Advanced separators for lithium-ion batteries

Kailin Chen\textsuperscript{1}*, Yingxin Li\textsuperscript{2}*, Haoxiang Zhan\textsuperscript{3}*

\textsuperscript{1}School of Energy and Power Engineering, Xi’an Jiaotong University, Xi’an 710049, China
\textsuperscript{2}School of Chemical Engineering, Dalian University of Technology, Dalian 116081, China
\textsuperscript{3}Department of Physics and Astronomy, University College London, London WC1E 6DH, England

\textsuperscript{*}chenkl2001@stu.edu.xjtu.cn, \textsuperscript{*}1029306485@mail.dlut.edu.cn, \textsuperscript{*}zcaphz1@ucl.ac.uk

These authors contributed equally

\textbf{Abstract:} The separator technology is a major area of interest in lithium-ion batteries (LIBs) for high-energy and high-power applications such as portable electronics, electric vehicles and energy storage for power grids. Separators play an essential part that physically prevents direct contact between positive and negative electrodes while acting as an electrolyte reservoir to transport lithium ions. The characteristics of different separators would directly affect the performance under cell abuse; hence separators are crucial for battery safety. This paper introduces the characteristics of separators, means to improve traditional commercial polymeric separators and novel materials for separators. Other novel high-performance separators are also briefly discussed in this paper. Insights from this paper illustrate that various strategies could enhance the performance of separators, and better performance and safety can be achieved in separators in high-energy lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) play an important role in electrical devices such as electric vehicles (EV) and smartphones due to their high energy density, prominent performance and longevity. Since they were shown to the public in 1991, the global demand over LIBs has grown to 68.9 billion dollars in 2021,[1], and they dominate a great market size in powering cell phones, lightweight laptops, electric vehicles and solar power storage. However, a major problem with this kind of application is that LIBs could have potential risks of short circuit or thermal runaway during operation, which endangers user safety. In recent years, there has been increasing research on a separator in LIBs, a membrane to prevent direct contact between anode and cathode in LIBs. Nowadays, microporous polyolefin membrane is widely utilized in commercial separators. Despite its outstanding mechanical strength, good chemical inertness and inexpensive cost, polyolefin separators have several problems in use. Since they have a low melting temperature, their weak thermal stability results in failures in secure operations during rapid temperature rises and other vigorous conditions.[2] In addition, polyolefin comes from non-renewable fossil fuels, accelerating the greenhouse effect and iceberg melting. Several attempts have been made to manufacture other types of separators with good wettability and thermal stability, such as polyamide and ceramic coated separators.
LIBs are mostly composed of 4 parts, including an anode, cathode, separator, and electrolyte. As you can see from Fig.1, during the charging phase, lithium ions leave the cathode, transmitting through the separator in electrolyte and embedded on the anode. While discharging, lithium ions would leave the negative electrode, passing through the separator and embed on the positive electrode. During charge and discharge, to maintain the balance of charges, a current is formed in the circuit during the transition of lithium ions. Electrodes and electrolytes are involved in electrochemical reactions. In comparison, the separator is a rather inactive part. A widely used material in anode for commercial lithium-ion batteries is a carbonaceous compound that is either coke or graphite.[3] As for cathode, layered structure lithium cobalt oxide is used frequently in commercial separators. In addition, It has commonly been assumed that the solution of LiF6 in linear and cyclic carbonates is a usual nonaqueous electrolyte.

As a crucial part of the LIBs, the separator plays a role to physically block the path between anode and cathode while allowing lithium ions to pass through. The separator is a key element to ensure safe cell operation under vigorous conditions, for example, burr, dendrites, cell abuse or even sudden crash. Punctures on the separator would result in a short circuit between anode and cathode. Therefore, certain characteristics are required for a high-performance separator: (1) chemical stability: separator should be inert for electrodes and electrolytes. (2) thermal stability: heat resistance and thermal shut-down required. (3) wettability: wet easily with electrolyte without stretch and deformation. (4) mechanical strength: possess good puncture strength so that separators’ structure is in contact during winding. (5) porosity: possess good ionic conductivity.

It is believed that the most common commercial separator material now is microporous polymeric membranes such as polyethylene (PE) and polypropylene (PP).[4] PE and PP materials are widely applied in separators due to their merits in mechanical strength, chemical and electrochemical stability. Commercial polymeric separators are mainly divided into 3 parts: monolayer PP or PE, two-layered PP/PE or PP/PP and three-layered PP/PE/PP. Multi-layered separators possess the advantage of a shut-down function as PE layers would melt and cease lithium-ion transmission with high temperature while PP layers would remain their dimensional structure and morphology to prevent a short circuit between electrodes.

This paper illustrates the separators’ characteristics, modifications for the microporous polymeric membrane to improve the performance and battery safety and novel separator materials.

