

Separators for Lithium-Ion Batteries: A Review on the Production Processes and Recent Developments

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Recently, much effort has been devoted to the development of battery separators for lithium-ion batteries for high-power, high-energy applications ranging from portable electronics to large-scale energy storage for power grids. The separator plays a key role in battery construction because it functions as the physical barrier to prevent electronic contact between the two electrodes and at the same time serves as an electrolyte reservoir, facilitating the ionic conduction. The purpose of this Review is to describe the requirements and

properties of membrane separators for lithium-ion batteries, the recent progress on the different types of separators developed, and the manufacturing methods used for their production. Specifically the large-scale manufacturing processes are highlighted along with the processing parameters that affect their properties. The outlook and future directions regarding the development of advanced separator technologies are also discussed.

1. Introduction

Lithium-ion battery (LIB) systems have revolutionized battery powered electronic devices with their potential to be lightweight, high energy-storage capability, and long cycle life. Since their introduction in 1991, they have grown into a \$2 billion market in 2010, and dominated powering in portal electronics including laptops, cell phones, and digital cameras.^[1a] Even so, intensive efforts are still under way to further improve the technology. Recently, the area of application of LIBs has been extended to power tools, battery-assisted bicycles, hybrid electric vehicles (HEVs), etc.^[1] The main target of the effort is not only the automobile industry by achieving higher energy and power densities, but also the energy storage market to supplement environmentally friendly power sources such as solar energy and wind turbine.

Each lithium-ion battery consists of an anode, a cathode, and a separator. The separator membrane separates the two electrodes and serves as the medium for the lithium-ion transport between the two electrodes to control the number of lithium ions and their mobility. The porous structure of the separator is filled with the liquid electrolyte (lithium salt dissolved in a mixture of one or more solvents). Upon charging the battery, an external electrical power source injects electrons into the anode. At the same time, the cathode gives up some of its lithium ions, which move through the electrolyte to the anode and remain there. During this process, electricity is stored in the battery in the form of chemical energy. Upon discharging the battery, the lithium ions move back across the electrolyte to the cathode, enabling the release of electrons to the outer circuit to perform the electrical work.

The separator is a critical component of a battery as its properties have a strong impact on cell production, cell performance, life, and most importantly reliability and safety, although it does not “directly” participate in any reactions.^[2–5]

Moreover, the new market needs, derived from emerging applications for stationary energy storage and electric drive train support in the automotive environment, have led to new requirements placed on the separator material. At present, the separator market is served by polyolefin membranes, which show some technological limitations regarding wettability, porosity, shrinkage, and meltdown. Having in mind that battery reliability and safety concerns are of paramount importance and that they are closely related to separator materials properties, there is an increasing need to boost battery safety and reliability without compromising on performance and cost, which brought separators back into the focus of increased worldwide research and development activities in academia and industry.

This Review is structured in four sections. The first gives an idea about the future battery industry growth and describes the key contributors to separator materials industry and their market share. The second section discusses the properties of the separator membranes and their impact on cell performance as well as safety, and the third highlights the manufacturing of separator membrane technologies. The last section is devoted to the most important types of separators developed. The perspectives and future challenges in this research field are also described.

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2. Market overview

The compound annual growth rate (CAGR) is a business- and investing-specific term (important here for lithium-ion battery production) for the geometric progression ratio that provides a constant rate of return over the time period. It's an imaginary number that describes the rate at which an investment would have grown if it grew at a steady rate. The total lithium battery market is expected to grow at a CAGR in excess of 16% through 2020 on an energy capacity basis, driven by the application of lithium battery technology in new markets such as electric drive vehicles and energy storage systems for grid support. Moreover, lithium-ion batteries are considered the "holy grail" of renewable energy because their ability to store electricity from intermittent sources of energy such as solar and wind. Global sales of energy storage systems that typically require lithium-ion batteries are expected to triple from less than \$2 billion in 2015 to roughly \$6 billion by 2020.^[6]

Due to the aforementioned estimations, it is believed that membrane separator growth

will exceed battery unit sales growth because of the many new applications that are incorporating large-format lithium batteries and require much greater membrane separator volume per battery.

2.1. Major lithium battery separator enterprises

The information included in this section has been mainly found from the companies' websites and annual reports. The major manufacturers of lithium-ion battery separators along with their typical products are listed in Table 1.

The Hipore lithium-ion battery separator is mostly used for mobile electronics and other consumer electronics. Asahi

Table 1. Commercial separator properties.

Separator manufacturers ^[a] Product	ASAHI HIPORE	TORAY SETELA	CELGARD Celgard	UBE UPORE	ENTEK Teklon
thickness [μm]	≥ 25	7–25	ML PP: 16–25 ML PE: 16–20 TL PP/PE/PP: 12–38	–	25
single (SL)/multilayer (ML) composition ^[b]	SL PE	SL PE	SL/ML SL: PP, PE ML: PP/PE/PP	SL PP, PE	SL PE
process	wet extruded	wet extruded	dry extruded	dry extruded	wet extruded

[a] Separator specifications are found on data sheets for each product. [b] PE: polyethylene, PP: polypropylene.

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focuses more on full-scale business expansion for automotive applications as well as industrial and infrastructure applications. The new lines for Hipore lithium-ion battery separators in Hyuga, Miyazaki, Japan was a major part of Asahi's strategic plan to increase production capacity and develop new membranes that match individual customer needs to expand sales in rapidly emerging automotive applications.

Toray Tonen Specialty Separator began business in January of 2010 with a 50% investment by Toray. In February of 2012, they embarked on a new start as Toray Battery Separator Film (TorayBSF), a 100% subsidiary of Toray, with the aim of increasing operational efficiency. Toray has upgraded separator films used in lithium-ion batteries to extend their life. Specifically, the company developed separator films for preventing short circuits that are only 5 μm thick, or half the previous film's thickness. This creates extra space inside the battery, thus enabling it to store approximately 10% more electricity. Toray plans to spend about \$62.4 million to increase the capacity of a Tochigi Prefecture factory by fiscal year 2015 to accommodate production of the new material.

Celgard, a Polypore's company, publicized that in 2012 and 2013, the demand for lithium battery separators was lower than originally anticipated, and it is currently operating production facilities at levels below full capacity. Polypore has announced that Celgard and Panasonic will jointly develop a component for use in advanced lithium-ion batteries. The two companies will work on the development of coated and uncoated Celgard brand separators for Panasonic's next-generation cylindrical battery cells' production for various appli-

cations globally. It is also expected that the parties will enter into the development of separators for electrical vehicles, which is a key growth area for Panasonic.

UBE announced in its 2014 annual report plans for expanding sales in the automotive market by reconciling coating functionalization with standardized dry process manufacturing methods and synchronizing appropriately timed capital investment with market expansion. However, in the same report was stated a decrease in earnings despite growth in separator shipments because the sales prices decreased substantially.

Entek International Ltd designs and builds battery separator lines and extruders with their in-house engineering, machining, and fabrication resources. Entek manufactures more than 130 million square feet per year ($10.7 \text{ ft}^2 \approx 1 \text{ m}^2$) of its Teklon-brand lithium-ion separator material in a new building in Lebanon. Recently, has announced a £10 million investment in a new generation of battery separators for the automotive industry.

In 2014, Sumitomo Chemical announced that it will expand production capacity at its Ohe Works (located in Niihama City, Ehime Prefecture) for lithium-ion secondary battery separators (marketed under the PERVIO brand name). The increased capacity will be phased in over time, with an increase of current capacity to approximately 1.7 times current capacity in the spring of 2014, approximately 1.9 times increase in the fall of 2014, and approximately 2.3 times by the spring of 2015.

