Poly(vinylidene fluoride) separators for next-generation lithium based batteries

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Abstract
Lithium-ion batteries (LIBs) have become star products in wireless electronic equipment, new energy vehicles and many other fields due to their advantages of high energy density, light weight, good stability, high charging-discharging efficiency, long service life and environmental friendliness. The separator is an indispensable part of batteries that does not participate in electrochemical reactions, separating the anode and cathode. It has a microporous structure, which can store electrolyte and allow ions to transfer freely. Poly(vinylidene fluoride) (PVDF)-based separators are characterized by strong polarity, high dielectric constant, stable electrochemical performance, excellent tensile properties and mechanical strength, favorable thermal stability and wettability. Therefore, they are proposed to be potential candidates for novel separators in the field of LIBs. This review introduces the recent researches and advances in PVDF-based separators for LIBs, with the characterizations and requirements for separators. It is mainly divided into the two types including monolayer and multilayer separators. Furthermore, the performance of the PVDF-based separators is summarized, and the challenges and prospects in their practical application are briefly analyzed.

KEYWORDS
lithium-ion batteries, monolayer separators, multilayer separators, PVDF

1 INTRODUCTION
With the rapid growth of population and the continuous development of science-technology in today’s world, humans’ demands for energy increase rapidly, leading to a rise of traditional fossil fuel consumption, which not only cause serious waste of natural resources, but also bring a series of global problems such as environmental pollution and the weather warming.¹ To alleviate the serious problems caused by fossil fuels, the development and utilization of renewable new energy like the solar wind energy and geothermal energy is definitely urgent.² However, renewable energies require efficient energy storage equipment to stockpile and distribute. Rechargeable batteries are viable solutions for storing these renewable energies.³ With the development of science and
technology, lithium batteries have become the mainstream of advanced energy storage devices. Lithium batteries can be divided into lithium-ion batteries (LIBs) and lithium-metal batteries (LMBs) (like lithium-sulfur batteries). PVDF-based separators are widely applied in LIBs and emerging LMBs.

LIBs are undoubtedly one of the most promising products among the energy storage devices depending on their high energy density, charging and discharging efficiency, light weight, good stability, long life and environmental friendliness. As can be seen from Figure 1, LIBs have been diffusely used in laptops, mobile phones, electric vehicles, power station, defense equipment, space vehicles and so on. Especially, portable electronic devices (PEDs) have become the information-exchange platforms in everyday life, which greatly demands rechargeable battery technology and promotes the exploitation of multifunctional batteries. Although LIBs dominate the market for PEDs, they are not energy-dense enough to sustain new-energy electric vehicles for a long driving distance. However, compared with LIBs, LMBs can provide higher energy density and increase the endurance of batteries, especially lithium-sulfur batteries. In addition, the natural abundance of sulfur makes Li-S batteries economical. Therefore, LMBs are of great significance to human life. Unsatisfactorily, LMBs are easy to produce lithium dendrites during cycling, resulting in rapid loss of capacity, low coulombic efficiency, even damage to the battery. To build highly stable LMBs remains a serious challenge. So far, in addition to the development of electrodes and electrolytes that can mitigate the shuttle effect, strategy of inhibiting polysulfide shuttle with the separator has significant advances. Usually, functionalizing/coating the separator with a barrier layer that can adsorb or convert soluble polysulfides is a simple and direct method for mitigating the shuttle effect in Li-S batteries. Recently, ionic exchange membranes have brought a new strategy to the field, introducing a cationic-selective membrane to prevent the diffusion of polysulfide anions in Li-S batteries. In order to address the problems faced by LMBs, the separators for LMBs need to meet special requirements. First of all, the separator should be able to uniformly deposit lithium metal and inhibit the growth of lithium dendrite, so as to build a stable and uniform protective interface layer on the LMBs. Last but not least, the separator should be able to prevent the dissolved polysulfide from traveling between the two electrodes, preventing side reactions from occurring. Today, advanced separators effectively prevent the shuttle effect of LMBs. A variety of functional LMBs separators have been developed. PVDF-based separators exhibit excellent physical and electrochemical properties in LIBs. Therefore, introducing functional groups that can inhibit polysulfide in PVDF-based separators or coating polysulfide barrier layers on PVDF-based separators is expected to promote the wide application of LMBs. The next-generation LIBs with high performance, low cost, good stability, safety, environmental benignity and long life is urgently expected to be developed.

In general, a lithium-ion battery is composed of four important parts: positive electrode (cathode), negative electrode (anode) and electrolyte and separator. In recent years, lithium metal anode has attracted extensive attention owing to its high theoretical capacity and low redox potential. The separator prevents the anode and cathode from contacting and avoids internal short circuits, as well as stores the liquid electrolyte at the same time, allowing ions to pass freely. In a normally working battery, the storage and release of electric energy is always accompanied by the migration of electrons and ions at the electrode-electrolyte interface. Moreover, the structure and properties of electrode materials and separators vastly impact the efficiency and stability of the interface transmission. In addition, the properties, structures and compositions of separators have a huge impact on electrical conductivity, cycling performance, capacity and safety of LIBs. Therefore, the separator is an indispensable part of LIBs without participating in the electrochemical reaction.

At present, the most commonly used commercial separators are mainly polyolefin separators, such as polypropylene (PP), polyethylene (PE) and multi-layer composite separators (PP-PE-PP). A large-scale application has been achieved on account of their lower production cost, higher mechanical strength and electrochemical stability. Nevertheless, the further development of polyolefin separators is hindered by low electrolyte absorption, surface hydrophobicity, poor wettability, low porosity, and poor thermal stability, which may result in the thermal shrinkage and short circuits.
Particularly, production of lithium dendrites on the surface of lithium metal in some extreme circumstances may cause short circuits and thermal runaway. Therefore, traditional commercial polyolefin separators cannot fully meet the requirements of the energy industries for the use of LIBs. Compared with polyolefin-based separator materials, PVDF-based separators have stronger polarity and higher dielectric constant, outstanding chemical stability, excellent mechanical properties, good thermal stability and affinity with liquid electrolyte. Figure 2B-D compare the key characteristics of commercial polyolefin separators with monolayer and multilayer PVDF-based separators. The commonly used polymer raw materials for the preparation of separators are the copolymers of PVDF like poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP), poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE), and poly(vinylidene fluoride-chlorotrifluoroethylene) (PVDF-CTFE). A performance improvement is realized by perfecting preparation techniques, adding inorganic/organic additives, innovating separator microstructure and blending other excellent polymers, and so on. Recently, the solid-state lithium battery prepared by adding lithium salt into the polymer has become the next-generation energy storage equipment with high energy density and safety.

In this review, the indagation and progress of PVDF-based separator for LIBs, as well as the characteristics and requirements of separator are discussed. This paper is divided into two categories: the monolayer separators and multilayer separators. Finally, the performance of PVDF-based separators is summarized, and the challenges and prospects in their practical application are briefly analyzed.

2 CHARACTERIZATIONS AND REQUIREMENTS FOR SEPARATORS

Separator is an indispensible part of LIBs so that its physical and chemical properties have a huge impact on the practical application of batteries. Therefore, various characterization methods are used to obtain the performance parameters of separators, such as porosity, mechanical strength, and permeability, thermal shrinkage stability, and so on. In order to prepare LIBs with high capacity, safety, long service life, and reasonable cost, each parameter of the separator has an ideal value. This section
will introduce the various characteristic parameters of the separator, as well as the correlation between each property, and point out the requirements of the separator in a perfect state.

2.1 Pore size

Separators are usually made of polymer materials with microporous structure. The electrolyte is stored in the pores to ensure the smooth transfer of lithium ions. The larger the pore size, the easier it is to transfer lithium ions, and the more possible it is for the battery to charge and discharge at a high rate.\(^2\) However, in order to play the role of separators in preventing short circuit, the diameter of the pore must be less than the size of particles of cathode active materials, so the diameter of the pore is generally less than 1 µm. In addition, the pore size distribution must be homogeneous to ensure the uniform current distribution and smooth lithium metal deposition on the lithium sheet so as to reduce the production of lithium dendrites and avoid the battery short circuits caused by the separators piercing. Therefore, reasonable pore size and pore distribution are crucial to making the battery work stably and efficiently.

2.2 Porosity

Similar to the pore size described above, the porosity is also a parameter that characterizes the electrolyte storage capacity and the ion conductivity. Higher porosity indicates that sufficient liquid electrolyte can be stored, the internal resistance of the battery is smaller, and its ionic conductivity will be correspondingly higher.\(^4\) Nevertheless, high porosity will inevitably reduce thermal stability and mechanical properties, further affecting the high temperature performance and service life of the battery. Under normal circumstances, the 10 year life of the battery can be guaranteed when the porosity of the separator is maintained between 40% and 60%.\(^5\) Usually, a separator with a mass of \(W_0\) and a volume of \(V_0\) is immersed in an electrolyte with a density of \(\rho_L\) to obtain the separator with a mass of \(W\), and then the porosity is calculated by the given Equation (1).

\[
\text{Porosity} \% = \frac{W - W_0}{\rho_L V_0} \times 100 \tag{1}
\]

2.3 Permeability

Permeability is another property that impacts the internal resistance of batteries. It is usually explained by the MacMullin number, which is expressed by the resistance ratio value of the separator filled with electrolyte and the simple electrolyte. The MacMullin number is directly proportional to the Gurley number. Lower Gurley number signifies the higher porosity of the separator. Uniform permeability makes the current inside the battery evenly distributed, reduces the generation of lithium dendrites, and prolongs the service life of the battery. Currently, the Gurley number of the separator is required to be less than 0.025 s µm\(^{-1}\).\(^6\)

