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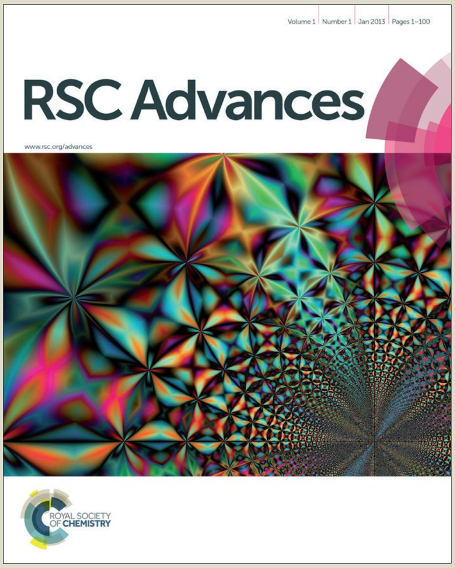

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Progress in Polymeric Separators for Lithium Ion Batteries

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Abstract

This paper reviews the recent developments and the characteristics of polymeric separators used for lithium ion batteries. According to the structure and composition of the separators, they are broadly divided into four types: (1) polyolefin microporous separator, (2) heterochain polymer microporous separator, (3) polymer electrolyte and (4) non-woven separator. Specially, polymer electrolyte was defined as one category of separators for the convenient description in this review, which features intermediate between the two electrodes and possesses transport properties comparable with the separaor in liquid LIB. For each category, the structure, characteristics, modification, and performance of separators are described. Finally, the guidelines for further improvements in this research are outlined.

Contents

1. Introduction

The constant increase in global energy demand together with the awareness on the finite supply of fossil fuels has sparked the need to explore alternative green energy sources (such as solar, wind and geothermal energy). Besides, the increasing pollution due to the growing CO_2 content in the atmosphere has boosted technological efforts to replace combustion-engine car with electric or hybrid vehicles. However, the success of these technology relies on the availability of suitable storage systems such as electrochemical batteries.

Among different varieties of batteries, lithium ion battery (LIB) is one of the vigorous competitors due to its high energy and power density, low self-discharge, and long cycle life. Already, LIBs have been widely used in various portable electronic devices such as cellular phones, laptops, and PDAs. Recently, their applications are further expanding to electric and hybrid vehicles. Basically a LIB consists of four functional components, i.e., the anode, the cathode, the separator and the electrolyte, as illustrated in Fig. 1[1].

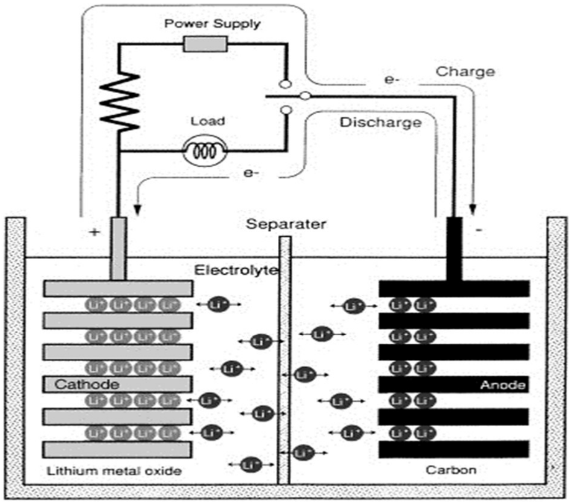

Fig. 1 Schematic illustration of a typical LIB. This figure was edited from Fig. 2 of ref.[1], with permission from Elsevier.

A separator is placed between the anode and the cathode. Its primary function is to prevent physical contact of the electrodes so that free ionics rather than electrons can transport between them[2]. Although, the separator itself does not involve in any cell reactions, its structure and properties considerably influence the interfacial structure and internal resistance of LIB thus making a difference on capacity, polarization, cycle life, and safety. Hence, the fabrication of high-performance separator is eager to develop the overall performance of LIB.

In principle, an ideal LIB separator must satisfy some basic requirements such as electronic insulation, mechanical and dimensional stability, chemical and electrochemical reliability, excellent wettability in liquid electrolyte, and uniform thickness. The detailed description have been extensively discussed elsewhere and are not included in this review[3-5]. However, it’s not easy to achieve all requirements simultaneously. For example, with the reduction of the separator thickness, the battery's energy and power densities increase while its mechanical strength and safety may be deteriorated. Herein, the order of importance of the various requirements varies depending on the application.

2. Types and properties

Based on their structure and composition, we broadly divide polymeric separators into four types: (1) polyolefin microporous separator, (2) heterochain polymer separator, (3) polymer electrolyte, and (4) non-woven separator. In this article we focus on the influence of the material, processing method, and structure on its properties for above separators. In addition, some remarks on the main strength and weakness of each separator as well as future directions are presented. Prior to introducing each system, however, one important concept has still to be clarified. As mentioned earlier, strictly speaking, there are some obviously difference between polymer electrolyte and traditional separator. Polymer electrolyte was defined as one category of separators in this review that features intermediate between the two electrodes and possesses transport properties comparable with the separaor in liquid LIB[6, 7].

2.1 Polyolefin microporous separators

Currently, the commercialized separators are mainly made of polyolefins, including polyethylene (PE) or polypropylene (PP) materials. The dry process and wet process are most widely used method to prepare the polyolefin separators. Generally, separators made by the dry process exhibit distinct slit-pore and straight microstructure, while those made by the wet process show interconnected spherical or elliptical pores. The typical surface morphology of the polyolefin separators made by both processes are displayed in Fig. 2[4]. From the viewpoint of porous structure, separators made by the dry process are more suitable for high power density batteries due to their open and straight-through porous structure, while the tortuous and interconnected porous structure of the wet process separators have more advantages in suppressing the growth of lithium dendritic during long cycle process. The detailed description on the various fabrication processes as well as the relationships between the structure and properties of polyolefin separators have been reported in numerous monographs and reviews[8-10].