2.2. Market size

The total revenue for lithium-ion battery components has been estimated to be \$4.64 billion for 2013.^[7] Among the various components of a lithium-ion battery (cathode, anode, electrolyte, binder), the separator possesses 21.6% (\$1 billion) of the aforementioned total revenue. Based on revenue, the market for separators is expected to triple, exceeding \$3 billion by 2020. Separator production in 2013 has estimated to be 1018 billion m^2 of which, 848 million m^2 was produced by wet processing and the rest by dry processing.^[8]

2.3. Market share

In 2013, Japan-based Asahi Kasei, U.S.-based Celgard, South Korea-based SKI and Japan-based Toray Tonen occupied a 56.8% share of the global market, showing a sharp decline as opposed to the market concentration in 2008, when Asahi Kasei, Celgard, Toray Tonen and UBE Industries, as the top four companies, accounted for 82.8%. This is mainly attributed to the production increase of Chinese manufacturers. The high-performance separator will become the main demand growth point for the future lithium battery separator market. In Table 2, the battery separator market share is presented.^[7]

Table 2. Battery separator market share.

Separator Manufacturers	2011	2012	Brand Name
ASAHI	25%	26%	HIPORE™
TORAY	21%	23%	SETELA™
CELGARD	26%	19%	Celgard®
SKI	12%	13%	—
UBE	7%	7%	UPORE®
ENTEK	3%	3%	ENTEK
SUMITOMO	1%	1%	PERVIO™
OTHERS	5%	8%	—

3. Requirements for Separators

Although classified as an inactive cell component, the separator properties play a critical role in obtaining practical and optimal cell-level performance and the inherent safety of the cell.

A number of factors should be considered to select the appropriate separator for specific applications. In addition to initially possessing optimal properties for meeting the requirements for a specific application, the material properties must be uniform and stable over the desired lifetime. These characteristics are essential to achieve high energy and power densities for applications requiring such performance attributes. A list of separator requirements is given in Table 3 and a detailed discussion about each is following.

Table 3. List of requirements for lithium-ion battery separators.

Parameter	Requirement
chemical and electrochemical stability	stable for a long period of time
wettability	complete wet out in typical battery electrolytes
thickness [μm]	20–25
porosity	40–60%
pore size [μm]	<1
permeability (MacMullin no. ^[9])	<11
air Permeability (Gurley, ^[2] sec)	~25/25.4 μm
mechanical property ^[2]	<2% offset at 1000 psi
puncture strength ^[13]	>300 g/25.4 μm
dimensional stability	lay flat and not curl up
thermal shrinkage ^[10]	<5% shrinkage after 60 min at 90°C
shutdown	effectively shut down the battery at elevated temperatures
high-temperature stability	preserve its mechanical integrity at high temperatures

3.1. Chemical stability

For longevity, the cell separators must have a high degree of chemical stability to resist degradation and/or loss of mechanical strength due to reactivity with or dissolution by the electrolyte.^[2,4a] They should not produce impurities that could interfere with battery's operation. Moreover, separa-

tors must be electrochemically stable against the strong oxidizing and reducing environments posed by the active electrode cell components.

3.2. Wettability

Wettability is a critical property, as the absorption of liquid electrolyte is essential for ion transport. Separators should have the ability to absorb significant amount of liquid electrolyte and also to retain the absorbed amount under cell operation. Both parameters contribute to enhancing the cell performance by lowering the separator and cell resistances. Additionally, the separator must be wetted quickly by the electrolyte to facilitate its filling and consequently the final cell assembly. The wetting speed is related to electrolyte filling time and depends on the polymer type of separator, pore size, porosity, and the tortuosity.^[2, 4a-c]

3.3. Thickness

A minimal separator thickness is required for high-energy and high-power applications. Currently thickness of 20–25 μm for commercial separators seems to be standard.^[2, 4a-c] However, this can have a negative impact on mechanical strength and safety. The thinner the separator, the lower the mechanical strength and the higher the probability of puncture formation during cell assembly, which can lead to internal short circuits. On the other hand, the thicker separators offer higher resistances, thus decreasing cell's performance. Thickness homogeneity is also desirable as variations in thickness could lead to premature cell performance fading.

3.4. Porosity

An optimal porosity is required for trapping sufficient amount of electrolyte within the pores to maintain high ion conductivity. Typically, the lithium-ion battery separators have a porosity of 40%.^[2] However, too high porosities could adversely affect the shutdown performance, as the pores could not be closed effectively. On the other hand, separators with very low porosities can retain less electrolyte, leading to internal resistance increase.

The separator porosity is defined as the ratio of void volume to apparent geometric volume and can be calculated by the following equation:^[2]

$$\left[\text{porosity}(\%) = 1 - \frac{\frac{\text{sample weight}}{\text{sample volume}}}{\text{polymer density}} \right] \times 100\%$$

It is usually calculated from the skeletal density, basic weight, and dimensions of the material and so may be not reflect the accessible porosity of the material.

The most practical method for measuring porosity is the weight before and after absorption of liquid electrolyte.^[4c]

$$\text{porosity}(\%) = \frac{W - W_0}{\rho_L V_0} \times 100$$

in which W_0 and W are the weights of the separator before and after impregnation in liquid, respectively, ρ_L is the density of the liquid, and V_0 is the geometric volume of the separator.

3.5. Pore size and pore size distribution

Uniform pore size distribution is also desirable within the total area of a separator film to avoid performance losses, originated from uneven current distribution. The pore size must be smaller than the particle size of the electrode components. In practical cases, sub-micrometer pore sizes have proven adequate in reducing the possibility of an internal short circuit by blocking the penetration of larger electrode material particles or by dendritic lithium metal. Mercury porosimetry has been traditionally used to characterize separators regarding porosity percentage, pore size distribution, and mean pore size.^[2]

3.6. Permeability

A critical functional separator property is its permeability, as the presence of a solid separator increases significantly the effective resistance of the ion-conducting electrolyte. The ratio of the resistance of the separator filled with electrolyte divided by the resistance of the electrolyte alone is called MacMullin number.^[9] MacMullin numbers as high as 8 have been used in high-power lithium batteries; however for batteries used in hybrid electric vehicles, MacMullin numbers should be as low as possible. Air permeability can be used indirectly to estimate the MacMullin number. Air permeability is expressed by the terms of the Gurley number,^[2] 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 number is an easy and accurate method to characterize membranes, and deviations from specific values are good indication of problems.^[2, 3, 5] A low Gurley number indicates that the separator has high porosity and low tortuosity. Typically, Gurley numbers of separators are less than 25 sec per 25.4 μm measured according to ASTM D726. 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 lithium on the negative electrode.

3.7. Dimensional stability

Separators should be flat and not curl up when they are laid out and impregnated with liquid electrolyte. In practice, however, some camber is often observed which could cause misalignment between the electrodes and separator during cell assembly.^[2] The separators should remain stable in dimen-

sions under battery storage and operation conditions over a wide temperature range.

3.8. Thermal shrinkage

Having in mind that all materials used for battery assembly must be dried before going into the cell at 80 °C under vacuum to avoid battery poisoning by water, separators must show minimal shrinkage and must not wrinkle under these drying conditions. The requirement of thermal shrinkage is generally less than 5 % after 60 min at 90 °C.^[10]

In addition to these requirements, the cost of the separators is also important, as it can exceed 20 % of the total cost of a high-power battery and can be a limiting factor for their extended applications. Therefore, research on new manufacturing methods that produce low-cost separators is a necessity towards the development of high-capacity lithium-ion batteries.

4. Role of the Separator in the Cell

The separator's properties play a critical role in obtaining optimum cell performance and the inherent safety of the cell.

4.1. Electrical resistance

Separators should possess a uniform pore structure and exhibit a low electrical resistance or high ionic conductivity to achieve good performance. The separator property of a low electrical resistance has a pronounced effect in capacity, rate performance, fast charge capability, overall cell resistance, and cycle life.^[2] Low electrical resistances can be achieved when separators absorb and retain big amounts of liquid electrolyte. However, due to safety concerns, the advantages of utilizing a thin film filled with liquid electrolyte separator must be weighed against the severe deterioration of its mechanical integrity, and the cell design should reflect such.

4.2. Thermal and shutdown properties

The separator must not shrink significantly and definitely must not wrinkle when the temperature is increased during cell operation. The temperature could be increased due to heat generation if the lithium-ion cell is accidentally overcharged or abused. Under these conditions, thermal runaway could take place as the temperature increase changes the conditions in a way that causes a further temperature rise.

