Synthetic Polymer-based Membrane for Lithium Ion Batteries

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Abstract: Efficient energy storage systems are increasingly needed due to advances in portable electronics and transport vehicles, lithium-ion batteries standing out among the most suitable energy storage systems for a large variety of applications. In lithium-ion batteries, the porous separator membrane plays a relevant role as it is placed between the electrodes and serves as a charge transfer medium and affects the cycle behavior. Typically, porous separators membranes are comprised of a synthetic polymeric matrix embedded in the electrolyte solution. The present chapter focus on recent advances in synthetic polymers for porous separation membranes, as well as on the techniques for membrane preparation and physicochemical characterization. The main challenges to improve synthetic polymer performance for battery separator membrane applications are also discussed.

Keywords: synthetic polymers, battery separators, porous membranes, processing techniques, lithium-ion batteries

1. Introduction

In recent years there has been a growing increase in the global energy market due to the population growth, the economic development and the increase in the quality of life of populations [1]. This growth has been mainly based in fossil fuel reserves and nowadays the focus is redirected to address these critical challenges and drive global research to develop clean energy technology and devices for energy storage systems [2]. This is particularly relevant considering the 4th Industrial Revolution and IoT (Internet of Things) concepts where efficient energy storage systems are needed to connect "smart" people and objects/devices able to share capable of information, data and resources, acting and reacting [3].

Among the different energy storage systems, what stands out most are lithium-ion batteries [4, 5]. Lithium-ion batteries are electrochemical cells that convert chemical energy into electrical energy, being one of the most efficient technologies for energy storage, highly needed for mobile applications and transportation [6-8]. The main characteristics of lithium-ion batteries are being light, cheap, showing high energy density (210Wh kg^{-1}), low charge loss, no memory effect, prolonged service-life and high number of charge/discharge cycles [6, 9, 10].

The basic constituents present in an electrochemical cell are the anode, cathode and the separator, as illustrated in Figure 1.1.
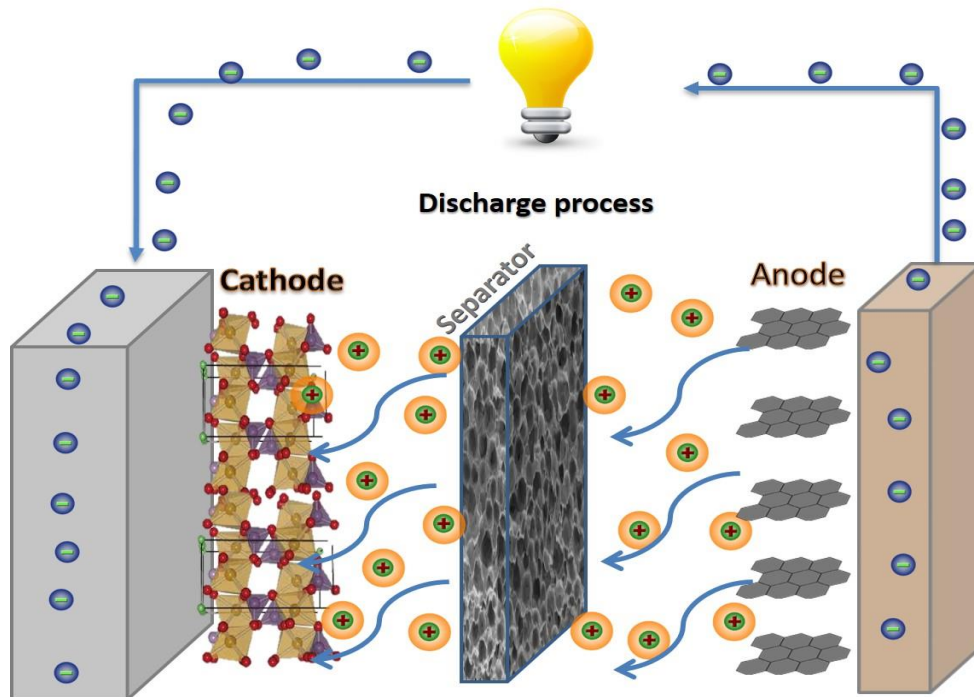
Figure 1.1 - Schematic representation of the main constituents and the discharge process of lithium-ion battery systems.

The two main processes of lithium-ion batteries are charging and discharging. During the charging process, for each lithium ion that leaves the cathode and crosses the separator to reach the anode, an electron exits through the external circuit, leading to an electric current and to the charging of the battery. In the discharge process, the movement of electrons and ions is in the opposite direction [11].

The separator separates the anode from the cathode and serves as the medium for the transfer of charges [12-14]. The separator can be constituted by a polymeric matrix in which the membrane is soaked by the electrolyte solution, i.e, a liquid electrolyte where salts are dissolved in solvents, water or organic molecules. Other possibility for the fabrication of polymer electrolyte separators is the incorporation of the lithium salts directly in the polymer matrix [15]. Typically, the liquid electrolyte solution is composed by lithium salts within one or more solvents. The solvents present in the electrolyte solution must meet the requirements

of battery applications, which are contradictory in some cases, such as high fluidity vs high dielectric constant [16]. The characteristics of an ideal solvent are: showing high dielectric constant to dissolve large salt concentrations, low viscosity for improving ion transport, being inert to all cell components and remaining in liquid state in a wide temperature range [16]. The non-aqueous solvents most used in electrolyte solutions belong to the classes of organic esters and ethers [17]: ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) [18-21]. The differences between the aforementioned solvents are mainly the melting temperature (-74.3ºC-36.4ºC), viscosity (0.50 cP-2.53 cP) and dielectric constant (2.8-90) [16]. The solvents can introduce modifications in the polymer matrix that can severely affect the battery performance [22].

In this chapter, the recent advances in separator membranes for lithium-ion battery applications based on synthetic polymers are presented and discussed, together with a general outlook on this field.

2.   Membrane structure and characteristics for lithium-ion batteries

The separator membrane is a key element in all lithium-ion batteries systems, as it allows to control the movement of ions between the anode and the cathode during charge and discharge of the battery [23]. The most commonly used separator types are microporous membranes, nonwoven membranes, electrospun membranes, membranes with external surface modification, composites membranes and polymer blends [23, 24]. The main parameters that determine the performance of the separator are permeability, porosity/pore size, electrolyte absorption and retention, chemical, mechanical and thermal stability and high ionic conductivity [15, 16]. All parameters are essential in the separator membrane, but the main issue is related to its morphology, as it correlates with the value of ion conductivity, mechanical properties, wettability and, consequently, battery performance [25]. Recently, biopolymers

such as silk fibroin [26], polyvinyl alcohol (PVA) [27], eggshell [28], chitin [29] and cellulose [30] have been used for separator membranes, but the most commonly used polymers are synthetic polymers, such as, poly(ethylene) (PE) [31], poly(propylene) (PP) [32], poly(ethylene oxide (PEO) [33, 34], poly(acrylonitrile) (PAN) [33, 35], poly(vinylidene fluoride) and its copolymers (PVDF-TrFE and PVDF-co-hexafluoropropylene, PVDF-HFP) [36-39].

In addition to these polymers, other synthetic polymers such as polyimide (PI) [40], poly (ether ether ketone) (PEEK) [41], polyetherimide (PEI) [42], polybenzimidazole (PBI) [43] and poly (m-phenylene) isophthalamide) (PMIA) [44] have been used to increase the thermal stability of the separator membranes, among other relevant parameters.

Regarding the processing techniques, separator membranes can be obtained through different techniques, the most used ones being e wet and dry processes [45, 46], including solvent casting, phase inversion, including thermally induced phase separation (TIPS) [47] and non-solvent induced phase separation (NIPS) [48], electrospinning [49] and particulate leaching [50], among others [51].

Further, efforts are also devoted to improve the surface properties of the separator membrane, such as wettability, compatibilization with electrodes or ionic conductivity, through surface treatments such as coating, grafting, plasma   or electron beam treatments [23, 52].

3.   Membrane preparation techniques

Together with materials selection, choosing the production technique is also paramount to control the physical-chemical properties and morphology of the materials. The final application also determines the requirements and specificities of the material, and consequently, the more appropriate technique to achieve such needs. Polymers are well known for their easy processability and for the many methods that allow producing very different structures. The polymeric membranes produced as separators for Li-ion batteries are no

exception and in this way, several techniques can be employed towards specific features. Properties such as chemical and thermal stability, porosity, pore size, pore distribution or tortuosity are essential envisaging this application. Different techniques can strongly affect those properties and ultimately the battery efficiency. In the following, some of the more used processing techniques in the framework of membranes for Li-ion batteries applications will be presented.