### 2. Physicochemical Characteristics of the Separator

A high-performance separator requires an infinite electronic resistance and a high conductivity of ions. Separators have to be inert chemically and electrochemically to both electrodes and electrolytes to achieve stability over a long-time span.[5] Ionic conductivity is related to separators’ structures such as porosity and tortuosity. An appropriate porosity is required to enable separators to store adequate electrolytes to achieve a high ionic transference. Prominent ionic conductivity is also correlated with tortuosity. Tortuosity is a quantity to describe the morphology of the separator. The smaller the value of tortuosity, the greater conductivity could be obtained. In addition, separators should have a good wettability to obtain an ideal ionic conductivity. Better electrolyte permeation could be achieved, which provides a fluent route for lithium-ion transference. On the other hand, uniform pore size and tortuosity are critical for battery stability because ununiform pore size and tortuosity could result in uniform current density over the separator. For ideal LIBs, separators must possess a strong mechanical strength to prevent them from puncture, which could cause a short circuit. A separators’ shut-down function is crucial for battery stability when encountering a short circuit or overheating. In addition, separators must not shrink or deform under sudden temperature rise during cell operation, which is significant for battery stability.

#### 2.1 Thickness, porosity, and mean pore size

LIBs with smaller thickness exhibit lower ionic resistance, resulting in a high charging rate and energy density. Separators equipped in LIBs are usually with a thickness of around 20-50 μm.[6] Despite the commercial separators being commonly reported to have a thickness of 20-25 μm, the thickness of the
separator is closely correlated with their mechanical strength and stability. Small thicknesses could result in more puncture formation in battery manufacturing, which leads to internal short circuits and explosions. The thickness equality is critical because non-uniform thickness could have consequences of electrodes dendrites forming and shorter cycle life of the batteries.

The separator porosity is defined by the ratio of the sum of the volumes of the pores and liquids to the apparent pore volume.\[7\] Porosity can be calculated by eq. (1)

$$\text{Porosity}(\%) = (1 - \rho_m/\rho_p) \times 100$$  \hspace{1cm} (1)

Where $\rho_m$ is the apparent density and $\rho_p$ is the density of the separator material.

Generally, the porosity is calculated by the weight difference before and after the separator is submerged in a liquid, as shown in eq. (2)

$$\text{Porosity}(\%) = W - W_0/\rho_L V_0$$  \hspace{1cm} (2)

Where $W$ is the weight of void separator and $W_0$ the weight of the separator submerged in the liquid, $\rho_L$ and $V_0$ represent the density of the liquid and the geometric volume of the separator, respectively.

Suitable porosity is required to ensure sufficient electrolytes are filled in the pores to guarantee prominent lithium-ion conductivity. If the porosity is too high, the separator itself would be fragile, so battery safety is affected; if the porosity is too small, inadequate electrolyte filled in separators so that ionic conductivity and battery performance may be diminished. Generally, a separator in a lithium-ion battery with 40% porosity is rather common in the market.

A prominent separator should possess a pore size that is big enough for the lithium ions to pass through while small enough so that all the active components and dendrite growths in the electrode can be cut off to avoid short circuits.\[8\] Uniform pore size distribution is also critical because it ensures uniform current density between electrodes and separator, hindering performance declines and dendrite growth.

2.2 Tortuosity, and permeability

Tortuosity simply indicates the fraction of the mean distance traveled to the direct distance. For separators, tortuosity is a factor describing the effect of the geometric shape of the separator on the ionic conductivity,\[9\] and it can be calculated by eq. (3)

$$\tau = \sqrt{\epsilon \times R_s/R_0}$$  \hspace{1cm} (3)

where $\epsilon$ is the porosity, $R_s$ and $R_0$ are the resistivity of the separator before and after submerging in liquid.

Geometric effective transport coefficient is a measure of effective ionic transport of separators’ morphology, and can be defined by $\delta = \epsilon/\tau$. For instance, with a typical porosity value of 45% and a tortuosity of 2.5, the effective transport coefficient is 0.18. The transport coefficient value of 0.18 indicates that the morphology change reduces the ionic conductivity by 18% compared to the pure electrolyte.

The definition of permeability is analogous to tortuosity. The permeability also refers to how the geometric structure affects the ionic conductivity under a certain pressure difference. Darcy’s law is used to determine fluid rate through a porous surface, which can be calculated by eq. (4)

$$u = -\kappa/\eta \nabla P$$  \hspace{1cm} (4)

Where $\eta$ is the viscosity, $\nabla P$ is the applied pressure gradient, $u$ is the average velocity of the fluid when penetrating the porous surface.

However, the Gurley value, $G$, which is correlated with the permeability, is frequently used instead.\[10\] It is referred to as the time taken for air to penetrate a unit area of a separator, which is retained by eq. (5):

$$G = \eta_{air} \times V \times L/\kappa \times \Delta P \times A$$  \hspace{1cm} (5)

Where $\kappa$ is permeability, $\Delta P$ is the pressure difference, $A$ represents the area, $V$ refers to air volume, $L$ is the thickness of the separator and $\eta_{air}$ is the air viscosity.
2.3 Wettability
Wettability is a crucial property for separators since they can rapidly absorb and retain electrolytes during assembling. Prominent wettability enables separators to possess a smaller internal resistance, which would effectively enhance the battery performance.[11] A longer life cycle could be achieved with better wettability as a shorter time is required to fill the pores of the separators. Although according to the recent reports, there are no effective methods to scale wettability quantitively, wettability relates to porosity, pore size, morphology and characteristics of different separators.