The shutdown property of a polymeric separator material can internally provide a margin of safety against an external short circuit, accidental overcharge, or an abuse condition resulting in an elevated cell temperature. However, the shutdown mechanism would provide very little protection from an internal short circuit or overcharge at high current densities accompanied by a rapid internal heating rate causing separator shrinkage or even melting.^[2-4a,5]

The separator material should also possess high-temperature melt integrity and exhibit mechanical robustness above the shutdown temperature. After a separator shutdown occurrence, the cell temperature is likely to continue to increase. The separator must maintain its mechanical integrity and high impedance as a function of time at elevated temperatures to prevent the electrodes from making physical contact and creating the safety hazard of an internal short circuit. Many of the multilayer separators are designed with a shutdown feature, by which two of the layers have different phase transition temperatures. As the temperature of the cell increases, the lower-melting component melts and fills the pores of the other solid layer and stops ion transport and current flow in the cell.^[4a] In PP/PE/PP separators incorporating polypropylene (PP) and polyethylene (PE), due to the difference in PP and PE melting points ($T_m = 165$ °C for polypropylene and 130–140 °C for polyethylene), the inner PE layer melts and fills the pores to inhibit ionic conduction, whereas the PP layers continue to provide the mechanical support up to their melting point.^[11,12] Thus, this multilayer design can prevent a catastrophic cell thermal runaway. The shutdown property of a separator material can be characterized by monitoring the electrolyte-saturated separator material impedance as the temperature is ramped.^[12-14]

4.3. Puncture strength

The puncture strength has been used to indicate the tendency of separators to allow short circuits during battery assembly. There are currently two major stack assembly processes for large-format lithium-ion batteries: the spiral winding and the stacked-plate process.^[5] In the spiral winding process, each electrode is tightly placed between two layers of separator during winding. The separator must have sufficient strength so that it does not break or reduce in width under the stress of winding. Moreover, during winding, small pieces of electrode materials can come off and be forced into the separator by the winding stress. The separator must not puncture, or else the battery will be shorted.

Puncture strength must also be provided by the separator in a stacked-plate process where the stack is compressed and forced into a can, or the electrodes and separator are laminated together before pouching. The compression or lamination steps put pressure on the separator. Separators must also be able to avoid penetration from dendritic lithium metal which could be formed under undesirable cell overcharge conditions.^[2]

The mechanical strength of separators is characterized in terms of the tensile properties and the puncture strength in the machine direction (MD) and the transverse direction (TD).^[2,3,4a] All these parameters are described by the Young's Modulus. As the Young's Modulus is difficult to measure, a 2 % offset yield is a good measure; less than 2 % offset at 1000 psi (14.5 psi $\approx$ 1 bar) is acceptable for most winding machines (ASTM D-882). High puncture strength is also required to withstand the penetration of electrode materials. The puncture strength is the maximum load that must

be applied to a needle to puncture a given separator.^[15] If particulate materials from the electrodes pass through the separator, an electrical short circuit of the battery occurs. The puncture strength for 25 μm separators for normal lithium-ion battery applications should be at least 300 g using ASTM D3763.

5. Manufacturing Processes

Separators can be broadly divided into 4 major categories (microporous, nonwoven mats, composite, and gel-polymer electrolyte) as will be discussed in the next section in detail. Different manufacturing processes have been followed for their production including dry processing, wet processing, phase inversion, electrospinning, and melt-blown. However, the two fundamental manufacturing processes for producing large-scale commercial microporous separators are the wet and dry processes. The phase inversion method is also applied to produce microporous separators, whereas nonwoven mats are prepared by various methods including dry laid, wet-laid, melt blown, and electrospinning processes.

5.1. Large-scale manufacturing processes of microporous separators

Wet and dry are the dominant processing technologies for large-scale manufacturing of commercially available microporous separators, including rolls as long as 1800 m.^[5] Commercial available separators are mainly polyolefins such as PE, PP, and their combinations such as PE/PP and PP/PE/PP (trilayer). Both methods consist of two basic steps, including an extrusion step to prepare a thin film and a stretching step to form the microporous structure (Figure 1). In the dry method, oriented micropores with slit-like characteristics are formed, whereas in the wet process, interconnected non-oriented spherical or elliptical pores are created as shown in Figure 2.

5.1.1. Dry processing

In the dry process^[16–18] (Figure 1a), polyolefins are melted, extruded into a sheet, and thermally annealed to induce crystallite formation and/or to increase the size and amount of crystallites. These crystallites have a row lamellae structure and are highly oriented as a consequence of the extrusion and annealing processes. The last step involves uniaxial stretching at a low temperature to form microporous initiators, a subsequent stretch at high temperature to form tightly ordered micropores,^[16–18] and relaxation to reduce the internal stresses induced by heat treatment. The microporous structure is formed by tearing apart stacked lamellae crystallites and is strongly oriented in the machine direction (MD). The microstructures before and after stretching is illustrated in Figure 3. Both uniaxial and biaxial stretching are adopted in industry, but only uniaxial stretching results in slit-like pore structures. Additionally, the uniaxial stretching imparts high anisotropy in the mechanical properties, leading to

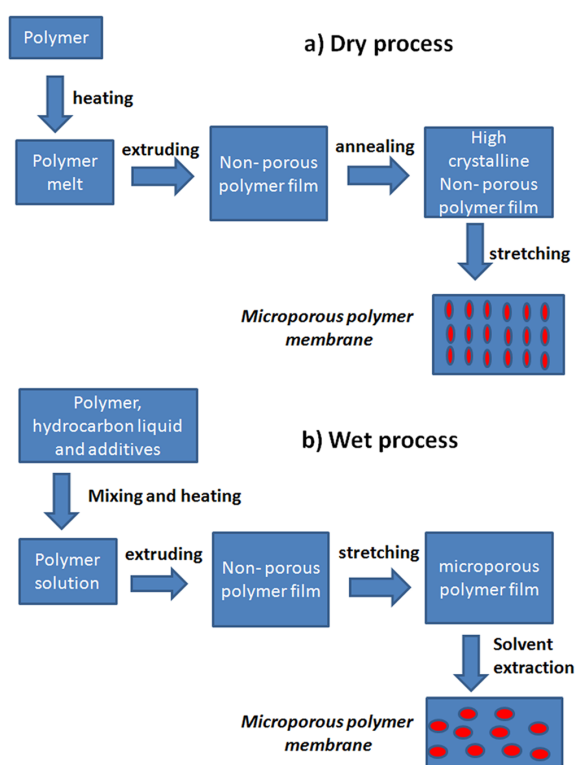


Figure 1. General procedures for producing microporous separators: a) dry process, b) wet process. Redrawn for Ref. [4c].

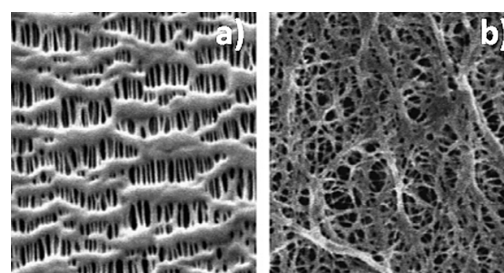


Figure 2. SEM images of the microporous polyolefin membranes made by using a) dry process and b) wet process, respectively. Reprinted with permission from Ref. [2], Copyright 2004, American Chemical Society.

membranes with much higher tensile strengths in the machine direction than in the cross-machine direction, which introduce handling concerns during battery assembly. However, the thermal shrinkage in the cross-machine direction is negligible. The porous structure of the separator is greatly affected by the morphology of the extruded film as well as by the processing parameters such as stretching ratio, speed, annealing temperature, time, etc.

