomposite membranes, key theories, and classic methods to avoid redundant research.

2. The classification of nanomaterials and the application of different nanomaterials in Lithium-ion battery

2.1. Inorganic nonamaterials

Considering the chemical composition, nanomaterials can be classified into three categories: inorganic nanomaterials, organic nanomaterials, and nanocomposite materials.

First of all, inorganic nanomaterials possess some classical features, ranging from excellent flame retardancy to remarkable chemical stability, and corrosion resistance. In lithium-ion batteries, most accidents such as spontaneous combustion, fire, and explosion, are mainly caused by thermal runaway inside the battery. Therefore, developing high-performance separators with high thermal stability and high safety is of great significance for the steady development of Lithium-ion batteries. Inorganic nanomaterials are predominantly composed of oxides, nitrides, and carbides. These compounds primarily consist of ionic bonds and covalent bonds, which are resistant to fracture at high temperatures. So on the separator of a lithium-ion battery, the inorganic coatings can establish a rigid framework for thermal insulation and significantly decrease the risk of thermal runaway.

Moreover, inorganic nanomaterials can also be applied in the anodes of lithium-ion batteries. Silicon dioxide (SiO_2) is regarded as an ideal anode material for lithium-ion batteries due to its high lithium storage capacity (1965 mAh g^{-1}) and low electrochemical potential ($0.01\text{--}1.0 \text{ V vs Li/Li}^+$). However, these silica-based materials still face challenges in practical applications due to their disadvantages such as drastic volume change and even pulverization during charge-discharge processes, low ion diffusion rate and poor conductivity [4, 5]. To solve these problems, some feasible strategies can be adopted, such as hollow nanocubes, nanospheres, nanotubes, and nanofilms. These special structures can provide a relatively large internal cavity structure to cope with the issues of volume expansion and contraction as well as subsequent pulverization occurring during charging and discharging processes.

Overall, inorganic nanomaterials are primarily used as the coating materials on lithium-ion battery separators to maintain thermal stability.

2.2. Organic nanomaterials

Organic nanomaterials mainly consist of polymers, organic molecules, and their size ranges from 1 to 100 nanometers. Organic compounds have attracted extensive attention from numerous researchers and have been studied as electrode materials for secondary batteries due to their advantages such as diverse structures, renewability, low cost and environmental friendliness.

Thus, at present, the most widely used separator for lithium-ion batteries is still polyolefin microporous membranes mainly composed of polyethylene (PE) and polypropylene (PP). However, because of their low melting point and softening temperature, these commercial membranes will easily lead to separator melting and trigger battery thermal runaway during overcharging or overdischarging.

In order to thoroughly address these problems, developing new high-temperature resistant material systems is a prospective path and inside it PI nanofiber membranes prepared via electrospinning offer exceptional heat resistance and wettability.

Furthermore, the thermal shutdown sensitivity of commercial lithium-ion battery separators is relatively low, meaning that the pore closure occurs slowly as temperature increases, which can lead to fatal safety problems. For example, when the battery temperature rises abnormally, separators cannot rupture current immediately and the temperature of the closed diaphragmatic pore is higher than the beginning temperature of thermal out of control.

To solve this issue, WEI Z et al. [6] prepared a thermally induced shutdown separator with high thermal sensitivity and stability via coaxial electrospinning using PAN (core) and polybutylene succinate (shell) (PAN@PBS). Composed of core-shell structure and crossed nanofibers, the PAN@PBS separator features high porosity, excellent electrolyte wettability, desirable electrolyte absorption, high safety and favorable electrochemical performance, making it a promising safety separator for lithium-ion batteries. In conclusion, the target of the application of organic nanomaterials in Lithium-ion battery separator is to radically improve the properties of separator itself.

2.3. Nanocomposite materials

Currently, nanocomposite materials are widely utilized in lithium-ion battery separators within the field of nanotechnology, nanocomposite. They can combine the advantages of both inorganic and organic nanomaterials. Moreover, classified by constituent components, nanocomposite materials can be divided into three categories, inorganic composite nanomaterials, organic composite nanomaterials, and organic-inorganic composite nanomaterials.