3.1 Thermally induced phase separation

Different means can be used in the production of polymeric membranes, and among them, phase inversion stands out as one of the most commonly used methods. This method comprehends two techniques that are often used, thermally induced phase separation (TIPS) and nonsolvent induced phase separation (NIPS)[53]. The first reference to TIPS dates back to the 80s [54], and since then, it became one of the most used techniques to produce porous membranes [55]. Typically, the TIPS method is used polymers such as poly(vinylidene fluoride), polyethylene, poly (methyl methacrylate, polyacrylonitrile, polypropylene, and polymers that are insoluble in the more common solvents [53, 56, 57]. For the TIPS process, the polymer dissolves in a solvent (high boiling point and low volatility) at a high temperature, and the polymer solution is cast into a film. Afterwards, the phase separation mechanism occurs by decreasing the temperature in a water bath (Figure 3.1) [58].
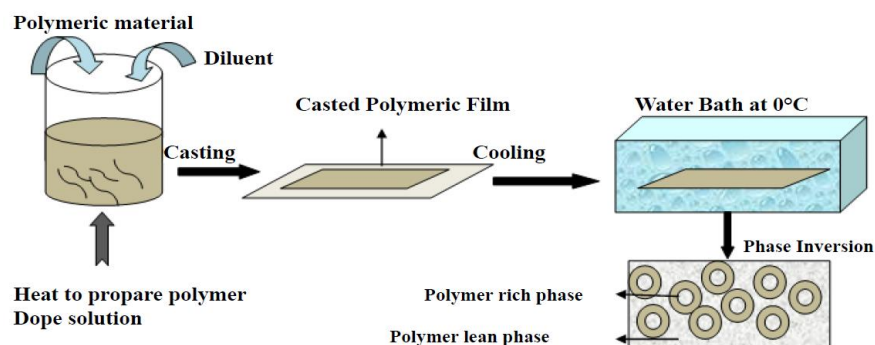
Figure 3.1. Representation of the main steps in the thermally induced phase separation technique (TIPS). Reprinted with the permission of [58].

TIPS allows to produce membranes with excellent mechanical properties and a highly porous structure with slight pores distribution [57, 59]. As this technique involves just two reactants (solvent and polymer), the produced membranes show high reproducibility and low level of imperfections [60]. It is relevant to notice that the phase diagrams of the binary system (solvent and polymer) can be valuable to understand the thermodynamics of the system, and consequently allows to foresee the porous structure of the membrane [61].

3.2   Nonsolvent induced phase separation

The NIPS method (also known as immersion precipitation or Loeb - Sourirajan method) is broadly used to produce asymmetric porous structures [62]. The NIPS is a straightforwardand versatile technique that provides wider pore size distribution resulting in high-performance membranes.

For the NIPS technique, polymer, solvent, and nonsolvent are necessary to produce the membranes [53]. Dissolution of the polymer at room temperature occurs, using the adequate solvent. The solution is then cast into a film, and afterwards, the membrane is placed in contact with a non-solvent bath (coagulation bath) such as water (Figure 3.2), which initiates an exchange between the solvent and the non-solvent - phase separation and phase inversion [57]. The nonsolvent must have a high affinity with the solvent and no affinity with the polymer, in this way, the phase inversion is induced to remove the solvent [62]. The NIPS technique usually employs solvents such as N-methyl- pyrrolidone (NMP), dimethylacetamide (DMAc), dimethylformamide (DMF), tetrahydrofuran (THF), and dimethylsulfoxide (DMSO) [63].
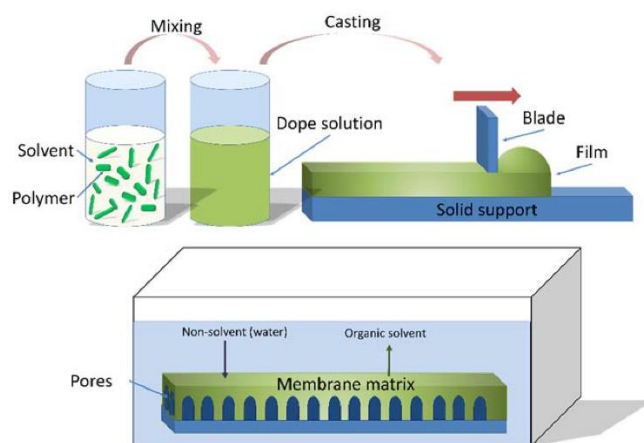
Figure 3.2. Illustration of the nonsolvent induced phase separation (NIPS) process. Reprinted with the permission of [64].

The control over polymer concentration, solvents and nonsolvents types, and the interaction between both allows tailoring membrane morphology finely [62]. Moreover, and similarly to the TIPS technique, ternary system (polymer, solvent, and non-solvent) phase diagrams are a helpful tool to predict the polymer crystallisation process [65]. A significant drawback of TIPS and NIPS techniques are the environmental problems caused by the extensive use of toxic solvents [53]. Therefore, green solvents such as Citroflex A4 and TEGDA (trie- thylene glycol diacetate) are under active research as a way to replace the toxic ones [66, 67].

3.3   Particulate leaching

Particulate leaching is one of the simplest and low-cost techniques to produce porous structures. The technique involves an initial dissolution of the polymer in an organic solvent. Afterwards, particles (e.g. water-soluble salts), also called porogen, with specific sizes are incorporated in the polymer solution. The solution is then transferred into a mould (e.g. petri dish) that will dictate the shape of the membrane. Subsequently, the solvent can be alternatively removed trough evaporation or lyophilisation leaving the particles leached in the polymer

structure. The last step involves the immersion of the mould in a bath that dissolves the particles/salt lodged in the polymer matrix [68]. Figure 3.3.1. shows the main steps of the particulate leaching technique.
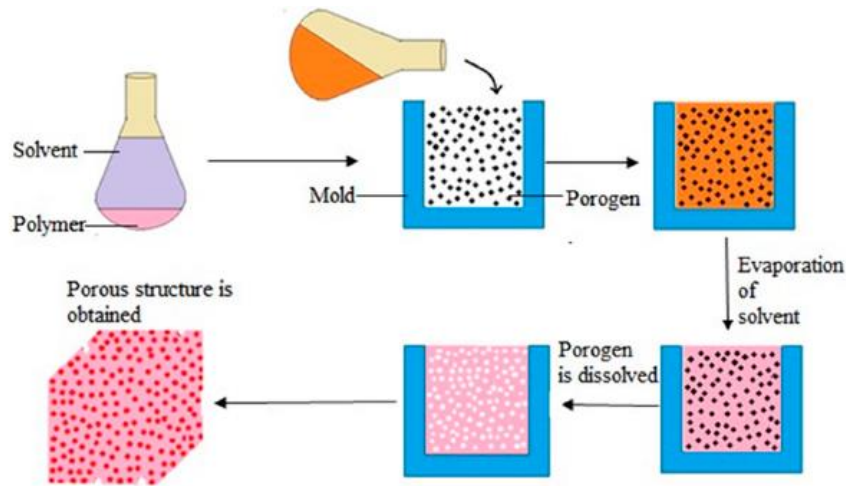

Figure 3.3. The schematic diagram of solvent casting and particulate leaching technique. Reprinted with the permission of [69].

Generally, this technique produces highly porous structures (> 93%) with a thickness of up to 3mm [70]. A major drawback of particulate leaching is that it is not possible to design a well interconnected porous structure with regular and reproducible structure [71].

3.4   Replica molding

Replica moulding is a technique that allows transferring the desired pattern from an elastomeric mould into the surface of a polymer. This technique allows duplicating 3D structure shapes, sizes and patterns in a wide range of materials [72]. Typically, a patterned poly(dimethylsiloxane) (PDMS) layer functions as the mould that is used to transfer the pattern to the surface of another polymer (prepolymer) [73]. The polymer is carefully spread into the PDMS patterned mould, and the crystallisation will occur. Depending on the crystallisation

temperature, the porous structure will be different [74]. Figure 3.4.) depicts the basic steps to use the replica moulding technique.
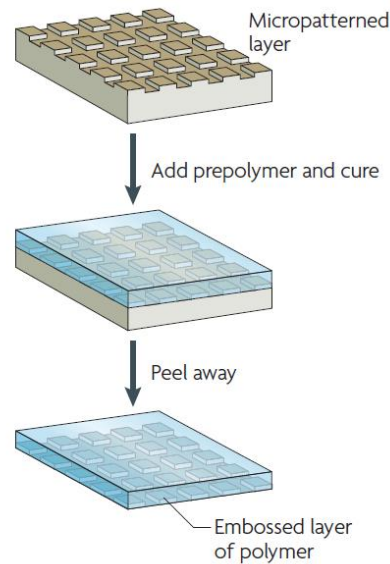

Figure 3.4. The key stages of replica moulding technique. Adapted and reprinted with authorization from [75].

