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REVIEW ARTICLE

Research progress on the electrospinning nanofiber lithium-ion battery separators

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ABSTRACT

Electrospinning nanofiber membrane has the advantages of wide raw materials, large specific surface area, and high porosity. It is an ideal separator material for lithium-ion batteries. This paper first introduces two common electrospinning nanofiber diaphragms: polymer, polymer, and inorganic composite, and then focuses on the modification methods of composite modification, blending modification, and inorganic modification, as well as the methods of electrospinning nano modified polyolefin diaphragm. Finally, the development direction of the electrospinning lithium-ion battery separator has prospected.

Keywords: Electrospinning Nanofibers; Lithium-ion Battery; Modification; Polyolefin; Separator

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1. Introduction

Lithium-ion batteries have the advantages of high specific capacity and long service life. They are widely used in portable electronic equipment, new energy vehicles, energy storage of large power grids, and other fields[1]. As the main component of the lithium-ion battery, the separator can effectively prevent the bad condition of short circuit between the positive and negative electrodes due to direct contact, and allow the lithium-ion battery to move rapidly between the positive and negative electrodes, so as to achieve the purpose of charging and discharging[2].

Nowadays, most commercial separators are polyolefin microporous separators. Although they have certain advantages in cost and processing technology, there are still many deficiencies in liquid retention, thermal stability, electrolyte wetting and ion permeability[3].

In order to improve the above shortcomings, researchers have done a lot of work in the preparation of nanofiber porous lithium-ion battery separators by electrospinning technology. Electrospinning technology is one of the most effective methods to prepare nanofibers at present. Its products have the advantages of wide raw materials, large specific surface area, and high porosity. It has been widely used in the fields of battery diaphragm, filtration and adsorption, medical supplies, and fashion[4–6]. At present, polyimide (PI), polyacrylonitrile (PAN), polyethylene terephthalate (PET), polyvinylidene fluoride (PVDF), polymethylmethacrylate (PMMA), polyvinylidene fluoride hexafluoropropylene (PVDF-HFP), and other materials are often used to prepare electrospinning nanofiber lithium battery separator[7–8]. This paper mainly introduces the research progress of electrospun lithium-ion battery membrane from three aspects: electrospinning nanofiber membrane material, electrospinning membrane modification and polyolefin membrane modification by electrospinning.

2. Electrospinning nanofiber separator

2.1 Polymer nanofiber separator

Priya *et al.*[9] prepared PAN porous nanofiber separator by optimizing the electrospinning process parameters as lithium-ion battery diaphragm. The fiber diameter distribution is 880 ~ 1260 nm. The obtained pan nanofiber membrane has good mechanical properties and high porosity, and the ionic conductivity is much higher than that of Celgard diaphragm. Xu Caidi *et al.*[10] dissolved heated PVDF in DMF through electrospinning method to prepare spinning stock solution and PVDF nanofiber separator. According to relevant tests, it can be concluded that when the concentration of PVDF is 12%, the spinning rate is better; when the voltage is 14 kV, the diameter of PVDF nanofiber diaphragm spun under electrospinning is better, the spindle is less and evenly distributed, which meets the relevant standards.

Although common organic polymer nanofiber materials show good electrochemical properties, their heat resistance is relatively poor. High temperature resistant polymers can be used to make up for this deficiency. Ye *et al.*[11] dissolves PEEK with two chloroacetic acid (DCA) at 180 degrees Celsius. After coating the PEEK solution in the nanofiber shell of the spinnable polymer PBS by coaxial electrospinning, the shell core structure nanofibers are obtained, and then the core shell fibers are treated at low temperature to convert PEEK solution into gel state. PEEK nanofibers were obtained by removing the shell. After heat treatment at different temperatures for 2 hours, it was found that PEEK separator could maintain a good shape even at a high temperature of 370 ℃, and the shrinkage rates along H and T directions were 3.1% and 2.8% respectively.

Xiao Ke[12] used the advantages of aramid nanofibers such as high melting point, good thermal stability and good affinity for electrolyte to obtain PMIA based nanofiber films with good multiple properties by using meta aramid (PMIA) and polyurethane (PU). The results show that electrospinning nanofiber membrane has high porosity. PMIA PU Blend Membrane with high tensile strength (>15.79 MPa) is produced by introducing PU and nano cobweb structure, and its ionic conductivity can be as high as 1.38 mS/cm; the introduction of PMIA makes the blend membrane have excellent thermal stability, flame retardancy and excellent electrolyte wettability, which improves the safety performance of lithium battery to a certain extent.