2.4 Mechanical properties and thermal behavior
An ideal mechanical strength of a separator is demanded to prevent the battery from dendrite forming, accidental break and short circuit. Tensile strength and puncture strength are the most crucial mechanical properties for separators. Adequate mechanical strength is required during separator handling and manufacturing stages. The traditional stretching procedure determines tensile strength properties, and high tensile strength is common among porous separators in the stretched directions. On the other hand, puncture strength is the weight needed for a needle to create a puncture on the separator.[12] This property has been widely used to determine how hard a separator encounters short circuits during assembly and manufacture. Sufficient puncture strength is required to ensure the separator does not break or puncture during battery assembly, or else a short circuit is likely to happen for the separator. The separator must not shrink or deform under temperature rise.[13] During battery operation, contact between electrodes is blocked by separators. Therefore the deformation of the separator during high temperatures should be minimized. In addition, separators must have a shut-down function. When a steep temperature rise occurs, a shut-down function would be involved to prevent cell abuse. Shutdown should step in before steep temperature, and thermal runaway occurs.

3. Modification of Polyolefin Separators
Currently, commercial separators of LIBs are mainly microporous polyolefin membrane, which has a low liquid absorption rate and are prone to side leakage of electrolytes.[14] The melting temperatures of PE and PP separators are 135°C and 165°C respectively, leading to severe heat shrinkage and contact between the anode and cathode, further leading to internal short circuits, fire and even explosion.[15] Although the newly developed electro-spinning nanofiber membrane has made great progress in porosity, liquid absorption rate and other aspects, it has the disadvantages of poor mechanical properties. Modification of separators is important in improving the performance of separators while developing new methods of separator preparation. The modification methods for polyolefin separators are coating, chemical grafting and blending.[16]

3.1. Coating
Nowadays, methodologies for coating are mainly by coating ceramic particles or gel polymer onto the separator or just a combination of the two methods. Ceramic materials can prevent the cell from being harmed from high temperature and maintain the stability of the cell’s structure, while gel polymer can absorb enough electrolyte, which can improve the ionic conductivity.

As a kind of composite material, ceramic-coating materials are gaining more and more interest from researchers for their combination of the heat resistance from inorganic powder and the characteristics of the coated material. Materials used for ceramic coating include ceramic particles, binder, solvent and additives, and the paint proportion varies according to application scenarios. Dhrupad Parikh et al. [17] developed a binary ceramic system and made each kind of ceramic yield its greatest returns on investment. As TiO₂ has more surface energy and Al₂O₃ is good at thermal conductivity, the two ceramics were used to develop the electrolyte affinity and thermal stability. A slurry formulation methodology was used by adding ceramic and PVDF-HFP into N-methyle-2-pyrrolidone (NMP) solution, and the slurries were tape cast onto PE separators (Fig. 1a). All the coated separators showed great thermal conductivity, especially that of the 100% Al₂O₃ coated separator, which was 3.2 times higher than that of the bare PE separator. Although the Al₂O₃ and TiO₂ both have a surface energy of
over 60 mJ·m⁻². And the coated separators were supposed to have better hydrophilicity. The contact angle of the coated ones towards deionized (DI) water was even higher than pristine PE (>100°). This may attribute to the low surface energy of PVDF-HF, which was used as the binder, the high surface roughness and the coating porosity. Even if so, this article still deserves to be mentioned since the combination of the two ceramic materials was an innovation in this field and its broad prospect is worth our research and exploration.

Aerogel is another acceptable coating material due to its rich pores, high thermal insulation, and electrolyte affinity. Feng, G. et al. [18] designed a hydrophobic silica aerogel composite (SAC) separator by coating the hydrophobic silica aerogel onto a PP separator (Fig. 1b). The contact angle of electrolyte (ethylene carbonate/dimethyl carbonate) with the SAC separator was 0° thanks to the “like dissolves like” theory, while that of the bare PP and PP/PVDF are 52° and 51°, respectively. At the same time, the SAC separator is rich in porosity, which significantly improves electrolyte uptake, with that increasing from 195% (PP) to 346% (SAC). Thermostability was tested, and the result showed that the SAC separator almost stayed unchanged when placed in an environment of 160° for 30 minutes, which can improve the safety of the battery, while PP and PP/PVDF both shrunk, as shown in Fig. 1c.

