Review

A review on the separators of liquid electrolyte Li-ion batteries

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Abstract

This paper reviews the separators used in liquid electrolyte Li-ion batteries. According to the structure and composition of the membranes, the battery separators can be broadly divided as three groups: (1) microporous polymer membranes, (2) non-woven fabric mats and (3) inorganic composite membranes. The microporous polymer membranes are characterised by their thinness and thermal shutdown properties. The non-woven mats have high porosity and a low cost, while the composite membranes have excellent wettability and exceptional thermal stability. The manufacture, characteristics, performance and modifications of these separators are introduced and discussed. Among numerous battery separators, the thermal shutdown and ceramic separators are of special importance in enhancing the safety of Li-ion batteries. The former consists of either a polyethylene (PE)–polypropylene (PP) multilayer structure or a PE–PP blend which increases safety by allowing meltdown of the PE to close the ionic conduction pathways at a temperature below that at which thermal runway occurs. Whereas the latter comprises nano-size ceramic materials coated on two sides of a flexible and highly porous non-woven matrix which enhances the safety by retaining extremely stable dimensions even at very high temperatures to prevent the direct contact of the electrodes.
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Keywords: Separator; Microporous membrane; Polyolefin; Non-woven; Thermal shutdown; Safety

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1. Introduction

The separator is a critical component in liquid electrolyte batteries, and is placed between the positive electrode and the negative electrode to prevent physical contact of the electrodes while enabling free ionic transport and isolating electronic flow. It mostly is a microporous layer consisting of either a polymeric membrane or a non-woven fabric mat. Essentially, it must be chemically and electrochemically stable towards the electrolyte and electrode materials, and must be mechanically strong to withstand the high tension during the battery assembly operation. Structurally, the separator should have sufficient porosity to absorb liquid electrolyte for the high ionic conductivity. However, the presence of the separator adds electrical resistance and takes up limited space inside the battery, which adversely affects battery performance. Therefore, selection of an appropriate separator is critical to the battery performance, including energy density, power density, cycle life and safety. For high energy and power densities, the separator is required to be very thin and highly porous while still remaining mechanically strong. For battery safety, the separator should be able to shut the battery down when overheating occurs, such as the occasional short circuit, so that thermal runaway can be avoided. The shutdown function can be obtained through a multilayer design of the separator, in which at least one layer melts to close the pores below the thermal runaway temperature and the other layer provides mechanical strength to prevent physical contact of the electrodes. In this paper, the separators used in non-aqueous liquid electrolyte Li and Li-ion batteries will be reviewed in terms of the separator type, manufacture, function and structural modification.

2. Requirements and characterization

The essential function of a separator is to prevent physical contact of the positive and negative electrodes while permitting free ion flow. The separator itself does not participate in any cell reactions, however, its structure and properties considerably affect the battery performance, including the energy and power densities, cycle life and safety. The requirements for use in rechargeable Li and Li-ion batteries are generally listed below.

2.1. Chemical stability

The separator material must be chemically stable against the electrolyte and electrode materials, especially under the strongly reductive and oxidative environments when the battery is fully charged. Meanwhile, it should not degrade and lose mechanical strength. An easy method to verify chemical stability is by calendar life testing.

2.2. Thickness

A low thickness is required for high energy and power densities. However, this adversely affects the mechanical strength and safety. In the current technologies, 25.4 μm (1 mil) seems to be the standard thickness for consumer rechargeable batteries. In addition, a uniform thickness is critical for long cycle life of the batteries. The thickness can be measured using the T411 om-83 method developed under the auspices of the Technical Association of the Pulp and Paper Industry.

2.3. Porosity

An appropriate porosity is necessary to hold sufficient liquid electrolyte for the ionic conductivity between the electrodes. However, too high porosity will adversely impact the shutdown performance because in this case the pores cannot be closed effectively and the membrane tends to shrink as it melts or softens. The porosity can be measured using liquid or gas absorption methods according to American Society for Testing and Materials (ASTM) D-2873. Typically, the Li-ion battery separators have a porosity of 40%.

2.4. Pore size

The pore size must be smaller than the particle size of the electrode components, including the electrode active materials and the conducting additives. In practical cases, membranes with sub-micron pore sizes have proven adequate to block the penetration of particles since the tortuous structure of the pores assists in blocking the particles from reaching the opposite electrode. The distribution and structure of pores can be analyzed using a Capillary Flow Porometer (Porous Materials Inc.) or scanning electron microscopy based on ASTM 1294 standard. Uniform distribution and a tortuous structure of the pores are both highly desirable since the former ensures a uniform current distribution throughout the separator and the latter suppresses the growth of dendritic lithium.

2.5. Permeability

Separator should not limit the electrical performance of the battery. Typically the presence of a separator increases the effective resistance of the electrolyte by a factor of 4–5. The ratio of the resistance of the separator filled with electrolyte divided by the resistance of the electrolyte alone is called MacMullin number. MacMullin numbers as high as 8 have been used in high power Li-ion batteries. For batteries used in hybrid electric vehicles (HEV) and in power tools, the MacMullin number should be lower for the purpose of safety and a long cycle life. Air permeability can be used indirectly to estimate the MacMullin

number. Air permeability is expressed by a terms of the Gurley value, which is defined as the time required for a specific amount of air to pass through a specific area of the separator under a specific pressure. The Gurley value can be measured according to ASTM D726. When the porosity and thickness of the separators are fixed, the Gurley value reflects the tortuosity of the pores. The separator with uniform permeability is essential for the long cycle life of a battery. Variations in permeability will result in uneven current density distribution, which has been verified as the main reason for the formation of dendrite Li on the negative electrode.

2.6. Mechanical strength

This is characterized in terms of the tensile strength along the machine direction (MD) and the transverse direction (TD) (ASTM D-638), the tear resistance (ASTM D-1004) and the puncture strength (ASTM D-822). All these parameters are described by Young's modulus. The separator must be mechanically strong, especially in the MD, and enough to withstand the tension of the winding operation during battery assembly. The puncture strength is defined as the maximum load required for a given needle to puncture a given separator and it can be measured with a tensile tester. The minimum requirement for the mechanical and puncture strengths is $1000 \, kg \, cm^{-2}$ and 300 g, respectively, for a 25 μm membrane.

2.7. Wettability

The separator should wet easily in the electrolyte and retain the electrolyte permanently. The former facilitates the process of electrolyte filling in battery assembly and the latter increases cycle life of the battery. There is no generally accepted test for separator wettability. However, placing a droplet of electrolyte on the separator and observing whether or not the droplet quickly wicks into the separator is an easy way to indicate sufficient wettability.

2.8. Dimensional stability

The separator should lay flat and not bow or skew when it is laid out and soaked with liquid electrolyte. The separator should remain stable in dimensions over a wide temperature range.

2.9. Thermal shrinkage

When the temperature rises to the softening temperature, the membrane tends to shrink, even if the porosity is very low, because of the difference in the density between the crystalline and amorphous phases of polyolefin materials. For example, the PE can shrink as much as 10% when exposed to a temperature of 120 °C for only 10 min. The thermal shrinkage should be minimized. For the Li-ion battery, the shrinkage is required to be not more than 5% after 60 min at 90 °C.