2.4 Electrolyte wettability

Electrolyte wettability can be detailed as the affinity between the separator and the electrolyte, which is related to the nature of the separator material itself and the microstructure of the separator (such as pore size, porosity, etc.).\(^4\) Electrolyte wettability is usually characterized by the contact angle measurement, liquid absorption rate and liquid retention rate.\(^5\) The separator must have good wettability, which can rapidly absorb electrolyte during the battery assembly process to prevent electrolyte loss and volatilization, and at the same time spread the electrolyte evenly on separators, thereby improving the Coulombic efficiency of the battery\(^1\). Moreover, the good wettability enables the separator to not only store sufficient electrolyte, prolong the service life of the battery, but also transmit ions smoothly, reduce ion resistance and impedance.\(^6\) Equations (2) and (3) are used to calculate the electrolyte absorption rate and retention rate of the separator, where \(W_{\text{dry}}\) and \(W_{\text{wet}}\) represent the mass of the dry separator and the separator after soaking in the electrolyte for a period of time.

\[
\text{Electrolyte absorption rate} \% = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{2}
\]

\[
\text{Electrolyte retention rate} \% = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100 \tag{3}
\]

2.5 Mechanical properties

Mechanical properties of the separator play a crucial role in the long-cycle stability and safety of batteries, which are connected with the properties of the material and the fabrication process. Normally the tensile strength, elongation at break and puncture strength of the separator are researched. The separator will be subjected to physical external forces such as extrusion during the battery assembly process.\(^7\) The high tensile strength can improve the robustness of separators and prevent the separator from
damage. The elongation at break can characterize the tensile performance of the separator. Simultaneously, the separator must have high puncture strength to prevent rough electrodes and lithium dendrites generated during charging and discharging from piercing the separator to ensure the long-term safe operation of batteries.\[48-50\] Nevertheless, the mechanical strength is not as large as possible because it is inversely proportional to the porosity and ionic conductivity of separators. It is necessary to find a suitable figure to balance the relationship between them so that the battery can reach the optimal working condition. Under the normal conditions, the mechanical strength of a separator with a thickness of 25 µm is required to reach at least 98.06 MPa.\[41,51\]

2.6 Chemical stability

The separator in the battery must have chemical stability that does not react with the electrolyte and the active material. If the separator reacts with the substances in the battery, it will destroy the electrochemical working environment, and the structure of the separator will be broke and cannot provide stable ion transmission. Therefore, the precondition of the separator is that it has chemical and electrochemical stability without participating in the electrochemical reactions.

2.7 Ionic conductivity

The ionic conductivity is connected with the porosity and pore structure of the separator. Proper ionic conductivity ensures the long service life of LIBs. In order to achieve a balance with the separator structure and other properties, when the ionic conductivity of fully wetted separator is within the scope of 10^{-3} to 10^{-1} S cm^{-1}, it can meet the performance requirements of the battery at different conditions. The MacMullin number can also be used for prediction. The smaller the MacMullin number is, the better the battery performance will be. Usually the MacMullin number is required to be less than eight. In the experiment, the ionic conductivity is calculated by the following Equation (5), where \( R_0 \) represents the volume resistance of the electrolyte, \( l \) signifies the thickness of the separator, and \( A \) represents the area of separator.\[27,52\]

\[
\text{Ionic conductivity } (\sigma) \ (S \ cm^{-1}) = \frac{l}{R_0A}
\]  (4)

2.8 Lithium ions migration and storage

The migration and storage state of lithium ions (Li\textsuperscript{+}) is a crucial index to evaluate whether the lithium battery can operate normally and efficiently. The separator and electrolyte provide an important route for the transport of Li\textsuperscript{+}. The lithium transference number (\( t_{\text{Li}^+} \)) is usually used to characterize the migration of Li\textsuperscript{+}. \( t_{\text{Li}^+} \) is defined as the relative quantity of the transported Li\textsuperscript{+} compared to the counter anion, which is generally less than 1.\[53\] In the experiment, \( t_{\text{Li}^+} \) is calculated by Equation (5). \( R_0 \) and \( R_s \) are the impedance before and after polarization. \( I_0 \) and \( I_s \) are the initial and final values of the variation of steady-state current. In addition, \( \Delta V \) is the constant voltage value of 10 mV.\[54\] \( t_{\text{Li}^+} \) impacts the discharge/charge rate, energy density and service life of lithium batteries. The closer the \( t_{\text{Li}^+} \) is to 1, the faster the charging rate of the battery will be. Meanwhile, higher capacity will be achieved even at high-rate cycles. The storage status of Li\textsuperscript{+} is basically determined by the porosity of the separator. The separator with high porosity can reserve plenty of electrolytes, which is conducive to the long-term cycle stability of the battery.

\[
t_{\text{Li}^+} = \frac{I_s (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_s R_s)}
\]  (5)

2.9 Thickness

The thickness of the separator influences the volume, energy density, actual specific capacity, cycle stability and safety of the battery.\[55\] Separator with a overlarge thickness would result in an excessive occupation of the battery volume, reducing the energy density of batteries as well as increasing the transmission distance of ions.\[56\] On the contrary, too thin separator will impact the mechanical strength, and will be easily pierced by the lithium dendrites. As the current increases, the separator may also be broken. Therefore, to ensure that the battery can be charged and discharged stably and efficiently, the thickness of the separator is ideally controlled within 25 µm.\[5\]

2.10 Dimensional stability

When the battery is assembled, the electrolyte is dripped on the flat separator. The separator may curl or shrink after absorbing the electrolyte. wrinkled separators cannot provide uniform current distribution, increasing the generation of lithium dendrites and causing a quiescent battery cycling performance. If the shrinkage rate is too large, the cathode and anode at the edge of the battery will be in direct contact, causing the short circuit. In order to avoid the occurrence of these abnormal situations, it is necessary to control the dimensional stability of separator.\[40\]
2.11 | Thermal stability and thermal shrinkage

Thermal runaway is a major problem that LIBs often encounter during high-rate and long-cycle operation. In most cases, thermal runaway is caused by overcharging. When the battery is charged, lithium deposits on the surface of the lithium metal to form branch-shaped dendrites, which can easily pierce the separator, causing a short circuit and overcharging. At this time, the good thermal stability of separators can prevent the battery from overheating and exploding. Thermal dimensional stability is another performance index to ensure the secure and normal operation of batteries. The heat generated by the electrochemical reaction of the battery during the working process will increase the temperature, and the separator with good thermal dimensional stability will not shrink at high temperature. Thermal stability can be characterized by Thermogravimetric Analysis (TGA) and thermal shrinkage rate. The ideal thermal shrinkage rate of the separator is < 5% at 100 °C/hour. The following is the calculation Equation (6) of thermal shrinkage.

\[
\text{Thermal Shrinkage} \% = \left( \frac{D_i - D_f}{D_i} \right) \times 100 
\]

where \( D_i \) is the area of the separator before annealing and \( D_f \) is after annealing.

2.12 | Shutdown effect

The shutdown effect of the separator is another important property to ensure battery safety. When the battery temperature is too high and reaches the shutdown temperature of the separator, the separator will melt and flow, and the pores will be closed to stop the flow of current and prevent thermal runaway of the battery. Nevertheless, the shutdown effect will not influence the mechanical integrity of the separator while blocking the cathode and anode from contacting and avoiding the short circuits. Since the resistance value of the separator will increase dramatically after the shutdown effect of the separator, the impedance of the battery during the temperature rise is usually measured. At least a threefold increment of the resistance value after the separator is shut is regarded as the standard to judge the shutdown effect. As a safety mechanism of the battery, the shutdown temperature should be lower than the thermal runaway temperature of the battery.

2.13 | Cost

The production cost is also a decisive factor for the commercialization of the separator. In the LIBs technology, the cost of separators accounts for about 20% of the overall cost, and it is concentrated on the preparation process of the separator. The traditional dry and wet production methods are cumbersome and complicated, and the cost is high. Therefore, the development of the low-cost, simple and intelligent separator manufacturing technology can accelerate the development of the battery industry.

2.14 | Section summary

In this section, the various properties of the separator and the interrelationship between the properties are introduced. The influence of separator performance on battery working status is also analyzed. It can be seen from the various properties summarized above that the separator does not have all the best properties at the same time, which requires us to choose according to different situations. For example, batteries used in new energy vehicles and drones must have excellent thermal stability and high mechanical strength to avoid the short circuits in the case of long-term intensive use or collisions. The batteries demanded in portable fast-charging mobile devices such as mobile phones are small in size, and thin and high-porosity separators are required to improve electrochemical performance. Therefore, usually without affecting other performance, the necessary performance is augmented to a large extent, and appropriate performance parameters are selected. In this way, the requirements of different devices can be met to a greater extent in practical applications.

3 | TYPES OF PVDF-BASED SEPARATORS

PVDF is endowed with high polarity, high dielectric constant, low crystallinity, good electrolyte wettability and chemical stability by the strong electron withdrawing group C-F. Therefore, PVDF-based separators have attracted more and more attention and many related literatures have been reported in recent years. Lithium-ion battery separators can be classified according to battery types (like liquid batteries and solid-state batteries), materials (like pure PVDF polymer, PVDF and inorganic composite material, PVDF and organic material composite material), structures (like microporous separator, nonwoven separator) and other forms. As shown
in Figure 2A, the latest research progress of each type of separators will be reviewed according to the layered structure.

3.1 Monolayer separators

3.1.1 Single polymer separators

The properties of pure PVDF separator are significantly affected by the preparation process and the type of solvent. The research progress of a single PVDF separator from the aspects of manufacturing technique and performance will be firstly summarized.

Electrospinning is a common method for fabricating PVDF separator, which can efficiently prepare nanofiber nonwoven separators.\[59] The separator manufactured by this method has the advantages of high porosity, small pore size, large specific surface area and ion conductivity. Hwang et al.\[60] prepared PVDF nanofiber electrospinning separators for high-rate charge and discharge secondary batteries. They used a 19% PVDF solution with a 3:7 weight ratio of DMAc and acetone for electrospinning. The pore structure of the separator is optimized by changing spinning qualification, post-processing and sheet forming. The upgraded PVDF separator has a high porosity of 48% and an electrolyte uptake of 142%. The tensile strength of PVDF separator is 14.8 MPa cm\(^{-2}\) and the elongation at break is 117%. Compared with ordinary commercial polyolefin separators, it exhibits higher thermal stability and does not deform significantly even at 135 °C under air. In battery testing, such PVDF separator has an excellent charge/discharge capacity and efficiency. Similarly, Barbosa et al.\[61] used electrospinning technology to prepare PVDF fiber separators mixed with different types of ionic liquids (ILs) with the same anion, bis(trifluoromethylsulfonyl)imide [TFSI]\(^-\), as shown in Figure 3A. The presence of ILs influences the content of the β phase and the decreased of crystallinity, as shown in Figures 3B and 3C. PVDF separator with 15% of [Emim][TFSI] has a maximum ionic conductivity value of 2.8 mS cm\(^{-1}\) at 25 °C. The electrochemical window stability of samples is 0.0-6.0 V. PVDF separator with 15% of [Emim][TFSI] reaches a maximum discharge capacity (119 mAh g\(^{-1}\)), and its coulombic efficiency reaches approximately 100%, and the discharge capacity is extremely stable in the rate cycle test, as shown in Figure 3D-F.