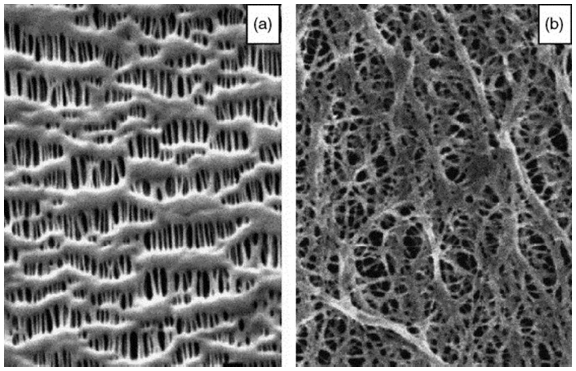

Fig. 2. The surface morphology of polyolefin separators made by (a) dry process and (b) wet process, respectively. This figure was edited from Fig. 3 of ref.[5], with permission from Elsevier.

Although the polyolefin separators are basically reliable for the portable applications, two major drawbacks have been identified. Firstly, due to their inherent hydrophobic and low surface energy, the polyolefin separators show a poor wettability and retention of the liquid electrolyte containing polar solvents such as ethylene carbonate (EC), dimethyl carbonate (DMC), γ-butyrolactone（γ-GBL）and propylene carbonate (PC), etc. Secondly, the polyolefin separators suffer from severe thermal shrinkage at high temperature because of their low melting points. Although they have the feature of thermal shut-down, which can turn the polyolefin separator into a nonporous insulating film around its melting point, the temperature of cell often continues to increase even after shutdown before it actually begin to cool[11]. Thus, the cell may experience an internal short-circuit or even explosion, especially when it is exposed to abuse conditions such as overcharge, crushing or overheating. Hence, the separator with excellent wettability in liquid electrolyte and high thermal stability is highly desired for the high preformance LIB.

Multilayer separator made from PE and PP has been patented as high heat resistance separator, which is a perfect combination providing both the safety assurance and sufficient mechanical strength[12-14]. In a multilayer structure (as shown in Fig. 3) , the low melting PE layer (135 ^{o}C) can act as a thermal fuse and block the pathway of ions when the temperature is close to its melting temperature. At the same time, the higher-melting PP layer (165 ^{o}C) retains its dimensional structure and mechanical strength and thus prevents the short circuit between two electrodes.

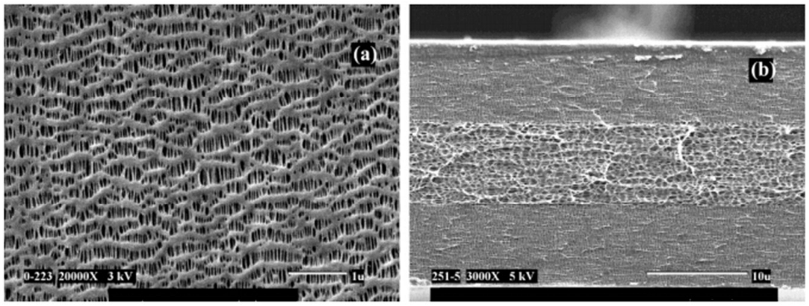

Fig. 3. Scanning electron micrographs of Celgard 2325(PP/PE/PP) separators: (a) surface and (b) cross-section. This figure was edited from Fig. 5 of ref.[14], with permission from American Chemical Society.

In addition, many methods have been attempted in the lab such as surface coating, surface grafting and blending.

2.1.1 Surface coating

Surface coating is widely adopted by the researchers because of its facile operating process. The coating materials are mainly divided into three categories: the functional polar components or gel polymer electrolytes to improve the wettability with liquid electrolyte; the high temperature polymers like polyimide and polyamide to improve the thermal stability; and the inorganic nanoparticles to improve both wettability and thermal stability. The properties of some surface coated polyolefin microporous separators are listed in Table 1.

Table 1 The properties of surface coated polyolefin separators

Polyolefin substrate	Coating materials	Liquid electrolyte	Electrolyte uptake (%)	Ionic conductivity (mS/cm)	Ref.
PE	AN-MMA	$LiClO_4$-EC/DMC	91	1.00	[15]
PE	PVDF-HFP/PMMA	$LiClO_4$-EC/DEC	403	1.69	[16]
PE	PVDF-CAB	$LiPF_6$-EC/EMC	152	2.48	[17]
PE	PDA	$LiPF_6$-DEC/EC/PC	126	0.41	[18]
PP	Catechol/ Polyamine	$LiPF_6$-EC/DMC	270	--	[19]
PE	PVDF	$LiPF_6$-EC/EMC/DMC	--	0.89	[20]
PE	Ethylcellulose (EC)	$LiPF_6$-EC/DMC	--	0.68	[21]
PE	PI (BTDA–TDI/MDI)	$LiPF_6$-EC/DEC	106	0.24	[22]
PE	SiO_2/PMMA	$LiPF_6$-EC/DEC	180	0.74	[23]
PE	Al_2O_3(cPET binder)	$LiPF_6$-EC/DEC	--	--	[24]
PE	Al_2O_3(SBR-CMC binder)	--	82	1.00	[25]
polyolefin	PMOTPA	$LiPF_6$-EC/EMC/ DMC	--	--	[26]
PE	SiO_2/ poly(lithium 4-styrenesulfonte)	$LiPF_6$-EC/DEC	242	0.75	[27]
PP	SiO_2/ Al_2O_3	EC/DEC	120	0.78	[28]
PE	SiO_2/PEI	$LiPF_6$-EC/EMC/DEC	398	0.49	[29]
PE	Al_2O_3/PVDF-HFP	$LiPF_6$-EC/DEC	-	0.53	[30]
PE	DMAET		108	0.29	[31]
PP	Polyamine/ catechol	$LiPF_6$-EC/DMC	270	-	[32]
PP	Tannic-Acid	$LiPF_6$-EC/DMC	125	0.46	[33]

Jeong et al[15] have reported a method to reduce interfacial resistance by coated gellable acrylonitrile (AN)-methyl methacrylate (MMA) copolymer onto the PE separator with a dip coating and followed phase inversion, which can trap large amount of liquid electrolyte and further assist in adhering the electrodes to the separator. Moreover, the cell assembled with this modified separator displayed a stable discharge capacity and an excellent rate performance.

Generally, the coating process produces a new interface between the support separator and coating material, which inevitably compromises the ionic conductivity and the electrochemical kinetics of the modified separator. To modify the interface properties between the support PE separator and coated material, Kim et al[34] have used gamma ray irradiation to treat the PE separator before coating the gel polymer electrolyte (PVDF-12% HFP). Compared to the non-irradiated separator, the electrolyte uptake, the ionic conductivity and cycle performance of the irradiated separator were improved.