The material composing the mould (micropatterned layer) should not react with the polymer solvent. Additionally, good wettability favors the process as it allows a suitable spread of the prepolymer solution over the pattern layer [76]. In the last years, replica moulding has upsurged as an interesting alternative to fabricating many materials such as poly(dimethylsiloxane) PDMS, hydrogels, thermoplastics, and thermoset composites in desired patterns [77] [78].

3.5   Freeze extraction

In the last decades, a straightforward freeze technique has been widely used to fabricate highly porous and crack-free structures [79, 80]. This method implies the dissolution of a polymer in a solvent with the addition of water. The solution is mixed until an emulsion is

formed and poured into a mould. Before phase separation, the solution is instantaneously cooled down to entrap the liquid in the structure. Later, solvent and water are removed by freeze-drying [81] – the space initially occupied with solvent originates the pores in the final structure [82]. Figure 3.5. Illustrates the steps involved in freeze extraction technique.
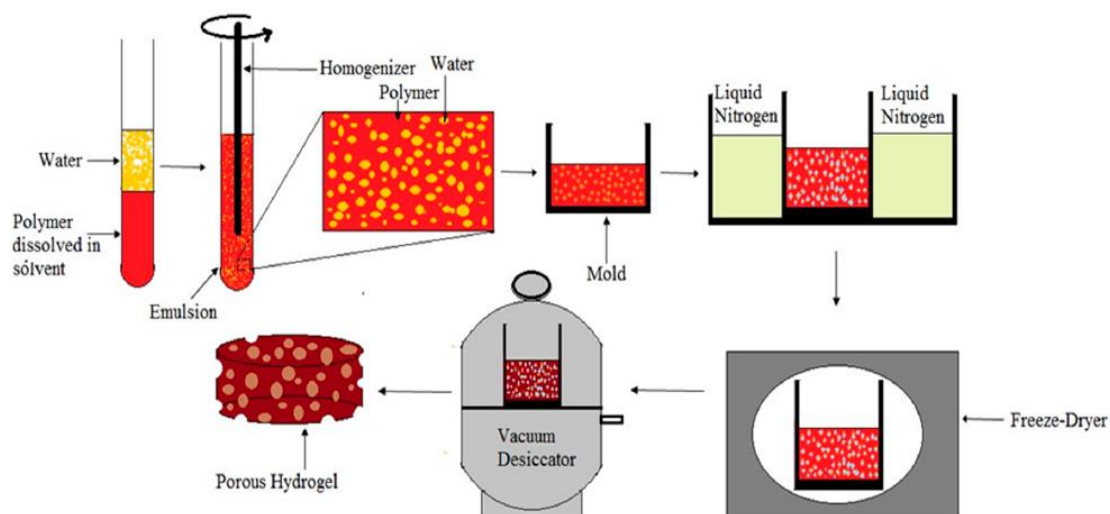

Figure 3.5. The schematic diagram of a freeze extraction process. Reprinted with the permission of [69].

In freeze extraction, the phase separation occurs in a solid-liquid unmixing – frozen solvent and polymer phases. Once the frozen solvent is removed, an interchange between solvent and non-solvent occurs, and the polymeric porous structure is formed [79]. Usually, this technique is used when the material requires porosities >90%, and when control over pore size is also necessary for the intended application [69].

Porosity and pore structure can be controlled by polymer concentration, solvent, and water phase percentage, and freeze-drying parameters [83]. When compared with TIPS and NIPS techniques, the freeze extraction is less time consuming, spares energy and reagents, and presents easier scalability [82].

3.6   Electrospinning

The first reference to something similar to the actual electrospinning occurred between 1934 and 1944 when Formalas published several patents [84]. Those documents describe a technique used to produce polymer filaments by electrostatic force. Only in 1994, the technique gained the nowadays name, electrospinning. In the '80s, electrospinning attracted further attentions, mainly caused by nanotechnology uprise as this technique allows to produce nanofibers efficiently [28].

Electrospinning is a technique that allows producing fibres with diameters in the range of micro to nanometers to form membranes using synthetic and natural polymers. The fibres produced by electrospinning are known to possess excellent mechanical properties. Moreover, the surface of the fibres can be easily changed owing to their remarkable high surface area to volume ratio [85]. This technique requires the application of a high electric field to produce fibres [86]. Afterwards, the formation of a polymer solution droplet occurs at the needle tip, and when the electrostatic repulsion overwhelms the surface tension of the solution, the shape of the suspended droplet will change into a cone (known as *Taylor* cone). As the jet and the *Taylor* cone gets thinner, the solvent evaporates leaving behind polymer fibres that are attracted to and deposited on a grounded collector [87]. Figure 3.6.1 illustrates the typical electrospinning set up that usually comprises four main components: (i) a high voltage source (1–30 kV) (ii) a metallic needle (iii) a syringe pump, and (iv) conductive collector (static or rotational) [88].
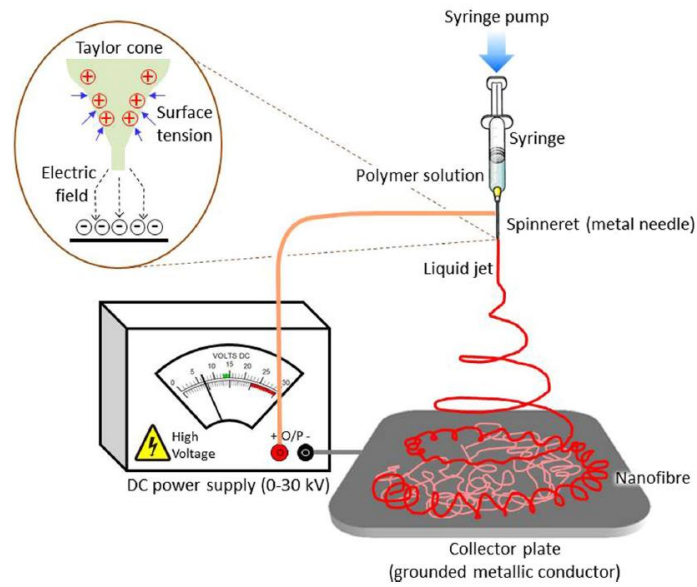
Figure 3.6. Schematic representation of the electrospinning technique. Reprinted with the permission of [89].

Table 3.1 outlines the parameters that directly affect the electrospinning process. It is from the interactive play between these parameters that the properties of the produced fibres will be defined [90]. Solution properties and process parameters mainly determine the very different possibilities related to surface topography, fibre morphology and orientation.

Table 3.1. Process parameters for electrospinning. Reprinted from [90].

Solution parameters	Process parameters	Environmental conditions
Concentration	Electrostatic potential	Temperature
Viscosity	Electric field strength	Humidity

Surface tension	Electrostatic field shape	Local atmosphere flow
Conductivity	Working distance	Atmospheric composition
Dielectric constant	Feed rate	Pressure
Solvent volatility	Orifice diameter	

The importance of controlling these parameters is illustrated with the variation of polymer concentration. Thus, if the electrospinning process is carried out under low polymer concentrations, beads will be produced instead of fibres [87]. However, when the polymer concentration increases, the beads shape change to fibres as a consequence of higher viscosity and higher polymer entanglement [91]. In short, all the mentioned parameters can define the materials/fibres properties dramatically, from thin to thicker fibre diameters or to form smooth to wrinkle fibres.

4. Physical-chemical characterization of the membranes

The physico-chemical characterization of polymer-based membranes encompasses the determination of a wide range of properties that allows to know the material itself and the expected performance when applied. Naturally, the type of application for which the membrane is intended for is the major factor in the selection of the characterization to be performed, in any case, there are a set of properties that are essential to know with respect to polymeric membranes regardless of the type of application.

In the field of polymer membranes for Li-ion battery separators the characterization is typically directed towards specific structural and functional properties that represent fundamental requirements for membranes performance as battery separator. It is important to keep in mind that the main function of a battery separator is to prevent physical contact between the electrodes while allowing the ion flow through its structure [92]. Some of these properties, as well as the techniques used for their determination are addressed in this section.

4.1   Thickness

The definition of a polymer membrane thickness for Li-ion battery separators requires a sensitive commitment between electrical and mechanical performance of the material. On the one hand a low thickness ensures high energy and power density, but at the same time thin membranes can compromise the mechanical strength of the membrane and consequently the safety of the system. The standard thickness for commercial separators is around 20-25 µm, additionally thickness uniformity is essential for the performance and long cycle life of the battery [23, 51, 93, 94]. The thickness can be measured by the standard method D645/D645M-97 [95] of the American Society for Testing Materials (ASTM).