Other methodologies such as coating organic polymer onto the separator are also popular nowadays. A flame retardant grafted porous organic polymer (POP) based separator was prepared by X Mu et al. [19]. Hydroxy-terminated hyperbranched phosphorous-containing flame retardant was grafted onto melamine-based POP to prepare P-POP, which was later coated onto Celgard 2325 (PP/PE/PP). The electrolyte absorption rate of P-POP coated separator (61%) has increased a lot compared to that of Celgard 2325 (60%) because of the polyhydroxy terminated hyperbranched flame retardant grafted on POP. The safety performance was excellent, too. They ignited Celgard 2325 and the coated one, respectively and tested the ignition time and extinguishing time. The result has shown that the coated separator’s combustion time and extinguishing time were short thanks to the gas source, acid source and carbon source in P-POP, which led to flame retardant effect, and the remaining flame can be extinguished very fast when the electrolyte started to burn. This makes batteries safer to use. However, because of the low crystallinity of P-POP, its mechanical strength was far lower than a ceramic-coated separator.

![Fig. 1 (a) Slurry formulation methodology; (b) Preparation of SAC separator; (c) Different separators after 160°C treatment (30min)](image)

### 3.2. Chemical grafting

Since the thermal properties, electric properties and structure of polymer will change when exposed to high-energy radiation. Some chemical groups can be grafted onto the surface of the polymer by ionizing radiation, ultraviolet radiation, and chemical initiator to develop the separator’s electrolyte wettability and compatibility with electrodes. [20]
Chen, L. et al. [21] anchored BTCEAD onto PP separator with the N-hydroxyphthalimide (NHPI) catalyst, and the BTCEAD will initiate the process of PEGMA being grafted onto PP separator by activators regenerated by electron transfer atom transfer radical polymerization (ARGET-ATRP) strategy to obtain PP(s)-g-PPEGMA. (Fig. 2a) The contact angle of the grafted membrane is much lower than that of the PP separator (47°) thanks to the great electrolyte affinity of EO units in PPEGMA, especially when the grafting degree (GD) is 31%, that of it fell to 10°. Electrolyte-uptake ratio saw a considerable increase, reaching 292% when grafting degree is 31%, which was almost 2.6 times higher than that of pristine PP (111%). However, too high GD can lead to low porosity (24.3% at 31%GD), leading to low ionic conductivity and higher internal resistance, which may affect the performance of cells. To solve this, choosing an appropriate GD is vital.

Most ceramic coating separators need polymer as the binder, and the coating must be thick enough to get a better thermal and mechanical stability because of the limited adhesion between the layer and the separator. However, this will block the pores and reduce the ionic conductivity of separators and the internal volume of the battery, which results in low energy density. [22] Scientists have now focused on methodologies that can graft ceramic materials onto separators without binder based on these problems. Wonjun Na et al. [23] developed a way of grafting SiO$_2$ nanoparticles (NPs) onto polyethylene separators (PE) that do not need a polymeric binder by activating the surface with UVO, radical grafting, and sol-gel chemistry. (Fig. 2b) They also compare the properties of SiO$_2$-grafted PE separators with SiO$_2$/PVdF-HFP-coated PE separators (19 and 23 µm thick respectively) and bare PE separators. (Tab. 1) The result shows that the SiO$_2$-grafted PE separator is pretty thin with fantastic wettability, ionic conductivities, thermal and mechanical properties, and it functions well in LIBs. Xingtao Qi et al. [24] prepare a polypropylene/mSiO$_2$ separator (PP-g-mSiO$_2$) by creating a covalent grafting interface based on the ring-opening reaction between modified mesoporousSiO$_2$ (mSiO$_2$) and PP separator. (Fig. 2d) PP and PP-SiO$_2$ are used as the control sample. PP-g-mSiO$_2$ shows greater thermal stability with no shrinkage at 170°C compared to PP and PP-SiO$_2$ separators. The decomposition temperature of the PP-g-mSiO$_2$ separator (450°C) is also much higher than that of the PP separator (330°C). PP-g-mSiO$_2$ separator shows great electrolyte wettability, and affinity as the contact angle dates are less than 4° (Fig. 2c). The enhanced wettability is attributed to mesoporous nanoparticles’ high specific surface area, intrinsical hydrophilic, and siphon and capillary effects.

**Table. 1 Property of different separators**

|                  | Gurley number (s/100 cm$^3$) | Water contact angle (°) | Ionic conductivities (mS/cm$^2$) | Thermal shrinkage (120°C, 30min) |
|------------------|------------------------------|-------------------------|---------------------------------|---------------------------------|
| PE               | 160                          | 128                     | 0.63                            | 41.3%                           |
| SiO2/PVdF-HFP-coated PE 1 | 186                          | 118                     | 0.77                            | 23.4%                           |
| SiO2/PVdF-HFP-coated PE 2 | 382                          | 107                     | 0.73                            | 7.6%                            |
| SiO2-grafted PE   | 168                          | 84                      | 0.84                            | 4.2%                            |
Fig. 2 (a) Procedure of preparing PP(s)-g-PPEGMA separator; (b) The fabrication of the PE separator grafted by SiO$_2$; (c) Average contact angle formed from water and electrolyte droplets on the separators with different coatings; (d) Creating covalent grafting interface based on the ring-opening reaction between mSiO$_2$ and PP separator

3.3. Blending

Blending refers to the preparation of the separator by mixing one kind of material with a nice performance that is used as matrix polymer with another or more kinds of polymer with complementary performance. The interaction between different materials offers chances to improve the prosperities of the separators.