Despite the success in achieving in superior wettability in liquid electrolyte, the all-covered gel coating layer usually causes a serious pore blockage and strong resistance for ion transportation, which in turn generates serious negative effects on the ionic conductivity and cycle performances. Park et al[35] have introduced a kind of closely packed poly(methyl methacrylate) (PMMA) nanoparticle arrays onto the surface of PE separator. In contrast to the conventional dense coating layer, the highly ordered nanoporous structure, i.e. well-connected interstitial voids formed between the closely packed PMMA nanoparticles, not only favored liquid electrolyte wettability but also a facile ionic conduction.

Inspired by the outstanding adhering ability of mussel, Ryou et al.[18] have prepared a polydopamine (PDA)-coated PE separator by the facile and "green" dipping process. The PDA coating decreased the contact angle significantly from 108 ° ± 1.4 ° to 39 ° ± 1.7 ° suggesting that the modified PE became more hydrophilic. Afterwards, Wang[19] et al have reduced the manufacturing cost by replacing dopamine with catechol and polyamine binary system.

Among all the standards that need to be satisfied, the safety issue is directly associated with human life and can thus eventually depress the entire market, which is more critical than others. In fact, the temperature-related safety issue is usually related to the dimensional shrinking or melting of the separator[36]. This would result in direct contact and chemical reactions between the strongly oxidative cathode and reductive anode.

To overcome this drawback, remarkable efforts have been taken to improve the thermal stability of the polyolefin separators. Chung et al[11] have coated a cross-linked polymer synthesized from diethylene glycol dimethacrylate (DEGDMA) on PE separator. For the uncoated separator, the reduction in the sample size (shrinking), which started at around 120°C, continued as the temperature increased, and then the sample was completely melted at around 150 °C. On the other hand, the sample coated with polymer synthesized from DEGDMA maintained its original shape until around 150°C.

In addition, a variety of high heat resistance polymers have also been investigated as coating materials[21, 22]. Song et al[22] have coated the PE separator with a co-polymerized polyimide (PI), which is composed of 3,3’,4,4’-benzophenone tetracarboxylic dianhydride having 80% toluene diisocyanate and 20% methylene diphenyl diisocyanate. The shrinkage ratio of the PI coated separator was only 10.0% after heated at 140 ^{o}C, while the bare PE separator shown a significant thermal shrinkage ratio of 83.3% under the same condition.

Many kinds of inorganic nanoparticles such as Al_2O_3[37, 38], SiO_2[31, 39, 40], TiO_2[41] and $BaTiO_3$[42] were directly coated onto the polyolefin separators to enhance their mechanical strength, wettability and thermal stability. Several properties of the inorganic composite separators, especially ionic conductivity are influenced by the type and size of the ceramic particle incorporated. Choi et al[43] have investigated the effects of SiO_2 particle size on the electrochemical performance of inorganic composite separators. In comparison to 530 nm SiO_2 composite separators, the 40 nm SiO_2 system showed a higher porosity and a shorter tortuous path, which could lead to a higher liquid electrolyte uptake and ionic conductivity.

A salient feature of this inorganic nanoparticles coated composite separators is their unusual porous structure, i.e., the interstitial voids formed between the closely-packed nanoparticles are interconnected by a binder. Lee et al[44] have controlled the morphology of coating layer by varying the SiO_2/PVdF-HFP ratio. At low SiO_2/PVdF-HFP ratios, SiO_2

domains in PVdF-HFP matrix with nonporous morphologies developed while PVdF-HFP serves as a binder to interconnect SiO_2 nanoparticles and a highly-percolated interstitial voids are formed between closely packed SiO_2 nanoparticles at high ratios. In comparison, the composite separator with high SiO_2/PVdF-HFP ratio showed a higher ionic conductivity and a superior cell performance.

However, the thick inorganic nanoparticles coated layer inevitably increases the thickness, weight, and decreases the ionic conductivity of the separator although it is helpful to improve the thermal stability[45]. To reduce the thickness of the inorganic layer, Jung et al[46] have employed an atomic layer deposition method to introduce inorganic materials into the pores of the PP separator. By this method, the thermal stability of the PP separator enhanced without any significant change in the thickness.

As the above mentioned inorganic nanoparticles were introduced, the improvement in separator's properties are mainly related to the physical actions without including lithium ion transport process. Kim et al[27, 47] have used a kind of core-shell structured SiO_2 particles containing lithium ions in their shells as the functional fillers. The presence of hydrophilic poly(lithium 4-styrenesulfonate) (PLSS) in the shells of the SiO_2 (Li^+) particles could hold the solvent more effectively, which leads to the enhancement of interfacial stability. For this coated separator, the liquid electrolyte is not only encapsulated in the pores but also retained in the coating layer composed of the SiO_2 (Li^+) particles and P(VdF-co-HFP). As a result, the liquid electrolyte uptake is greater than that of the PE separator. Together with the reason that the lithium ions dissociated from the SiO_2 (Li^+) particles can also contribute to the ionic conductivity, the maximum value of the ionic conductivity of the coated separator can be up to 6.0×10^{-3} $S\cdot cm^{-1}$ at room temperature.

The potential issues related to inorganic nanoparticles coated separators are the increased separator weight due to the introduction of heavy inorganic nanoparticles, particle detachment due to the insufficient binding, and the unknown electrochemical stability of the inorganic nanoparticles and the binder in the high oxidizing and reducing environments encountered in LIB[10]. Additionally, it is troublesome during drying process because that any drying temperature above 100 - 120 °C can cause a permanent morphological change in the polyolefin separator skeleton[48].

Some electroactive redox coating materials such as poly (4-methoxytriphenylamine) (PMOTPA) [26], polytriphenylamine (PTPAn)[49], polydiphenylamine (PDPAn)[50], which can make the microporous separators to effectively shut down during overcharging, have also been coated onto the polyolefin separators. Once the cell overcharged (i.e. the cathode potential exceeds the oxidation potential of the electroactive polymer), the incorporated polymer will be electrochemically p-doped so as to convert it into a conducting state. This in turn produces a current bypass for the charging reaction through the conductive polymer bridge formed between the two electrodes.