4.2   Pore size and distribution

The pore size of the polymer membranes for Li-ion separators is an essential requirement for battery operation, the pores should be small enough to block the penetration of particles constituting electrode materials, such as active materials or conductive additives. Pores in the sub-micron range (< 1 µm) have proven to be adequate for a good battery performance reducing the possibility of internal short circuit. A homogeneous pore distribution along the polymer matrix and a good interconnection between the pores is also of utmost importance since it ensures uniform current distribution through the separator and inhibits

problems related to lithium dendrites. The pore size and its distribution can be evaluated by capillary flow porosimetry or scanning electron microscopy (SEM). The methods are described in the ASTM 1294-89 standard [96]. The SEM micrography allows an overall assessment of membrane morphology, including porosity type and pore homogeneity throughout the matrix [15, 23, 51, 93, 94].

4.3   Porosity

A suitable membrane porosity is essential to retain the liquid electrolyte in order to ensure an appropriate ionic conductivity, typically porosities around 40-60% being adequate for Li-ion batteries. Low porosity levels lead to high internal resistance due to insufficient liquid electrolyte, whereas excessive porosity negatively affects battery safety, namely the shutdown performance because the pores cannot be closed effectively, and the membrane tends to shrink with the increasing temperature. Uniform porosity along the matrix is also highly desirable to ensure uniform current density, and hence, high battery performance [23, 94]. The porosity is defined as the ratio of void volume to apparent geometric volume and can be calculated by the following equation:

$$\text{Porosity (\%)} = \left(1 - \frac{\rho_M}{\rho_P} \right) \times 100$$

where ρ_M is the apparent density of the membrane and the ρ_P is the density of the polymer. Commonly, the porosity is calculated through the masses of the membrane before and after liquid electrolyte absorption using the following equation:

$$\text{Porosity (\%)} = \left(\frac{m - m_0}{\rho_L v_0} \right) \times 100$$

where m_0 is the mass of the dry membrane, m is the mass of soaked membrane after immersion on liquid electrolyte, ρ_L is the density of liquid and the v_0 is the geometric volume of the separator [15, 23]. The method is described in the ASTM D-2873 standard [97].

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4.4   Tortuosity

The tortuosity (τ) is defined as the ratio between mean effective capillarity length and the thickness of the membrane and can be determined by:

$$\tau = \frac{l_s}{d}$$

where l_s is the ion path through the membrane and d is the thickness.

The tortuosity is called a long-range property of a porous material describing qualitatively the average pore conductivity of the material and can be also determined from the electrical measurements and porosity through the equation:

$$\tau = \sqrt{\frac{\sigma_0 \varepsilon}{\sigma_i}}$$

where σ_0 is liquid electrolyte conductivity, σ_i is the conductivity of the membrane soaked in the electrolyte at room temperature and ε is the membrane porosity.

This parameter is often used to characterize the ionic transport providing information about the pore blockage of the membrane. A $\tau = 1$ corresponds to an ideal porous material with cylindrical and parallel pores, while $\tau > 1$ corresponds to a hindered porous material [15, 98].

4.5   Permeability

The permeability of a membrane is typically described by the MacMullin number and the Gurley value. The MacMullin number is the ratio between the resistivities of the separator soaked with the electrolyte and in the dry state and should be as low as possible, numbers between 10-12 are usually found in commercial cells. The Gurley value is defined as the time required for a specific amount of air to pass through a specific area of the membrane under a specific pressure, the typical values being below 0.025 s/µm. A lower Gurley value indicates

high porosity and low tortuosity of the membrane separator [15, 51, 94]. The Gurley value can be measured by the ASTM D726-94 [99] and ASTM D737-96 [100] standards. Membrane separators permeability should be uniform to ensure a long cycle life of the battery, since non-uniform permeability leads to irregular current density distribution and dendritic formation on the electrodes [93, 94].

4.6   Wettability

The wettability of the membrane is a key factor since liquid electrolyte entry into the structure is essential for battery performance. An easily soaking of the membrane in the electrolyte leads to high absorption which is required for the ion transport and facilitates the battery assembly process. A good and permanent liquid retain capacity is also required as it results in low internal resistance and high ionic conductivity increasing the cycle life of the battery [51, 93, 94]. The evaluation of the wettability of the membrane can be performed by measuring the electrolyte content ($E_{content}$) into the membrane after immersing it into the liquid electrolyte during 24 hours. The masses of the wet and dry membrane are determined and correlated by the following equation:

$$E_{Content}=1-\frac{m_0}{m_E}\times100$$

where m_0 is the mass of the dry membrane and m_E is the mass of the membrane filled with the electrolyte after the uptake [98]. The dynamic contact angle measurements is another possible method to measure the wettability of the membrane since it enables to observe the ease and speed of liquid entry into the membrane [15, 93].

4.7   Mechanical strength

The mechanical strength of a membrane separator is characterized in terms of tensile strength and puncture strength in the machine direction and in the transversal direction, and all

the parameters are typically described by the Young's Modulus. As this parameter is difficult to measure for these materials a 2% offset yield is a good measure and < 2% offset at 1000 psi is acceptable for most winding machines. The separator must be able to withstand the winding tensions during battery assembly, for a membrane with the thickness of 25 µm the minimum tensile strength, measured according to ASTM D882 [101] and D638 [102] standards, should be around 98.06 MPa. The puncture strength corresponds to the maximum load applied by a needle to force it completely through the separator. It can be measured by a tensile tester and the minimum requirement is 300 g for a 25 µm separator, measured according to the ASTM D3763-18 [103]standard. The puncture strength indicates the tendency of the membrane separator to allow short-circuits due to particulate electrode material penetration in the separator [15, 23, 51, 93, 94].

4.8 Thermal stability

Membrane separators should maintain flat geometry and not curl when soaked with the liquid electrolyte. Additionally, shrinkage during battery storage and operation must be avoided over a wide range of temperatures, so that the separator remains dimensionally stable. The shrinkage tests are performed in both directions, machine and transversal, and the dimensions of the separator are measured at 90 ℃ for a fixed time; generally, the requirement of thermal shrinkage for Li-ion batteries is less than 5% after 60 min at 90 ℃. This characterization is usually performed by thermal mechanical analysis (TMA) and the shrinkage calculated by:

$$\text{Shrinkage (\%)} = \frac{L_i - L_f}{L_i} \times 100$$

where L_i is the initial length and L_f is the final length of the separator after higher temperature storage [15, 23, 51, 93, 94].

4.9   Chemical stability

The longevity of the membrane separator is intimately associated with its ability to withstand chemical degradation and loss of mechanical integrity due to the reactivity or even dissolution by the electrolyte. The membrane should be inert to both strong reducing or oxidizing conditions for long periods of time and not produce impurities which may affect the operation of the battery [15, 51].

4.10   Electrical resistance

Membrane separators should exhibit low electrical resistance since it influences decisively battery capacity, rate performance, charge capability and cycle life. The lowering of electrical existence is ensured through high absorption and retention of the liquid electrolyte, which in turns allows the separator being ionic conductive. The ionic conductivities of the membrane separators soaked with the liquid electrolyte should be in the range of 10^{-3} to 10^{-1} S/cm at room temperature to ensure a good battery performance.

The impedance electrochemical spectroscopy (EIS) is typically used to characterize the electrical resistance of the membrane separators and the ionic conductivity (σ_i) calculated by the following equation:

$$\sigma_i = \frac{d}{R_b}$$

where R_b is the bulk resistance obtained by EIS, d is the thickness and A is the electrochemical active area of the membrane [15, 23, 51, 94, 104].

4.11   Electrochemical stability

The electrochemical stability of the membrane separator is of utmost importance for the performance of the battery. It is important that separator being stable in reactive and oxidative

environments between 0 to 5 V, and this characteristic is typically evaluated by cyclic voltammetry [23].

4.12 Shutdown

A membrane separator must be able to shut down the Li-ion battery in cases of overheating or short circuits before thermal runaway is reached thus avoiding loss of mechanical integrity. Therefore, the separator material should present high temperature melt integrity and mechanical robustness above the shutdown temperature. Typically, the thermal runway temperature of polymer separators is 130 ºC. This property is usually examined by differential scanning calorimetry (DSC) or by analyzing resistance variation as a function of temperature for a membrane filled with electrolyte [51, 93, 94].

5. Recent advances in separator membranes for Li-ion batteries

Recently, strong efforts have been devoted to improve the performance of the different types of separator membranes, Table 5.1 showing the separator types, materials and properties for some relevant separator membranes based on synthetic polymers. Many of those works are mainly focusing on improving processing techniques for morphology control and on surface modification to improve thermal stability and other relevant properties, such as interface properties with the electrodes. PVDF is one of the most widely used polymer for battery separators and different approaches have been recently used to improve its properties.