2.3.1. Organic composite nanomaterials

Organic composite nanomaterials can fundamentally and comprehensively enhance the performance of membranes, ranging from the physical properties to chemical properties. DONG T et al. [7] used PAN, dimethylformamide (DMF) and tetrahydrofuran (THF) as raw materials to prepare an organic nanocomposite material separator, which is not coated with an inorganic material nor housed in ceramic shells, via electrospinning. Compared with commercial Celgard Separator, this separator possesses better porosity, tensile strength, ionic conductivity, electrochemical stability and battery performance, which provides strong confirmation of organic nanocomposite materials effectively strengthening the performance of lithium-ion battery separators.

2.3.2. Inorganic nanocomposite materials

At present, inorganic nanocomposite materials are normally used as diaphragm coating and ceramic shells in lithium-ion battery separators, but in addition to their application in separator, inorganic nanocomposites are also utilized in battery anodes. For instance, the inorganic composite nanomaterial, formed by combining carbon materials such as carbon nanotubes [8] and porous carbon [9] with ZnO, serves as an ideal anode material for lithium-ion batteries. When ZnO is applied as the anode material for lithium-ion batteries, its theoretical capacity reaches up to 978 mA h g^{-1} [10], and its lithium ion diffusion coefficient is higher than that of most metal oxides, but the ZnO anode undergoes severe volume expansion during the cycling process of lithium-ion batteries [9, 11], leading to poor cycling stability and capacity fading issues. Whereas, the design of ZnO nanostructures effectively alleviates volume expansion of the ZnO anode during charge-discharge cycling, thereby improving the battery's cycling performance. Besides, carbon materials will alleviate the volume expansion of nanoparticles during the alloying process. Therefore, the combination of nano-sized ZnO and carbides can effectively reduce the defects of individual materials while amplifying their advantages.

2.3.3. Organic composite inorganic nanomaterials

The organic composite inorganic nanomaterials bind the advantages of inorganic and organic nanomaterials, and addresses their shortcomings. For instance, Polyimide (PI) nanofiber membranes prepared by electrospinning possess excellent thermal stability, chemical stability and comprehensive properties owing to the imide ring structure on their main chains, and are known as top-tier materials and problem-solving solutions. In addition, their three-dimensional tortuous pore structure also helps prevent lithium dendrites from directly piercing through the membrane, reducing the likelihood of short circuits and thermal runaway in lithium-ion batteries. However, the nano-scale rough structure of nanofiber membranes themselves and the inherent surface inertness of PI result in a significant gap in electrolyte wettability, temperature resistance and flame retardancy compared with inorganic ceramics. Therefore, Dong et al. [12] applied zirconium dioxide via coaxial inorganic coating to the outer surface of each PI nanofiber, combining the zirconium dioxide's high wettability, excellent thermal stability, superior dimensional stability under heat, and flame retardancy with the ceramic layer. In this way, the PI nanofiber membrane participates in battery cycles with the surface properties of full ceramics, and meanwhile possesses flexibility that pure ceramic separators do not have. In summary, the nanocomposite separator can combine the excellent thermal stability and mechanical properties of inorganic nanomaterials without compromising the high porosity and high ionic conductivity of organic nanomaterials. This approach efficiently addresses the most crucial safety concern in Lithium-ion batteries-thermal runaway-and thereby resolves the challenge of achieving both high energy density and enhanced safety simultaneously. Next, this essay will compare nanocomposite separators with non-nanocomposite separators, with relevant diagrams and charts attached.

3. Performance comparison between nanocomposite separators and non-nanocomposite separators

The application of composite nanotechnology can significantly improve the overall performance of diaphragm across multiple dimensions. This article will present several examples to compare the performance differences between nanocomposites and their non-nanocomposite counterparts. For

instance, Gao et al. [13] fabricated a fiber separator using PES and SiO₂ through electrospinning and in-situ growth processes, ensuring uniform SiO₂ coating on the fiber surface. This approach fully leverages PES's inherent thermal stability, while the presence of SiO₂ endows the composite separator with flame-retardant properties.