2.1.2 Surface grafting

Many practical problems exist during the surface coating process such as uniformity of the coated layer, thickness of the coated layer and adhesive to the substrate, etc. For these reasons, a permanent surface grafting is highly desirable for the surface hydrophilic modification of polyolefin separators, which can immobilise the functional chains, brushes or layers on the separator surface through covalent bonding interaction. Generally, graft polymerization can be carried out by UV-irradiation[51, 52], plasma treatment[53], high energy radiation (γ-rays, ion beams, or electron beams)[54] and so on. The uptake and retention of liquid electrolytes were greatly influenced by the degree of grafting and the type of monomers. Table 2 shows the properties of some of the surface grafted polyolefin microporous separators.

Table 2 The properties of the surface grafted polyolefin separators

Polyolefin materials	Grafting materials	Grafting method	Liquid Electrolyte	Electrolyte Uptake(%)	Ionic conductivity (mS/cm)	Ref.
PE	MMA	electron beam radiation	$LiPF_6$-EC/DMC	210	1.01	[55]
PP	PEG	mussel-inspired dopamine coating	$LiPF_6$-EC/DMC/EMC	145	0.99	[56]
PE	MMA	γ-rays	$LiClO_4$ -EC/DEC	320	2.0	[54]

PE	AN	Plasma-induced pre-irradiation	$LiPF_6$-EC/EMC/DEC	-	1.4	[53]
PP/PE/PP	MMA	electron beam syn-irradiation technique	$LiPF_6$-DMC/ EC	240	1.21	[57]
PE	MMA	surface-initiated ATRP	$LiPF_6$-EC/DMC/DEC	195	1.25	[58]
PE	GMA	electron beam technology	$LiPF_6$-EC/DMC	-	-	[59]
PE	siloxane	electron beam technology	$LiPF_6$-EC/DMC	-	0.7	[60]
PP	AA+DEGDM	electron beam technology	$LiAsF_6$-PC/EC/DME	-	-	[61]
PE	PVDF-HFP/PEGDMA	electron beam technology	$LiClO_4$-EC/DEC	125	0.38	[62]
PE	PMMA	γ-rays	$LiClO_4$-EC/PC	380	1.3	[63]

Gao et al[55] have prepared PE-g-MMA separators with different degrees of grafting (DG) using the electron beam radiation technique. The DG was controlled by varying the total electron dose. But, the electrolyte uptake did not increase linearly on increasing DG. The reason can be explained as follow. At low DG, the separators still retained pore structures. With the increase of DG, the micropores are gradually filled by PMMA and the porosity decreased.

Li et al[57] have introduced a pre-irradiation method to avoid the generation of thick and compact PMMA-grafted layer. In this method, a high energy radiation source was used to chemically activate the ungrafted polyolefin separators before the graft copolymerization process. Compared with the electron beam-induced syn-irradiation technique, this method produced a much looser and spongier grafted PMMA layer, which could apparently reduce the activation time. Moreover, the grafted separator showed a smooth surface morphology and excellent adhesion property toward electrodes, which led to a low interfacial resistance.

In UV-irradiation grafting process, the introduction of photo-initiator would inevitably degrade the electrochemical reactions during battery operation. While, in the high energy radiation-induced graft polymerization, the usual uncontrolled and high energy projectiles such as electrons, ions, and radicals often result in the degradation of polymer backbone (-C-C- bond), the formation of undesirable chemical functionalities, and damage to the target molecules. Even worse, these surface grafting approach usually causes deterioration of separator’s mechanical strength. To bypass those disadvantages, Man et al[64] have developed a hyperthermal hydrogen induced cross-linking (HHIC) technology to graft PEO onto the PP separator. In the HHIC process, the energy-controlled hydrogen projectiles collided with both PEO and PP chains to selectively cleave only the -C-H- bonds. The adjacent carbon radicals generated from the -C-H- bond cleavages would bond themselves, leading to an effective and efficient cross-linking. The PEO layer on the PP separator obtained by HHIC treatment was extremely thin such that the pore size and structure remain intact.

2.1.3 Blending

In surface coating and grafting modifications, the modified sites usually exclude the pores inside the separators due to the limited diffusion ability of the modifying agents into the separator pores. By blending modification, both the surface and inside-pores of the separator have an opportunity to be modified simultaneously[65]. However, to date, studies on the blending modification of polyolefin separators have rarely been investigated.

Shi[65] has successfully prepared hydrophilic PE/poly(ethylene-block-ethylene glycol) (PE-b-PEG) blend separators via thermally-induced phase separation (TIPS) process. It has been found that the incorporated polyether chains greatly enriched in the surface layer and improved the compatibility between separator/liquid electrolyte and the electrodes. Also, such modified separator matrix could absorb liquid electrolyte and swell to some extent showing the characteristics of an “active separator”(as shown in Fig. 4).

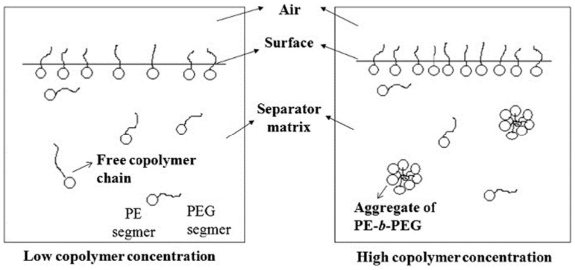

Figure 4 Model of the configurations of PE-b-PEG chains in blend separators with different additive contents. This figure was edited from Fig. 3 of ref.[65], with permission from Elsevier.

2.2 Heterochain polymer microporous separators

To develop the high performance separator with excellent wettability in liquid electrolyte and high heat resistance, various heterochain polymer microporous separators have also been studied such as brominated poly(phenylene oxide) (BPPO) [66], isotactic poly(4-methyl-1-pentene)[67], polyoxymethylene[68], polystyrene (PS)-PP[69] blend, and poly(ethylene terephthalate) (PET)-PP [69] blend polymers.

A series of sponge-like porous polyimide separators have been prepared by Wang et al using a wet phase inversion process[70]. The obtained separators exhibited excellent thermal stability, whose thermal shrinkage was less than 1% after stored at 200 °C. Moreover, due to their high surface polarity and high porosity, the liquid electrolyte uptake can be up to 190 - 378%.

A polyetherimide (PEI) based three dimension heat resistance skeleton has been constructed via vapor induced phase inversion process[71]. This PEI separator can provide a good short circuit protection function, which shown unobvious deformation on the dimension even at 180 °C due to its relatively high heat deflection temperature (210 °C).