Thus, an active-oxide-incorporated separator is proposed and it was observed that the anode/electrolyte architecture with strong CuO/graphene and PVDF-HFP/CuO interactions leads to an anode-separator interface featured with low interfacial resistance and structural integrity with suppression of the volumetric expansion/contraction of the oxide anode in the charge/discharge process [105].

An efficient and scalable method has been developed to obtain hierarchically constructed microporous PVDF-HFP separators for lithium-ion batteries as shown in Figure 5.1 [106].
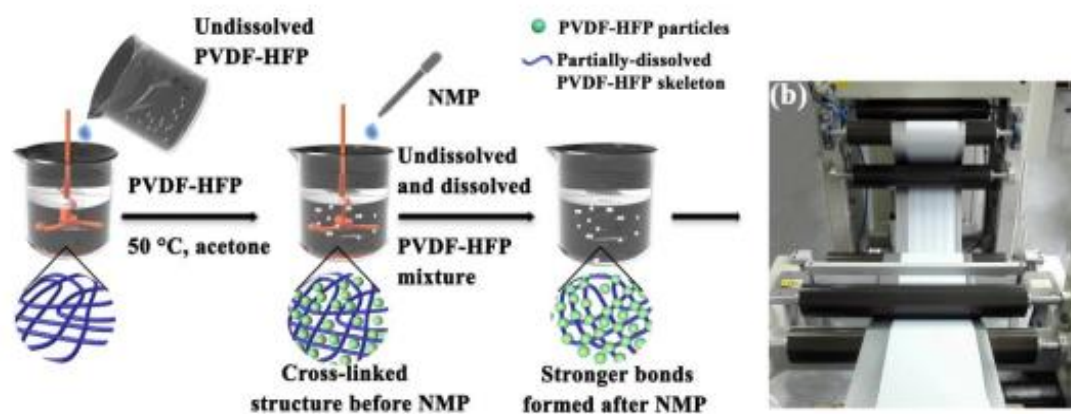

Figure 5.1 – Schematic representation of the large-scale preparation of PVDF-HFP separators [106].

This method produces separator membranes with excellent mechanical strength, notable porosity and high ionic conductivity, allowing battery operation over 1000 cycles with near-zero capacity fading even at 10 C [106].

Table 5.1 – Recent advances in different separator membrane types with the indication of their main properties.

Types	Polymer matrix	Filler /Polymer	Porosity/ %	Ionic conductivity / mS.cm at RT	Capacity / mAh.g^{-1}	Ref
Composites	PVDF-HFP	CuO	----	0.028	637.2 mAh.g^{-1} for Graphene oxide electrode	[105]

Single	PVDF-HFP	----	----	3.27	95 mAh.g^{-1} at 10C	[106]
Single	PVDF-HFP	----	80.17	3.97	~140 mAh.g^{-1} at 2C	[107]
Composite	PVDF-HFP	$Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$	----	1.46	93 mAh.g^{-1} at 5C	[108]
Blend	PVDF-HFP	PEGMEMA), vinyl-functionalized Al_2O_3 nanoparticles	63	1.37	150 mAh.g^{-1} at 0.5C	[109]
Single	PVDF-HFP	----	----	0.81	270 mAh.g^{-1} at 1C	[110]
Composites	PVDF-HFP	PE-BN	50.8	0.44	120 mAh.g^{-1} at 2C	[111]
Composites	PVDF-TrFE	ZnO	65	1.6	107 mAh.g^{-1} at 2C	[50]
Single	PVDF-TrFE	----	----	3	85.5 mAh.g^{-1} at 2C	[112]
Composites	PVDF-CTFE	Sb_2O_3	72	2.88	167 mAh.g^{-1} at 1C	[113]
Composite	PVDF	TEOS	----	1.22	~140 mAh.g^{-1} at 4C	[114]
Blend	PVDF	PMIA	75	1.7	~130 mAh.g^{-1} at 2C	[115]

Composite	PVDF	CA-AgTiO$_2$	88	7.7	170 mAh.g^{-1} at 0.1C	[116]
Composite	PVDF	SiO$_2$	43	1	179 mAh.g^{-1} at 0.05 C	[117]
Composite	PVDF	Zirconia	77.69	0.96	120 mAh.g^{-1} at 4C	[118]
Blend	PI	PAA (polyamic acid)	72.5	2.2	~140 mAh.g^{-1} at 5C	[119]
Composite	PI	TiO$_2$	77.8	1.24	132.8 mAh.g^{-1} at 5C	[120]
Blend	PI	PBI	84	3.24	130.2 mAh.g^{-1} at 5C	[43]
Blend	PAN	PI	87	0.2	153 mAh.g^{-1} at 0.5C	[121]
Single	PI	----	69.8	0.829	~140 mAh.g^{-1}	[122]
Composite	PI	AlOOH	65.8	2.18	115 mAh.g^{-1} at 8 C	[123]
Single	PPESK	----	70	1.39	91.1 mAh.g^{-1} at 4C	[124]
Composites	PP	boron nitride (BN)	----	----	1027 mAh.g^{-1} at 1C in Li/S	[125]
Composites	PP	boron nitride (BN)	----	----	90.1 mAh.g^{-1} at 10C	[126]

Composite	PE	Al$_2$O$_3$/PDA	----	----	90.1 mAh.g^{-1} at 5C	[127]
Blend	PE	Al$_2$O$_3$/ePOSS/ PVdF-HFP		0.86	~130 mAh.g^{-1} at 5C	[128]
Single	PE	benzoyl peroxide	----	0.8	-----	[129]
Single	PE	Graphene oxide coating	----	----	----	[130]
Composite	Glass Fiber	MOFs	----	2.54	2 mAh.cm^{-2} at 1C	[131]
Blend	PAN/PMMA	PDA	56.1	3.61	170.6 mAh.g^{-1} at 0.2C	[132]
Single	PEEK	----	84	1.68	154.3 mAh.g^{-1}	[133]
Single	PAN	----	67.26	1.60	117.92 mAh.g^{-1} at 1C	[134]

To enhance the mechanical properties, thermal and dimensional stabilities, cross-linked membranes covalently integrated with hybrid silsesquioxane components were fabricated by in-situ crosslinking method, obtaining armor-like shell structures coated on PVDF-HFP fibers [107]. This novel cross-linked PVDF-HFP based electrospun membrane shows high porosity and affinity, enhanced mechanical strength, dimensional stability and high lithium ionic conductivity [107].

PVDF-HFP/LLZO composite separators (Figure 5.2) have been developed through the dispersion of LLZO particles into PVDF-HFP polymer matrix, the composite separator with

4.29 wt % LLZO showing significantly enhanced mechanical, thermal and electrochemical performance [108].
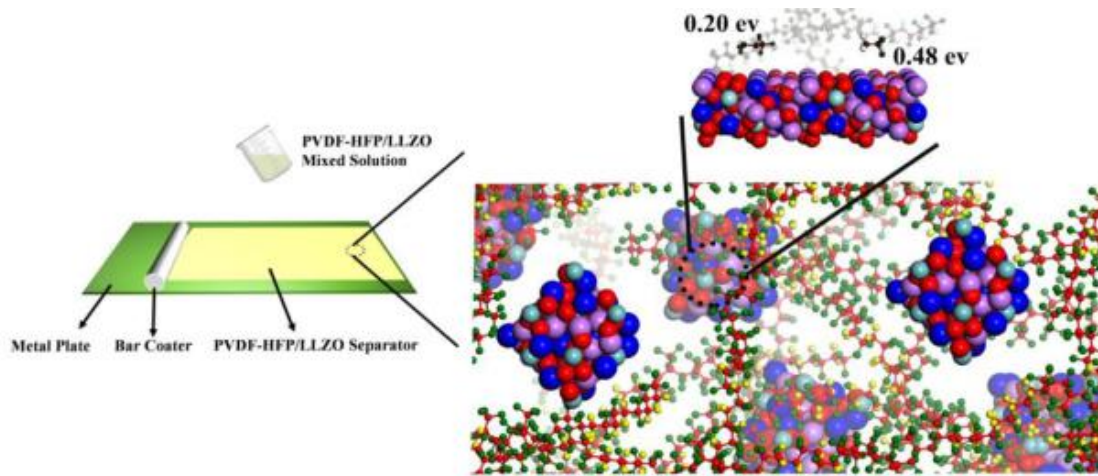

Figure 5.2 – Schematic representation of the preparation method and the proposed microstructure of the PVDF-HFP/LLZO composite separator [108].