2.10. Shutdown

In a Li-ion battery, the separator is required to be capable of battery shutdown at the temperature below that at which thermal runaway occurs, and the shutdown should not result in loss of mechanical integrity. Otherwise, the electrodes could come into direct contact and the resulting chemical reactions cause thermal runaway. The shutdown characteristics can be examined by differential scanning calorimetry or by observing the resistance change of the electrolyte-soaked membrane with temperature increase. For the PE–PP bilayer separators used currently in Li-ion batteries, they have ~130 °C shutdown temperature and ~165 °C melting temperature.

2.11. Cost

According to the current material prices and Li-ion technology, the cost of the separator can be over 20% of the total cost of a Li-ion battery. The majority of the separator cost is in the manufacturing process. Therefore, a cost-effective process is necessary for the reduction of separator cost.

Many of the properties above are associated with each other and may be in a trade-off relationship. For example, reducing the separator thickness increases battery energy and power densities, but it inevitably lowers the mechanical strength of the separator. In practical applications, the requirements above should be appropriately weighed among the performance, safety and cost.

3. Type and manufacture of the separators

According to the structure and composition, battery separators can be broadly divided into three types: (1) microporous polymer membranes, (2) non-woven fabric mats and (3) inorganic composite membranes. These three types of separators are, respectively, featured by the thinness, high porosity and excellent thermal stability. Among them, the microporous polyolefin membranes have been most widely used in liquid electrolyte batteries due to their comprehensive advantages of performance, safety and cost [1,2]. These three types of separators are reviewed below with focus on the relationships of the material, process, structure and properties.

3.1. Microporous polymer membrane

Nearly all microporous polymer membranes used in the current Li-ion batteries are based on semi-crystalline polyolefin materials, including polyethylene (PE) [3,4], polypropylene (PP) [5–10] and their blends such as PE–PP [11–14] and high density polyethylene (HDPE)-ultrahigh molecular polyethylene (UHMWPE) [15,16]. The methods for manufacturing the microporous membranes can be divided into dry process and wet process. Both methods include an extrusion step to make thin films and employ one or more orientation steps to impart porosity and increase the tensile strength. Separators made by the dry process generally show a distinct slit-pore and straight microstructure, while those made by the wet process exhibit interconnected spherical or elliptical pores.
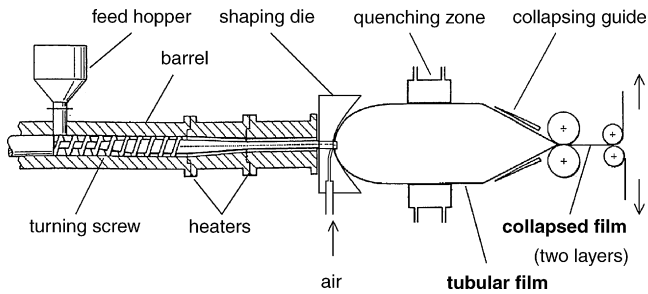
Fig. 1. Schematic chart of a screw extrusion process. Polyolefin pellets are fed from a hopper into the barrel of the extruder, where the pellets are gradually melted by mechanical energy generated by a turning screw and by heaters arranged along the barrel. The molten polymer is forced through a shaping (tubing) die to expand into a balloon shape by a stream of air, which subsequently shapes and quenches into a tubular film, followed by collapsing and drawing forward by rollers to get a collapsed film (two layers), whose two sides are trimmed to obtain two identical films.

The dry process can be generally described as three steps [3,5,7–10,12,13,19–28]: (1) extruding, (2) annealing and (3) stretching. The first step, as shown in Fig. 1, is operated at a temperature higher than the melting point of polymer resins. In this step, the polymer resins are melt-extruded into a uniaxially oriented tubular film or called precursor film, whose morphology and orientation depend on the processing conditions and the characteristics of the polymer resins. Generally, the resulting film is required to have a crystalline row structure with lamellae arranged in rows with their long axis perpendicular to the MD. Such a structure is critical for the formation of micropores because only stacked lamellae are able to "open" in the next stretching process.

The second step is to anneal the extruded precursor film at a temperature slightly lower than the melting point of the polymer. Its purpose is to improve the crystalline structure so as to facilitate the formation of micropores in the subsequent stretching step. Variables of this step include annealing temperature and time. In the third step, the annealed film is deformed along the MD by a process consisting of a cold stretch, a hot stretch and a relaxation. The cold stretch is to create the pore structure by stretching the film at a lower temperature with a faster strain rate, and the hot stretch is to increase the size of the pores by further stretching the film at a higher temperature with a slower strain rate. The relaxation is a heat treatment to reduce internal stresses within the film. The porosity of the final film depends on the morphology of the precursor film, annealing conditions and the stretching ratios/conditions. Both uniaxial [5,10,13,24–26] and biaxial [3,7,8,9,12,20] stretches have been adopted in the third step. In the former, the precursor film is stretched only in the MD, while in the latter the film is stretched in the MD at a lower temperature (70–10 °C, depending on the melting point of polymer), followed by stretching of the film in the TD at a higher temperature (110–140 °C). The tensile strength and its orientation of the final microporous film depend on the ratio of the MD and TD stretches. Both the pore shape and the tensile strength of the uniaxially stretched films are strongly MD-oriented since the film is stretched only in the MD. Significant difference between the MD and TD strengths may result in a splitting problem, i.e. tearing as a result of puncture, which increases difficulties in handling the separators during battery assembly.

Fig. 2 shows the microstructure of a melt extruded HDPE film before and after a uniaxial stretch. Before the stretch, the film shows a stacked lamellar morphology with the lamellae oriented along the TD (Fig. 2a). On stretching, the film is deformed along the MD, during which some of the stacked lamellae separate to form a microporous structure while others remain with their initial morphology. Obviously, the pores formed by a uniaxial stretch are MD-oriented, which is almost perpendicular to the TD (Fig. 2b). As described above, the formation of pores by stretching is based on a lamellae-arranged crystalline structure. Therefore, the dry process is only applicable to the polymers with high crystallinity. Apart from semi-crystalline polyolefins, other polymers such as polyoxymethylene [24,25] and isotactic poly(4-methyl-1-pentene) [26] also have been reported to make microporous membranes. In addition, the dry process also is
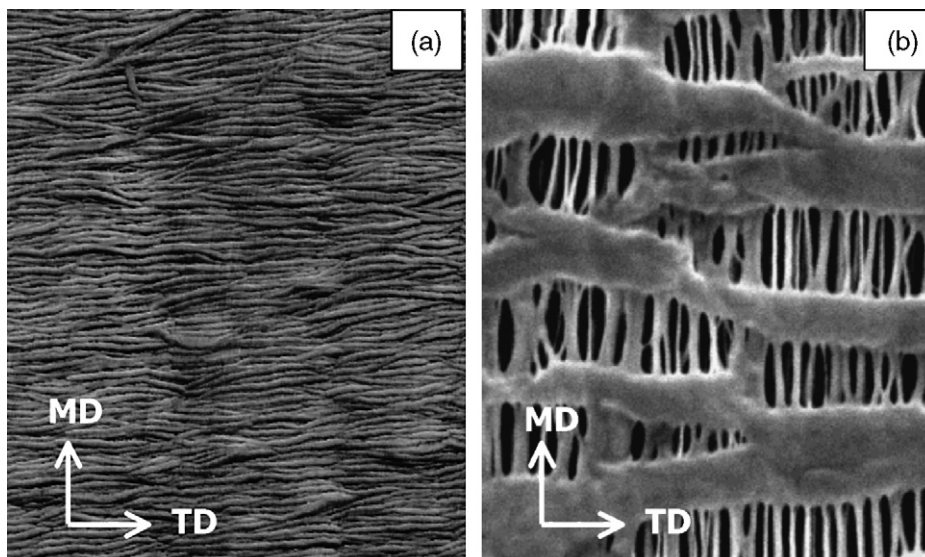

Fig. 2. Microstructure of a uniaxially oriented HDPE film before (a) and after (b) uniaxial stretch.

applicable to the blends of two immiscible polymers, in which at least one polymer has a crystalline structure, such as PE–PP [13], polystyrene (PS)–PP [27] and poly(ethylene terephthalate) (PET)–PP blends [27]. The membranes thus obtained exhibit such microporous structures with two polymer phases interconnected throughout the membrane.