Phase inversion method is also diffusely applied to fabricate the separators for LIBs.\[15] This method uses some physical ways to transform the homogeneous polymer solution into polymer-rich and polymer-lean phases. At last, the polymer-lean phase evaporates to obtain a separator. Phase inversion method mainly includes the two technologies: nonsolvent-induced phase separation (NIPS), thermally induced phase separation (TIPS).\[62,63]

The operation procedure of NIPS is shown in Figure 4A, as shown in Figure 4A, Tabani et al.\[64] prepared a PVDF porous separator by the NIPS method. The mixture of N-methyl-2-pyrrolidone (NMP) and acetone were used as the solvent. Meanwhile, ethanol and deionized water were non-solvent. The results show that as the NMP content in the solvent increases, the electrolyte uptake of the separator increases. In addition, the use of ethanol as a non-solvent contributes to a more uniform separator with higher porosity. When the weight ratio of NMP/acetone is 40:60, the optimal separator with excellent physical and electrochemical properties can be obtained. The thermal shrinkage rate of the optimal sample is 37.5% at 160°C, while of Celgard 2400 is 90.7%. Its ionic conductivity is 1.2 mS cm\(^{-1}\), and its electrochemical stability can reach 5 V. The initial capacity of PVDF separator is 141 mAh g\(^{-1}\), indicating that the PVDF porous separator manufactured by the NIPS method for LIBs has excellent electrochemical stability and cycle performance. Karabelli et al.\[66] prepared macroporous PVDF separators by phase inversion method with and without TAIC/MEP cross-linking agents. The resulting cross-linked separators prepared with TAIC have excellent thermal and mechanical strength (250 MPa at 25 °C) and ionic conductivities (14 mS cm\(^{-1}\)).

The process of TIPS is shown in Figure 4B, as shown in Figure 4B, Liang et al.\[67] fabricated dual-asymmetric PVDF separators by TIPS method with the mixed diluents of dimethyl sulfoxide (DMSO2) and glycerol. This dual-asymmetric porous structure has a porous volume and two surfaces with large interconnected pores and small pores, respectively. This structure endows separators with higher electrolyte wettability, as shown in Figure 4C. The thermal dimensional stability of the separator can be maintained up to 160°C. At this temperature, the pores in the surface are closed, resulting in a shutdown effect, as shown in Figure 4D. The separators filled by electrolyte show high ionic conductivity (1.72 mS cm\(^{-1}\) at 25 °C). LiFePO\(_4\)/Li batteries using these separators show the superior capacity and rate performance. The study provides new thoughts into the design and application of separators for high-performance LIBs.

In some studies, different types of technologies are combined to prepare lithium-ion battery separators. He et al.\[69] prepared PVDF ultrafine porous separators with three dimensional network structure, superm porosity and electrolyte absorption through combining electrospinning and phase separation processes, as shown in Figure 5A. The microstructure and modalism of PVDF separators are investigated via the scanning electron microscope (SEM), as shown in Figure 5B. PVDF ultrafine porous fiber separators have suitable pore structure and
high electrolyte wettability and uptake (360 wt.%), as shown in Figures 5C and 5D.

Kundu et al. [70] prepared PVDF and its copolymer separators by solvent casting method, and researched their physical and electrochemical properties in depth. They revealed that PVDF is semi-crystalline polymer, which was composed of small crystallites arranged in the lamellae as shown in Figure 6A. The study found that the β-phase content and the crystallinity for PVDF separator were higher when compared with the copolymer separators, as shown in Figure 6B. Simultaneously, all separators illustrated a sponge-like porous structure with micrometer sized interconnected pores. The pores were evenly distributed along the thickness of separators, as shown in Figure 6C-F. The electrochemical performance of separators in Li/C–LiFePO₄ half-cells displays good cycle and rate capability, as shown in Figure 6G-I. Finally, the article points out that the larger β-phase content in the separator leads to higher polarity, which is conducive to faster lithium ion migration.

The researches show that the physical properties such as porosity, electrolyte absorption rate, thermal stability and mechanical strength of single PVDF separators are diverse based on different preparation methods. Monolayer PVDF separator prepared by electrospinning method and phase conversion method has outstanding electrolyte wettability and high porosity, which is beneficial to the storage of electrolyte inside the battery. The production process of pure
PVDF separator is simple and low-cost. However, there is a big gap between the mechanical strength of pure PVDF separator and that of commercial polyolefin separator. Hence the mechanical strength of pure PVDF separator has a large room for improvement. Pure PVDF separators have far-reaching significance in the development of PVDF-based separators as a basic research.

3.1.2 Surface-modified separators

With the large-scale application of LIBs in many fields, only improving the performance of the separator by improving the preparation process of the pure PVDF separator can no longer meet the requirements of modern society. Therefore, many novel preparation methods have been exploited to enhance the performance of PVDF separators. The surface modification of the separators is to improve specific functions, such as thermal stability, mechanical stability, and electrolyte wettability. Generally, separator modification can be achieved by introducing inorganic nano-ceramic particle coatings and other polymer coatings on the surface of PVDF separators. Simultaneously, a composite separator with a core-shell structure based on PVDF materials can be prepared. The following will introduce the performance optimization and research progress brought by the surface modification of the separators.

Wu et al.[71] reported a PVDF/Al₂O₃ composite separator fabricated by tip-induced electrospinning (TIE) and dip-coating process for LIBs, as shown in Figures 7A and 7B. PVDF/Al₂O₃ separator prepared by this method shows a good thermal stability that mechanical shrinkage is less than 2% at high temperature (140 °C) for an hour, as shown in Figure 7C. PVDF/Al₂O₃ separators have remarkably good electrolyte affinity that the contact angle of PVDF/Al₂O₃ separator are almost zero, while it is 56° for commercial separators, as shown in Figure 7D. The porosity of PVDF/Al₂O₃ separator is 55.8%, and its ionic conductivity is 2.23 mS cm⁻¹. The discharge capacity loss of LIBs with PVDF/Al₂O₃ separator is lower (1.8%, after 100 cycles at 1 C), and its retention rate is 92.9% in the current density of 4 C. This research reveals the LIBs with PVDF/Al₂O₃ separator have great potential for applications under high temperature and power operations. Wang et al.[72] used a method similar to Wu et al.[71] They made a composite nonwoven fabrics coated with different contents of nano-SiO₂ and PVDF. They found that the coated separator had higher electrolyte uptake as well as better thermal stability compared with the polyolefin separators. LIBs with the composite nonwoven fabrics revealed higher
discharging capacities, better C-rate and cycling performance than with the polyolefin separator.

Li et al.\textsuperscript{[73]} prepared polyether gel-filled PVDF (GF-PVDF) separators by means of thermal crosslinking. They found that a relatively better gel polymer electrolyte (GPE) could be obtained when the filled polyether content did not exceed 60 wt.%. The ionic conductivity of the GPE could reach $1.3 \times 10^{-3}$ S cm\textsuperscript{-1}. The electrochemical window of LIBs with GPE is 4.6 V (vs. Li/Li\textsuperscript{+}). This shows that GPE is compatible with the positive and negative electrodes of LIBs under high voltage. The coulombic efficiency of LIBs using such GPE could reach 94% after 100 cycles. The research shows a potential composite polymer electrolyte applied in lithium cells. Further, Xu et al.\textsuperscript{[74]} developed a functional separator which was constituted by conventional polypropylene (PP) coated water-based PVDF powder particles by simple dipping method to improve the performance of LIBs. SEM images shows that the PVDF particles assembled and dispersed on the both surfaces of PP separator. The thermal shrinkage of separator with 20% of PVDF particles was minimum (12.7%, at 130\degree C for 1 hour), and its electrolyte uptake was up to 140%. The modification separator coated with PVDF on the surface can decrease the interface resistance and improve the ionic conductivity because of the tough affinity between PVDF and polar solvents, as well as the pores of PVDF particles to provide the passage for Li-ions.

Wei et al.\textsuperscript{[75]} demonstrated a novel approach for embellishing the separator with a PVDF-carbon(PVDF-C) layer through phase inversion process, leading to the polysulfides produced in the LSBs being limited on the cathode side, as shown in Figures 8A and 8B. The strong microporous adsorption capacity of PVDF-C layer and the conductivity of the C network improve the long-cycle
stability of the LSBs. Furthermore, the PVDF-C layer can block the shuttle of polysulfides in the battery and improve the conductivity of the electrode. LSBs using the separator delivered a discharge capacity of 669.1 mAh g⁻¹ after 500 cycles at 0.5 C. Even when the current density is 5 C, the battery can still maintain a discharge capacity of 393 mAh g⁻¹, thus exhibiting excellent rate performance and high stability, as shown in Figures 8C and 8D. This frugal and straightforward strategy to restrain the polysulfide dissolution supplies a commercially viable method for LSBs. Cao et al.⁷⁶ successfully proposed a PVDF electrospun nanofibrous separator coated with polydopamine (PDA) for LIBs, as shown in Figure 8E. The presence of the PDA coating makes the surface of PVDF hydrophilic (Figure 8F), thereby elevating the electrolyte absorption and ionic conductivity, leading to an enhanced battery performance. The battery with the PDA-PVDF nanofibrous separator demonstrates better cycling and rate performance than that of the battery with the exposed PVDF nanofibrous separator. This study provides a promising technical method of PDA-coating for the preparation of advanced electrospun nanofiber separators among the LIBs domain.