Xiao et al[72] have prepared pure PVA microporous separators by the non-solvent induced phase separation (NIPS) process, with notable features, such as the lower thermal shrinkage, the superior electrolyte adsorption/retention capacity and the higher ionic conductivity compared to the commercial PP separator.

2.3 Polymer electrolytes

Because of the high oxidation potential of the metal oxide cathodes in LIB, the cell with the above-mentioned micropore separator may suffer from decomposition reactions of the liquid electrolyte solutions. Therefore, the replacement of the liquid electrolyte with polymer electrolyte would be highly desirable. The motivation and advantages of using polymer electrolyte can be concluded and listed as follows: (1) suppress the growth of lithium dendritic; (2) enhance the endurance to the varying electrode volume during cycle process; (3) avoid the reactivity of liquid electrolytes; (4) improve the security; (5) provide the better shape flexibility and manufacturing integrity [73-75].

The development of polymer electrolytes has gone through three stages: (1) solid polymer electrolytes, the polymer host itself is used as a solid solvent along with lithium salt and does not contain any organic liquids; (2) gel polymer electrolytes, in which organic electrolyte solution is introduced into a polymeric matrix such as PEO[76], PVDF[77-79], and PMMA[80, 81]; (3) composite polymer electrolytes, formed by incorporating inorganic particles into the polymeric matrix.

2.3.1 Solid polymer electrolytes

The study of poly(ethylene oxide) (PEO) containing lithium salt complexes was first reported by Wright's group in 1973[82]. Later, Armand et al. have highlighted the possible applications of these polymer-salt complexes as polymer electrolytes[83]. However, the practical applications of solid polymer electrolytes are hindered by their relatively low ionic conductivity. The ionic conductivity of solid polymer electrolytes, typically less than 10^{-4} S·cm^{-1}, is restricted by chain mobility above their glass transition temperature[84]. Many valuable investigations have therefore focused primarily on the enhancement of the room-temperature conductivity, via various approaches such as blending[85], co-polymerization[86, 87], and cross-linking[88]. All these improvements have been achieved either by lowering the glass-transition temperature or reducing the crystallinity of polymers and some reported polymer electrolytes and their ionic conductivity was listed at Table 3.

Table 3 Some polymer electrolytes and their ionic conductivity

Polymer electrolytes	Lithium salt	Ionic conductivity (S/cm)	Ref.
POSS-PEG/methyl cellulose	$LiClO_4$	1.6×10^{-3}	[89]
HPG-PPEGMA	LiTFSI	1×10^{-4}	[90]
Oligo(ethyleneoxy)cyclotriphosphazenes	$LiN\text{-}(SO_2CF_3)_2$	1.98×10^{-4}	[91]
Oligo(ethyleneoxy)cyclotriphosphazenes	$LiSO_3CF_3$	1.16×10^{-4}	[91]
Poly(oxetane)- polyDDOE	$LiBF_4$	3.7×10^{-5}	[92]
PVA	$LiCF_3SO_3$	-	[93]
P(EO/MEEGE)	LiTFSI	1×10^{-4}	[88]
PMPEA	LiTFSI	10^{-3}	[94]
P(EO/MEEGE)	$LiClO_4$	3.3×10^{-4}	[95]
P(EO/PO)	LiTFSI	2.2×10^{-5}	[96]
TEC	$LiClO_4$	1.5×10^{-4}	[97]
PEP	$LiClO_4$	10^{-4}	[98]
P(EO/MEEGE/AGE)	LiTFSI	-	[99]
PME-GE	$LiClO_4$	10^{-4}	[100]
PEO-PEGEEM-MMA	$LiClO_4$	-	[101]
Siloxy-aluminate polymer	$LiAlH_4$	2.3×10^{-5}	[102]
PLMA-b-POEM	$LiCF_3SO_3$	10^{-5}	[103]
cyanuric chloride/PEO	LiTFSI	3.9×10^{-5}	[104]
PEG-PDMS	LiTFSI	6.7×10^{-4}	[105]

PEO	POSS-phenyl-$(BF_3Li)_3$	4×10^{-4}	[106]
TPEO-MA_9LC_{19}	$LiClO_4$	2.2×10^{-5}	[107]

To improve the mechanical strength of the solid polymer electrolytes, block copolymer electrolytes, containing both well-defined conducting pathways and a sturdy supporting matrix, have been proposed[108]. This class of polymer electrolytes includes Poly(styrene-b-(styrene-g-ethylene oxide)-b-styrene) [109], Poly(styrene-b-oligooxyethylene methacrylate-b-styrene) [110], Poly(styrene trifluoromethanesulfonylimide of lithium-b-ethylene oxide-b-styrene trifluoromethanesulfonylimide of lithium) (P(STFSILi)-PEO-P(STFSILi)) [111] and Poly(ethylene glycol) methyl ether methacrylate-Polystyrene-Poly(ethylene glycol) methyl ether methacrylate (POEM-PS-POEM)[112].

Meador[86] and coworkers have reported a branched PI-PEO copolymer and confirmed the possibility of using it as solid polymer electrolyte for LIB. Therein, the PEO coil phase allowed the high ionic conductivity, while the PI rod phase provided a strong mechanical strength.

Higa et al[87] have prepared a graft copolymer electrolyte consisting of a PI main chain and POEM side chains using atom transfer radical polymerization method. Compared with the solid polymer electrolyte with the PMMA main chain, the tensile strength of this solid polymer electrolyte is about 15 times higher with its ionic conductivity approximately 6.5×10^{-6} S/cm at 25°C.

All the above mentioned solid polymer electrolytes are dual-ion conductors, in which both cation and anion are mobile[113]. The motion of lithium ion is only a small fraction in the overall ionic current, which may lead to a strong concentration gradient and generate internal polarization. To improve the lithium ion transference number of the polymer electrolytes, Bouchet et al[111] have designed a BAB triblock copolymer P(STFSILi)-PEO-P(STFSILi), in which the anions were immobilized by covalently linking to the polymeric backbone such that the lithium ion transference number could approach to 0.85.

Zhu et al[114] have synthesised a novel single-ion conducting polymer electrolyte, lithium polyvinyl alcohol oxalate borate (LiPVAOB), whose monomer is structurally similar to lithium bis(oxalate)borate LiBOB. The obtained polymer electrolyte has shown good electrochemical performance and stable electrochemical window up to 7V (vs. Li^+/Li).