Poly(4-methyl-1-pentene) (PMP) was first used to combine with ultra-high molecular weight polyethylene (UHMWPE) by sequential biaxial stretching [25] (Fig. 3a) because of its nice thermal behavior, and it can enhance the electrochemical performance of UHMWPE separator. The result of thermogravimetric analysis (TGA) showed that the decomposition rate at high temperatures slowed down as the content of PMP increased. Besides, porosity and air permeability also increased thanks to DMP (Fig. 3bcd), and this led to electrolyte uptake rising from 134.1% to 259.7% and ionic conductivity increasing from about 0.9 to 1.17 mS cm$^{-1}$. Liao, H. et al. [26] prepared a hydrophilic high-density polyethylene/methylcellulose (HDPE/MC) blend microporous separator through thermally induced phase separation (TIPS) (Fig. 3e). This was the first time that natural polymers and PE were blended. The water contact angle decreased significantly as the content of MC increased (Fig. 3f), which indicated the nice wettability HDPE/MC had. The ionic conductivity reached its highest when the content of MC was 2wt%, at 1.01 mS cm$^{-2}$. Besides, the MC acts as a rigid particle that strengthens the HDPE matrix, which increases tensile strength.

Blending is quite beneficial since it combines the advantages of each component to develop the properties of membranes. However, there is usually a huge difference in physicochemical properties between components, making it vital to choose a suitable solvent. Besides, to prepare high-performance separators, the weight ratio of each component also needs experiments to be decided.
4. Novel Materials for LIB Separators

As mentioned in the previous section, there are several disadvantages of polyolefin materials. Apart from modifying polyolefin materials, researchers are also looking for substitute materials for separators of LIB. Some progress has been made [27]. In this section, a few substitute materials to serve as new types of separators are introduced.

4.1 Polyamide separators

Polyamide is a kind of polymer, which is constructed by repeating units of amide bonds. It has relatively high chemistry and thermal stability, and good solvent resistance. And it has great insulation when it is dry. These properties make it an excellent separator for LIB. Besides, as a substitute polymer material of polyolefin, polyamide has a better affinity for lithium-ion electrolytes because of its polarity groups. [28] In the application as the separator of the lithium-ion batteries, researchers tend to modify polyamide materials or combine them with other materials for better performance.

For instance, Saleh and his colleague [29] insert alumina nanoparticles into polyamide (PA) nanocomposite membrane by situ interfacial polymerization. These particles in the membrane help improve the permeate flux and maintain the salt rejection. And these nanoparticles also enhance the hydrophilicity of the material.

Additionally, polyamide materials are often used in conjunction with other materials to produce a single-ion electrolyte membrane as a separator for LIB. A polyamide single-ion electrolyte membrane was synthesized by Sun et al. [30]. More specifically, it is a bis(sulfonyl)imide incorporated, high-molecular-weight gel single-ion polyamide polymer electrolyte membrane (LiPA) synthesized by using a polycondensation reaction. Then they exchanged the H+ ions with Li+ ions. As a single ion polymer electrolyte membrane, all the bis(sulfonyl)imide anions have refrained in the polymer chains, helping the number of transferred Li+ ions rise and reach 0.88. Besides, the new material provides smooth channels for the transport of Li+. They also found that polyamide could help raise the stability of separators in high temperatures when combined with other materials. Li et al [31] reported a novel electrospun single-ion conducting polymer electrolyte (SIPE), which is consisted of nanoscale mixed...
poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and lithium poly (4,4′-diaminodiphenylsulfone, bis (4-carbonyl benzene sulfonyl) imide) (LiPSI). The material has a much better performance as the separator in LIB than polyolefin materials with better thermal stability, electrolyte wettability and higher porosity. Li/LiFePO4 battery cells using such a SIPE show great rate capacity and excellent electrochemical stability for 1000 cycles. It is an ideal material to serve as the separator in high-energy-density LIB.

4.2 Polybenzoxazole separators

Scientists recently devised a new separator for high power density LIB, called thermally rearranged poly(benzoxazole-co-imide) (TR-PBO) electrospun membrane. It has great nanoporous cavities distribution and extraordinary permeability and selectivity. [32] Besides, it shows excellent thermal stability, chemical resistance and processability. All of these properties make it an outstanding material for lithium-ion battery separators.