Dry processing is typically a batch process and, as there is no requirement for solvent use, it is inherently a simpler method than wet processing. Moreover, due to the fact that

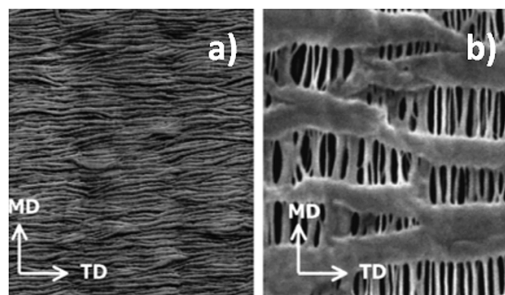


Figure 3. SEM micrographs of the surface of HDPE film before (a) and after (b) uniaxial stretching. Reprinted with permission from Ref. [4a], Copyright 2007, Elsevier.

only polyolefin resin is used, battery contamination is more difficult. However, this method requires only the use of semi-crystalline polymers, and particularly only PE and PP. PE and PP microporous separators are available from Celgard (Polypore)^[17,19,20] and Ube Industries Ltd.^[21] Blends of PE and PP are possible to be prepared using dry processing, although they have not proved advantageous.^[22]

5.1.2. Wet processing

This process^[23–26] involves several steps: (1) mixing of a polyolefin resin with plasticizers or low-molecular-weight substances, for example, paraffin oil, (2) melting of the mixture, (3) extruding the mixture into a gel-like film, (4) stretching of the film either in the machine direction or biaxially, and (5) extracting the plasticizer with volatile solvents^[27] to form sub-micrometer pores (Figure 1b). The stretching step can be conducted either before or after extraction to achieve high porosity and large pore size.^[24,26] It has been reported that membranes produced by stretching before extraction have a smaller mean pore size and a narrower pore size distribution than those produced by the process of stretching after extraction.^[28] Figure 4 shows the microstructure of two polyolefin based separators (Asahi Kasei Hipore) prepared by wet processing with different characteristics (pore size and porosity).^[29]

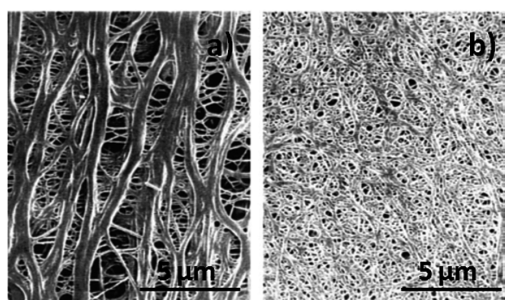


Figure 4. SEM images of the surfaces of Asahi Kasei Hipore polyolefin separators with a) large pore size and b) small pore size. Reprinted with permission from Ref. [29], Copyright 2002, Elsevier.

The wet process is a more versatile method compared to dry as can be used in a wide range of polymers (both semi-crystalline and amorphous) and processing conditions. The wet process can be operated as a continuous process and can use ultrahigh-molecular-weight polyethylene (UHMWPE). Due to its high viscosity, UHMWPE-based separators can only be produced using the wet method, because the addition of plasticizer significantly reduces the viscosity, thus improving polymer processability. However, solvent extraction and recovery as well as biaxial stretching are expensive operations in separator production. Typically, UHMWPE separators produced by using wet processing are stretched biaxially to enlarge the pore size and increase porosity. Although biaxial orientation imparts exceptional mechanical strength, separators tend to shrink in both machine and transverse directions upon heating.

Approximately 80 % of the global market relies on the wet process and separators made by this method are available from Asahi Kasei,^[30] Toray,^[31,32] Mitsui Chemicals,^[33] and more recently from Entek.^[34]

The structure and the properties of the separators produced can be influenced by several parameters such as solution composition, quenching temperature, stretching rate, and solvent evaporation/removal in the gelation and solidification processes. For example, blend separators comprised of high-density polyethylene and UHMWPE have been prepared and studied, thereby demonstrating that both the mechanical strength and drawing characteristics were influenced by the weight ratio of UHMWPE in the polyolefin blends as well as its molecular weight.^[24]

5.1.3. Phase inversion

Phase inversion has long been used for the formation of porous structures.^[35–39] It allows pore formation without stretching the structures, thus minimizing the membrane thermal shrinkage and product defects associated with the stretching step. Typically, a polymer solution is cast onto a thin film and then is immersed into a coagulation bath of a non-solvent. The solvent/non-solvent are miscible and their exchange leads to a thermodynamically metastable and/or unstable system, thus resulting in the formation of a porous structure.^[35] Therefore, the properties of the two solvents significantly affect the morphology and porosity of the resulting membrane. It has been reported that the morphology of poly(vinylidene fluoride) (PVdF) homopolymers and co-polymers^[37,38,40–44] and polyimide^[45] based microporous separator membranes vary from “sponge-like” to “finger-like” with asymmetric distribution of the pores on both sides of the membrane depending on the solvent and non-solvent pair used. For instance, the immersion of a PVdF/*N*-methyl pyrrolidone (NMP) solution in a water bath^[46] induces a very fast precipitation process with the formation of an asymmetric porous structure being composed of a skin layer on the top surface and some macrovoids on the bulk. On the other hand, cellular pores are dominant over the lower half of the membrane, as evidenced in Figure 5a. The immersion of

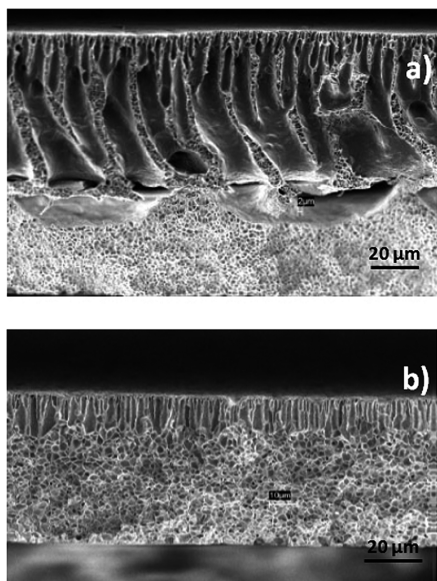


Figure 5. SEM images of the cross section of 20 wt% PVDF/NMP microporous membrane a) in H_2O precipitation bath and b) in 50 wt% NMP/water precipitation bath. Reprinted with permission from Ref. [46], Copyright 2004, John Wiley and Sons.

a PVdF/NMP solution in a soft bath (50 wt % NMP/ H_2O) induces a delayed-type phase demixing process which results in macrovoids that degenerate into parallel columnar voids, as shown across the upper quarter of the membrane and the rest is composed of cellular pores (Figure 5b). The presence of the skin layer on the porous membrane induces an internal resistance increase due to the poorly conducting surface layer, which is fatal for high-charge-rate performance of batteries. In addition, the porosity of the membrane can be controlled by the concentration of the polymer solution, the gap of the doctor blade and the temperature of the coagulation bath. Polyacrylonitrile (PAN) or PAN-copolymer membranes^[47] have also been fabricated using this phase-inversion process and evaluated as lithium-ion battery separators.

A similar method to the phase inversion is the solvent-evaporation-induced phase separation^[48,49] where a polymer is dissolved in a mixture of a volatile solvent and a less-volatile non solvent. The resulting polymer solution is coated or cast onto a flat substrate to form a thin polymer doping layer, where after evaporation of the good solvent the film is solidified due to the phase separation, followed by the subsequent removal of the non-solvent, which results in the formation of a porous structure. Similarly the solvent, non-solvent, and polymer concentration, all affect membrane's morphology.

5.2. Manufacturing processes of nonwoven separators

Although nonwoven mats are common separator formats for rechargeable alkaline batteries because of their low processing cost, high porosity, low weight, and scalability to roll-to-

roll manufacturing, they have limited applications in lithium-ion secondary batteries nowadays.

Nonwoven mat separators are fibrous mats that are typically made by bonding randomly oriented fibers together through chemical, thermal, or mechanical methods. Both natural materials and synthetic materials have been used to fabricate the fibers for nonwoven separators. Nonwoven mats are traditionally produced by using a dry-laid method, wet-laid method,^[50–52] melt-blown method,^[53–55] or electrospinning.^[56,57] These processes allow fiber adhesion by sprayed resin bonding, thermoplastic fiber bonding, fiber self-bonding, or mechanical bonding.