In addition, plastic crystal electrolytes (PCEs) have also been studied in the laboratory, which are prepared by doping lithium salts into a plastic crystalline matrix. Due to the rotational disorder and the existence of vacancies in the lattice, they usually exhibit a fast lithium ion motion[115]. For example, succinonitrile (SN, $NC\text{-}CH_2\text{-}CH_2\text{-}CN$) plastic crystal electrolyte exhibited a high ionic conductivity of more than 10^{-3} $S{\cdot}cm^{-1}$ at room temperature[116].

2.3.2 Gel polymer electrolytes

Gel polymer electrolyte (GPE) has been attractive due to its combined advantages of liquid electrolyte (high ionic conductivity) and solid electrolyte (free of leaking)[73, 117, 118]. Various types of polymers have been selected as the matrix for GPEs such as poly (ethylene oxide) (PEO), polyacrylonitrile (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinyliden Fluoride) (PVDF), polyvinyl butyral (PVB)[119] and polyvinyl formal (PVFM)[120].

Currently, these available homopolymers cannot simultaneously attain the optimal requirements in mechanical strength, ionic conductivity, and electrochemical stability. To overcome these drawbacks to some extent, copolymers formed by cross-linking or copolymerization with different functional monomers have been used as the matrixes of GPE. Some of such copolymers are poly(methyl methacrylateeacrylonitrile) (P(MMA-AN))[121, 122], poly(butyl methacrylateestyrene) (P(BMA-St))[123], poly(methyl methacrylate acrylonitrile vinyl acetate) (P(MMA-AN-VAc))[124, 125] and poly(methyl methacrylate vinyl acetate)-co-poly(ethylene glycol) diacrylate (P(MMA-VAc)-PEGDA)[126]. Costa et al[3] have summarized the developments and main characteristics of PVDF and its copolymers for LIB separators. Being a semi-crystalline polymer, PVDF is hard to swell liquid electrolyte into the polymer matrix. Moreover, the affinity between PVDF and liquid electrolyte is not strong enough to hold the entrapped liquid electrolyte. Thus, various PVDF/copolymer blending systems have been prepared to decrease the crystallinity of PVDF as well as to increase its affinity with the liquid electrolyte, and the “active separator” concept was proposed. Here, the copolymers are mainly amphiphilic copolymers such as P(hexafluorobutyl methacrylate-co-poly(ethylene glycol) methacrylate) (P(HFBMA-co-PEGMA))[77] and P(methyl methacrylate-poly(ethylene glycol) methacrylate) P(MMA-co-PEGMA)[127]. Table 4 shows PVDF-based gel polymer electrolytes and their properties.

Table 4 PVDF-based gel polymer electrolytes and their properties

Gel polymer electrolytes	Liquid Electrolyte	Electrolyte Uptake(%)	Ionic conductivity (mS/cm)	Ref.
PVDF	$LiPF_6$-EC/EMC/DMC	230	1.3	[128]
PVDF-HFP	$LiPF_6$-EC/DEC	-	1.2	[129]
PVDF/ PEO-b-PMMA	$LiClO_4$-EC/PC	211	2.79	[130]
PVDF/PEO-PPO-PEO	$LiPF_6$-DMC/EMC/EC	188	2.94	[131]
PVDF-HFP/PSx-PEO_3	LiTFSI-EC/DMC	520	0.42	[132]
PVdF-TrFE/PEO	$LiPF_6$-EC/DMC	45	2.3	[133]
PVDF/ P(MMA-co-PEGMA)	$LiPF_6$-EC/EMC/DMC	372	3.01	[134]
PVDF/PDMS-g-(PPO-PEO)	$LiPF_6$-EC/EMC/DMC	520	4.5	[135]
PVDF/ PMMA	$LiPF_6$-EC/EMC/DMC	129.3	3.38	[136]
PVDF/PSF	$LiPF_6$-EC/EMC/DMC	129.7	2.03	[137]
PVDF/P(HFBMA-co-PEGMA)	$LiPF_6$-EC/EMC/DMC	387	3.19	[138]
PVDF/PVDF-PEO	$LiClO_4$-EC/PC	387	3.03	[139]

To explain the stability mechanism of liquid electrolyte in PVDF- based blend GPE, Li et al[127] have synthesized a brush-like amphiphilic copolymer P(MMA-co-PEGMA) and blended it into PVDF matrix. They classified the status of electrolyte in GPEs into three phases: filled in pores, swollen in the amorphous phase (swollen phase), and absorbed by the PEG chains which enrich at the separator surface and pore walls (fixed phase), as shown in Fig.5.

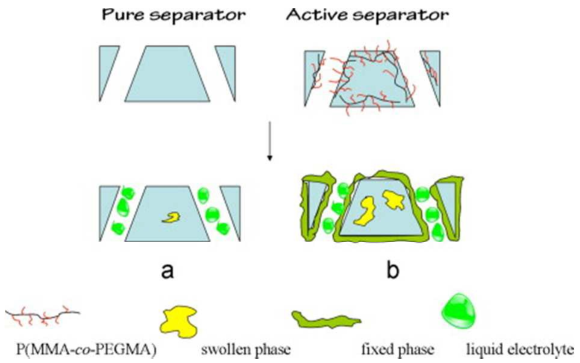

Figure 5. Status of electrolyte in pure and active separators. This figure was edited from Fig. 11 of ref.[127], with permission from Elsevier.

A dense instead of porous gel polymer electrolyte for LIB has been reported by Li et al[140]. Hydroxyethyl cellulose (HEC) has been chosen as the host for this gel polymer electrolyte. The results demonstrated that this dense gel polymer electrolyte can effectively avoid the short circuit of LIB.

Cai et al[141] have used lithiated perfluorinated sulfonic (PFSA-Li) ion-exchange membrane swollen with non-aqueous solvent as the polymer electrolyte for LIB. The results demonstrated that a LIB can be operated by using only ion-exchange membranes as electrolyte with no doped salts.

2.3.3 Composite polymer electrolytes

The high ionic conductivity of GPE is due to the high liquid electrolyte uptake, but it is accompanied by a loss of mechanical strength and increases its reactivity toward the lithium metal anode. It is difficult to combine good conductivity and mechanical properties over a wide temperature range. To improve the ionic conductivity as well as the mechanical properties, one of the simple ways is to form a composite polymer electrolyte by adding some ceramic fillers. These ceramic fillers are believed to kinetically inhibit crystallization from the amorphous state. X-ray and Raman spectroscopy results shown that the effect of fine ceramic fillers can influence the ion aggregation in amorphous polyether electrolytes by promoting ceramic-salt interactions[142].