M.J. Lee and his colleagues first developed TR-PBO materials [32] in 2015. All of the samples exhibited better rate capability and cycle retention than commercial separators. In the next year, they improved the material. [33] The pristine membranes were coated respectively by spherically shaped hydroxyl copolyimide 1(HP11) and sea-squirt shaped HPI4 nanoparticles. And they are converted into TR-PBO1 and TR-PBO4 nanocomposite membranes through heat treatment. These membranes exhibited excellent wettability of the electrolyte, good pore size distribution and thermal stability. Moreover, both of the membranes showed better cycle retention than the Celgard membrane. These advantages demonstrate that TR-PBO membranes are outstanding candidates for high power density LIB separators.

4.3 Multi-layer separators

With the increasingly enhanced performance of LIB, a single material can no longer satisfy the high performance needed as the separators in cells. Therefore, researchers have been studying composite materials, among which multi-layer materials are becoming increasingly popular. By constructing multi-layer separators, benefits from different materials could be integrated. One of the most common ways to synthesize a multi-layer material is electro-spinning. A special fiber manufacturing process is electrostatic spinning. Polymer solution or melt will be sprayed in a strong electric field in this process. [34]

Cai and his colleague [35] successfully fabricated a PVDF-HFP/PI side-by-side bicomponent electrospun separator with a cross-linked structure for LIB, as shown in Fig.4. This material integrates the outstanding characteristics of PVDF-HFP and PI and improves the material’s mechanical strength by keeping the porosity at a high level. In addition, the composite material shows great thermal
dimensional stability (up to 200°C), good ionic conductivity \((1.78 \times 10^{-3} \text{ S/cm})\), high electrolyte uptake \((483.5 \%)\), wide electrochemical stability window (up to 4.94 V vs. Li+/Li), self-extinguishment and favorable interface structure and other great performances. Besides, the lithium-ion batteries which use this kind of material as the separator emerge good discharge capacity under different discharge C-rate at 45°C. All of the above advantages show that the composite material can serve as the separator in cells. A tri-layered SiO\(_2@\)PI/m-PE/SiO\(_2@\)PI nanofiber composite membrane was reported. [36] In the sandwich-like structure, as shown in Fig.2, two layers of SiO\(_2\) nanoparticles doped polyimide membranes serve as the sheath layers to protect ethylcellulose modified PE membrane, which is the core layer. This tri-layered composite separator integrates thermal runaway function and thermal stability from the core layer at high temperature with the function of thermal shut-down at low temperature and the mechanical stability from the sheath layers, making it an ideal separator for lithium-ion batteries. For better performance, multi-layer materials will be doped with other substances sometimes. Wang and her team [37] modified the PVDF-CTFE material, which could help improve the strength of the composite material. Furthermore, the modified PVDF-CTFE membrane exhibited good synergistic flame retardancy, superior thermal stability, excellent wettability, high ionic conductivity and lower interfacial resistance.

Certainly, there are other ways to fabricate multi-layer materials besides electro-spinning. For instance, Zhen et al. [38] synthesized a non-woven tri-layer membrane featured with double amido functionalized poly (ether ether ketone) outer layers and a poly (methyl methacrylate) interlayer as the separator of the LIB, which shows high thermal stability and wettability with thermal shut-down function.

4.4 Other novel of LIB separators
Undoubtedly, apart from the three kinds of new separators, several other advanced materials have great potential to be processed into separators for LIB, such as non-oxide inorganic compounds, γ-Li\(_3\)PO\(_4\) oxides, garnet-type oxides, NASICON-type oxides, perovskite-type oxides, single crystalline silicon and the like. [39] It is not just that scientists are discovering new materials for separators, they are also building mathematical and physical models to carry on the analytical work towards separators to find better materials theoretically. [40]

As the technique of LIB matures, separators with higher performances are required. The current separators are still facing many problems. An ideal separator should possess great wettability, thermal stability, mechanical strength, high ionic conductivity, and great tortuosity to prevent dendritic lithium growth. And it should be as thin as possible. Nonetheless, it is almost impossible to achieve all these properties simultaneously, so it is essential to balance them and focus on several properties according to
different lithium-ion batteries. [40] In general, there is still much work to be done to generate better separators for the safety and better performance of lithium-ion batteries.

5. Conclusion
Building the relationships between the separator structure and the cell’s electrochemical performance is the basis for preparing high-performance separators and is also the premise of fabricating high energy density and high safety batteries. This paper introduces the main functions and properties of the lithium-ion battery separator and summarizes the commonly used methodologies to modify the separators. There are some limitations. The market demand for separators is gradually increasing, while the existing researches mainly focus on significantly improve the performance of a certain aspect of the separator, but cannot comprehensively and greatly improve the performance. At the same time, some high-performance separators are either expensive or not environmentally friendly to manufacture, which means they are hard to meet the target of marketization. At present, most kinds of separators are universal, which might make it a research focus to develop specific separators for specific batteries.