However, the nonwoven separators produced by wet- and dry-laid methods show excessively large pore sizes (20–50 μm) and increased thickness (100–200 μm), which is a desirable property for preventing short circuits, but at the expense of battery energy density. Thus, a more sophisticated method, the electrospinning technology, has been adopted for the production of thin nanofiber separators with fiber diameters at the sub-micrometer or nanometer scale, providing the potential for lithium-ion battery applications. Melt-blown technology can also be used for the production of nanofiber separators.

5.2.1. Wet- and dry-laid methods

The air-laid mat formation (dry process) involves individual staple fibers that are transported through the air toward a permeable conveyor belt to form a mat.^[4b] The formed mat can be bonded with thermal, mechanical, or chemical methods. For instance, chemical bonding of fibers involves adding a wet chemical adhesive (binder) to the web to impart mechanical integrity.

Wet-laid nonwovens are nonwovens made by a modified papermaking process, by which the fibers to be used are suspended in water.^[50–52] A major objective of wet-laid nonwoven manufacturing is to produce structures with textile-fabric characteristics (primarily flexibility and strength) at speeds approaching those associated with papermaking. Specialized paper machines are used to separate the water from the fibers to form a uniform sheet of material, which is then bonded and dried. The most common material used in bonding wet-laid nonwovens is a water-based emulsion or dispersion (“latex”) of a cross-linkable synthetic polymer, such as a polyacrylate, styrene-butadiene polymer, etc. In the roll good industry, 5–10 % of nonwovens are made by using the wet-laid technology. An example of the wet-laid process is described by Kritzer,^[50] where a polyester mat with an average pore size of 20–30 μm and porosity of 55–65 % has been fabricated using this method. Despite its high thermal and electrochemical stability, due to its big pore size it could not be directly used as a separator but only as a supporting layer for battery separators.

5.2.2. Melt-blown process

In melt-blown process, the mats are made directly from filaments extruded from plastics in liquid form. The hot, molten, liquid polymer is forced through nozzles to form a stream of polymer. At the nozzle tip, the filaments are picked up by hot, high-velocity air streams that stretch the filaments by drag forces into very fine diameters. The filaments gradually cool as they travel across to the collector where they are collected into rolls and subsequently bonded by calendaring at high temperature and pressure to form a nonwoven mat of sufficient strength. The preparation of thin, mechanically robust separators made of polyester, polyamide, and polymethylpentene and its copolymers through this method has been suggested.^[53–55]

5.2.3. Electrospinning

Electrospinning^[56,57] is a simple, versatile method for generating ultrathin continuous polymeric fibers with diameters at the sub-micrometer or nanometer scale. Thus, electrospun mats can have much smaller thickness compared with those fabricated by using other mat-forming processes. The technique of electrospinning polymers into mat sheets for the production of lithium-ion battery separators has recently been scaled using commercial equipment for large-scale manufacturing processing,^[58] although the low production capacity as well as the high cost of production are limiting factors. A typical electrospinning setup consists of a high-voltage power supply, a syringe, a spinning nozzle, and a grounded collector (Figure 6a). An electrical potential is applied between the electrospinning polymer solution contained in the syringe and the grounded metallic collector. Once the applied electric field overcomes the surface tension of the droplet of the polymer solution at the tip of the nozzle, a charged liquid jet is ejected. Nanofibers deposit on the grounded collector to form the nonwoven structure. The SEM micrograph of the poly(ethylene terephthalate) (PET) fibrous membrane prepared by electrospinning is illustrated in Figure 6b.^[59]

The mat morphology is affected by the solvent evaporation rate, the polymer concentration, the distance from the nozzle tip to the target, the accelerating voltage, etc. Electrospun nonwoven mats show higher porosity, smaller pore size, higher permeability compared to the conventional nonwoven mats, making them excellent candidates for separators in lithium-ion batteries.

Some electrospun nonwoven membranes such as polyacrylonitrile (PAN),^[60–62] poly(vinylidene fluoride) (PVDF),^[63,64] (PET)^[59] have already been developed and evaluated in lithium-ion batteries. For example, electrospun nonwoven PAN membranes with average diameters of 380–250 nm, porosities of 58–76%, and thicknesses of 25–35 μm have been obtained.^[60]

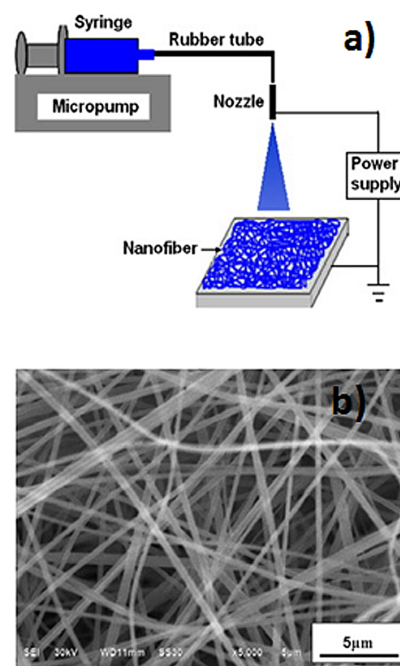


Figure 6. a) Schematic illustration of the preparation of a PET fibrous membrane (electrospinning method), b) SEM micrograph of a PET fibrous membrane prepared by electrospinning. Reprinted with permission from Ref. [59], Copyright 2013, Elsevier.

6. Classification of Separators

Separators for lithium-ion batteries can be classified into four major categories, with respect to their structure, composition and related properties: microporous membranes, nonwoven mats, composite membranes, and gel-polymer electrolyte membranes. A detailed discussion regarding the different types of separators follows.

6.1. Microporous membrane separators

Microporous polymeric membrane separators are characterized by pore sizes in the micrometer scale and are mainly based on polyolefin materials, such as PE, PP, and blends of the two, as they afford both excellent chemical stability and mechanical properties. These membranes can be comprised of one or more distinct layers, where the simplest are monolayer separators. The performance, porosity, pore size, gas permeability, mechanical/thermal properties, and safety issues regarding commercial PP and PE monolayer separators have been studied by several groups.^[10,65–67] For example, Djian et al.^[65] reported that commercially available separators with higher pore volumes and larger pore diameters exhibited increased conductivity after swelling with liquid electrolyte and higher charge capacities in high C-rate in lithium cells. Love^[67] studied the thermomechanical properties of commercial PP and PE separators. Anisotropic separators that were produced by using the dry method showed limited

mechanical properties in the transverse direction. On the other hand, separators prepared by using a wet technique behaved more uniformly (or biaxially) and nearly showed identical mechanical properties within the separator plane. The mechanical integrity of the separators after immersion in electrolyte solution as a function of temperature and time has been studied as well.

However, due to their low wettability and poor electrolyte retention as well as limited thermal stability, other polymer such as PVdF^[44, 68, 69] and its copolymers,^[41, 42, 70, 71] PAN^[72, 73] poly(methyl methacrylate) (PMMA)^[74] have also been used for the preparation of microporous membranes. PVdF and its copolymers show advantages over the commercially available polyolefin separators due to their high polarity and high dielectric constant, which can assist in the ionization of lithium salts. Saunier et al.^[69] have studied how the affinity of PVdF for the liquid electrolyte impacts the mechanical strength of the microporous structure. They determined that if too much solvent is incorporated into the polymer, it causes deterioration of the thermal and mechanical stability and introduces safety concerns for the battery operation.

The high crystallinity of PVdF is one of the major obstacles to obtaining high ionic conductivity in these systems; to overcome this problem, PVdF copolymers and specially polyvinylidene fluoride-co-hexafluoropropylene (PVdF-co-HFP)^[41, 42, 70] have attracted significant attention due to their low crystallinity, which can lead to improved ionic conductivity, high mechanical flexibility, and good compatibility with electrodes. Microporous PVdF-co-HFP membranes^[42] have been prepared by using the phase inversion method and activated with a liquid electrolyte to form a gel-polymer electrolyte, which showed good mechanical strength and high ionic conductivity.