The preparation of a separator with a core-shell structure has become a popular way in the field of contemporary lithium-ion battery separators. The new structure of separator brings a breakthrough in battery performance. Recently, Park and companions⁷⁷ put forward a multicore-shell (MCS) nanofibrous separator with the shell of PVDF wrap multiple cores of polyimide (PI), using a simple one-pot electrospinning technique to obtain the unique structure, as shown in Figure 9A. The multi-core PI nanofibers have strong thermal stability, and the PVDF shell has good compatibility with the electrolyte (electrolyte uptake of 427%) so that this unique separator shows better thermal stability (Figure 9B) and high-temperature electrochemical performance than commercial PE membranes, as shown in Figures 9C and 9D. And as can be seen from Figures 9E and 9F, the cell with MCS1 separator has higher discharge capacities than the cell with the bare PE separator within the operating temperature range. The long-term cycle performance of the cell with MCS separator was better than that with PE separator at 1 C as well as the c-rate performance, as shown in Figures 9G and 9H.
Analogously, Wang et al.\(^{[78]}\) successfully synthesized a poly-m-phenyleneisophthalamide@PVDF (PMIA@PVDF) nanofiber separator with a novel core-shell structured by coaxial electrospinning (Figure 10A). The high melting point and great rigidity character of the PMIA core acting as a stable skeleton for the PMIA@PVDF separator strengthen the thermal stability and structural integrality of the whole separator, as shown in Figures 10B.
and 10C. At the same time, the hydrophilic PVDF shell and the electrospun separator with interconnected open pore structure ensure the wettability of the PMIA@PVDF separator against electrolyte, thereby promoting the conduction of ions. Under high temperature treatments (180 °C), the PVDF shell could melt to shut down the battery. Thus, PMIA@PVDF nanofiber separator shows superiorities in electrochemical performance for LIBs, as shown in Figure 10D.

Surface modification of PVDF separator is carried out to improve the performance. Inorganic nanoparticles introduced into the surface-modified PVDF separator enhance the thermal shrinkage performance and electrolyte absorption rate of the separator, whereas increasing the thickness of the separator to some extent. The wettability and thermal stability of PVDF separators can be boosted by introducing hydrophilic polymers or high-melting-point polymers on the surface of PVDF separators. Surface modification of PVDF separator can further perfect the performance effectively, with strong selectivity. However, the process of surface modified PVDF separator is complicated and the cost is high, which hinders its commercialization advancement.

3.1.3 Polymer blends separators

Another strategy to improve PVDF separators’ performance (such as thermal stability, mechanical stability, electrolyte wettability, and ionic conductivity) is to introduce another one or more polymers with complementary characteristics to prepare a polymer blends separator. This method has simple process and strong operability to fabricate PVDF-based separators with various excellent properties. In the past decade, various combinations of diverse polymers and PVDF have been reported in the literature to achieve the expected output. Next, the research progress of PVDF-based blending separators will be introduced.

Wu et al. [79] prepared PVDF/ polyacrylonitrile (PAN) blend porous separators for LIBs via TIPS method, as shown in Figure 11A. The introduction of PAN improves the mechanical strength and the thermal stability while decreasing the aperture and porosity of separators with an increase content of PAN. The diminution of the aperture and the porosity causes a corresponding decrease in electrolyte absorption and ionic conductivity. However, the C/LiFePO₄ batteries with PVDF/PAN separators show higher C-rate performance and cycle stability than the
batteries with PVDF separators or the commercial Celgard 2400, as shown in Figures 11B and 11C. Similarly, Zhu et al.\cite{80} also prepared PVDF/PAN blended separators, the difference is that they used the electrospinning technology. The obtained PVDF/PAN blend fiber separator was soaked in PVDF/acetone solution for modification. The mechanical strength of the modified PVDF/PAN (at a weight ratio of 5:5) separator reaches more than 20 MPa. Moreover, the modified blend separators exhibited good dimensional stability at 200°C due to the presence of PAN, as shown in Figure 11D. In addition, separators based on the modified PVDF/PAN blended separators impart LIBs with superior C-rate and cyclic performance, high coulombic efficiency and capacity, as shown in Figure 11E-G.

Recently, Sivaraj et al.\cite{81} had applied PVDF/PAN separators to all-solid-state batteries, preparing a freestanding PAN/PVDF/LiClO$_4$/Li$_{0.5}$La$_{0.5}$TiO$_3$ solid polymer electrolyte by solution casting technique, as shown in Figure 12A. Composite solid polymer electrolytes exhibited a high thermal stability (500°C), evaluated by TG/DSC analysis, owing to the filler incorporated composite samples, as shown in Figure 12B. PAN/PVDF/LiClO$_4$ solid polymer electrolyte containing 10 wt.% Li$_{0.5}$La$_{0.5}$TiO$_3$ nanoparticles presented an excellent ionic conductivity ($1.43 \times 10^{-3}$ S cm$^{-1}$ at room temperature), which was better than the filler-free separators ($\sim 10^{-5}$ S cm$^{-1}$). The addition of Li$_{0.5}$La$_{0.5}$TiO$_3$ into the PAN/PVDF/LiClO$_4$ polymer electrolyte enhanced the concentration of Li$^+$ and provides Li$^+$ conduction channels. The all-solid-state batteries using PAN/PVDF/LiClO$_4$/Li$_{0.5}$La$_{0.5}$TiO$_3$ (10 wt.%) electrolyte exhibited outstanding electrochemical cycling, and rate stability, as shown in Figure 12C.

Zhai et al.\cite{82} manufactured a x-polyethylene glycol diacrylate (x-PEGDA) coated polyetherimide/PVDF (PEI/PVDF) fiber separator, as shown in Figure 13A. Successful cross-linking of PEGDA augments the average fibers diameter and reduces the packing density, leading to the mechanical property and flexibility of x-PEGDA-PEI/PVDF separators increasing and the average pore diameter decreasing, as shown in Figures 13B and 13C. Besides, owing to the great appetency of PEGDA and PEI with electrolyte, the x-PEGDA coated PEI/PVDF separators acquired good electrolyte wettability, high electrolyte absorption and ionic conductivity, as well as improved electrochemical stability window, as shown in Figures 13D and 13E. The x-PEGDA-PEI/PVDF separators demonstrate excellent thermal stability and nonflammability, as shown in Figures 13F and 13G, which can guarantee the safety of LIBs. What’s more, the Li/LiFePO$_4$ batteries assembled with the x-PEGDA-PEI/PVDF separators exhibits better...
cycling stability and rate capability compared with the cell using Celgard separators, as shown in Figures 13H and 13I. This research provides a promising solution for the preparation of next-generation lithium-ion battery separators with good wettability and safety.

Recently, Wu et al. [83] proposed the semi-interpenetrating polymer networks (IPNs) of poly(butyl acrylate) (PBA)/PVDF made by free radical polymerization for gel polymer electrolyte (GPE). A novel type of PBA/PVDF separator was produced in different molar ratios. When the semi-IPNs PBA/PVDF separators were soaked with commercial liquid electrolyte, separators demonstrated a chemically cross-linked structure (Figure 14A), leading to an outstanding electrolyte uptake (120%), as shown in Figure 14B. When the PBA/PVDF molar ratio is 1:0.5, the resistance value is the smallest so that the best performance of the GPE will be obtained, as shown in Figure 14C. The prototype cell assembled with GPE as the electrolyte shows an outstanding cycling stability and rate capability (Figures 14D and 14E). Cui et al. [84] obtained a polymer separator, blending PVDF and cellulose acetate doping the Al(OH)$_3$ particles through NIPS method, as shown in Figure 14F. The addition of Al(OH)$_3$ particles enhanced the thermal stability (shrinkage ratio of 4.6% at 160°C), porosity (68.6%), electrolyte absorption (403.9%), ionic conductivity (2.85 mS cm$^{-1}$), and electrochemical properties of the PVDF-CA/Al(OH)$_3$ separator. In addition, the batteries with PVDF-CA/Al(OH)$_3$ separators presented an outstanding rate capability (128.28 mAh g$^{-1}$ at 8 C) and cycling stability (151.97 mAh g$^{-1}$ after 100 cycles at 1 C) compared with the commercial polypropylene separator, as shown in Figures 14G and 14H. The study demonstrates a novel PVDF-CA/Al(OH)$_3$ separator for the high-safety and stabilized LIBs.

Fu et al. [85] found that the usage of electrospun polymeric separators was limited due to their poor mechanical property. In this study, they introduced Polymethyl methacrylate (PMMA) and nano-SiO$_2$ into electrospun PVDF separators to generate a PVDF/PMMA/SiO$_2$ non-woven separator. Then they controlled the thickness of the separator by a hot-pressing method, improving their mechanical performance at the same time. It can be observed from the SEM test (Figure 15A) that the melt of PMMA bonding the neighbor electrospun fibers and uniform-distributing nano-SiO$_2$ reinforced the mechanical strength of the separator. DSC and hot oven tests
manifest that the PVDF/PMMA/SiO$_2$ composite separator has excellent thermal stability. Moreover, adding PMMA and SiO$_2$ can reduce the crystallinity of PVDF to increase the uptake of liquid electrolyte. The PVDF/PMMA/SiO$_2$ nonwoven separator exhibits a lower interfacial resistance compared with the Celgard separator. The LIBs assembled with the PVDF/PMMA/SiO$_2$ separator shows more stable cycle performance, better capacity retention and higher discharge capacity (158 mAh g$^{-1}$).