References
[1] Tarascon, J.M., Armand, M. Issues and challenges facing rechargeable lithium batteries. Nature 414, 359–367 (2001).
[2] Jianjun Z., Zhihong L., Qingshan K., Chuanjian J., Shuping P., Liping Y., Xuejiang W., Jianhua Y., and Guanglei C. ACS Applied Materials & Interfaces 2013 5 (1), 128-134 DOI: 10.1021/am302290n
[3] Scrosati, B. (2000). Recent advances in lithium ion battery materials. Elsevier sci, 45(15–16), 2461–2466.
[4] W. Zhenhua, P. Daichong, S. Kening. Research progress of separator materials for lithium ion batteries[J]. CIESC Journal, 2018, 69(1): 282-294
[5] Lagadec, M.F., Zahn, R. & Wood, V. Characterization and performance evaluation of lithium-ion battery separators. Nat Energy 4, 16–25 (2019). https://doi.org/10.1038/s41560-018-0295-9
[6] Huang, X. Separator technologies for lithium-ion batteries. J Solid State Electrochem 15, 649–662 (2011).
[7] Deimede, V. and Elmasides, C. (2015), Separators for Lithium-Ion Batteries: A Review on the Production Processes and Recent Developments. Energy Technology, 3: 453-468.
[8] Zhang, L., Li, X., Yang, M., & Chen, W. (2021). High-safety separators for lithium-ion batteries and sodium-ion batteries: Advances and perspective, energy storage materials. ScienceDirect, 41, 522–545. https://doi.org/10.1016/j.ensm.2021.06.033
[9] Lee, H., Yanilmaz, M., Toprakci, O., Fu, K., & Zhang, X. (2014). A review of recent developments in membrane separators for rechargeable lithium-ion batteries. Energy Environ. Sci., 7(12), 3857–3886.
[10] Francis, C. F. J., Kyratzis, I. L., Best, A. S., Lithium-Ion Battery Separators for Ionic-Liquid Electrolytes: A Review. Adv. Mater. 2020, 32, 1904205.
[11] Xie, Y., Zou, H., Zhang, H., Xia, R., Liang, D., Shi, P., Dai, S. H. E. N. G., & Wang, H. A. I. H. U. I. (2016). Enhancement on the wettability of lithium battery separator toward nonaqueous electrolytes. ScienceDirect, 503, 25–30.
[12] Francis, C. F. J., Kyratzis, I. L., Best, A. S., Lithium-Ion Battery Separators for Ionic-Liquid Electrolytes: A Review. Adv. Mater. 2020, 32, 1904205.
[13] Ren, D. O. N. G. S. H. E. N. G., Feng, X. U. N. I. N. G., & Liu, L. I. S. H. U. O. (2021). Investigating the relationship between internal short circuit and thermal runaway of lithium-ion batteries under thermal abuse condition. Elsevier Sci., 34, 563–573.
[14] H Wen, J Zhang, J Chai, J Ma, L Yue, & T Dong., et al. (2017). Sustainable and superior heat-resistant alginate non-woven separator of linio.5mn1.5o4/li batteries operated at 55 degrees c.
[15] Song, J., Ryou, M. H., Son, B., Lee, J. N., Dong, J. L., & Yong, M. L., et al. (2012). Copolyimide-coated polyethylene separators for enhanced thermal stability of lithium ion batteries. Electrochimica Acta, 85(none).

[16] Fergus, J. W.. (2010). Ceramic and polymeric solid electrolytes for lithium-ion batteries. Journal of Power Sources, 195(15), 4554-4569.

[17] D. P., C. J., B. P. T., J. S., H. M., C. S., J. Li, et al. (2021). Al2O3/TiO2 coated separators: Roll-to-roll processing and implications for improved battery stability and performance. Journal of Power Sources, volume 507, 0378-7753.

[18] Feng, G., Li, Z., Mi, L., Zheng, J., Feng, X., & Chen, W.. (2018). Polypropylene/hydrophobic-silica-aerogel-composite separator induced enhanced safety and low polarization for lithium-ion batteries. Journal of Power Sources, 376(feb.1), 177-183.

[19] X Mu, X Zhou, Wang, W., Xiao, Y., & Song, L.. (2021). Design of compressible flame retardant grafted porous organic polymer-based separator with high fire safety and good electrochemical properties. Chemical Engineering Journal, 405, 126946.

[20] Lee, J. Y., Yong, M. L., Bhattacharya, B., Nho, Y. C., & Park, J. K.. (2009). Separator grafted with siloxane by electron beam irradiation for lithium secondary batteries. Electrochimica Acta, 54(18), 4312-4315.

[21] Chen, L., Yue, F. S., Zhao, Y. M., Wang, S. S., & Ge, X. C.. (2021). Surface tailoring of polypropylene separators for lithium-ion batteries via n-hydroxyphthalimide catalysis. European Polymer Journal, 152, 110487.