Another strategy for enhancing the ionic conductivity as well as the mechanical and thermal properties is the preparation of microporous monolayer membranes made using polymer blends. PVdF/poly(methyl methacrylate) (PMMA),^[75, 76] PVdF-HFP/PAN,^[77] PVdF/poly(ethylene oxide) (PEO),^[78] PVdF-HFP/poly(ethylene glycol) (PEG),^[79] PVdF-HFP/poly(methyl methacrylate-co-poly(ethylene glycol) methacrylate) (P(MMA-co-PEGMA)),^[80] PVdF/poly(dimethyl siloxane) graft poly(propylene oxide)-block-poly(ethylene oxide) (PDMS-g-(PPO-PEO))^[81] and poly(vinylidene fluoride-co-trifluoroethylene) (PVdF-TrFE)/PEO^[82] blends have been used for the preparation of microporous membranes through the phase-inversion method. For example, it has been reported that the addition of PEO to the PDVF can improve the porosity and pore connectivity resulting in ionic conductivity enhancement.^[78] Large-scale microporous separators have been prepared based on blends of aromatic polyethers containing main-chain pyridine units with PEO after water treatment using a two-step procedure.^[83] This versatile procedure includes the preparation of the blend solution and the formation of the nonporous membrane through the solvent-casting method, followed by water treatment to impart porosity. The prepared blend membranes showed improved liquid electrolyte uptake and lower thermal shrinkage compared to com-

mercial separators; upon use in lithium cells, they exhibited good discharge rate capability and stable cycle performance.

It should be taken into consideration that although alternative microporous separators based on PVdF, PAN, PMMA, and their blends have shown some advantages, they suffer from poor mechanical integrity in liquid electrolytes; thus further improvement in terms of mechanical stability is needed.

Microporous monolayer membranes cannot easily include all of the optimal characteristics required that are related to battery safety and performance. Thus, microporous multilayer separators combining different polymers with different functions have been prepared. A variety of processes, including lamination, slot-die, dip coating, gravure, casting, and phase inversion can be used to prepare multilayer separators.

Commercial available separators such as Celgard 2325, U-Pore are composed of a PP/PE/PP trilayer structure that provides good puncture strength as well as shutdown and thermal stability. As already mentioned, the low-melting PE layer can act as a thermal fuse, and the higher-melting PP layers provide the mechanical strength. Although the PE layer melts and loses porosity at elevated temperatures, which effectively stop current flow between electrodes, the mechanical integrity is still preserved by the PP layers. This way, an external short circuit, accidental overcharge, or an abuse condition can be prevented, thus leading to safety improvement. Nonwoven mats, and particularly PE^[84] and PET,^[85] have also been used as substrates to produce microporous multilayer membranes. For example, polymers such as PVdF were coated onto the nonwoven PET substrate and the resulting membranes showed high wettability, high ionic conductivity, good mechanical stability and excellent electrochemical stability.^[85]

Cross-linked microporous multilayer membranes with enhanced thermal stability have been prepared by coating polymer-blended layers such as poly(ethylene glycol) diacrylate (PEGDA)/poly(ethylene glycol) methyl ether acrylate (PEGMEA) onto polyolefin microporous membranes and then irradiating to form chemically cross-linked membranes.^[86] PVdF-co-HFP/poly(vinyl chloride) (PVC)-based trilayer porous membranes have been prepared by using electrospinning, and they exhibited improved electrochemical properties compared to conventional separators.^[87]

6.2. Modification of microporous membrane separators

Another way to improve the poor wetting capability of conventional separators by liquid electrolytes is the modification of their surface through grafting of hydrophilic functional groups onto the membrane surface using UV irradiation, electron beam irradiation,^[88, 89] and plasma treatment.^[90] For example, Ko et al.^[88] and Gao et al.^[89] modified microporous PE membranes by grafting glycidyl methacrylate (GMA) and methyl methacrylate (MMA) respectively, onto the surface of PE membranes by using electron beam irradiation. Grafting of the PMMA layer has increased both electrolyte

uptake and electrolyte retention ability, leading to performance enhancement.

Modification of the surface can also be accomplished by using a coating method; for example, polydopamine was used as a thin coating layer on the PE separator to induce hydrophilicity and thus to improve wettability, electrolyte uptake, and ionic conductivity.^[91] In another report, PEG chains were grafted onto polypropylene separators based on a mussel-inspired dopamine coating.^[92] The introduction of PEG chains enhanced the liquid electrolyte uptake and the ionic conductivity, reduced the interfacial resistance, and improved the cycling stability. The coating of thermoplastic ethylene–vinyl acetate copolymer microspheres onto a PP/PE/PP separator resulted in improved thermal shutdown protection and this had no negative impact on the normal battery performance.^[93]

6.3. Nonwoven mat separators

Both natural materials and synthetic materials have been used for fiber production of nonwoven separators. Many recent reports highlight the preparation of separators based on natural materials, including celluloses and their chemically modified derivatives.^[94–100] Very recently, Jiang et al.^[95] reported on the preparation of bacterial cellulose nanofiber-based separators. The bacterial fibers used were covalently cross-linked, leading to high strength, high porosity, and excellent thermal and dimensional stability. Moreover, these separators showed superior cycling performance, electrolyte affinity, and rate capability to those of Celgard polyolefin separators. Eco-friendly cellulose microfibrils were modified by mussel-inspired polydopamine coating layer and a cellulose/polydopamine membrane was fabricated by using a facile and cost effective papermaking process.^[97] The prepared separator displayed superior mechanical strength as well as the best cycling stability and rate capability, compared with those of the commercial polypropylene and pristine cellulose separators. Moreover, eco-friendly cellulose nanofiber paper-derived separator membranes have also been prepared and, due to their nanoscale labyrinth structure, established between cellulose nanofiber with nanometer-scale diameters; these separators exhibited improved ionic conductivity, electrolyte wettability, and thermal shrinkage compared to the commercialized PP/PE/PP separator.^[100]

In another work, porous structure-tuned cellulose nanofiber paper separators were developed using a facile fabrication strategy based on colloidal SiO₂ nanoparticle-assisted structural control, by which SiO₂ nanoparticles were used as a cellulose nanofiber disassembling agent.^[99] The cellulose nanofiber paper separators containing 5 wt% SiO₂ showed the highest ion conduction due to the well-balanced combination of nanoporous structure and separator thickness, thus contributing to the excellent cell performance.

The synthetic materials used in nonwoven fabrics typically involve a single polyolefin, or a combination of polyolefins, such as PE, PP, polyimide (PI), polytetrafluoroethylene (PTFE), PVdF and its copolymers, PET, PAN and polyvinyl

chloride (PVC). Conventional nonwovens cannot be directly applicable as separators in lithium-ion batteries originated from their native macroscaled porosity and nonuniform pore size distribution. However, nonwovens can be used as support materials after impregnation with polymer-gel electrolytes due to their high porosity and large pore size, and they find application as separators in lithium-ion batteries. The nonwoven matrix acts as the mechanical support and the gel-polymer electrolyte provides the necessary ionic conductivity.

For example, a PVdF layer was coated onto the nonwoven material made of strongly compressed PE with relatively coarse fibers.^[101] The pore structure is generated in the PVdF region by phase inversion of the polymer solution. The PE nonwoven matrix imparts mechanical strength, and the PVdF component provides a hydrophilic ionic-conducting phase. Moreover, an improvement of the capacity retention of the prepared lithium cells using these separators has also been observed. Another effort reported by Jeong et al.^[102] describes a nonwoven separator that consists of a microporous PVdF–HFP gel-polymer electrolyte and a PET nonwoven matrix. The separator exhibited high ionic conductivity (0.81 mS cm^{−1}) and superior cell performance at high voltages and high current densities. Another strategy has been reported to prepare nanoporous PVdF–HFP scaffold-embedded PET nonwoven separators by using silica nanoparticles which have been selectively removed, allowing the formation of a nanoporous structure. The prepared separators showed facile ion transport, excellent electrolyte wettability, and thus superior cell performance.^[103]

Xia et al.^[104] prepared a nanoporous separator composed of a PET nonwoven sandwiched between two interconnected poly(vinyl alcohol-co-ethylene) nanofibrous membranes. This separator shows superior electrolyte wettability, lower thermal shrinkage, and higher ionic conductivity compared to commercial PP separator. In addition, a polyimide nonwoven matrix-impregnated with a cross-linked PEO gel-polymer electrolyte has been fabricated by using simple dip-coating and heat treatment.^[105] The PI nonwoven substrate provides high thermal stability and the cross-linked gel portion enhances the affinity with the liquid electrolyte. Thus, these separators showed better cyclability and rate capability than the traditional PP separators.