The wet process for the manufacture of microporous PE membranes was reviewed by Weighall [29], and since then, the technology has moved forward [4,6,11,14–17,29–34]. The wet process generally consists of these steps: (1) mixing of polymer resins, paraffin oil, antioxidant and other additives and heating to make a homogenous solution, (2) extruding the heated solution through a sheet die into a gel-like film and (3) extracting the paraffin oil and other additives with a volatile solvent to form the microporous structure. In the second step, the same extrusion process as described in the dry process can be used. In most cases, methylene chloride is used in the last extraction process. The wet process is applicable to both crystalline and amorphous polymers, and its resulting membrane is non-oriented for both pore structure and mechanical strength. For semi-crystalline polymers, a stretching step is often added before or after the extraction in order to achieve high porosity and a large pore size [4,11,15,16]. It has been proven that the membranes produced by the process of stretching after extraction have a much larger pore size and a wider pore-size distribution than those produced by the process of stretching before extraction [16]. Fig. 3 shows a distinct difference in the orientation of the pore structure for two microporous polyolefin membranes made by the dry and wet processes, respectively. In consistence with the pore structure, other physical properties also exhibit a distinct difference between the membranes made by the dry and wet processes. Table 1 summarizes the properties of the microporous polyolefin membranes made by these two different processes. It is obvious that the membranes made by the dry

process distinguish themselves by a high orientation-dependent tensile strength and a low Gurley value. The low Gurley value reflects their less tortuous pore structures. From the viewpoint of microporous structure, the membranes made by the dry process seem to be more suitable for a high power density battery due to their open and straight porous structure, while those made by the wet process are more suitable for a long cycle life battery because of their tortuous and interconnected porous structure that is helpful in suppressing the growth of dendritic Li on the graphite anode during fast charging or low temperature charging.

Most of microporous polyolefin membranes used in Li-ion batteries have a thickness below 50 μm and an average pore size below 1 μm. Typical thickness is 25 μm or even lower with a tendency towards 10 μm for the higher energy density batteries. However, reducing the thickness may raise the safety risk regarding mechanical penetration. Thermal properties of the membranes are dependent on the properties of the polyolefin materials. Membranes made from an HDPE melt at 135 °C and have no mechanical integrity above the melting point. Membranes made by laminating layers of PP and PE have mechanical integrity up to 165 °C (the melting point of PP). An extensive study on the structure–property relations of the microporous polyolefin separators can be found in the work by Venugopal et al. [35].

A thermal shutdown separator has been manufactured based on the difference in the melting point of PE (120–130 °C) and PP (165 °C). The shutdown separators are generally designed as a multilayer structure, in which one or more PE layers serve to shutdown the battery and at least one PP layer as the mechanically dimensional support. Typically, PE–PP bilayer [17,20] and PP–PE–PP trilayer [18,21–23,28,36,37] structures have been widely adopted by many separator manufacturers. With such structures, the PE layer is capable of melting and filling the pores at a temperature lower than thermal runway,
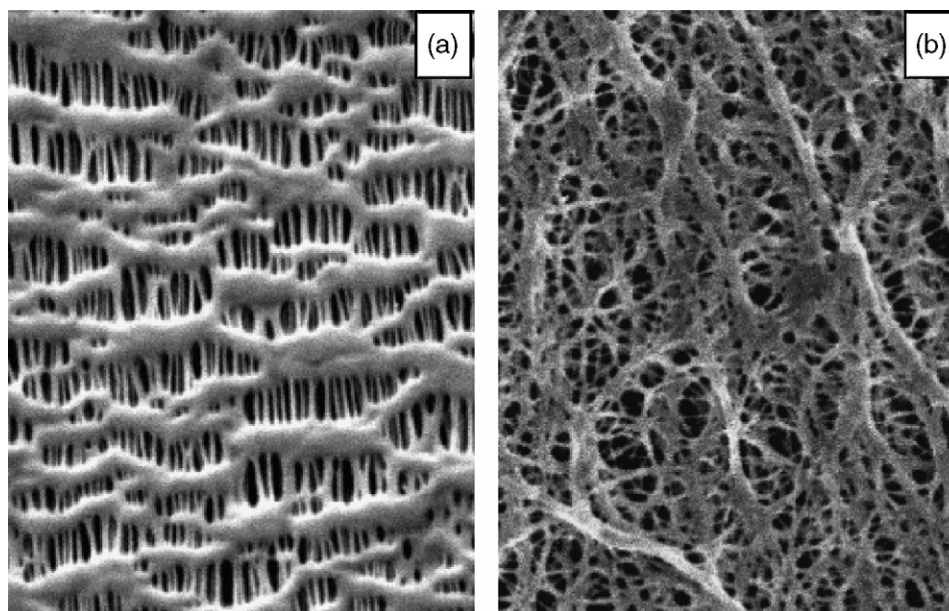

Fig. 3. Microstructure of the microporous polyolefin membranes made by dry process (a) and wet process (b), respectively. This figure was edited from Figs. 4 and 6 of ref. [2], with permission from American Chemical Society.

Table 1
Comparison of the properties of the microporous polyolefin membranes by different processes

Manufacturer	Celgard	Celgard	Exxon Mobil	Exxon Mobil
Membrane name	Celgard 2325	Celgard 2340	Tonen-1	Tonen-2
Process	Dry	Dry	Wet	Wet
Composition	PP–PE–PP	PP–PE–PP	PE	PE
Thickness (μm)	25	38	25	30
Porosity (%)	41	45	36	37
Pore size (μm)	0.09×0.04	0.038×0.9		
Gurley value [a] (s) per 100 cm^3	575	775	650	740
Tensile strength (MD) (kg cm^{-2})	1900	2100	1500	1500
Tensile strength (TD) (kg cm^{-2})	135	130	1300	1200
Melting temperature (°C)	134/166	135/163	135	135
Thermal shrinkage[b] (%)	2.5	5	6.0/4.5[c]	6.0/4.0[c]
Reference	Data sheet	Date sheet	[34]	[34]

[a] Gurley value was based on per gauge (piece of membrane) [34].

[b] The shrinkage was measured at 90 °C for a fixed time for Celgard membranes according to ref. [2] and at 105 °C for 8 h for Tonen membranes [34], respectively.