[22] D. Zhou, Y.-B. He, R. Liu, M. Liu, H. Du, B. Li, Q. Cai, Q.-H. Yang, F. Kang In situ synthesis of a hierarchical all-solid-state electrolyte based on nitrile materials for high-performance lithium-ion batteries Adv. Energy Mater., 5 (2015), p. 1500353

[23] Wonjun Na, Ki Hwan Koh, Albert S. Lee, Sangho Cho, Byoeri Ok, Suk-Won Hwang, Jin Hong Lee, Chong Min Koo. (2018). Binder-less chemical grafting of SiO2 nanoparticles onto polyethylene separators for lithium-ion batteries.

[24] Xq, A., Zz, A., Ct, A., Chao, Z. A., Jwa, B. , & Zy, A. . (2020). Covalent grafting interface engineering to prepare highly efficient and stable polypropylene/mesoporous sio 2 separator for li-ion batteries. Applied Surface Science.

[25] J. H., Z. U., R. Yu, M.D., C. Wan, X. Chen, L. Li.Thermally stable and high electrochemical performance ultra-high molecular weight polyethylene/poly(4-methyl-1-pentene) blend film used as Li-ion battery separator, Applied Materials Today, Volume 24, 2352-9407.

[26] Liao, H., Hong, H., Zhang, H., & Li, Z.. (2016). Preparation of hydrophilic polyethylene/methylcellulose blend microporous membranes for separator of lithium-ion batteries. Journal of Membrane Science, 498, 147-157.

[27] Heidari, A. A., & Mahdavi, H. (2020). Recent Development of Polyolefin-Based Microporous Separators for Li–Ion Batteries: A Review. Chem. Rec., 20(6), 570-595.

[28] Palmer, R. J., & Updated by Staff. (2000). Polyamides, plastics. Kirk-Othmer Encyclopedia of Chemical Technology.

[29] Saleh, T. A., & Gupta, V. K.. (2012). Synthesis and characterization of alumina nanoparticles polyamide membrane with enhanced flux rejection performance. Sep. Purif. Technol., 89, 245-251.

[30] Sun, Y., Rohan, R., Cai, W., Wan, X., Pareek, K., Lin, A.,... & Cheng, H. (2014). A Polyamide Single-Ion Electrolyte Membrane for Application in Lithium-Ion Batteries. Energy Technol., 2(8), 698-704.

[31] Li, C., Qin, B., Zhang, Y., Varzi, A., Passerini, S., Wang, J.,... & Cheng, H. (2019). Single-ion conducting electrolyte based on electrospun nanofibers for high-performance lithium batteries. Adv. Energy Mater., 9(10), 1803422.

[32] Lee, M. J., Kim, J. H., Lim, H. S., Lee, S. Y., Yu, H. K., Kim, J. H.,... & Lee, Y. M.. (2015). Highly lithium-ion conductive battery separators from thermally rearranged polybenzoxazole. ChemComm, 51(11), 2068-2071.
[33] Lee, M. J., Hwang, J. K., Kim, J. H., Lim, H. S., Sun, Y. K., Suh, K. D., & Lee, Y. M. (2016). Electrochemical performance of a thermally rearranged polybenzoxazole nanocomposite membrane as a separator for lithium-ion batteries at elevated temperature. J. Power Sources, 305, 259-266.

[34] Wang, H. G., Yuan, S., Ma, D. L., Zhang, X. B., & Yan, J. M. (2015). Electrospun materials for lithium and sodium rechargeable batteries: from structure evolution to electrochemical performance. Energy Environ. Sci., 8(6), 1660-1681.

[35] Cai, M., Yuan, D., Zhang, X., Pu, Y., Liu, X., He, H., ... & Ning, X. (2020). Lithium ion battery separator with improved performance via side-by-side bicomponent electro-spinning of PVDF-HFP/PI followed by 3D thermal cross-linking. J. Power Sources, 461, 228123.

[36] Liu, J., Liu, Y., Yang, W., Ren, Q., Li, F., & Huang, Z. (2018). Lithium ion battery separator with high performance and high safety enabled by tri-layered SiO2@ PI/m-PE/SiO2@ PI nanofiber composite membrane. J. Power Sources, 396, 265-275.

[37] Wang, L., Wang, Z., Sun, Y., Liang, X., & Xiang, H. (2019). Sb2O3 modified PVDF-CTFE electrospun fibrous membrane as a safe lithium-ion battery separator. J. Membr. Sci., 572, 512-519.

[38] Li, Z., Xiong, Y., Sun, S., Zhang, L., Li, S., Liu, X., ... & Xu, S. (2018). Tri-layer non-woven membrane with shut-down property and high robustness as a high-safety lithium ion battery separator. J. Membr. Sci., 565, 50-60.

[39] Jang, J., Oh, J., Jeong, H., Kang, W., & Jo, C. (2020). A review of functional separators for lithium metal battery applications. Materials, 13(20), 4625.

[40] Li, A., Yue, A. C. Y., Wang, W., De Cachinho Cordeiro, I. M., Wang, C., Chen, T. B. Y., ... & Yeoh, G. H. (2021). A Review on Lithium-Ion Battery Separators towards Enhanced Safety Performances and Modelling Approaches. Molecules, 26(2), 478.