2.2 Polymer and inorganic composite nanofiber separator

A common method for preparing polymer and inorganic composite nanofiber separators is to dope inorganic nanoparticles[13]. Peng Shujing *et al.*[14] added SiO_2 nanoparticles into PVDF solution to make composite membrane. For PVDF separator and Cel-gard 2400 separator, the composite separator has better charge discharge performance and battery cycle performance. Through relevant tests, it can be seen that its performance is the best when 5% SiO_2 is added. Zhang Zhixiong[15] prepared PVA-SiO_2 nanofiber composite separator by electrospinning technology. The separator has a unique three-dimensional network pore structure, and the porosity is as high as 73%; the porous structure and surface polar functional groups make the composite membrane have better electrolyte wettability. Its liquid absorption rate is as high as 405%, which is more than 3 times that of PP separator. Its ionic conductivity is as high as 1.81 mS/cm. After heat treatment at 170 ℃ for 0.5 h, the composite separator has no obvious thermal shrinkage and shows good thermal dimensional stability.

Ding Jun[16] prepared PI and TiO_2 composite nanofiber films by electrospinning. The addition of TiO_2 reduces the average fiber separator, increases the porosity and improves the electrochemical performance of the composite nanofiber separator, which makes its battery performance better than that of PI nanofiber separator. Li Lin *et al.*[17] used electrospinning technology to blend PVDF and nano-TiO_2, and nano-TiO_2 particles played an auxiliary role in the process of pore formation. According to the relevant experiments, when the mass ratio of PVDF to TiO_2 is 22:3, the porosity of the composite separator is improved; the liquid absorption rate is 20 times higher than that of commercial PP separator, with excellent performance and obvious improvement effect after compounding.

The prepared composite membrane has good porosity and provides more and better channels for the passage of Li^+. Due to its superior battery performance, the charge and discharge performance of lithium-ion batteries with PVDF and TiO_2 composite membrane can be tested.

Compared with the doping process, the inorganic nanoparticles produced by the electrostatic spraying method can be directly attached to the positive and negative electrodes of the polymer, and the inorganic composite separator can be directly attached to the surface of the polymer and inorganic composite separator, so as to further optimize the separator performance[18]. Jiao Xiaoning *et al.*[19] made a sandwich structure of polymer and inorganic composite separator by spraying electrostatic spraying technology between two layers of nanofibers. The test results show that the composite separator has an excellent liquid absorption rate, thermal dimensional stability, and electrochemical stability.

3. Modification of electrospinning nanofiber separator

Although electrospinning nanofiber diaphragm has certain advantages, it also has some problems, such as low strength and electrochemical performance to be further improved. Therefore, researchers at home and abroad have done a lot of research on the modification of electrospinning nanofiber separator in order to obtain separator materials with better performance[20].

3.1 Composite modification

Zhao Jianmeng[21] prepared PVDF, PMMA and PVDF multilayer composite separators by electrospinning technology. Compared with single-layer separators, the tensile strength of multilayer separators was improved, and the electrochemical potential was stable at 5.2 V, meeting the needs of lithium-ion batteries. Chen *et al.*[22] prepared interleaved and disordered polyimide (PI) and polyvinylidene fluoride Hexafluoride (PVDF-HFP) composite fiber separators by cross spinning process. The separator not only combines the advantages of the two materials but also melts part of PVDF-HFP through a special hot rolling treatment to realize the adhesion between fibers and improve the strength of the separator.

Although the multi-layer composite modified electrospinning separator optimizes the strength and electrochemical properties of the separator to some extent, there is no strong interaction between the composite separator layers, and the battery performance may be affected by the separation of swelling and other effects after the separator absorbs the electrolyte[23].

3.2 Blending modification

Gopalan *et al.*[24] mixed PVDF and PAN by electrospinning to prepare lithium-ion battery separator. It was found that compared with pure PVDF separator, the affinity of mixed polymer membrane to electrolyte was better. When the mass fraction of PAN reached 25.0%, the membrane had higher liquid absorption rate, and the ionic conductivity at room temperature was as high as 7.80 mS/cm. When the mass fraction of PAN is 0.5%, the average diameter of the prepared separator fiber is different from that of PVDF separator fiber. At the same time, the fibers in the separator are entangled and knotted, which is very helpful to improve the electrochemical performance of polymer electrolyte.

Yang *et al.*[25] the preparation of PAN@PVDF-HFP composite fiber separator with core-shell structure is carried out by coaxial electrospinning technology. PVDF-HFP and PAN were used as shell and core materials respectively to study the structure, surface morphology, porosity and thermal properties of core-shell fiber separator. Compared with the traditional commercial porous PE separator, PAN@PVDF-HFP fiber composite separator has better porosity, thermal stability and electrochemical performance.