[c] The numbers show MD and TD shrinkage, respectively.

which, as a result, considerably increases the resistance of the electrolyte layer between the two electrodes to terminate the operation of the battery, while the PP layer still has sufficient mechanical strength to prevent a short circuit between the electrodes. About a 35 °C buffer between the PE shutdown and PP melting may be enough for the protection of most Li-ion batteries. However, it cannot provide protection against serious safety tests, such as nail penetration and overcharge at a high current density, since the local overheating under these conditions can cause separator shrinking or even melting, which results in physical contact between the strongly oxidative cathode and the strongly reductive anode, and the resulting chemical reactions then would lead to thermal runaway. The multilayer separators usually are made by laminating different functional layers together by calendaring, adhesion or welding. Preferably, a cross-plied lamination, where the axis of one ply is angularly biased relative to the axis of another ply, can increase the mechanical strength and puncture resistance. Alternatively, multilayer separators can be made through a co-extrusion processes, in which all the precursor layers are extruded simultaneously and then are annealed and stretched to form a multilayer microporous structure [28,36]. In consideration of the impurities brought in by the resin materials, antioxidants, and other possible additives during extrusion, Kinouchi et al. [37] claimed that dispersing a small amount of metal oxide particles into the two PP layers of the PP–PE–PP trilayer membrane could effectively adsorb these impurities and consequently reduce their negative impact on battery performance. Meanwhile, the presence of the inorganic fillers favors increasing the wettability and retention of the liquid electrolyte.

By the same principle as the solvent extraction, a microporous structures can be formed through a phase inversion or selective solvent evaporation. The phase inversion method [38–43] generally consists of: (1) dissolving the polymer into a good solvent, (2) applying the polymer solution as a thin doping layer and (3) precipitating the polymer to form a porous membrane through solvent exchange between the good solvent in the polymer dope and the non-solvent in a coagulation bath by immersing the polymer dope into a coagulation bath. The selective solvent evaporation or thermally induced liquid–liquid phase separation [44–46] uses a mixture of a good solvent and a non-solvent to dissolve polymer, in which the good solvent is required to be more volatile than the non-solvent. The resulting polymer solution is coated or cast onto a flat substrate to form a thin polymer dope layer, which is left to evaporate the volatile good solution until a porous membrane is formed due to the phase separation and solidification of the polymer. It has been proven that both the methods above lead to an asymmetrical porous structure, depending on many factors such as the properties and concentration of the polymer, the type of the good solvent and the non-solvent, solution temperature, dope thickness and so forth. In most cases, the membranes thus made show an open-pored structure on the top surface (the side facing air), a dense surface on the bottom (the side in contact with the substrate) and a sponge-like layer sandwiched between them, as shown in Fig. 4. Such asymmetric porous structures greatly restrict the application of these membranes as a battery separator due to the concerns that the dense surface blocks electrolyte absorption and the path of ionic conduction. To eliminate this adverse effect, the polymers that are able to swell or dissolve in the liquid electrolytes, such as polyvinylidene fluoride (PVDF) based homo- and co-polymers [41,47], polyacrylonitrile [42], and their related blends [43], have been selected to prepare asymmetric porous membranes because such membranes can be gelled by the liquid electrolyte to form in situ a microporous gel polymer electrolyte inside the batteries [41].

3.2. Non-woven fabric mat

A non-woven separator is a fibrous mat made by bonding numerous fibers together through chemical, physical or mechanical methods. Both natural and synthetic materials have been used to manufacture the fibers for non-woven separators. Natural materials include celluloses and their chemically modified derivatives [48–50]. The synthetic materials include polyolefin [51–56], polyamide (PA) [57,58], polytetrafluoroethylene (PTFE) [59], PVDF [60], polyvinyl chloride (PVC) [60], polyester [61,62] and so forth. The principal bonding methods
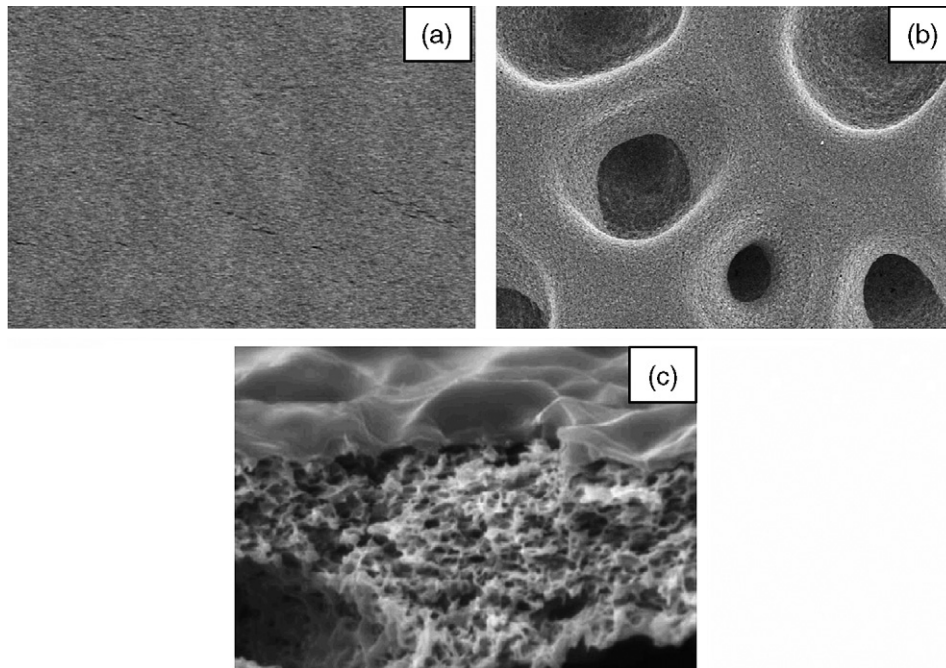
Fig. 4. Typical structures of a microporous membrane made by the phase inversion method. (a) Bottom surface facing the substrate, (b) top surface facing air and (c) cross-sectional view.

for the battery separators are resin bonding and thermoplastic fiber bonding. In the former, the resin as an adhesive is sprayed onto the web of fibers, and then dried, heat-cured and in some instances pressed. In the latter, a fusible (thermoplastic) fiber having a lower melting point than the base fiber as the bonding agent is blended with the base fiber to form a web, followed by pressing between two heated rollers to promote bonding of the thermoplastic fibers and the base fibers. To minimize the adverse effect of foreign adhesives on the battery performance, the thermoplastic bonding method is most preferable for the manufacture of battery separator [53–55,63]. The fibrous webs can formed either by a wet process such as a paper-making process [51,60], a solution extrusion method using a spinning jet [49] and wet-laid method [48,60,61,63] or by a dry process such as a melt blowing method [53,55,56,64]. As an example, the melt blowing process can be described as two steps: (1) forming fabric web and (2) boning of the web. In the first step, both base polymer resin and fusible polymer are molten and blown to form a non-woven fabric web. In the second step, the resulting web is thermally bonded by calendaring it at a temperature higher than the melting point of the fusible polymer to form a non-woven mat with sufficiently high mechanical strength. Beside the polymers and their composition, the blowing conditions such as temperature, spinning speed and the parameters of the fiber-forming die greatly affect the properties of the final non-woven mats. In order to reduce thickness while still remaining good mechanical strength, an electrospinning method has been adopted to prepare the highly porous non-woven separators by applying a high voltage between the solution capillary jet and the membrane-collecting substrate [65,66]. By optimizing the correlation among the polymer concentration, deposition distance, applied electric field strength, feed rate of the solution,

Kim et al. [66] successfully made a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP) membrane composed of fibers with an average diameter of 0.5–2.3 μm, a thickness of 30 μm and a porosity of 68–82%.