Recently, Zhou et al.\[86\] fabricated PMMA/PVDF hybrid polymer separator through an in-situ reaction for lithium metal batteries (LMBs), as shown in Figure 15B. This separator provided a stretchable and stable SEI layer with the high ionic conductivity and excellent mechanical strength, as shown in Figures 15C and 15D. The interface between the PMMA/PVDF layer and lithium anode existed Li-F and Li-O bond, which supplied the fast ion transport channels, as shown in Figure 15E. In addition, the robust and flexible polymer layer can synchronously adapt the volume change and restrain dendrite growth. Therefore, the cells with PMMA/PVDF hybrid polymer separator shows excellent long-term cycling performance and high-rate performance, as shown in Figures 15F and 15G. From the EIS results (Figure 15H), it is further testified the low interface impedance and supernal lithium ion-conductivity of the cells with PMMA/PVDF-Li. The SEM test of the lithium anode after cycling revealed that the PMMA/PVDF-Li anode presented a flat and compact surface, which was almost the same as the lithium anode without current cycling, once again confirming the mechanical and chemical stability of the PMMA/PVDF separator and the effective inhibition of lithium dendrites, as shown in Figure 15I. For the full cells, the PMMA/PVDF separator also exhibits an electrochemical performance. This research provides a reliable idea for the preparation of high-stability and dendritic-free lithium metal batteries.

Huang et al.\[87\] prepared the perfluorosulfonic acid (PFSA)-PVDF blending separators with different ratios through electrospinning technology. The material structure of PFSA and the crystal of PVDF in nanofiber were impacted by each other, which was related to the main chain interaction between PFSA and PVDF. The average diameter of the PFSA/PVDF nanofiber separator is between 75 nm and 170 nm, which has high
hydrophobicity. The lithium-ion battery assembled with PFSA/PVDF nanofiber separator with high PFSA content has a higher capacity than PVDF nanofiber after 100 cycles, and has more stable cycle performance. Using the same production method, Monaca et al.\textsuperscript{[88]} prepared the PVDF/polyethyleneoxide (PEO) separator by blending and electrospinning. The PVDF-PEO based separators contributed to the increased conductivities, greater electrolyte absorptivity and higher porosities than commercial polyolefin separators, result in an enhanced cell performance. Due to the lower shutdown temperature, PVDF-PEO based separators are much more secure than PVDF separators, although their mechanical properties are not as robust as PVDF separators. Liu et al.\textsuperscript{[89]} made a sponge-like PVDF/high density polyethylene (PVDF/HDPE) separator demonstrating high ionic conductivity for LIBs via NIPS method. HDPE fillers with smaller size (250 nm) are prepared through moderate reverse phase emulsion. The ionic conductivity of the PVDF/HDPE separator can reach to 2.54 mS cm$^{-1}$ at room temperature, which is higher than pure PVDF separator (1.85 mS cm$^{-1}$). The ion transport number of lithium-ion battery with PVDF/HDPE separator is 0.495, higher than that with commercial separator (0.33) and pure PVDF separator (0.27). Furthermore, LiCoO$_2$/Li batteries assembled with PVDF/HDPE separator exhibit great C-rate and cycling performance. PVDF/HDPE separator has great potential as the excellent candidate separator for the application of LIBs.

The inherent mechanical property of PVDF separator limits its wide application. The primary reason for preparing polymer blends separators is to compensate for the poor performance of PVDF separators. The electrochemical performance of LIBs is enhanced on the basis of ensuring its safety. In general, PVDF is mixed with other polymers to improve the overall performance. In this way, the process is simple and operable, and the capability of the separator (such as thermodynamic stability, electrolyte affinity, mechanical strength, inhibition of lithium dendrite, etc.) can be controlled and balanced by adjusting the proportion of PVDF and additives. Nonetheless, when the
polymers are mixed, the solvent of the polymer is more demanding. It is inevitable to find out the solvent that can
dissolve two kinds of polymer at the same time.

3.1.4  Inorganic material-filled separators

Another way to improve the thermal stability, mechanical strength, microstructure and electrochemical performance of the separator is to mix PVDF with various inorganic fillers to prepare a composite separator. Over the years, this technique has been frequently reported in various ways. The mixed fillers are mainly oxides (SiO₂, TiO₂, Al₂O₃, ZrO₂), clay, lithium salts, carbonaceous materials or organic biomass materials. Due to the limitations of pure PVDF polymer separators, the research of inorganic material-filled separators have become the main concern in recent years. In this section, we will discuss the recent progress in single-layer inorganic material-filled polymer separators.
Yanilmaz et al.\textsuperscript{[91]} reported a nanoparticle-on-nanofiber hybrid separator manufactured via simultaneously electrospaying SiO\textsubscript{2} dispersions and electrospinning PVDF solution, as shown in Figure 16A. On the surface of PVDF nanofibers, a uniform, bead-free fiber structure can be observed doped with a large number of SiO\textsubscript{2} nanoparticles, as shown in Figure 16B. The dispersion of SiO\textsubscript{2} nanoparticles on the surface of PVDF nanofibers enhances the wettability of electrolyte, thermal dimensional stability (Figure 16C), and ion conductivity. Because the particular hybrid structure of SiO\textsubscript{2} ceramic nanoparticles and PVDF nanofibers increases the specific surface area, the electrochemical performances are improved. Compared with industrial polyolefin separators, SiO\textsubscript{2}/PVDF composite separators have larger electrolyte uptake and higher electrochemical oxidation limit, as well as lower interfacial resistance (Figure 16D). The battery assembled with SiO\textsubscript{2}/PVDF composite separator exhibits high battery capacity, good cycle performance and C-rate performance at room temperature, as shown in Figure 16E.

Similarly, Costa et al.\textsuperscript{[92]} prepared a silica (SiO\textsubscript{2})/PVDF composites separator with a SiO\textsubscript{2} filler content of 20% using the NIPS process (Figure 16G). The dispersed SiO\textsubscript{2} filler was prepared by a sol-gel method with an average particle size of about 400 nm mesoporous silica spheres (SS), as shown in Figure 16F. The separators obtained after 1 minute exposure to air were assembled in cells, which contributed to the best cycling and C-rate performance, as shown in Figure 16I. The PVDF/SS separator reveals a capacity retention of 79% and capacity fade of 4% at 2 C after 50 cycles, as shown in Figure 16H. The study concluded that this novel separator is suitable for the applications of LIBs.

Gao et al.\textsuperscript{[93]} fabricated a gel polymer electrolyte (GPE) of PVDF mixed with poly (ethylene oxide) (PEO) and nano zirconia dioxide (ZrO\textsubscript{2}) with a compact morphology by a simple solution-casting method, which can block polysulfides penetration and guarantee electrolyte uptake and Li\textsuperscript{+} migration, as shown in Figure 17A. Superior to the commercial liquid electrolyte separators, the LSB assembled with non-additive GPE shows an excellent rate performance, high initial capacity (1429 mAh g\textsuperscript{-1}) and coulombic efficiency (retention of 96% after 200 cycles at 0.2 C), as shown in Figure 17B. Moreover, the LSB could still exhibit a high capacity (847.2 mAh g\textsuperscript{-1} after 500 cycles at 1 C) and a low fading rate (0.05% per cycle),
as shown in Figure 15C. Through the scanning electron microscopy (Figures 17D and 17E) comparing the surface morphology of anode before and after the rate tests, it is found that PVDF/PEO/ZrO₂-GPE can protect the lithium anode from the erosion of polysulfide effectively. Therefore, this new type of hybrid PVDF-based GPE separator supplies an effective method for the establishment of high-performance LSBs.

Fang et al. fabricated PVDF/montmorillonite (MMT) composite separators with diverse contents of MMT for LIBs via electrospinning. The introduction of MMT increases the mechanical strength and thermal stability of PVDF electrospun separators. Simultaneously, the PVDF/MMT-5% composite separator shows maximum ionic conductivity (4.2 mS cm⁻¹) and best electrochemical stability. The cells assembled with PVDF/MMT-5% composite separator exhibits higher capacity and more excellent cycle performance than that with commercial Celgard PP separator. Recently, Khalifa et al. used a concept similar to Fang et al. They synthesized a PVDF/halloysite nanotube (HNT) electrospun nanocomposite as gel polymer electrolyte (GPE) for LIBs. The addition of HNT reduces the average diameter and crystallinity of electrospun nanofibers and increases the porosity of the nonwoven fabric, thereby increasing the electrolyte absorption rate of the composite separator and the ionic conductivity (1.77 mS cm⁻¹). Moreover, this GPE separator possessed high mechanical strength, slight thermal shrinkage and higher melting point compared with commercial separators, which is vital to the safety, as shown in Figures 17F and 17G. The cycling performance of Li/GPE/LiCoO₂ battery exhibited a high capacity (138.01 mAh g⁻¹) and
coulombic efficiency (97%), as shown in Figure 17H. This polymer-based separator with high ionic conductivity, tensile strength and low thermal shrinkage rate is worthy of attention.

Solid electrolyte is a new type of electrolyte prepared by combining the polymer separator and lithium salt. It has been widely researched as a substitute for liquid electrolyte. The key issue is to research the interface
resistance of solid electrode with solid electrolyte. Lim et al.\textsuperscript{[97]} combined 80 wt.% Li$_{1.3}$Ti$_{1.7}$Al$_{0.3}$(PO$_4$)$_3$ (LTAP) with 10 wt.% of PVDF, and 10 wt.% LiPF$_6$ in EC/DMC to develop a novel composite electrolyte, as shown in Figure 18A. The ceramic-based composite electrolyte exhibited high thermal stability and ionic conductivity (8.9×10$^{-4}$ S cm$^{-1}$ at 25°C) with reduction of the interface resistance, as shown in Figures 18B and 18C. The composite electrolyte based on LTAP/PVDF can be used as potential high-safety LIBs electrolyte. He et al.\textsuperscript{[98]} developed a mesoporous PVDF-LiPF$_6$ piezoelectric electrolyte film for the all-solid-state flexible SCPC by fixing the liquid electrolyte into the mesoporous PVDF film, as shown in Figure 18D. Among this, the mesoporous PVDF film is synthesized via using SiO$_2$ microspheres, as shown in Figure 18E. The flexible SCPC is effectively charged through mechanical deformation to directly obtain/store body movement energy. This kind of separator design not only contributes to the SCPCs, but also provides an innovative way for the development of LIBs separators in the future.