Next, a comparative analysis will be conducted to examine the various properties of PES and nano silica-dioxide-encapsulated PES. Additionally, the performance characteristics of the commercial lithium-ion separator Celgard will be also evaluated in detail for a comprehensive comparison. As shown in Figure 1 the assessment will focus primarily on separator porosity and liquid absorption rate. Porosity indicates the number of Li⁺ migration channels in the fiber separator. The higher the porosity, the more channels for Li⁺ to pass through, and the lower the resistance during Li⁺ migration. The fiber separator prepared by electrospinning has internally crisscrossed fibers that form numerous voids for electrolyte storage, with a porosity as high as 72.8%, while the porosity of commercial Celgard separators is only 34.5%. The porosities of the three separators are 68.9%, 65.3% and 59.1% respectively. With the gradual increase of SiO₂ concentration, the particle size and quantity of SiO₂ particles increase continuously, the voids inside the fiber separator for electrolyte storage become smaller, and some gaps are blocked, thus leading to a decrease in porosity.

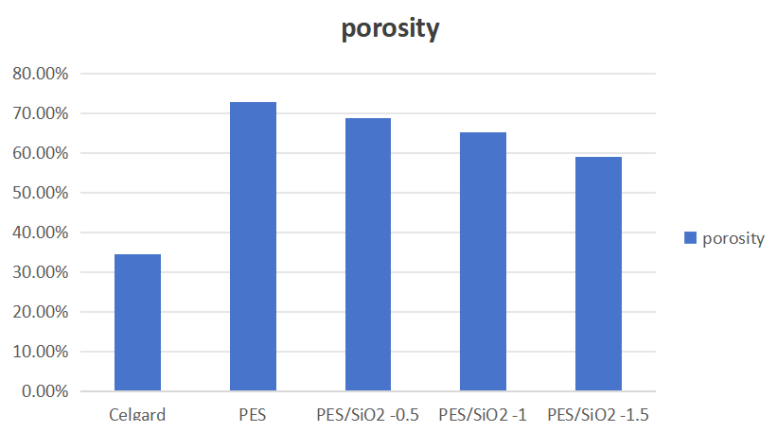


Figure 1. The porosity of Celgard, PES, PES/SiO₂-0.5, PES/SiO₂-1.0, PES/SiO₂-1.5

The electrolyte uptake rate reflects the electrolyte absorption capacity of the fiber separator. The higher the electrolyte uptake rate, the better the electrolyte absorption capacity of the fiber separator and the stronger the transport capability of Li⁺, thereby endowing the battery with superior electrochemical performance. It can be seen from Figure 2 that the saturated electrolyte uptake rate of the commercial Celgard separator is only 78%, while the electrolyte uptake rate of the pure PES fiber separator prepared by electrospinning can reach 360%. In addition, the liquid absorption rates of fiber separators treated with different concentrations of TEOS are 301%, 288% and 256%, respectively, because silica filling partially blocks micropores within the diaphragm and reduces the porosity, leading to a slight reduction in electrolyte uptake. Furthermore, nano particles coat the PES surface, decreasing the available contact sites for electrolyte infiltration.