Non-woven separators are featured by a high porosity (60–80%) and a large pore size (20–50 μm). Fig. 5 shows the microstructure of typical non-woven mats made by different process and used in exploratory research for a Li-ion battery separator. Their structures are featured by the labyrinth-like pores, which are very helpful in preventing the growth of dendritic Li in rechargeable Li and Li-ion batteries. These separators generally have a thickness of 100–200 μm and a base density of 9–30 g cm^{-2}. In an effort to reduce the thickness, recent technology has made it possible to produce non-woven mats with a thickness of 20 μm or less [61]. The diameter of the fibers is a critical parameter to determine the evenness of the non-woven surfaces, and must not exceed 5 μm. When the fiber diameters are in the range of the non-woven thickness, the thickness only allows one layer of fibers. Such a structure might result in the presence of locally "open" areas when two or more of fibers are neighbored, so that the separator cannot effectively prevent a short circuit between the two electrodes. Except for a few exploratory investigations by Kuribayashi [67], the non-woven separators are mainly used in rechargeable alkaline batteries such as nickel–cadmium and nickel–metal–hydride batteries. They have not been used in Li-ion batteries mainly because their "open" structure and the rough surface cannot effectively prevent short circuits unless their thickness is increased to at least 6 mils at a considerable expense to the battery energy density.

In Li-ion batteries, the non-woven mats are mainly used as the supporting framework to make gel polymer electrolyte (GPE) batteries. Due to the high porosity and large pore size of
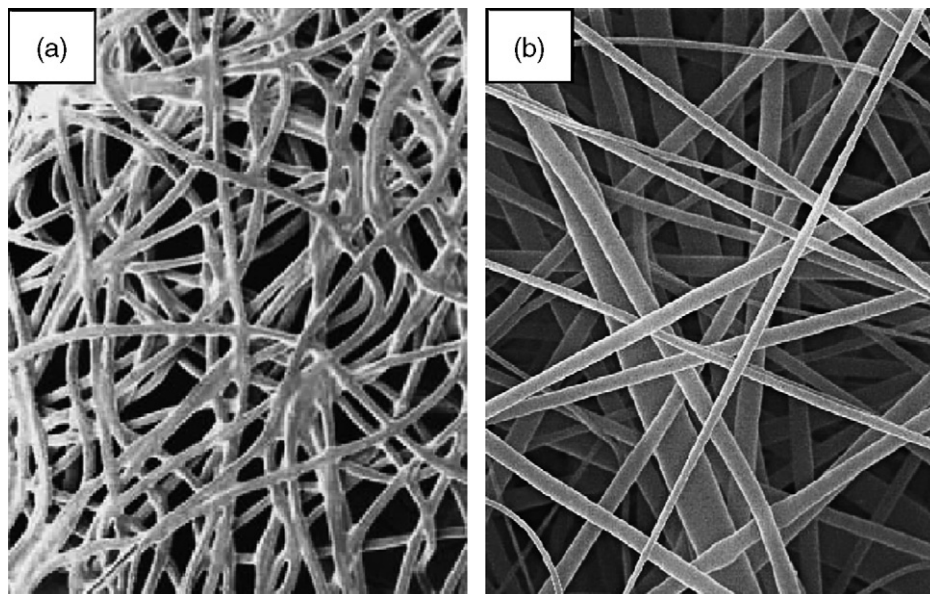
Fig. 5. Microstructure of the non-woven mats made by: (a) wet-laid method and (b) electrospinning method, respectively.

non-woven separators, the GPE can be readily impregnated into the non-woven separator and fill up the uneven surface. Thus, the non-woven nature serves as the mechanical support while the GPE provides the necessary ionic conductivity between the electrodes. Based on this concept, Song et al. [68] impregnated a blend of polyethylene glycol diacrylate (PEGDA), PVDF and poly(methyl methacrylate) (PMMA) into a 85 μm PET non-woven by ultraviolet (UV) cross-linking method. Beside the improved mechanical strength and surface integrity, they found that the resulting separator exhibited a very stable conductivity and liquid electrolyte retention at high temperatures, as compared with the untreated gel polymer electrolyte. More simply, Pekala and Khavari [52] employed a continuous coating machine to pass a porous UHMWPE non-woven mat having a thickness of 18 ± 0.5 μm through a hot PVDF solution bath. Due to the reduced viscosity of the hot polymer solution, the polymer (PVDF) not only coated on the surface, but also was impregnated into the web. Such a structure improved the overall permeability of the liquid electrolyte and resulted in a reduction of the time required to achieve a uniform electrolyte distribution throughout the separator. In order to increase the permeability of the liquid electrolyte through the polymer coating layer, Lee et al. [69] coated a microporous PVDF layer on the rough surface of a 20 μm PE non-woven mat by the phase inversion method. Thus, the PE non-woven matrix imparted mechanical strength and a thermal shutdown property to the separator, while the PVDF layer provided a hydrophilic ionic conducting phase. Their results showed a good improvement in the capacity retention of the Li-ion cells using such separators. In their continued efforts [70], they applied a poly(vinyl acetate) (PVAc) to the surface of the PVDF-coated separator and found that the additional PVAc layer resulted in a small increase of the ionic conductivity, as compared to the bare separator. Due to the increased evenness of the separator surface and the improved adhesion of the separator to the electrodes, the Li-ion

cells using such separators presented a lower resistance and a higher capacity than those using bare separators. Microporous structure of the surface coatings also can be created by a method of removing the plasticizer [71]. In this method, an acetone solution of PVDF and diethylsuccinate (as a plasticizer) was spread onto the surfaces of a porous non-woven mat. Upon evaporation of acetone, the plasticizer-contained separator was laminated with the electrodes, and the resulting cell stack was heated under vacuum to remove the residual placticizer, which in turn created a "dry" cell stack with highly porous structure.

Aiming at increased safety and cycle life of the polymer battery, Kritzer [61] proposed polyester non-woven as the mechanical supporting matrix. The suggested non-woven matrixes are made using the conventional wet-laid method, and they have a thickness of below 20 μm, a porosity of 55–65%, a pore size of 20–30 μm, and an average fabric diameter of 3–4 μm. Due to the high melting point of polyester, such non-woven matrixes can tolerate temperatures up to 180 °C with very low shrinkage. Furthermore, the homogeneous and labyrinth-like non-woven structures offer an increased safety and cycle life in relation to the formation of Li dendrite because such structures can more effectively prevent the growth of dendrite Li.