Nasrallah et al.\textsuperscript{[99]} prepared nanocomposite films of PVDF/Li$_4$Ti$_5$O$_{12}$ (LTO) with diverse volume scores of LTO nanoparticles. As the volume fraction of LTO increases, the melting temperature of the composite films is slightly decreased and the crystallinity is significantly reduced, which is confirmed by the augment in the relative content of β-phase in the PVDF base material. The presence of LTO NPs contributes to a porous spherical structure
and improves the hydrophilicity of PVDF. In this paper, the dielectric constant $\varepsilon'(\omega)$, AC conductivity $\sigma_{ac}(\omega)$, loss $\varepsilon''(\omega)$, complex impedance $Z^*(\omega)$, as well as Nyquist curve of PVDF/LTO nanocomposites separators are also studied. LTO NPs are used as dopants to enhance the physical and chemical properties of PVDF substrates applied to high-power-density LIBs electronic devices. Li et al.\cite{62} prepared a novel PVDF-based microporous separator blended cyanatoethyl cellulose (CEC) and cellulose nanofiber (CNF) cellullosic biomass-material by using an ordinary non-solvent induced phase separation technique, as shown in Figures 19A and 19B. The PVDF/CNF/CEC blend composite separators had a reduced crystallinity and electrolyte wettability, good ionic conductivity (1.26 mS cm$^{-1}$) as well as enhanced dielectric properties. The addition of CEC improves the thermal stability (Figure 19C) and mechanical properties (Figure 19D) of the composite separators. CEC and CNF play a vital part in augmenting the Li$^+$ content and promoting the safety of LIBs. In addition, the LIBs with the PVDF/CNF/CEC blend composite separators exhibited preferable cycle stability and rate performance (Figures 19E and 19F). This fascinating separator...
was fabricated through an eco-friendly and cost-effective way and has great application prospects for high-power-density LIBs.

Li et al.[100] exploited a HTPB-g-MPEG/PVDF porous separators by phase inversion process. HTPB-g-MPEG represents Hydroxyl-terminated polybutadiene that was grafted with methoxyl polyethylene glycol. Compared with pure PVDF porous separator, the use of HTPB-g-MPEG could not only reduce the crystallinity, but also enhance liquid electrolyte uptake and corresponding ion conductivity. Meanwhile, the cells assembled with HTPB-g-MPEG/PVDF separators revealed high initial discharge capacity and outstanding cyclic stability. Aadheeshwaran et al.[101] prepared a PVDF(80%) /PEG (10%) / BaTiO₃ (5%) composite polymer electrolyte separator based on PVDF matrix by the spinning immersion precipitation method. The PVDF/PEG/BaTiO₃ composite separator improves the porosity and electrolyte wettability of the separator, and has a larger electrolyte retention rate. At the same time, the PVDF/PEG/BaTiO₃ separator has excellent mechanical
properties and thermal stability. These good physical properties result in the batteries exhibiting outstanding electrochemical properties. The research suggests that the porous composite electrolyte has broad application prospects in LIBs. de Moraes et al.\textsuperscript{[67]} have studied a composite separator prepared by mixing carbon-coated hexagonal boron nitride (hBN) nanosheets and PVDF via dry phase inversion (Figures 20A and 20B), which possesses high thermal stability, porosity and electrolyte wettability, as shown in Figures 20C and 20D. Among them, the carbon-hBN nanosheets are procured by a scalable liquid phase shear stripping method. The resulting hBN nanosheet composite separators with high-porosity possessed high ionic conductivity. The LIBs with hBN/PVDF separators show a high rate capability and cycling stability, as shown in Figures 20E and 20F. Overall, this work provides a promising strategy for manufacturing separators in LIBs that enhance electrochemical performance and working temperature.

In this section, the recent development of monolayer inorganic material-filled separators is discussed. In general, organic polymer molecules can be combined with inorganic ceramic molecules in three-dimensional space in the form of adsorption or covalent bond to form a more compact composite structure, showing the optimal properties of raw materials and additives, to further improve the thermal stability, wettability, interface stability and ionic conductivity. The addition of active substances can also increase the energy density of LIBs. However, the non-uniform distribution of inorganic additives in the polymer matrix will affect the porosity and electrochemical property.

\section*{3.2 \ Multilayer separators}

\subsection*{3.2.1 \ Multilayer single polymer separators}

The previous section introduced the research progress of single-layer polymer separators. The introduction of other polymers, organic materials and inorganic materials into the PVDF matrix improve the physical and chemical performances of the separator to a certain extent, and speed up the process of LIBs developing. This section will introduce another preparation method to achieve high-performance
separator which use PVDF, pure polymers, organic or inorganic materials to produce a single multi-layer polymer separator composed of only one material per layer. By combining materials with different properties, a comprehensive design with physical and chemical properties, safety and practicability can be achieved.

According to the research progress of multilayer single polymer separators, we will divide the multilayer single polymer separators into two categories: double-layer polymer separators and sandwiched polymer separators. Fang et al.\textsuperscript{102} developed a porous PVDF-layer-coated polyethylene (PE) separator using the dip-coating method and dry-cast process, as shown in Figure 21A. Distinctively, they employed the non-volatile N, N-dimethyl formamide (DMF) solvent and the relatively volatile distilled water non-solvent to yield the PVDF coating layer with porous structure (Figure 21B). The porous PVDF coating separators reveal better affinity with electrolyte and higher ionic conductivity at the modified porous coating separator/liquid electrolyte system. Especially, the cell assembled with porous PVDF layer-coated PE separator shows better thermal stability and cycle performances. The double-layer separator preparation process is a simple, governable and effective way for separator modification. Wang et al.\textsuperscript{103} demonstrated a new carbon nanofiber (CNF)/PVDF composite separator used for LSBs to effectively obstruct dissolved lithium polysulfide, as shown in Figures 21C and 21D. This CNF/PVDF separator shows high electronic conductivity, reducing the internal resistance and helping inhibit the polysulfide. The LSBs assembled with CNF/PVDF bilayer separators exhibit high capacity, excellent long-cycle and rate performance.
Simultaneously, the CNF/PVDF exhibits an excellent cycling stability, which retains a capacity of 768.6 mAh g$^{-1}$ and a high coulombic efficiency of 99% after 200 cycles at 0.5 C, as shown in Figures 21E and 21F. In addition, CNF/PVDF composite separators have the advantages of low raw materials cost and simple preparation process, which are suitable for industrial production.

Wu et al.$^{[104]}$ combined the polyethylene terephthalate (PET) nonwoven with electrospun PVDF separator via hot-pressing to compensate for the disadvantages of poor mechanical strength of electrospun nanofiber membranes, as shown in Figure 22A. The double-layer composite PET/PVDF separator presents an excellent mechanical property (tensile strength of 13.70 MPa and longitudinal tensile strength of 34.85 MPa), favorable wettability, higher thermal stability, as well as improved electrochemical performance, as shown in Figures 22B and 22C. Recently, Zhu et al.$^{[105]}$ adopted the same concept. They developed a novel type of filmy bilayer polymer separator formed by the combination of electrospun PVDF nanofiber subject and PET ultrafine fiber layer for LIBs through mechanical pressing process, as given Figure 22D.
The PVDF layer decides the pore size and enhances porosity, whereas the PET layer intensifies mechanical and thermal stability. The reported PVDF/PET separator possesses a highly porous structure which contributes to a complete and quick absorption of liquid electrolyte, as shown in Figure 22E. Moreover, the separator exhibits outstanding thermal and dimensional stability, which has almost no shrinkage even at 135°C. And the meltdown temperature of PVDF/PET separator is 252°C, higher than the shutdown temperature (131°C), to protect against internal cell short circuits, as shown in Figure 22F.

Wu et al.\cite{106} fabricated a sandwich-type structure of Polyimide/PVDF/Polyimide (PI/PVDF/PI) separator by the electrospinning process for LIBs, as shown in Figure 23A. This construction utilizes PI as the top and bottom layers. Under high temperature operations, PVDF nanofiber, as a middle layer, can melt and constitute a pore-free separator to shut the battery down, as shown in Figure 23B. The electrolyte uptake of the PI/PVDF/PI separator is 476%, which is superior to that of commercial separators, and its ionic conductivity is 3.46 mS cm⁻¹. The battery assembled with PI/PVDF/PI separator manifests better impedance performances, high discharge capacity and long cycling life. PI/PVDF/PI can realize self-shutdown function within 10 minutes at a high temperature above 170°C, which could be used as a safety mechanism to prevent the thermal runaway of LIBs.

Similarly, Yang et al.\cite{107} prepared a novel sandwiched PVDF/PMMA/PVDF gel polymer electrolyte (GPE) as separator for rechargeable LSBs using a facile method, as shown in Figures 24A and 24B. The PVDF as the top and bottom layers could absorb liquid electrolyte completely and then enhance Li⁺ transfer. As a result of this sandwiched GPE separator, the batteries not only suppress the shuttle effect of polysulfides in liquid electrolyte, but also increase the utilization of sulfur significantly. LSBs with the sandwiched PVDF/PMMA/PVDF GPE separator displays an encouraging electrochemical performance. It has a higher initial discharge capacity (1711.8 mAh g⁻¹) and better capacity retention (1145.3 mAh g⁻¹ after 50 cycles) compared with the commercial PP separator, as shown in Figure 24C. This reported GPE separator has further promoted the application of LSBs.

Zhang et al.\cite{108} reported a sandwich structure PVDF/HEC/PVDF polymer separator of GPE for LIBs. The HEC (hydroxyethyl cellulose), as a middle layer, is compact to avoid micro short-circuits. Because of the simple and efficient electrospinning process for PVDF layer and environmentally friendly HEC layer, the production capacity of composite membranes is guaranteed. This structure combines the advantages of the HEC with that of PVDF. Therefore, it presents a high electrolyte uptake (135.4%), high ionic conductivity (0.88 mS cm⁻¹ at room temperature), low lithium movement activation energy (0.016 eV), all properties are better than those of the pure HEC separator and commercial separator. The Li//LiFePO₄ cell assembled with the PVDF/HEC/PVDF-GPE exhibits an observably high discharge capacity.
(140 mAh g\(^{-1}\) after 140 cycles). Depending on the non-flammable nature of PVDF and HEC polymers, the PVDF/HEC/PVDF separators are supposed to be given priority to for LIBs in high-temperature operating environments. This kind of sandwiched GPE is prospective for further progress in LIBs particularly those needing advanced safety and reliability.