Blending modification uses the complementary effect of polymer properties to optimize the performance of electrospinning separator in some aspects. However, due to the large property differences between complementary polymers, it is still a difficult problem to select the appropriate solvent for the preparation of blended polymer solution, and this research still has certain development possibility.

3.3 Inorganic modification

In the polymer doped with inorganic particles, not only polymer and inorganic composite nanofiber separator can be prepared, but also electrospinning nanofiber separator can be modified. Inorganic nanoparticles have good thermodynamic stability. The composite nanofiber separator prepared by doping inorganic particles into polymer can effectively improve the thermal size and electrochemical properties of the separator. In order to disperse nano-SiO_2 particles, Wang Yuan *et al.*[26] used PVDF-HFP as the basic material to prepare SiO_2 and PVDF-HFP composite lithium-ion battery separator by electrospinning. It is found that the addition of SiO_2 significantly improves the liquid absorption rate and electrochemical performance of the separator. The fibers obtained by electrospinning are not only small in diameter, but also loosely and irregularly stacked. Therefore, the porosity of the fiber separator can reach 87%, the liquid absorption rate of the prepared composite separator can reach 620%, and the ionic conductivity at room temperature can reach 2.92 mS/cm. The discharge specific capacity of the button battery assembled by the composite separator is 175 mAh/g, and the battery capacity retention rate is 92% after 100 cycles, showing excellent cycle performance.

Wang Zhenyu[27] formed a SiO_2 inorganic layer on the surface of PEI nanofibers by in-situ growth method on the basis of the prepared polyetherimide (PEI) nanofiber film. The introduction of SiO_2 ensures the three-dimensional storage space of the electrolyte, which provides more space for the internal storage of SiO_2 groups, and it is found that the introduction of SiO_2 has a good affinity for the electrolyte. Compared with commercial separator, PEI-SiO_2 separator has better electrolyte affinity and heat resistance.

The composite nanofiber separator prepared by mixing inorganic metal materials and polymers can not only make the composite separator material take into account the advantages of metal materials and polymers, but also improve the mechanical properties and thermal stability of the membrane. Wang Ya *et al.*[28] made films with PI and Ag composite nanofibers. The test shows that the dielectric constant of the composite film is 6 times that of the pure PI film. The relevant experiments show that the PI nanofiber separator modified by nano Ag has excellent mechanical properties, thermal stability and better dielectric constant. The modified PI lithium battery separator also has other advantages.

4. Electrospinning modified polyolefin separator

Due to the limitation of its processing technology, the liquid absorption rate and liquid retention performance of commercial polyolefin separator are poor, while electrospinning nanofiber membrane has a unique three-dimensional network structure. Electrospinning nanofibers can be deposited on one or both sides of polyolefin separator to prepare composite diaphragm, so as to improve the thermal stability, wettability and liquid retention of diaphragm, and to improve the electrochemical performance of the battery[29]. Lee *et al.*[30] deposited polyvinylidene fluoride, chlorotrifluoroethylene and aluminum oxide composite nanofibers on both sides of polyolefin separator to prepare three-layer composite separator. The results show that the prepared three-layer composite separator has good thermal dimensional stability and good battery cycle performance.

In order to improve the adhesion between polyolefin separator and polyvinylidene fluoride nanofibers, Liang Yinzheng[31] treated the surface of polyolefin separator under the condition of argon atmospheric pressure plasma, which improved the adhesion between nanofibers and polyolefin separator and reduced the delamination of composite separator. Wang Yuan[32] analyzed the wettability, thermal stability, mechanical properties and electrochemical properties of PVDF modified polyethylene lithium ion battery separator. The results showed that PVDF modified PE separator showed better mechanical properties, the tensile strength and elongation at break of the separator were improved accordingly, and the modified separator also showed excellent ion conductivity battery charge discharge cycle and rate performance.

5. Expectation

To sum up, the development of lithium ion spinning equipment should focus on reducing the production efficiency of lithium-ion separator; second, continuously improve the mechanical and electrochemical properties of existing separator materials through modification technology; third, continuously develop new materials to meet the needs of lithium-ion battery separator, such as high temperature resistant and low-cost power lithium-ion battery separator materials.

6. Conclusion

With the continuous development of portable electronic equipment, new energy vehicles and other industries, it not only brings high-speed development opportunities to the lithium-ion battery separator industry, but also brings demand challenges in terms of high performance and low cost. Electrospinning nanofiber separator as lithium-ion battery separator has many advantages, but also has some shortcomings. It still needs long-term discussion and research in the future.

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Conflict of interest

The authors declare that they have no conflict of interest.

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