3.3. Inorganic composite separator

An inorganic composite separator, or "ceramic separator", is a porous mat made of ultrafine inorganic particles bonded using a small amount of binder. Due to the high hydrophilicity and high surface of the small inorganic particles, such separators exhibit exceptional wettability with all non-aqueous liquid electrolytes, especially those containing a high content of cyclic carbonate solvents such as ethylene carbonate (EC), propylene carbonate (PC) and γ-butyrolactone (GBL), which have a high dielectric constant and are known to be unable to wet the

non-polar polyolefin separators. Meanwhile, these separators have extreme thermal stability and show zero-dimensional shrinkage at high temperatures. The outstanding wettability allows one to use a high content of PC and EC in the liquid electrolytes, which is very helpful to increase the cycleability of the Li-ion batteries at high temperatures, while the extreme thermal stability offers the batteries excellent temperature tolerance, which is critical to large-size Li-ion batteries. In fact, temperature-related safety issues are mostly related to the dimensional shrinking or melting of the separator. Both shrinking and melting of the separator could result in physical contact of the electrodes so that direct chemical reactions between the strongly oxidative cathode material and the strongly reductive anode material occur, and the generated heat causes thermal runaway. Therefore, the inorganic composite separators with excellent wettability and zero shrinkage are highly desirable for the development of large-size Li-ion batteries, especially these for hybrid electric vehicles and power tools.

Early reports about the composite separators were given by Prosini et al. who dispersed metal oxides powders (γ-LiAlO$_2$, Al$_2$O$_3$, MgO, respectively) into a PVdF–HFP solution in a 1:2 (w/w) ratio of the inorganic filler to polymer, and spread the resulting suspension over a glass substrate to obtain a free-standing and intrinsically porous film with a thickness of 30–50 μm [72]. They examined the resultant separators using Li half-cells of LiMn$_2$O$_4$ and MCMB, respectively, and found that the performance of such separators depended on the type of inorganic fillers. Among the separators made of these three fillers, the one made of MgO showed the best capacity retention. Since the solution method used by Prosini et al. [72] resulted in the formation of a dense polymer phase, which inevitably increased the difficulty in filling with electrolyte, especially when the content of the polymer is high. To solve this problem, Kim et al. [73] adopted a phase inversion method to make a TiO$_2$/PVDF–HFP composite separator. Due to the formation of a highly porous polymer phase, the membranes thus obtained not only facilitated the electrolyte filling process, but also were superior in electrochemical properties, such as ionic conductivity and interfacial stability with a Li electrode. Regarding the composition–property correlation of the membranes, Takemura et al. [74] systematically studied the impact of particle size and the powder–binder (P/B) ratio on the Al$_2$O$_3$–PVDF composite. It was shown that the pore size of the composite membrane was nearly equal to the powder particle size, and that the small powder particle size and high P/B ratio favored increasing electrolyte retention in the membrane pores and air permeability through the membrane. For example, a Li-ion cell using a 0.01 μm powder membrane exhibited almost the same capacity retention as that using a PE separator. On the other hand, aiming at reducing the acid-induced dissolution of LiMn$_2$O$_4$ active materials, Zhang et al. [75,76] proposed alkali CaCO$_3$ power as the main component of the composite separator so that the acidic products formed due to the hydrolysis of LiPF$_6$ can be neutralized in situ. They adopted the thermal pressing (calendaring) method to make a freestanding and flexible porous membrane by using 2–8 wt.% of Teflon as the binder. The obtained separators were wetted with a 1.0 M LiPF$_6$ 3:7 (w/w) EC/ethylmethyl carbon-

ate (EMC) electrolyte, and their ionic conductivities at 20 °C were measured to be 2.5–4 mS cm^{-1} (depending on the content of Teflon) versus 3.4 S cm^{-1} of the Celgard membrane. They also found that the cells using alkali CaCO$_3$ composite separator showed better capacity retention, as compared with the one using Celgard membrane. They attributed such an improvement to the removal of acidic impurities such as HF by the alkali CaCO$_3$.

The small solid particles tend to aggregate and theoretically the thickness of the composite separators cannot be less than the diameter of the aggregated particles. To reduce the thickness of the composite separators, Carlson et al. [77] used a sol–gel method, which allows the making of less than 10 μm thick membranes. In their method, a water suspension of a Boehmite sol and polyvinyl alcohol in a 10:1 solid weight ratio was prepared and then coated onto a PET sheet, followed by drying at 130 °C to obtain a composite film, which was subsequently soaked in a water–isopropanol solution to delaminate the film. They claimed that the thickness of the membranes could be easily controlled by multiple coating and drying processes. Since each coating led to a 12.5 μm thick membrane, a 25 μm membrane could be obtained by a second coating after the first coating was dry. The apparent porosity of such membranes was measured to be 65% versus 48% of Celgard 2500 membrane when the same measuring method was used.

Although the composite separators described above offer excellent wettability and extremely thermal stability, they are not mechanically strong enough to withstand handling in cell winding and assembly. To solve this problem, Degussa developed a series of Separion (a trade name) separator by combining the characteristics of polymeric non-woven and ceramic materials [78–82]. The Separion separator is a flexible perforated non-woven mat coated with a porous ceramic layer on its each side, as illustrated in Fig. 6. The pore size of Separion separator can be selectively set by an appropriate choice of the ceramic materials. Generally, the ceramic materials used in these separators are alumna, silica, zirconia, or their mixture, and their particle size is required to be of nano-size. To keep the excellent hydrophilic properties of the ceramic materials, an inorganic binder is highly recommended for the production of such separators. As an example [82], the inorganic binder sol can be prepared by hydrolyzing a mixture of tetraethoxysilane, methyltriethoxysilane and (3-glycidyloxypropyl) trimethoxysilane in the presence of HCl aqueous solution. The resulting sol was used to suspend aluminum oxide powders, and then the homogenized suspension was coated on a porous non-woven PET, followed by drying at 200 °C to obtain the separator. This method resulted in a separator having an average pore size of 0.08 μm, a thickness of about 24 μm and a Gurley value of about 65 s, and the separator thus made was thermally stable up to 210 °C, which is limited by the melting point of PET non-woven matrix. Typical physical properties of the Separion and Celgard membranes are summarized in Table 2, which clearly shows that the Separion separators have excellent wettability, high permeability (i.e. low Gurley value), a high meltdown temperature and negligible shrinkage at high temperatures. Remarkable improvements of the Separion separators on the battery safety have been demonstrated by a
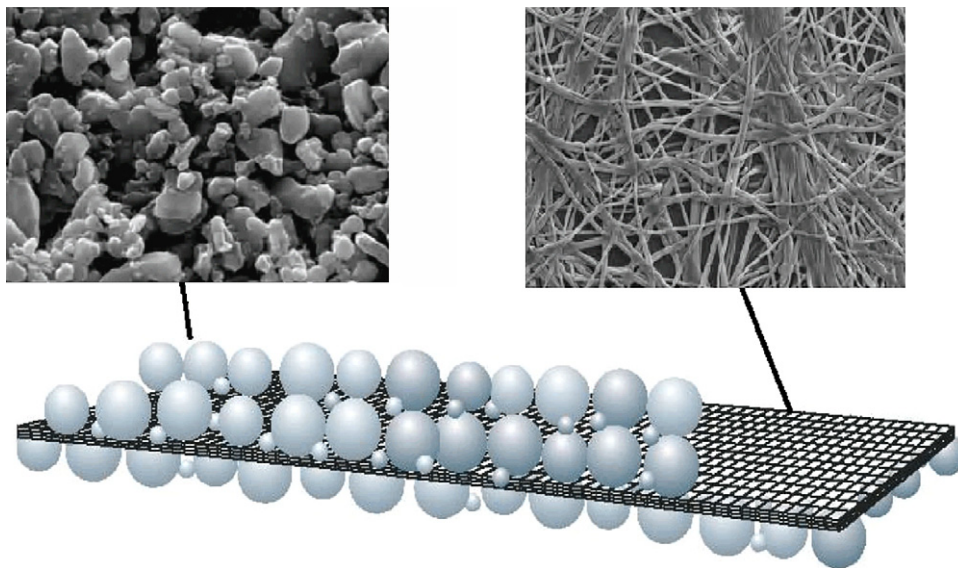
Fig. 6. Schematic structure of the Separion separators. This figure was redrawn based on Fig. 1 of ref. [78] and product brochure of Separion separators.