Electrospun nonwoven mats show higher porosity, smaller pore size, higher permeability, and larger surface area compared to the conventional nonwoven mats, making them excellent candidates for separators in lithium-ion batteries. Several polymers have been used to prepare electrospun polymer membranes, among them, PVdF is the most promising polymer candidate due to its good electrochemical stability and excellent affinity for lithium ions. Electrospun PVdF membranes have been prepared showing high porosity, large surface area, and fully interconnected pore structure. The gel-polymer electrolytes prepared after swelling of electrospun PVdF membranes with liquid electrolyte showed electrochemical stability and excellent wettability due to the high surface area of nanofibers as well as the good affinity with

the liquid electrolyte.^[106] A gel-polymer separator consisting of PVdF and lithium vinyl alcohol oxalate borate (LiP-VAOB) has been prepared after swelling with liquid electrolyte.^[107] The synthesized separator showed higher conductivity, higher lithium transference number compared to the commercial separator, and good capacity retention. Polydopamine (PDA)-coated electrospun PVdF nanofibrous membranes have been prepared and used as separators in lithium-ion batteries.^[108] The PDA coating makes the PVdF surface more hydrophilic, thus increasing electrolyte uptake and ionic conductivity. Moreover, the battery using PDA-coated electrospun PVdF nanofibrous separators exhibited better cycling performance and higher power capability than the battery using the bare electrospun PVdF nanofibrous separators.

Nanofibrous electrospun PAN membranes^[109] have also been prepared with an average fiber diameter of 350 nm and activated with liquid electrolyte, resulting in gel-polymer electrolytes with high electrolyte uptakes, high ionic conductivity ($\approx 10^{-3} \text{ Scm}^{-1}$), good cycle performance, and good discharge capacity upon use in cells. As polyethylene terephthalate shows good mechanical properties and excellent thermal stability, electrospun terephthalate-based separators with improved thermal stability and comparable or even better performance than commercial separators have been reported as well.^[58, 63]

6.4. Composite membrane separators

The incorporation of inorganic particles into the porous or nonwoven separators leads to the formation of composite separators with improved properties. In specific, ceramic compounds such as SiO_2 , Al_2O_3 , and TiO_2 are added to polymer hosts to promote the mechanical strength, wettability, ionic conductivity, and thermal stability.^[110] Inorganic particles can be either coated with a polymer binder onto a microporous membrane separator (ceramic particles coated onto composite membranes) or be incorporated directly into the polymer matrix (ceramic particle filled composite membranes). There is also another possibility to be directly introduced to nonwoven mats (ceramic particle-filled nonwoven mats).

In the case of composite membranes coated with ceramic particles, commercially available powders such as SiO_2 , Al_2O_3 , TiO_2 are dissolved together with a polymer to form a solution that is then coated onto PP and PE microporous membrane separators. The polymer acts as a binder to bond the inorganic particles onto the surface of the porous separator.^[111–117] For example, a functional ceramic-coated separator was developed by coating core-shell structured silica-poly(methyl methacrylate) (SiO_2 -PMMA) sub-microspheres onto one side of a porous PE separator.^[113] The presence of the PMMA shell facilitates the liquid electrolyte absorption and retention. This newly developed separator showed improved thermal shrinkage behavior, good wettability by the liquid electrolyte, and outstanding electrolyte retention ability. Moreover, cycle performance and C-rate capability were en-

hanced by the incorporation of the ceramic particles. Trilayer composite membranes have also been prepared by dip coating inorganic particle layers on both sides of a PMMA thin film.^[114] The coating solution was prepared by mixing Al_2O_3 and PVdF-co-HFP binder with a filler/binder weight ratio of 9:1. The schematic diagram and the SEM image of organic/inorganic trilayer separator are depicted in Figure 7. The tri-

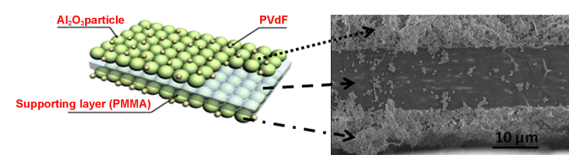


Figure 7. Schematic diagram as well as SEM image of an organic/inorganic trilayer separator. Reprinted with permission from Ref. [114], Copyright 2010, Elsevier.

layer separator showed exceptional thermal integrity due to the inorganic layers and adequate capacity retention with increasing C-rate.

In another work, a bilayer separator was prepared with a ceramic layer directly coated on the anode to provide high thermal stability and a porous PVdF layer formed on the top of the ceramic layer to provide good adhesion to the counter electrode.^[118] This separator showed stable cyclic performance and significantly improved rate capabilities compared to conventional polyolefin separators.

Although in all cases the resulting composite membranes exhibited good thermal stability and good capacity retention, they show some drawbacks related to the thickness of the coating layer. The coating process has consequences including an increase in the separator thickness and decrease in the porosity, which both increase the cell resistance.

The preparation of inorganic-particle-filled composite membranes involves the incorporation of inorganic particles directly into the polymer matrix. PVdF-co-HFP membranes filled with SiO_2 ,^[48] TiO_2 ,^[119] and ZrO_2 ^[120] have been fabricated and the resulting composite membranes with uniform pore size showed better wettability, higher ionic conductivity, and enhanced electrochemical and interfacial stability than the corresponding pure PVdF-co-HFP membranes. Recently, Nunes-Pereira et al.^[121] reported that the optimum montmorillonite (MMT) amount for battery application in terms of electrochemical stability and mechanical properties was 4% for MMT/poly(vinylidene-co-trifluoroethylene) P(VdF-TrFE) microporous membranes prepared with different MMT contents. The same group also explored the possibility of employing NaY zeolite/P(VdF-TrFE)^[122] and ferroelectric barium titanate (BaTiO_3)/P(VdF-TrFE)^[123] porous membranes. Lee et al.^[124] reported that the addition of the ceramic filler BaTiO_3 in P(VdF-TrFE)/PEO blend porous membranes resulted in ionic conductivity enhancement up to $1.2 \times 10^{-4} \text{ Scm}^{-1}$ for a 15 wt % of BaTiO_3 .

With respect to the ceramic-filled nonwoven mats, the introduction of the particles helps to decrease the excessive

pore size of the nonwoven substrate. For example, PVdF/SiO₂ composite nonwoven membranes have been successfully fabricated using electrospinning.^[125] Highly porous separators with improved porosity, liquid electrolyte uptake, thermal shrinkage behavior, and C-rate performance due to the addition of SiO₂ nanoparticles were obtained. The preparation of electrospun PVdF-co-HFP^[126,127] and PAN^[128] nonwoven mats with inorganic particle fillers has also been described.