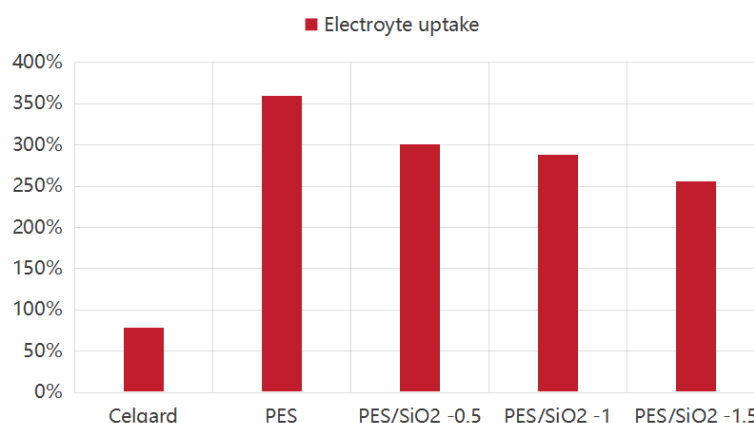


Figure 2. The electrolyte uptake of Celgard, PES, PES/SiO₂-0.5, PES/SiO₂-1.0, PES/SiO₂-1.5

Based on the analysis of the above figures, it can be concluded that composite nanomaterials demonstrate significantly superior performance in porosity and liquid absorption rate when compared to Celgard. Therefore, nanocomposites are highly effective in enhancing the electrochemical performance of lithium-ion battery separators.

Figure 3 shows the histogram of mechanical properties of fiber separators treated with different TEOS concentrations. The maximum stress of pure PES fiber separator is 3.8 MPa, and the elongation at break is 16.4%. It demonstrates good toughness but poor tensile strength. The tensile strength of the diaphragm increases with the rise of TEOS concentration, reaching 4.8 MPa, 5.8 MPa and 6.7 MPa respectively. The direct reason for the increased tensile strength of the diaphragm with higher TEOS concentration is the greater amount of nano-silica produced through hydrolysis. This silica forms a more complete and denser coating on the PES surface. Conversely, the elongation at break decreases with the increase of TEOS concentration, to 12.7%, 9.8% and 8.7% respectively. The fibrous separator exhibits increased rigidity and decreased toughness, and the composite separator's high molecular rigidity and stability provide it with sufficient mechanical properties to meet battery assembly requirements.

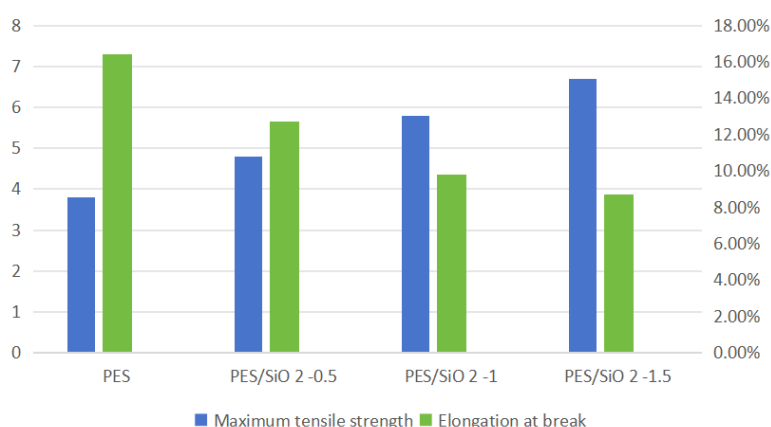


Figure 3. The Maximum tensile strength and Elongation at break of Celgard, PES, PES/SiO₂-0.5, PES/SiO₂-1.0, PES/SiO₂-1.5

Overall, nanocomposites demonstrate superior overall performance compared to their non-nanocomposite counterparts. Consequently, they are the preferred choice for use as separator

materials in lithium-ion batteries. However, the inability to produce nanocomposites on a large scale and their high cost remain key obstacles to their practical application in commercial lithium-ion separators. Therefore, reducing the cost of nanocomposites and exploring industrial-scale production methods will be the primary focus of future research.