Table 2
Comparison of the properties of the Separion and Celgard separators[a]

Trade name	Separion	Separion	Celgard	Celgard
Separator brand	S240-P25	S240-P35	Celgard 2340	Celgard 2500
Composition	Al_2O_3/SiO_2	Al_2O_3/SiO_2	PP–PE–PP	PP
Support matrix	PET non-woven	PET non-woven	N/A	N/A
Thickness (μm)	25 ± 3	25 ± 3	38	25
Average pore size (μm)	0.24	0.45	0.038×0.90	0.209×0.054
Gurley value[b] (s)	10–20	5–10	31	9
Porosity (%)	>40	>45	45	55
Temperature stability (°C)	210	210	135/163	163
Thermal shrinkage[c] (%)	<1	<1	5	3
Tensile strength (MD)[d]	>3 N cm^{-1}	>3 N cm^{-1}	2100 kg cm^{-2}	1200 kg cm^{-2}
Tensile strength (TD)			100 kg cm^{-2}	115 kg cm^{-2}
Wettability for PC, EC, GBL	Excellent	Excellent	Not wet	Good

[a] The data were cited directly from the product brochures.

[b] Gurley value was expressed as the time in seconds required to pass 100 ml of air through 6.45 cm^2 (1 in.^{2}) of membrane under a pressure of 31.0 cm (12.2 in.) of water.

[c] Separion shows a value measured at 200 °C for 24 h, while Celgard a value measured at 90 °C for a fixed time according to ref. [2].

[d] Different units were used to express tensile strength by two companies.

series of abuse tests [80,81]. During a hot oven test on the 1.1 Ah Li-ion pouch cells by heating the cells at 5 °C min^{-1} to 150 °C and holding at 150 °C for 30 min, the cells with Separion separators had no change while the cells with PE separators showed numbers of short circuit voltage peaks as a result of the shrinkage of the separator [80]. In a nail penetration test on the 8 Ah Li-ion pouch cells, it was shown that the maximum temperature of the cell using Separion separators was only 58 °C with a weight loss of 0.4% after nail penetration test, while that of the control cell using PE separators reached over 500 °C with a weight loss as high as 56.1% [81]. Since the maximum temperature (58 °C) in the nail penetration test is far from the melting point of the PE materials, one may assume that the exceptional safety behavior of the Separion separator is more related to the nano-size ceramic materials, instead of the PET non-woven matrix. Therefore, a composite separator that combines both character-

istics of the thermal shutdown and ceramic zero-shrinkage could be made by replacing PET matrix with a highly porous PE non-woven matrix if the Separion separators can be produced at the temperature below the softening temperature of the PE.

4. Property improvement of the separators

4.1. Surface modification

Due to the inherent hydrophobic properties of non-polar polyolefin separators, the electrolytes containing a high content of polar solvents, such as EC, PC, GBL, etc., exhibit a poor wettability and electrolyte retention. In this case, surface modification is necessary to make the polyolefin separators hydrophilic [83]. The modification either treats the separator with a wetting agent (mostly a surfactant) [84,85] or grafts hydrophilic functional

groups onto the surface and pore wells of the separators [86–93]. The use of a surfactant generally improves wettability, but it is unable to increase electrolyte retention. To increase the electrolyte retention, Taskier [84] combined a surfactant and a hydrophilic polymer (cellulose acetate) together to treat the polyolefin membranes. He found that the membrane thus treated exhibited much better wettability and electrolyte retention. In general, the surfactant treatment only makes the membrane hydrophilic temporarily since the surfactant is subjected to washing away by the liquid electrolyte upon cycling or storage. Therefore, permanent grafting of hydrophilic functional groups is preferable for the modification of the polyolefin membranes. Physically, the hydrophilic groups can be grafted onto polyolefin membranes by a means of plasma treatment, which usually is carried out between two electrode plates and applied with a radio-frequency field in a gas atmosphere [87,94]. By selecting the appropriate gas, the hydrophilic groups of hydroxyl, carbonyl, carboxyl, amino, imino, sulfonyl, etc., can be grafted. Chemically, the polyolefin membranes can be modified through sulfonation, fluorination and grafting polymerization. The sulfonation [94,95] has been used mainly for the treatment of these membranes used in aqueous alkali batteries. An additional benefit of the sulfonated membranes is that the introduced sulfonic groups are able to trap unwanted ammonia, which is present in NiMH batteries and has been identified to be the main source of self-discharge [94,95]. Due to the extreme reactivity of fluoride gas, fluorination can be carried out by exposing directly the membrane to fluorine gas for a short time [53]. The grafting polymerization can be initiated by high-energy radiation [86,89–93] and UV-irradiation [88], respectively. In the former, the polyolefin is radiation-induced to cleave the C−C or C−H bonds to generate polymeric radicals and the resulting polymeric radicals subsequently initiate the hydrophilic monomer to polymerize. In the latter, a photo-initiator should be used to increase the sensitivity of the polymer to UV-irradiation, and with the aid of the photo-initiator the monomer polymerizes and grafts onto the membrane surface. In these efforts, Senyarich and Viaud [88] developed a device that allowed the UV-induced grafting process to be operated continuously. In their method, the polyolefin membrane was first passed through a solution bath containing the monomer and photo-initiator, and then the wetted membrane was moved into a UV-chamber where the polymerization was initiated by the UV-irradiation. According to the chemical structure, the monomers bearing carboxylic acid, such as acrylic acid [86,88–91] and methacrylic acid [90], are suitable for the treatment of the membranes used in aqueous electrolyte batteries, while the monomers being polar but aprotic such as glycidyl methacrylate [92] and methylmethacrylate [93] are suitable for those used in non-aqueous electrolyte batteries. In both cases, the uptake and retention of the liquid electrolytes are affected by the degree of grafting and the type of monomer.

4.2. Surface polymer coating

Compact contact of the separator and electrodes is critical to the long-term reliable performance of a rechargeable battery. Even a small failure at the interface can give rise to a significantly uneven current distribution due to the high contact resistance in failure areas, which can cause the formation of dendritic Li on the negative electrode and further can contribute to an increase in battery impedance. To improve the interfacial contact, a thin polymer layer that can be gelled by the liquid electrolyte has been proposed to coat the surfaces of the microporous membranes [96–99]. The polymers that are suitable for this purpose include PEO [96,97], PVDF and its related copolymers such as PVDF–HFP [98,99]. Upon gelling with the liquid electrolyte, the polymer becomes a gel electrolyte and it in turn serves as an adhesive to bond the separator and electrodes together, which meanwhile increases uptake and retention of the liquid electrolyte. In practical processes, the polymer coating can be applied to the microporous membrane by a means of dipping or spraying. A heating step is required to promote the in situ formation of the gel polymer electrolyte when the polymer-coated membranes are used as the separator.