It has been well established that several parameters influence the electrochemical properties of the composite polymer electrolytes: the nature and content of lithium salt ($LiCF_3SO_3$, $LiClO_4$ and $LiPF_6$), the nature of nanoparticles (TiO_2, SiO_2 and Al_2O_3), the size of nanoparticle, etc. In general, the ceramic fillers for the composite polymer electrolytes are broadly classified into two categories: active and passive. The active component materials such as Li_2N, $LiAl_2O_3$, are involved in conduction process, while the materials such as Al_2O_3, SiO_2, MgO are passive. Raghavan et al[143] have prepared a series of nanocomposite polymer electrolytes comprising nanoparticles of $BaTiO_3$, Al_2O_3 or SiO_2 by electrospinning technique. Among these particle fillers, $BaTiO_3$ gave the best electrochemical performance, which has a significant lewis acid character. The effect of these ferroelectric ceramic fillers appeared to be highly dependent on the nature of the salt used in the PEO-based systems, with $LiClO_4$ showing the most dramatic effects[144]. But in both the cases, the particle size and the characteristics of the ceramic fillers play a vital role on the electrochemical properties of the composite polymer electrolytes. The smaller the size of ceramic fillers, the better they influence the crystallization kinetics of the polymer chains. It also has been proved that the nanosized ceramic fillers showed better compatibility with lithium metal than the micron sized fillers[145]. Table 5 shows the properties of some of the composite polymer electrolytes[146].

Table 5 Properties of some PEO-based composite polymer electrolytes

LiX	Ceramic fillers	Conductivity (S cm^{-1})	Ref.
$LiCF_3SO_3$	γ-$LiAlO_2$	9.0×10^{-4}	[146]
$LiBF_4$	γ-$LiAlO_2$	6.0×10^{-4}	[146]
$LiClO_4$	TiO_2	1.8×10^{-3}	[146]
$LiClO_4$	Al_2O_3	1.1×10^{-3}	[146]
$LiClO_4$	$BaTiO_3$	1×10^{-5}	[42]
$LiCF_3SO_3$	ZrO_2–TiO_2	1.2×10^{-5}	[147]
$LiN(C_2F_5SO_2)_2$	nanochitin	-	[148]
$Li(C_2F_5SO_2)_2N$	$BaTiO_3$	1.5×10^{-5}	[149]
Li-montmorillonit	Li-montmorillonit	1.6×10^{-6}	[150]

Kumar et al[145] have reviewed the state of art of the composite polymer electrolytes based on ionic conductivity, lithium ion transference number and electrode-electrolyte interfacial reactions. Stephan et al[151] have also reviewed various CPE hosts in the view of their electrochemical and physical properties for the applications in LIBs, mainly focusing on PEO, PAN, PMMA, and PVdF.

2.4 Non-woven separators

The non-woven separators are traditionally prepared by wet processes such as the paper-making method[152, 153], the solution extrusion method[154], and the wet-laid method[155] or by a dry processes such as the melt-blown method[156]. In general, these non-woven separators have certain advantages such as relatively low processing cost, high porosity, and lightweight. They are not, however, able to compete with polyolefin separators in LIBs due to the inferiority in their low tensile strength and excessively large pore size[155]. The large-sized pores would cause internal short circuit, overgrowth of lithium dendrite, self-discharge, and further deteriorate the battery cycle performances and safety. For tackling the above mentioned shortcomings, several attempts have been carried out including the incorporation of inorganic powders [157, 158], fibrillated fibers (poly(paraphenylene terephthalamide) (PPTA)) [155], and gel polymer electrolytes[159, 160] into the non-woven separators. Table 6 shows the properties of some non-woven microporous separators.

Table 6 The properties of non-woven microporous separators.

Non-woven matrix	Liquid electrolyte	Electrolyte Uptake(%)	Ionic conductivity (mS/cm)	Ref.
glass-microfiber/PVA-β-CN	LiTFSI-EC/DMC	-	0.89	[161]
PP/PVDF	$LiPF_6$ -EC/DMC	116	0.65	[79]
PP/PVDF-HFP/PMMA	$LiPF_6$ -EC/DMC	212	1.85	[162]
PI/PEG	$LiPF_6$	140	1.45	[163]
PVDF/PEGDA	$LiPF_6$-EC/DMC	-	3.3	[164]
PET/PVDF-HFP	$LiPF_6$-EC/DEC	-	0.86	[2]
PET/PVA-co-PE	$LiPF_6$-EC/DMC	160	0.55	[165]

PE/P(AN-Vac)	$LiPF_6$-DMC/DEC/EC	380	3.8	[166]
TPU/PVDF	$LiClO_4$-EC/PC	342	3.2	[167]
PVDF-PVC	$LiClO_4$-PC/EC	290	2.25	[168]
PVDF-10CTFE	$LiPF_6$ -EC/DMC	800	2.57	[169]
PAN	$LiPF_6$-EC/DEC	-	2.6	[170]
PET	$LiPF_6$-EC/DMC	484	2.27	[171]
SiO_2/PVdF-HFP coated PET	$LiPF_6$-EC/DEC	1.08gcm^{-3}	0.91	[43]
PMMA coated PET	$LiPF_6$-EC/DEC	160	0.96	[172]
SiO_2 coated PET	$LiPF_6$-EC/DEC	-	0.91	[173]
PVDF coated PET	$LiPF_6$-EC/DEC	185	0.81	[174]
PI/PET	LiPF6-EC/DMC/ EMC	200	0.66	[175]
PBT	$LiPF_6$-EC/EMC	-	0.27	[176]
cellulose	$LiPF_6$-EC/DEC		0.77	[177]
cellulose/PSA	$LiPF_6$-EC/DEC	260	1.2	[178]
PI-PEO	$LiPF_6$-EC/PC/DMC/ EA	178	0.65	[159]
Carboxymethyl cellulose	$LiPF_6$-EC/DMC	340	1.75	[179]
PPESK	$LiPF_6$-EC/DMC	1210	3.79	[180]

Degussa has developed a series of *Separion* (a trade name) separator by coating a porous ceramic layer on each side of a flexible perforated non-woven separator as illustrated in Fig. 6. Generally, the ceramic materials can be alumna, silica, zirconia, or their mixture, and their particle size is required to be few nanometers. It is proven that the *Separion* separators have excellent wettability with liquid electrolyte and show negligible shrinkage at high temperatures.