4. Conclusion

Nanocomposites integrate the exceptional porosity, ionic conductivity, and electrochemical stability of organic nanomaterials with the superior mechanical strength, flame retardancy, and thermal stability of inorganic nanomaterials. When applied in lithium-ion battery separators, they effectively mitigate critical safety issues such as separator deformation—which can cause electrode contact and short circuits—as well as thermal runaway. Moreover, incorporating nanocomposites into lithium-ion battery anode materials improves the overall energy density of the battery. The significance of this article lies in its comprehensive exposition of the various types of nanomaterials, along with the characteristics and functions of each category. It further discusses the advantages of composite nanomaterials and identifies future research directions. Additionally, the article provides scholars with accessible knowledge in areas such as nanomaterials and lithium-ion batteries, facilitating academic exchange. However, this article still has several shortcomings. The limited data provided fail to effectively support its arguments; the examples of nanocomposites cited are insufficient, and the discussion on lithium-ion batteries is flawed. Therefore, future research should incorporate more data and examples to substantiate its claims, and the description of the primary subject should be more detailed and comprehensive. Overall, this study summarizes the applications of nanomaterials and nanocomposites in lithium-ion batteries, and highlights the importance of advancing research on nanocomposite separators.

References

- [1] N. Nitta, F. Wu, J. T. Lee, et al., Li-ion battery materials: present and future, [J]. *Mater. Today*, 2015, 18: 252–264.
- [2] A. A. Heidari, H. Mahdavi, Recent development of polyolefin-based microporous separators for Li-ion batteries: a review, [J]. *Chem. Rec.*, 2020, 20: 570–595.
- [3] Gu Q Q, Xue H J, Li Z W, et al. High-performance polyethylene separators for lithium-ion batteries modified by phenolic resin [J]. *J. Power Sources*, 2021, 483: 229155.
- [4] N. Yan, F. Wang, H. Zhong, et al., Hollow porous SiO₂ nanocubes towards high-performance anodes for lithium-ion batteries, [J]. *Sci. Rep.*, 2013, 3: 1568–1573.
- [5] P. Lv, H. Zhao, J. Wang, et al., Facile preparation and electrochemical properties of amorphous SiO₂/C composite as anode material for lithium ion batteries, [J]. *J. Power Sources*, 2013, 237: 291–294.
- [6] Wei Z, Gu J, Zhang F, et al. Core-shell structured nanofibers for lithium ion battery separator with wide shutdown temperature window and stable electro-chemical performance [J]. *ACS Applied Polymer Materials*, 2020, 2(5): 1989–1996.
- [7] Dong T, Arifeen W U, Choi J, et al. Surface -modified electrospun polyacrylonitrile nano - membrane for a lithium - ion battery separator based on phase separation mechanism [J]. *Chemical Engineering Journal*, 2020, 398: 125646.
- [8] A. Mohammed M K, Ahmed D S, Mohammad M R, Studying antimicrobial activity of carbon nanotubes decorated with metal-doped ZnO hybrid materials [J]. *Mater. Res. Express*, 2019, 6: 055404.
- [9] Ren Z, Wang Z Y, Chen C, et al. Preparation of Carbon-Encapsulated ZnO Tetrahedrons as an Anode Material for Ultralong Cycle Life Performance Lithium-ion Batteries [J]. *Electrochim. Acta*, 2014, 146: 52–59.
- [10] Ashrafi A, Jagadish C, Review of zincblende ZnO: Stability of metastable ZnO phases [J]. *J. Appl. Phys.* 2007, 102: 071101
- [11] Zhang Y G, Wei Y Q, Li H P, et al. Simple fabrication of free-standing ZnO/graphene/carbon nanotube composite anode for lithium-ion batteries [J]. *Mater. Lett.*, 2016, 184: 235–238.

- [12] Dong Nanxi. Polyimide Nanomaterials: Microstructure Regulation, Functionalization and Their Application Research in Lithium Batteries [D]. Beijing University of Chemical Technology, 2021. DOI: 10.26939/d.cnki.gbhgu.2021.000127.
- [13] Gao Liang, Gong Guifen, Cui Weiwei, et al. Preparation and Properties of Flame-retardant and Safe PES@SiO₂ Separators for Lithium-ion Batteries [J]. Acta Materiae Compositae Sinica, 2025, 42(10): 5725-5735. DOI: 10.13801/j.cnki.fhclxb.20241129.003.