A negative effect of the approaches above is that the polymer layer made by the solution method is structurally dense, which inevitably blocks the penetration of liquid electrolyte into the pores of the microporous membrane. Therefore, the polymer layer with a porous structure is highly desirable so as to facilitate the electrolyte filling process. In such efforts, Jeong and Kim [100] employed a phase inversion method to replace the solvent evaporation step to form the microporous polymer layer. In their method, they first applied a dilute dimethylformamide (DMF) solution of acrylonitrile–methyl methacrylate copolymer (AMMA, AN:MMA = 84:16) to the micropouous PE membrane with a thickness of 25 μm and a porosity of 40%, and then immersed the coated PE membrane into a water bath to induce phase inversion. Due to the fast solvent exchange between the good solvent (DMF) in the polymer solution and non-solvent (water), the polymer layer with highly microporous structure is formed. They found that a Li-ion cell using the separator with a 14 μm polymer coating layer exhibited a very stable capacity retention and excellent rate performance, which is attributed to the strong bonding between the separator and electrodes. Based on the work above, Kim et al. [101] introduced different amounts of an inorganic filler, SiO_2, into the polymer coating layer, and they found that the presence of hydrophilic SiO_2 significantly reduced the contact angle of the liquid electrolyte and accelerated the wetting of electrolyte to the separator. As a result of the improved interfacial characteristic, the Li-ion cell using such a separator exhibited excellent capacity retention and rate performance. As a comparison, Fig. 7 exhibits the surface images of a microporous PE membrane before and after the polymer coating by different methods. The differences in the surface morphology of the polymer layers coated by the solution and phase inversion methods are very clear.

4.3. Impregnation of gel polymer electrolyte

In the same manner as described in the non-woven section, the microporous polyolefin membrane can be employed as a dimensional support to enhance the mechanical strength of the GPE. The impregnation of GPE into the pores of membranes is
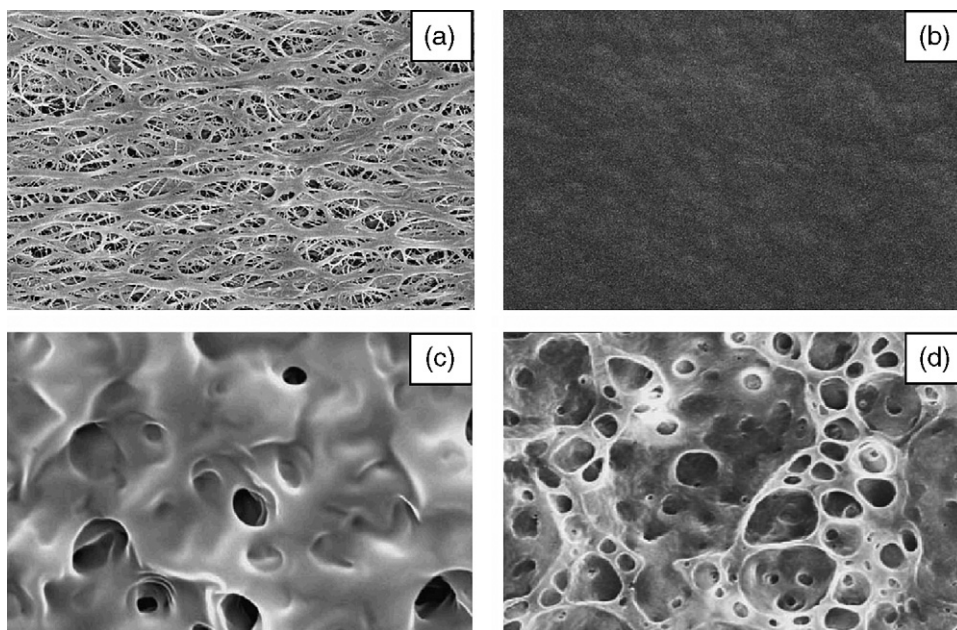
Fig. 7. Micrographs of the surface structure of a microporous PE membrane before and after polymer coating treatment. (a) Bare membrane, (b) with polymer coating by solution method, (c) with polymer coating by phase inversion and (d) with polymer/silica coating by phase inversion. This figure was reprinted selectively from Figs. 4, 1 and 2c of refs. [104,70,101], respectively, with permission from Elsevier.

carried out mainly through dipping [102–104] and in situ polymerization [105,106]. In the former, the operation is required to conduct at elevated temperature to reduce the viscosity of GPE so that the GPE can be easily impregnated into the small pores of the membrane. It has been reported [102] that when a copolymer is used, the composition of the copolymer plays a critical role in determining the electrolyte uptake and ionic conductivity due to the different functions of the copolymeric components. Alternatively, the GPE-impregnation can be conducted by diluting GPE in a volatile aprotic solvent to reduce the viscosity, and then applying the solution onto the porous membrane, followed by evaporation of the volatile solvent to obtain GPE-impregnated membrane [104]. This method generally is applicable to the GPE composed of the placitizer with high boiling point, such as EC, PC and GBL. In the latter, the GPE is formed in situ by a means of polymerization. In this approach, Abraham et al. [105] first reported the impregnation of GPE by UV-irradiation of the microporous membrane soaked with a solution containing a lithium salt, an oligo(oxyethylene) monomer, a non-volatile electrolyte solvent and a photoinitator. Due to the combined advantages of the GPE and microporous membrane, the GPE-impregnated membrane offers better protection against internal short circuit than the GPE alone, and the cells using it exhibit more stable capacity retention than the ones using the microporous membrane as the separator and the plasticizer as the solvent of liquid electrolyte.

5. Concluding remarks

The separator is a critical component of a battery, its main function is to prevent physical contact of the electrodes while permitting ions to flow freely. The separator itself does not participate in any cell reactions, however, its properties significantly determine the performance and safety of the batteries. For high energy and power densities, the separator is required to be very thin and highly porous, while it adversely affects the safety and cycle life of the battery as a result of the reduced mechanical strength. The safety requirement is a top priority for rechargeable Li-ion batteries, especially these used in hybrid electric vehicles and power tools. The PE-based shutdown separators are able to protect the battery in the temperature range of 90–130 °C, depending on the properties, such as average molecular weight and distribution, of PE and the composition of the blend if a blend is used. However, none of polyolefin separators can withstand temperatures above the melting point (near 165 °C) of PP. The melting of the polyolefin separator results in a direct contact of the electrodes, which induces very dangerous chemical reactions between the strongly oxidative cathode materials and the strongly reductive anode materials. When stored near the softening temperature of polyolefin, the polyolefin separator is subjected to shrinking, and therefore a safety concern is present as a result of a potential internal short circuit. The ceramic separator, which combines the characteristics of flexible polymers and hydrophilic ceramic materials, exhibits exceptional thermal stability and excellent wettability. Therefore, the ceramic separator exhibits overwhelming advantages in terms of safety and electrolyte wettability. In the view of battery safety, Separion separators could be very promising for high energy and power Li-ion batteries if their other performances and their cost can be made competitive with the current polyolefin separators. Future development of Li-ion battery separators will be made by balancing the performance against safety and cost. 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. The separators that combine the features of thermal shutdown and ceramic separators

are highly desirable, and such separators could be developed based on the Degussa Separion separators by replacing the PET matrix with a porous PE shutdown matrix.

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