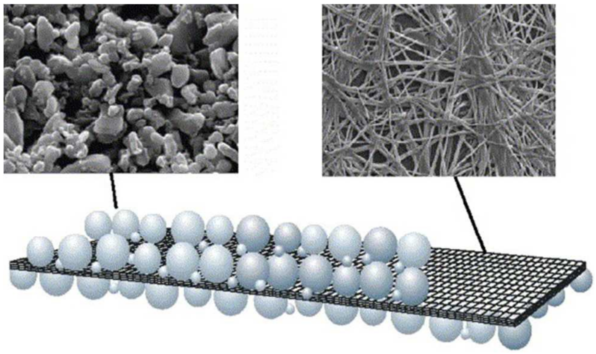

Figure 6. Schematic structure of the Separion separators. This figure was edited from Fig. 6 of ref.[5], with permission from Elsevier

Lee et al[44, 157, 181, 182] have developed various kinds of colloidal particles or inorganic nanoparticles coated non-woven separators. The introduction of poly(methyl methacrylate) (PMMA) colloidal particle arrays on poly(ethylene terephthalate) (PET) non-woven effectively helped to decrease the pore size of non-woven substrate[181]. Meanwhile, due to the well-connected interstitial voids between the PMMA particles and the strong affinity between PMMA and liquid electrolyte, the composite non-woven separator allowed facile ion transport and high electrolyte retention. But they have also been pointed out that the long-term durability of the colloidal particle embedded nonwoven separators still need to be improved[163].

Zhu et al[118] have coated PVDF onto the PP/PE non-woven separators. The surface pore size was effectively minimized from 50 mm to 100 nm by the formation of the PVDF gel layer. However, the PVDF gel has also permeated into the inner space of the non-woven separator that suppress the rapid diffusion of lithium ions. To retain large pores in the interior of the non-woven separator, Shi et al[163] have designed a kind of sandwich-like composite separator, i.e., a crosslinked polyethylene glycol (PEG) skin layer was formed on both sides of the non-woven separator by in-situ polymerization. It was demonstrated that the large pores remaining in the interior of non-woven separators could provide a quick access for the fast transportation of lithium ions, and thus contribute to a superior rate capability.

Among all the preparation methods of non-woven separator, electrospinning has drawn considerable attention due to its capacity to create a fully interconnected pore structure with a large surface area and high porosity. By controlling the processing parameters, the obtained electrospun separators will be endowed with porosities in the range of 30% - 90% and pore sizes in the range of sub-micrometers to a few micrometers[183].

However, the single layer non-woven separator show an insufficient mechanical property (not free-standing) for using it in LIBs. To address this problem, Angulakshmi et al[184] have prepared a PVDF-HFP/PVC/PVDF-HFP trilayer non-woven separator by electrospinning technology. By adding the second PVC and third PVDF-HFP layer to the PVdF non-woven separator, the tensile strength of this trilayer non-woven separator became superior to the commercial Celgard separator. Also, due to the increase of fiber diameter, the formation of inter fiber bonding, and the enhanced crystallinity, a heat treatment can be used to improve the mechanical properties of this electrospun non-woven separator [185].

A polymethylpentene (PMP) non-woven separator has been formed directly on the anode through the electrospinning process by Huang[48]. This PMP separator exhibited a much improved thermal stability and interfacial adhesion between the separator and the deposited electrode compared to the commercial polyolefin separator.

Non-woven separators with heat-resistant engineering polymers such as polyimide (PI)[186-189], polyester (PET)[43, 171, 190], poly(phthalazinone ether sulfone ketone) (PPESK)[180, 191], cellulose[152, 177, 192, 193], poly(m-phenylene isophthalamide) (PMIA)[194, 195], aramid[153] etc., as the matrix have also attracted lot of attention in recent years. These kinds of non-woven separators could still retain dimensional stability and effectively isolate the electrodes, further preventing battery short-circuit and explosion at high temperature. They are proved to be promising separators for high heat-resistance lithium ion batteries.

3. Conclusions and further works

Separator is a critical component in LIB, which is placed between the cathode and the anode to prevent physical contact of the electrodes so as to isolate the electronic flow but enables free ionic transport. Although, the separator itself does not involve in any cell reactions, its structure and properties considerably make a difference in the internal resistance and cycle performances of LIBs.

The polyolefin separators have been the most dominant ones for commercial lithium ion batteries over the decades due to their superior properties such as low cost, electrochemical stability, proper mechanical strength and pore structure. However, all of these properties have not been completely optimized till now. One of the most serious issues is their hydrophobic nature and lower surface energy, which would cause poor compatibility with the liquid electrolyte. Moreover, the polyolefin separators suffer from severe thermal shrinkage at high temperature because of their low melting points. Accordingly, it is important to develop some novel separators for a high performance and safety LIB.

Polyolefin separators have been modified by using various techniques such as surface coating, surface grafting and blending. The modified separators are endowed with certain improved properties such as thermal stability, wettability, and ionic conductivity. Compared to the polyolefin separators, there are two advantages of incorporating inorganic particles. One is the suppression of thermal shrinkage and other is the enhanced liquid electrolyte wettability. However, the increased thickness and weight inevitably reduces the power and energy densities of the corresponding cell.

Solid polymer electrolytes have several advantages over their liquid counter parts such as no leakage of electrolytes, better shape flexibility, and non-combustible reaction products at the electrode surface that exist in the liquid electrolytes. Further, the incorporation of substantial amounts of organic solvents to form a gel polymer electrolyte has effectively improved the ionic conductivity of polymer electrolytes. However, the requirements of high ion conductivity and good mechanical strength were still could not be met simultaneously.

Non-woven separators are now deemed as an important candidate for separators to be used in high power lithium ion batteries due to their low processing cost, high porosity, and lightweight. However, till now, the non-woven separators are mainly used in rechargeable alkaline batteries to date. The application in lithium ion batteries is limited by their low tensile strength and excessively large pore size.

In future, the development of lithium ion battery separators need to balance the performance against the safety and cost. The separators that combine the features of high ionic conductivity and excellent thermal stability are highly desirable for high performance lithium ion batteries. Besides, the high cost of separators is mainly due to their production process. Therefore, developing a more cost-effective process is very important for the reduction of battery separator cost.

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