This separator is very stable in Li/Li symmetrical cells indicating that promotes homogenous Li$^+$ flux and facilitates the suppression of Li dendrite growth [108]. A new separator based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) blended with a mixture solution containing poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), vinyl-functionalized Al$_2$O$_3$ nanoparticles (VTMO@Al$_2$O$_3$) as the cross-linker and poly(vinyl pyrrolidone) (PVP) as the pore-forming agent has been developed showing good mechanical strength, excellent thermal stability and stable capacity retention [109].

In order to improve the separator–electrode interface and, thus, to improve operational safety, a novel separator was produced based on nanostructured PVDF–HFP membranes directly deposited on a carbon anode through efficient, scalable electrophoretic deposition (EPD) in a surfactant-free colloidal system [110]. The as-assembled half battery with this approach exhibits ultra-high cycle stability and high discharge capacities [110].

Porous poly(vinylidene fluoride-cotrifluoroethylene) (PVDF-TrFE) separators with different patterned surfaces constituted by arrays of hexagons, lines, zig-zags and pillars microstructures were developed (Figure 5.3) and their influence on battery performance was evaluated.
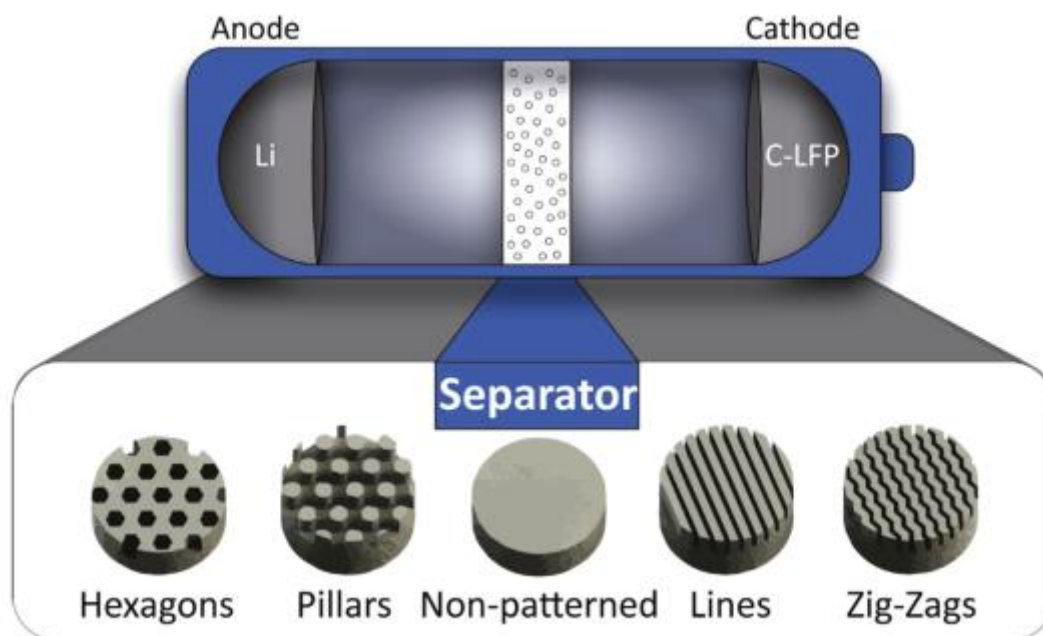

Figure 5.3 - Schematic representation of separators with different patterns -hexagons, lines, zig-zags, pillars and conventional non-patterned– designed to improve battery performance [112].

It was demonstrated that the zig-zag surface micropatterning leads to a higher electrolyte current density (472.6 A.m^{-2}), improved uptake value (262%), and larger ionic conductivity (3.00 mS.cm^{-1}) than the non-patterned separator and micropatterning of separator membranes allow to significantly improve battery performance [112]. A Sb_2O_3-modified poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) fibrous membrane was produced by electrospinning, leading to a separator with superior wettability toward nonaqueous electrolytes, higher ionic conductivity, lower interfacial resistance and improved electrochemical stability compared to the commonly used polyethylene separator [113].

A poly(vinylidene fluoride)/tetraethyl orthosilicate silane (PVDF/TEOS) composite separator with a fingerlike pore structure for lithium-ion batteries has been prepared by non-solvent-induced phase separation (NIPS) [114]. This novel PVDF/TEOS composite separator shows an ion conductivity of 1.22 mS.cm^{-1} at 25 °C, lithium-ion transference number with 0.7% TEOS of 0.481and show good cycling performance and rate capability [114].

A novel core-shell structured poly-m-phenyleneisophthalamide@polyvinylidene fluoride (PMIA@PVDF) nanofiber separator was successfully synthesized via facile coaxial electrospinning as shown in Figure 5.4a). Figure 5.4b presents the schematic functional principle of this separator [115].
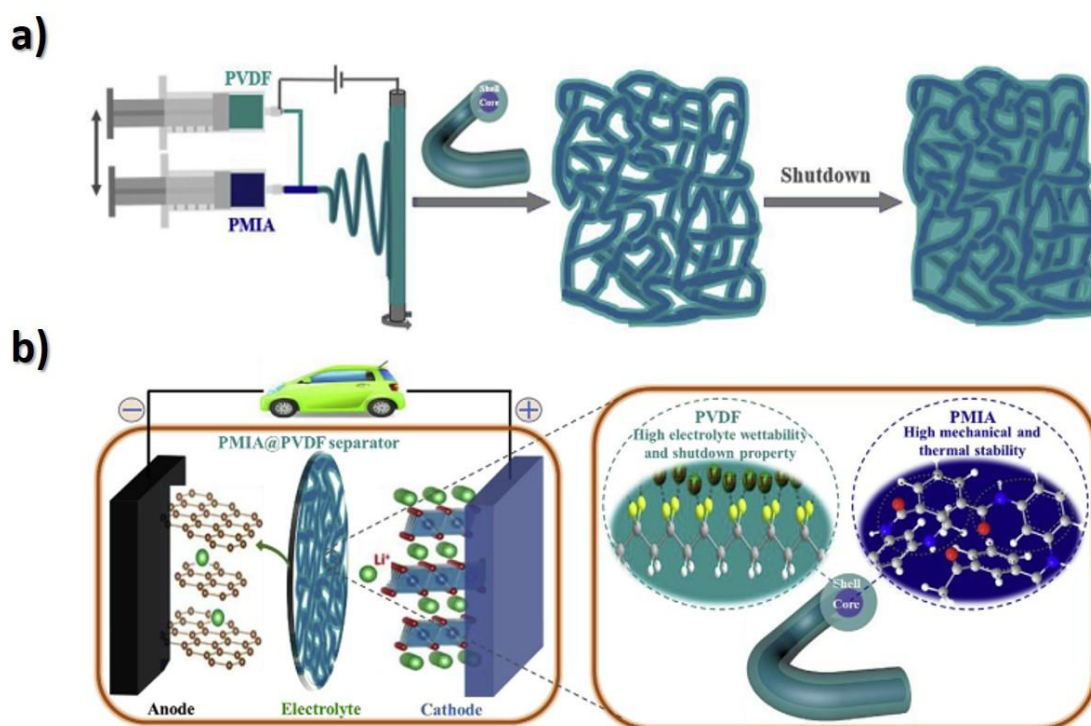
Figure 5.4 - Schematic illustration for the: a) preparation and b) functional principle of PMIA@PVDF nanofiber separators [115].

This PMIA@PVDF separator presents a prominent improvement on electrolyte uptake and ionic conductivity and maintains its integrity to prevent thermal shrinkage [115].

Hybrid PVDF with cellulose acetate/AgTiO$_2$ (CA-AgTiO$_2$) nanofiber membranes have been successfully fabricated by electrospinning with excellent thermal stability, high porosity and superior electrolyte compatibility [116].

Polyimide (PI) nanofibrous membrane separators with bonding microstructures have been prepared via a dipping method by employing PAA (polyamic acid) as shown in Figure 5.5, which turned the loose-weak nonwoven structure to a compact robust fabric structure. This separator exhibits excellent high-rate capability and cycling stability at high temperature [119].
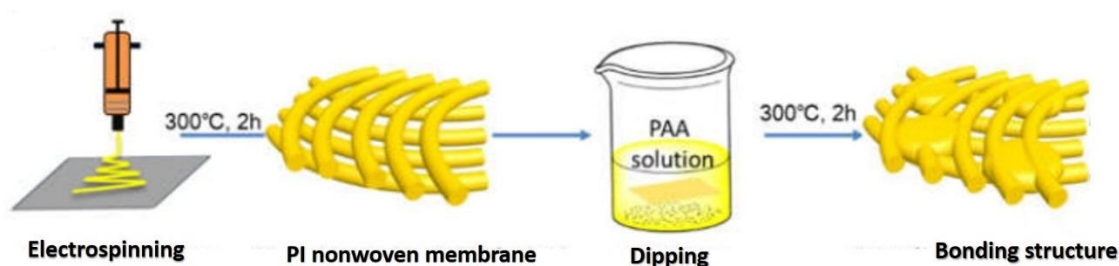
Figure 5.5 – Illustration for the preparation of PI nanofibrous membrane separator [119].