Recently, Soomro et al.\[109\] developed a multilayer Al\(_2\)O\(_3\)/PVDF/Celgard separator with the deposition of ultrathin PVDF and Al\(_2\)O\(_3\) layers on polyolefin separator through roll-to-roll atmospheric atomic layer deposition (R2R-AALD) and electro hydro dynamic atomization (EHDA) methods, as shown in Figure 25A. The coatings of ultrathin PVDF and Al\(_2\)O\(_3\) layers improve the thermal stability and mechanical strength, as well as the electrolyte wettability and electrolyte uptake (256\%) (Figure 25B), thus increasing the ionic conductivity. The separator reveals excellent thermal stability and robust mechanical strength (Figures 25C and 25D). The LCO/graphite cells based on the reported Al\(_2\)O\(_3\)/PVDF/Celgard multilayer separator display excellent discharge capacity (130.9 mAh g\(^{-1}\) at 0.5 C after 150 cycles and 99.6 mAh g\(^{-1}\) at 5 C after 100 cycles at 25 °C), as shown in Figures 25E and 25F. Moreover, the LCO/graphite cells assembled with Al\(_2\)O\(_3\)/PVDF/Celgard separators exhibit prominent cyclic performances at high temperatures, as shown in Figure 25G. The reported multilayer separators have proved to be better candidates for high-capacity LIBs, particularly for high-temperature conditions.

This section describes multilayer single polymer separators. Materials with diverse properties are combined to achieve a comprehensive design with both physicochemical properties and security. The multilayer polymer separator can introduce a porous polymer layer to close the separator at high temperature to avoid the potential safety hazard caused by thermal runaway of the battery. At the same time, the multilayer structure elevates the mechanical properties and dimensional stability. However, the multilayer structure increases the thickness and weight of the separator, resulting in a lower energy density of the battery.

### 3.2.2 Multilayer composite polymer separators

The previous section introduced the research progress of multilayer single polymer separators prepared by combining multiple pure material layers. In fact, on this basis, in
order to achieve more performance improvements, each layer can also be composed of composite materials to manufacture multilayer composite polymer separators, so as to design separators with specific functions. In recent years, many researches on PVDF-based multilayer composite polymer separators have been reported, and the research contents will be reviewed in the following.

Recently, Zhu et al.\textsuperscript{[110]} fabricated a novel, dual functional bistratal reduced graphene oxide (rGO)-PVDF/PVDF separator via a simple electrospinning technique for LSBs, as shown in Figure 26A. This double-layer separator provides two diverse functionalities. The porous PVDF delivers good thermal stability and keeps the separator structural integrity. The rGO-PVDF layer ensures the rapid transportation of lithium ions. Compared with traditional polypropylene separators, this novel multilayer separator design can prominently promote the cycling stability and rate performance of the LSBs, as shown in Figures 26B and 26C. Overall, this new type of double-layer separator provides an alternate way for the design of high-performance LSBs. Mao et al.\textsuperscript{[111]} prepared a double-layer PVDF/ZSM-Si@PE separator with three dimensional porous structure by dip-coating method to enhance Li\textsuperscript{+} ion transport number and ionic conductivity, as shown in Figure 26D. Especially, the Li\textsuperscript{+} ion transport number is greatly increased from 0.28 to 0.44 due to the specific pore structure of ZSM-5 and the interaction between ZSM-5 and the electrolyte. The ionic conductivity of PVDF/ZSM-Si@PE separators is up to 0.54 mS cm\textsuperscript{–1}. Consequently, the cells with PVDF/ZSM-Si@PE separators show excellent C-rate and cycling stability, which exhibits a capacity retention of 94.2\% after 100 cycles, as shown in Figures 26E and 26F.

Feng et al.\textsuperscript{[112]} proposed a polypropylene/hydrophobic silica-aerogel-composite (SAC) double-layer separator. The SAC is fabricated by combining silica aerogel and PVDF, as shown in Figure 27A. The rationally design of SAC effectively improves the thermal stability of separators (after heating at 160\°C for 30 minutes, the area retention rate is only 30\%), but the weight increases slightly.
Furthermore, the hydrophobic silica aerogel layer of SAC observably improves the electrolyte wettability owing to the introduction of the -Si(CH$_3$)$_3$ hydrophobic functional groups and porous structure, as shown in Figure 27B. The LIBs with SAC separators own a low polarization, contributing to preferable electrochemical performance and cycle stability. This work offers a new strategy to significantly improve the safety, implying promising application prospects in power batteries. Pan et al.$^{[113]}$ demonstrated an ultrathin (∼20 µm) PVDF/PE/PVDF porous separator by electrospinning, as shown in Figure 27C-E. The separator displays high mechanical strength (∼11.2 MPa) and porosity, as well as high electrolyte uptake (∼380%), which leads to a high ionic conductivity (∼2.5 mS cm$^{-1}$). The LiFePO$_4$/Li cell with such thin separator delivers a great initial discharge capacity (134.3 mAh g$^{-1}$ at 10 C) and sustains a discharge capacity of 129.2 mAh g$^{-1}$ after 300 cycles, exhibiting excellent high-rate performance, as shown in Figures 27F and 27G. Most importantly, this research provides a new way to develop ultrathin and high-mechanical-strength electrospinning separators for the high-rate LIBs.

Ma et al.$^{[114]}$ reported a new type of ultrathin hybrid electrolyte with PVDF/hydroxyethyl cellulose (HEC) as the substrate and polyethylene (PE) as the supporting matrix for high-voltage LIBs, as shown in Figure 28A. PE-supported PVDF/HEC separators (PVDF : HEC = 3 : 1, weight ratio) exhibit the best mechanical property, thermal and wettability performance (Figure 28B). The GPE has high ionic conductivity (0.78 mS cm$^{-1}$ at room temperature) and favorable electrochemical stability (5.25 V,
The cell with this GPE shows a superior cycling stability and good rate performance, as shown in Figures 28C and 28D. This study suggests that the PE-supported PVDF/HEC ultrathin polymer electrolyte with outstanding performance, lower cost and strong operability can be employed for 5 V LIBs.

Recently, Zuo et al. [115] developed a PVDF/ethyl cellulose/amino-functionalized nano-SiO$_2$ (PVDF-EC-(A-SiO$_2$)) composite polymer coated on PE layer as the functional double-layer separator of high-voltage LIBs, as shown in Figure 29A. The composite separator has a uniform interconnected structure (Figure 29B), resulting in an increased melting temperature of 140.8°C, small contact angle of 23.2° (Figure 29C), and high ionic conductivity of 0.79 mS cm$^{-1}$. In particular, LiNi$_{0.5}$Mn$_{1.5}$O$_4$/Li batteries with PVDF-EC-(A-SiO$_2$)/PE separator reveal a high discharge capacity and a superior cycling stability. The PVDF-EC-(A-SiO$_2$)/PE separator has broad application prospects in the field of high-voltage LIBs. Li et al. [116] fabricated sandwiched structure solid-state electrolytes (SSEs) with the properties of ultrathin (9.6 μm), flexible and mechanically strong via a tape casting process, which are constituted by the 75 wt.% LLTO/PVDF-CPE (LLTO-75) as middle layers and the 15 wt.% as the top and bottom layers, as shown in Figures 29D and 29E. The soft and stable LLTO-15 layer could create favorable interfacial contact with electrodes. The LLTO-75 layer with physical rigidity could restrain the Li dendrites growth. Therefore, sandwiched SSE possesses high ionic conductivity (4.7 × 10$^{-4}$ S cm$^{-1}$ at 25 °C), an excellent mechanical strength (7.2 MPa), and homogeneous Li plating/stripping. The battery assembled with sandwiched SSE has high capacity retention ratio (91.7%) and Coulombic efficiency (99.7%) after 1000 cycles, as shown in Figure 29F. The sandwich structure SSE proposed in this research is expected to be an alternative to high-performance solid-state LMBs.

The multilayer composite polymer separator is supported by PVDF-based composite separator, which is layered with other composite materials to significantly highlight the performance of each layer. Coating the composite layer with inorganic nanoparticles or other particular additives on the PVDF composite layer extremely improve
the thermal stability, mechanical strength, wettability and pore distribution of the monolayer separator, and further enhance the security, ionic conductivity and rate capacity of LIBs. Furthermore, for LMBs, the substrate can be coated with a functional protective layer to inhibit the growth of lithium dendrites and further enhance the safety under long-term charge-discharge cycles or high current density. Nevertheless, the thickness of the separator inevitably increases. In addition, the connections between the layers can be affected while the battery is running.

3.3 | Section summary

With the wide application of PVDF-based separators in the battery fields, more and more researchers have developed high-performance separators based on PVDF polymers. This chapter introduces the research progress of monolayer and multilayer separators prepared by combining pure PVDF polymers, other polymers, organic/inorganic materials, and natural raw materials in recent years. Researchers use various preparation methods and techniques to fabricate separators to meet the expected application requirements. It has been reported that the electrosprinning method, phase inversion method, NIPS, TIPS, impregnation method and other methods have been utilized to prepare PVDF-based separators with different structures and properties.