Besides PVdF/PVdF-co-HFP and PAN, polyimide,^[129] PET,^[130–132] Nylon 6,6,^[133] polyetherimide-polyurethane (PEI-PU)^[134] membranes were used to fabricate high-performance membranes by incorporating inorganic particles into the nonwoven structure. For instance, SiO₂/PVdF-co-HFP coated PET nonwoven separators have been prepared for high-voltage/high-rate lithium-ion batteries,^[132] where the well-connected interstitial voids formed between close-packed SiO₂ nanoparticles were interconnected by PVdF-HFP binders. In comparison to the conventional PE separator, the nonwoven composite separator provided superior cell performance owing to facile ion transport and retarded growth of cell impedance during cycling. The SiO₂/PEI-PU nanofibrous membranes,^[134] benefiting from the high porosity, interpenetrating network structure, and synergistic effect of PU, PEI and SiO₂ particles showed high ionic conductivity, robust tensile strength, improved safety, excellent cycling stability, and improved rate capability compared with the Celgard separator. In another work, a nanometer-sized TiO₂@Li⁺ single ionic conductor containing a P(AALi-MMA) polymer layer grafted onto a nanometer-sized TiO₂ surface was prepared and used as functional filler in composite PVdF-HFP electrospun membranes.^[135] The prepared separators showed unique mechanical properties and battery performance.

6.5. Gel-polymer electrolyte membranes

All of the aforementioned separator types should be filled with liquid electrolyte to facilitate the lithium-ion transport between the electrodes for use in lithium-ion batteries. Gel-polymer electrolyte membranes are formed after swelling of the polymer matrix with the liquid electrolyte and can serve both as electrolytes and separators at the same time. They exhibit wide electrochemical operating windows, good compatibility with electrodes and high ionic conductivity. The ionic conduction mechanism in gel-polymer electrolytes should be very similar to that in liquid electrolytes and is also greatly affected by segmental polymer chain mobility. It should be mentioned that is beyond the scope of this article to fully collect and discuss the wide range of gel-polymer electrolytes, thus only some representative examples are reported below.

Various polymers including PEO, PVdF, PAN, and PMMA have been investigated as gel-polymer electrolyte matrices. The gel-polymer electrolytes have been prepared by using different methods such as solvent casting, phase inversion, electrospinning, and liquid extraction/activation. For example, Bellcore's plastic lithium-ion battery is a successful dem-

onstration of the use of a PVdF-co-HFP nanoporous membrane^[136] prepared by a liquid extraction/activation technique as the host matrix. However, unfortunately, the performance of the aforementioned homopolymers in terms of mechanical strength, ionic conductivity, and electrochemical stability cannot meet the requirement of commercial lithium batteries. Thus, an alternative method to avoid these drawbacks to some extent is to prepare copolymers through copolymerization^[137–140] or cross-linking with different functional monomers. For instance, a statistical copolymer comprising oligo (ethylene glycol) methyl ether methacrylate and cyclic carbonate methacrylate (OEGMA/CCMA), was chosen as a matrix for the preparation of gel-polymer electrolytes, due to the fact that both monomers enable the interaction with the liquid electrolyte. Indeed, the prepared gel-polymer electrolyte showed high liquid electrolyte retention ability, high ionic conductivity (2.3 mS cm⁻¹ at 25 °C), good C-rate capability, and constant cycling performance.^[137] In another report, a gel-polymer electrolyte comprised of a poly(acrylonitrile-co-vinyl acetate) copolymer blended with poly(methyl methacrylate) as a host showed high ionic conductivity (3.5 mS cm⁻¹ at 30 °C), excellent lithium transference number, improved performance, and stable cycling performance.^[138]

Chemical cross-linking is a method that can significantly enhance the thermal and dimensional stability of gel-polymer electrolytes.^[141–144] A semi-interpenetrating polymer network gel-polymer electrolyte membrane based on the cross-linked poly (ethylene glycol) diacrylate-co-poly(vinylene carbonate) [P(EGDA-co-VC)] and PVdF-HFP linear polymer was successfully synthesized by using UV-cured technology. This gel-polymer electrolyte presented good mechanical properties, superior thermal stability, excellent interfacial stability to the lithium-metal electrode, good electrolyte retention ability, and thus high ionic conductivity (1.49 mS cm⁻¹ at 25 °C). Moreover, it showed superior cycling stability and rate performance compared to the conventional liquid electrolyte.^[141]

In another example, cross-linked gel-polymer electrolytes were synthesized by *in situ* chemical cross-linking of the liquid electrolyte with an appropriate amount of cross-linking agent [poly (ethylene glycol) dimethylacrylate]. These gel-polymer electrolytes exhibited better capacity retention and stable cycle performance, which resulted from the strong interfacial adhesion between the electrodes and the electrolyte as well as the suppression of the dendritic growth of the lithium powder electrode.^[143] A polyacrylonitrile-interpenetrated cross-linked polyoxyethylene (PEO) network, which serves both as separator and gel-polymer electrolyte, showed excellent electrolyte uptake and electrolyte retention as well as significant higher ionic conductivity (1.06–8.21 mS cm⁻¹, at 25 °C) than that of commercial separator. The high ionic conductivity is attributed to the high electrolyte retention ability of the membrane and the good compatibility between the separator/gel-polymer electrolyte and the electrode.^[144]

Blending is another strategy to address the mechanical and electrochemical stability issues. Polymer blends such as PAN/PMMA,^[145] PAN/PVdF,^[146] PVdF/PEO-b-PMMA,^[147] PVdF/

poly(dimethylsiloxane),^[148] PVdF/[lithium poly(4-styrene sulfonyl (phenylsulfonyl) imide)] (PSSPSI),^[149] PVdF/polysulfone (PSF),^[150] and PVdF/lithium poly(pyromellitic acid borate) (PPAB)^[151] were also used as polymer-gel electrolytes. Gopalan et al.^[146] blended PAN with PVDF and the resulting gel-polymer electrolytes exhibited higher liquid electrolyte uptake with adequate dimensional stability, high ionic conductivity (7.8 mS cm^{-1} at 25°C), lower interfacial resistance, and a higher electrochemical stability window than pure PVdF. In another report, PVdF/PSSPSI blends have been prepared by the solution-casting method where the PSSPSI serves as a single-ion-conducting electrolyte.^[149] These gel-polymer electrolytes showed high thermal and mechanical stability, high ionic conductivity (1.1 mS cm^{-1} at 25°C), and high lithium cation transference number (0.87) due to the immobilization of the bis (sulfonyl imide) anions in the polymer chains and a wide electrochemical window.

7. Summary and Outlook

Although the separator component of lithium-ion batteries for high-specific-energy and/or high-power-density applications does not “actively” participate in the battery operation, it plays an important role in realizing optimal levels of performance and safety. The separator should be as thin as possible and porous, but yet possess the required physical strength to maintain the mechanical and electrical separation between the solid electrodes. The separator should also have the inherent ability to shut the battery down if overheating occurs, for battery safety.

The separator market is mostly served by conventional microporous polyolefin-based separators, which can be manufactured at a large scale using dry and wet processes. These two processes involve two basic steps, including an extrusion step to prepare a thin film and a stretching step to form the microporous structure. However, due to important technological limitations such as wettability, porosity, thermal shrinkage arising from polyolefin material selection, and stretching processes, other separator technologies such as nonwoven, modified microporous, composite, gel-polymer electrolyte separators have been developed. Modified microporous separators can be modified by various techniques (plasma treatment, UV irradiation, etc), and polymer coating, and the corresponding separators show improved wettability and ionic conductivity. Nonwoven separators can be produced by using different methods; specially electrospun nonwoven mats are the most promising candidates for separators as they combine high porosity, small pore size, and large surface area, thus enabling the wettability and ionic conductivity enhancement, although mechanical strength needs to be improved. Composite separators offer important improvements in terms of thermal stability, mechanical strength, and conductivity due to the incorporation of inorganic particles into the membrane, making them an advanced separator technology that can be used in the next generation lithium-ion cell technology. Gel-polymer electrolytes are formed after swelling of the polymer matrix with the liquid

electrolyte acting both as electrolyte and separator at the same time and showing high ionic conductivity.

As lithium-ion cell technology continues to advance and mature, the requirements for and function of the separator will become more demanding and complex. Eventually the goal of realizing an “infinitely-thin” separator with negligible resistance will be met by a future generation of lithium-ion-based cell technology that will practically employ advanced separators with a strong performance boost toward more reliable, longer-lasting, and safer batteries.

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Keywords: composite materials • ionic conduction • large-scale manufacturing • lithium-ion batteries • separators

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