Novel blend separators have been developed by electrostatic spinning based on PAN/polyimide (PI) to improve the mechanical and electrochemical performances, the addition of PI increasing the porosity and fluid absorption rate of the membrane [121]. This membrane shows high ionic conductivity (0.2 mS.cm^{-1}), wide electrochemical window (about 4.0 V), and excellent cycling performance (153 mAh.g^{-1} even after 50 cycles at 0.5 C) [121]. Organosoluble polyimide (PI) was used to fabricate high-performance separators with excellent thermal and mechanical stabilities, leading to separators with high heat resistance when compared to PP separators as shown in Figure 5.6 [122].
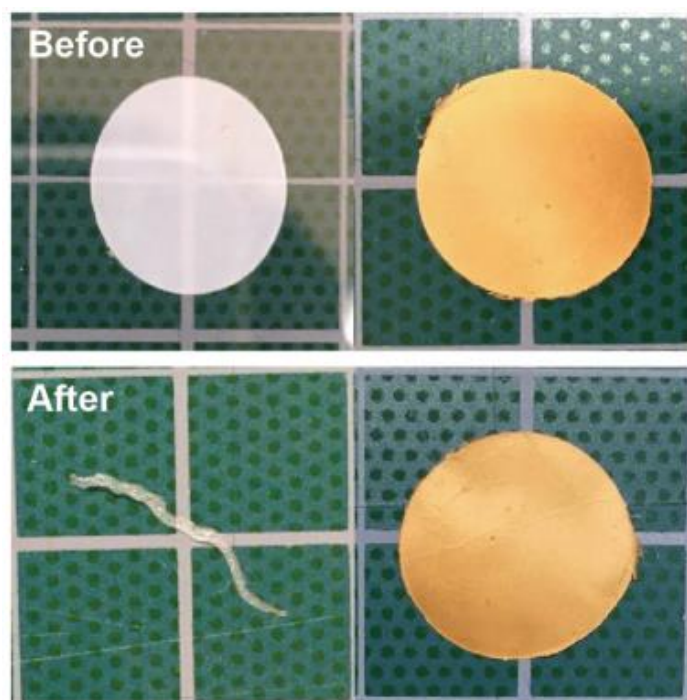
Figure 5.6 – Thermal shrinkage of a PP separator (left) and PI membrane (right) over a temperature range from 150 to 200 ℃ [122].

A PI fibrous membrane as a battery separator was prepared by combining a PI electrospun matrix with an AlOOH coating via an electrospinning technique and a subsequent blade-coating process, the morphology being presented in Figure 5.7 [123].
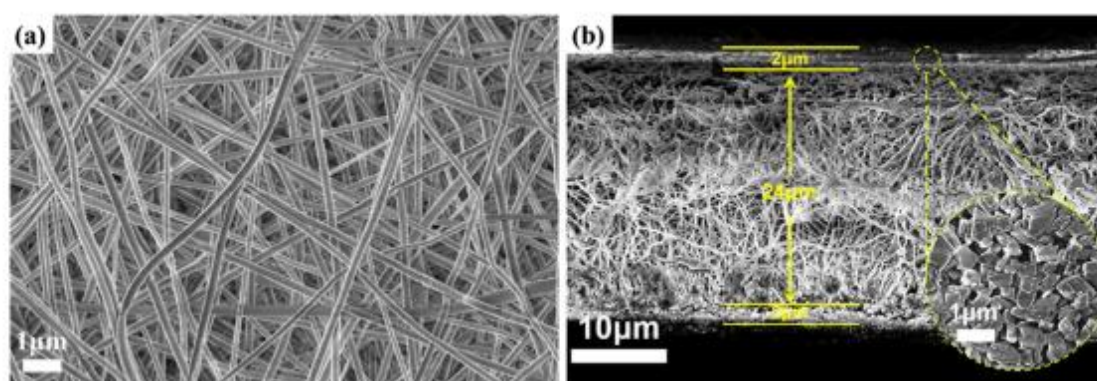

Figure 5.7 - (a) Surface SEM image of PI matrix. (b) Cross-sectional SEM image of the API separator (inset is the surface image of AlOOH coating layer) [123].

This separator shows excellent flame retardance, high ionic conductivity, good electrolyte wettability and superior rate capability [123]. Novel oriented poly(phthalazinone ether sulfone ketone) (PPESK) fibrous membranes were fabricated by electrospinning technique with high porosity (70%), superior electrolyte uptake (525%), low interfacial resistance (268 Ω) with electrodes and excellent ionic conductivity (1.39 mS/cm) [124].

Further advances in the field of separator membranes are based on surface modifications of synthetic polymer membranes to improve specific properties. A multifunctional separator based on the incorporation of functionalized boron nitride nanosheets with negative charged groups onto a commercial Celgard separator has been developed. The boron nitride separator is capable to prevent polysulfide migration through the separator effectively due to strong ion-repelling of negatively charged polysulfides [125]. A heat setting treatment (preset heat setting ratio λ and heat setting temperature $T_{setting}$) on polypropylene separator for Lithium Ion Batteries has been also implemented, leading to a decrease of the ionic conductivity of the separator while increasing the dimensional stability of the membrane [135].

A new BNNT separator was produced through incorporation of thermally and chemically stable BNNTs onto polyolefin (PP) separators via a dip coating process, the morphology being shown in Figure 5.8 [126].
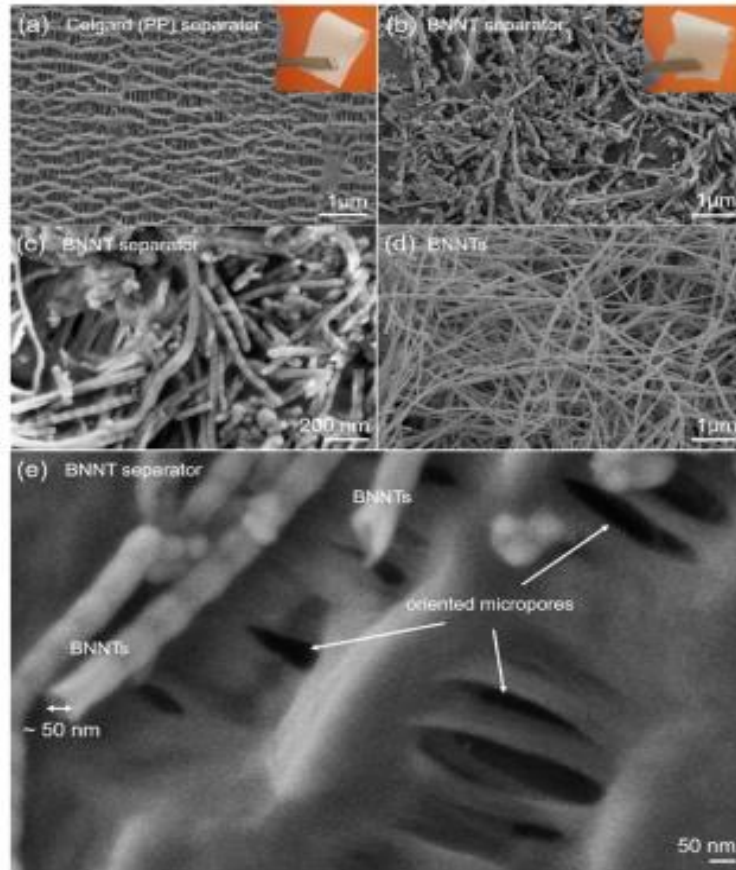
Figure 5.8 - SEM images: (a) Celgard-PP separator, (b, c, e) BNNT separators, and (d) low magnification image of BNNTs (Inset shows digital photographs of Celgard PP and BNNT separators) [126].

This separator exhibits superior thermal stability over commercial polyolefin (PP) separators and allows the cells to operate normally at high charge-discharge currents and high temperatures in which the lower orientation also determines more connections between the coarse fibrils, which delayed the micropores formation [126]. Also for the PP separator, it was evaluated the morphological evolution and pore formation mechanism [136]. Novel separators based on sequential deposition of Al_2O_3 via atomic layer deposition (ALD) and polydopamine (PDA) via solution dip coating on the surface of a commercial PE separator confirmed to be a powerful approach for the fabrication of battery separator with excellent properties [127].