In the research history of monolayer PVDF-based separators, it is found that pure PVDF polymer separators will have different pore size, porosity, electrolyte absorption rate, thermal stability and mechanical strength of physical properties. At the same time, it will affect the electrochemical performance of the assembled LIBs, such as impedance, cycle stability, charge-discharge capacity, coulombic efficiency, rate performance, and so on. Among them, electrosprinning and TIPS methods are the most commonly used preparation technologies that can adjust the microstructure (like pore size, porosity, pore shape). PVDF separators prepared with these two methods generally have high porosity and good electrolyte wettability, so that a larger ionic conductivity is obtained to the benefit of the electrochemical performance of LIBs. In addition, the type of solvent is another important factor that affects the pore size and porosity of PVDF separators. The pore size and porosity of PVDF separators prepared with volatile solvents (such as acetone, etc.) are greater than those with nonvolatile solvents (such as NMP, DMF,
DMSO, etc.). Moreover, a PVDF separator with a controllable pore size can be made by mixing a solvent with a non-solvent (like water, ethanol). In order to improve the PVDF separators, in recent years, people have modified the surface of PVDF separators by coating inorganic nanoparticles or other polymers on the surface, or preparing PVDF with other polymers with excellent properties. Nanofibers with a core-shell structure are also used to prepare PVDF-based modified separators with special functions, which are suitable for LIBs with diverse performance requirements. Coating inorganic nanoparticles into the surface of PVDF separators can enhance thermal dimensional stability and electrolyte absorption. And coating with hydrophilic polymers and refractory polymers can specifically elevate the electrolyte wettability and thermostability of the PVDF separators. PVDF-based blended polymer separators are also fabricated by blending PVDF with other polymers (such as PAN, PEI, PBA, PMMA, PFSA, PEO, PE). Among them, the most widely used are PAN and PEO polymers, which have revised mechanical properties, wettability and electrochemical properties, respectively. Generally speaking, the addition of fillers can improve battery performance by enhancing the ionic conductivity of polymer composites, but the best fillers for PVDF and its composite separators remain a mystery. The most universally used fillers are inert oxide ceramics, carbon materials and lithium active fillers, which increase mechanical properties, interface stability, the relationship between the electrode and the separator, and ionic conductivity, respectively. The use of active materials not only enhances the thermal, mechanical and chemical stability of the separator, but also improves the energy density of LIBs.

The most crucial reason for the design of the multilayer structure is to enhance its basic properties, and to introduce a shutdown effect to ensure safety. Compared with monolayer separators, multilayer separators have higher mechanical strength, thermal stability, shut-off capability, and ionic conductivity. However, its preparation method and technology are relatively complicated. The preparation of multilayer composite polymer separators with various materials and preparation methods has been reported. The polymer-composite separator projected with a multilayer structure is superimposed on the performance of a variety of pure polymers or composite materials, and the multilayer separator improves their performance without affecting the excellent performance obtained when the polymer is formed solely. The superposition composite separator has good wettability, liquid absorbability, super
mechanical strength and thermal stability due to symmetric/asymmetric polymerization strong interaction between the object and the matrix.

4 \ SUMMARY AND FUTURE TRENDS

The separator is an indispensable part of LIBs and plays a key role in the sustainability of LIBs and LMBs. PVDF-based separators have attracted more and more attention due to their excellent properties, which are widely applied in the field of LIBs. Appropriate thickness, good electrolyte wettability, ionic conductivity, chemical stability, thermal stability and high mechanical strength are the basic requirements of high-performance PVDF-based separators. This article reviews the recent developments in the use of different materials and methods to prepare layered structures (monolayer and multilayer) in PVDF-based separators of LIBs and LMBs.

For monolayer structure, separators developed from pure PVDF polymer, surface modification of PVDF polymer, blends of PVDF and other polymers, polymer composite materials of PVDF and organic/inorganic materials have been widely researched. Pure PVDF is often covered for its advantages such as high electrolyte wettability, thermal stability, and good ionic conductivity. Electrosticking and phase inversion methods are usually used to prepare PVDF separators with various microstructures and different properties. However, there is still a significant gap between the mechanical strength of PVDF polymer separators and that of commercial separators. Therefore, in order to improve the overall performance of PVDF separators, the modification of PVDF was studied. The surface of the PVDF separator is coated with inorganic nanoparticles, other polymers, or PVDF-based nanofibers with a core-shell structure, and then the surface of the PVDF separator is modified. Coating inorganic nanoparticles into the surface of PVDF films can vastly improve thermal dimensional stability and electrolyte absorption. Coating with hydrophilic polymers and refractory polymers can particularly improve the electrolyte wettability and thermal stability of PVDF separators. PVDF is blended with different polymers, combining the beneficial properties of a single polymer to enhance the overall performance. The addition of inorganic materials, especially metal oxides, can improve the mechanical and thermal stability of the polymer separator. However, the uneven distribution of inorganic additives in the polymer matrix affects the porosity and electrochemical performance of LIBs. The porosity, electrolyte absorption, mechanical strength, ionic conductivity and thermal stability of monolayer PVDF-based blends and composite polymer separators reported in recent years are higher than those of pure PVDF separators.

The fundamental reason for the development of multilayer separators is that the introduction of a porous structure can shut the separator at high temperatures to avoid thermal runaway, improve thermal stability and ionic conductivity, and increase the affinity between the liquid electrolyte and the separator. A single and multilayer polymer membrane is made of PVDF, pure polymer, organic or inorganic materials, and each layer is composed with only one material. By combining materials with different properties, a comprehensive design with both physical and chemical properties, safety and practicality is realized. Alternatively, PVDF-based composite materials are used to prepare multilayer composite polymer separators with specific functions. According to the reports, the methods for preparing multilayer separators are usually surface coating, hot pressing, mechanical pressing, R2R-AALD and EHDA. Multilayer separators realize a shutdown effect by blocking pores at high temperatures. However, the multilayer structure increases the thickness and weight of the separator, leading to a reduction of the energy density of the battery. Moreover, due to the interaction between the polar matrix of the polymer or polymer composite material and the coating, after a period of time, layer-to-layer detachment may occur. Potential safety problem remains an issue that needs to be further researched. The recently developed multilayer composite polymer separators exhibit excellent performance (close to the ideal separator requirements). For the LMBs, functional protective layer can be coated on the surface of the separator to protect the lithium metal surface, reduce the generation of lithium dendrite and eliminate the hidden trouble of short circuit. For the Li-S batteries, special structure designing and group modification of the separator are usually carried out to prepare a new-type separator that inhibit the shuttle of polysulfide. An ion-selective membrane can also be prepared to produce electrostatic shielding effect on the anions of polysulfide. The development of advanced separators that can both capture polysulfide physically and repel polysulfide through chemical interaction is expected to prevent shuttle effect more effectively.

As an important part of lithium ion storage and migration, the structure and characteristics of the separator play a decisive role in the storage and migration of Li\(^+\). The monolayer separator can maintain porous structure at extremely thin thickness, obtaining high porosity to store abundant Li\(^+\). However, the monolayer separator has a single preparation process and lacks of structural diversity, which limits the storage and migration of Li\(^+\) to a certain extent. The multilayer separator can be prepared into a multilayer structure with special pore channels to
facilitate the rapid migration of lithium ions. The increase in thickness also ensures that more electrolyte is stored. Nevertheless, the incompatibilization between layers has a negative effect on the migration of lithium ions. Improving the separator based on the storage and migration of lithium ions can greatly improve the comprehensive performance of batteries and promote the development of lithium industry.

The electrochemical performance of LIBs can be improved by developing PVDF-based separators with high efficiency. The real performance of the PVDF-based separator in the application of LIBs is still far from satisfactory, and further improvement is needed. In the process of scientific development in the future, energy storage technology will become an indispensable part. Lithium-ion battery is bound to develop in the direction of high energy density, fast charging, low cost and adaptability to various complex extreme environments such as high temperature, low temperature, mechanical impact, acid and alkaline environment. As a significant component of lithium battery, the separator will inevitably develop towards thinner thickness, lower cost, degradable and pollution-free, high temperature resistance, faster lithium ion transmission and diversified functions in the future. By analyzing the development of PVDF-based separator in recent years and looking forward to the future development trend, LIBs can be guided to work efficiently and sustainably to boost its electrochemical performance. In the future, the property of PVDF-based separators can be accelerated from the following aspects.

The prospective development trend of a single PVDF separator is to obtain a single polymer with a porosity of more than 50% but a pore size of less than 500 nm to alleviate lithium dendrite growth. Moreover, the mechanical strength of pure PVDF separators still needs to be improved, and updated manufacturing techniques can be developed to further improve mechanical properties. In terms of surface modification, due to the weak force between the polar PVDF and the polymer or inorganic material coating, separation will occur after a period of time. In the future, more surface grafting technologies should be introduced to form chemical bonds between PVDF polymers and other polymers or polymer composites through ultraviolet, gamma rays or electron beam radiation to alleviate the problems caused by surface coatings. Meanwhile, considering the environmental issues, it is also meaningful to use polyionic liquids and natural polymers as modification coatings for PVDF polymer separators. For PVDF-based composite materials, the future direction is to improve the interaction between the PVDF matrix and the filler to optimize the content of the filler without reducing the electrical properties and mechanical stability of the material. Furthermore, the use of multiple fillers with complementary properties may be a way to improve cycle performance. Through analyzing the research progress and preparation process of PVDF and other polymer blends, it is found that future research can improve the interaction and compatibilization of the two polymers. Properly introducing specific chemical bonds can strengthen the interaction between polymers and achieve the purpose of increasing thermal and mechanical stability. It has been demonstrated in existing studies that PVDF-based separators have been used in solid-state LIBs in high-temperature environments. Solid electrolytes are an available substitute for next-generation batteries and can alleviate fire and explosion problems associated with traditionally used liquid electrolytes in high-temperature environments. However, the low ionic conductivity of solid electrolytes requires further research to achieve better electrochemical performance. Therefore, ionic additives and flame retardants can be added to the PVDF-based solid electrolyte, and the preparation process can be improved to advance the high-temperature performance and safety of the PVDF-based solid electrolyte. Adding active materials to the separator can improve the energy density and electrochemical performance of the batteries. In order to achieve high-energy-density batteries, it is necessary to further promote the development of the combination of PVDF and active materials. Generally, the separator is the inactive component of the battery. The electrode materials as additives in the separator can participate in the electrochemical reaction and boost the electrochemical performance of LIBs. In addition, not only will the electrochemical performance be increased, but the thermal and mechanical stability of the separator will also be improved. For multilayer PVDF-based composite separators, the bonding relationship between layers will directly affect the property and life of the separator. Coating and pressing methods cannot make the layers permanently connected. This requires the addition of crosslinking agents or the surface reaction between layers to form strong chemical bonds.

In short, PVDF-based separators of batteries will be a new generation of LIBs separators with high power density and excellent cycle performance that satisfy the vast majority of requirements now and in the future.

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