Another coating into PP separators was realized with 4A zeolite with the objective to improve wettability and thermal resistance of the separators [137].

Further, PE separators have been coated with a crosslinkable binder in the form of inorganic polyhedral oligomeric silsesquioxane with epoxy functional end groups (ePOSS) leading to a flame retarding property without compromising electrochemical performance [128]. PE separators have been also improved by chemical treatment with benzoyl peroxide (BPO), oxygen containing functional groups such as carbonyl leading to improved ionic conductivity [129].

A surface modification of PE separators has been developed via a simple solution-based coating of graphene oxide (GO) with hydrophilic groups as shown in Figure 5.9 [130].
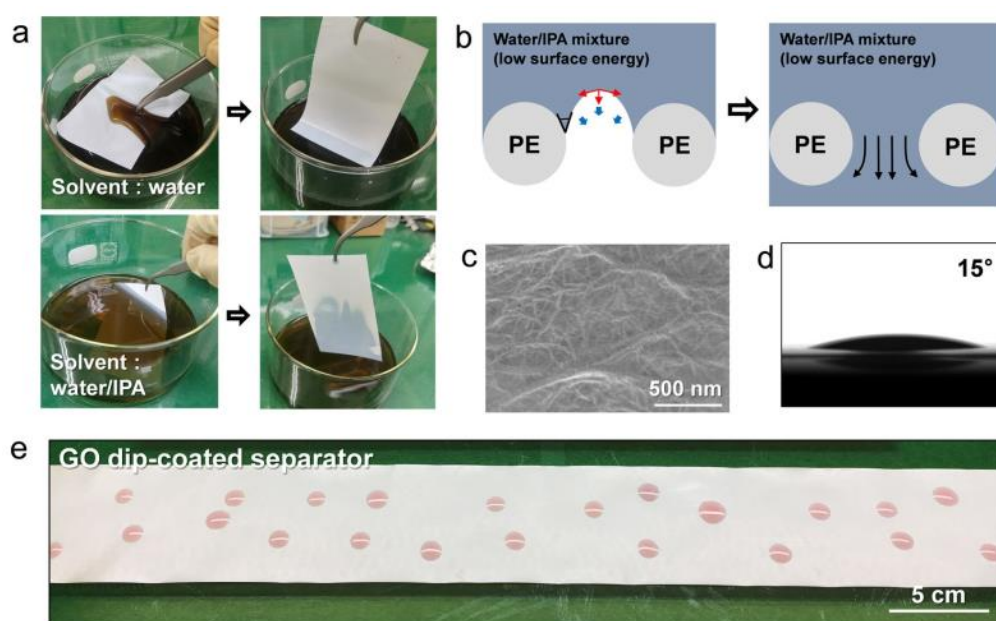

Figure 5.9 - (a) Photographs of graphene oxide (GO) dip-coating depending on the polarity of GO solution. (b) Schematic illustration of the wettability of the solvent with low surface energy on the conventional hydrophobic separator. (c) SEM image of the GO dip-coated separator. (d) Water contact angle measurement and (e) photograph of large-area wetting feature on the GO dip-coated separator [130].

This modification leads to superior wetting properties and preserves the ionic conduction through defect-induced ion transport and thin deposition thickness [130]. A new separator was designed and manufactured by applying multilayer functional coatings on both sides of a polyethylene separator as shown in Figure 5.10 [138].
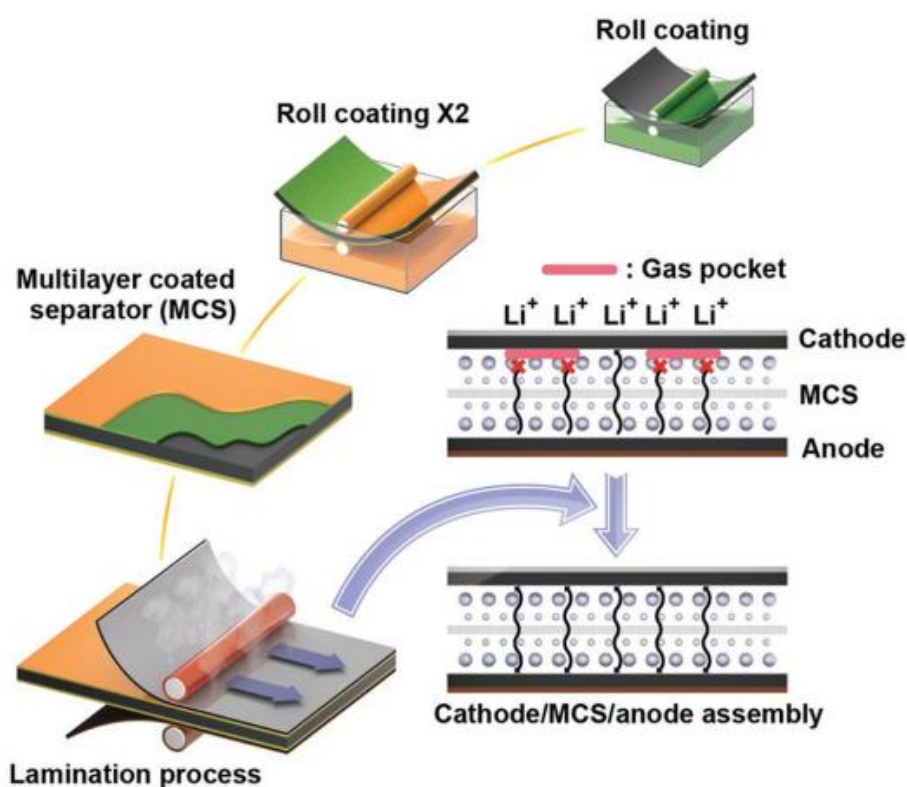

Figure 5.10 - Schematic illustration of the fabrication of MCS and integrated cathode/MCS/anode assembly [138].

This separator demonstrates that the ceramic and adhesive layers, composed of uniform micron-sized spherical particles, prevent the suppression of Li^+ diffusion between the NMC532 cathode and graphite anode while performing its intrinsic function and imparting thermal and mechanical stability [138]. Other strategy for the modification of PE separator was realized by coating with poly(p-phenylene terephthalamide) (PPTA) through a dip-coating and phase separation process in order to enhanced thermal-shutdown function [139]. PPTA coating does

not affect pore structure and this separator features superior wettability, ionic conductivity and cell performance [139].

In order to solve the thermal runaway, alumina coating has been performed leading to separators with improved safety and performance characteristics compared to the pristine polymeric separators [140]. Another strategy to improve the Li^+ transference number (t_{Li+}) was to produce a nanocomposite separator fabricated via the functionalization of a glass fiber (GF) separator with a metal–organic framework (MOF). The open metal sites in the MOF serve as the anchoring sites for anions, and the resulting t_{Li+} is increased by 100% as shown in Figure 5.11 [131].
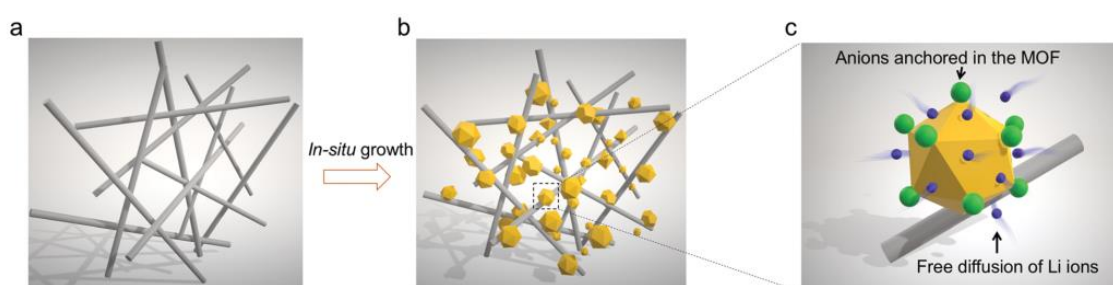

Figure 5.11 - Schematic illustrations of (a) glass fiber (GF) and (b) the MOF-GF composite separator (MOG) and (c) an enlarged view showing ion transport behavior in MOG [131]. This separator functionalized with MOFs enables the stable operation of Li metal anodes and improves the electrochemical performance [131].

The same approach was used with MOFs but in PVA composite membranes, leading to an enhancement of the electrode reaction kinetics and a reduction of the interface resistance between the electrolyte and the electrodes [141]. A new vapor-induced phase separation method was used for preparing poly (ether ether ketone) (PEEK) membranes with different pore structures as shown Figure 5.12.
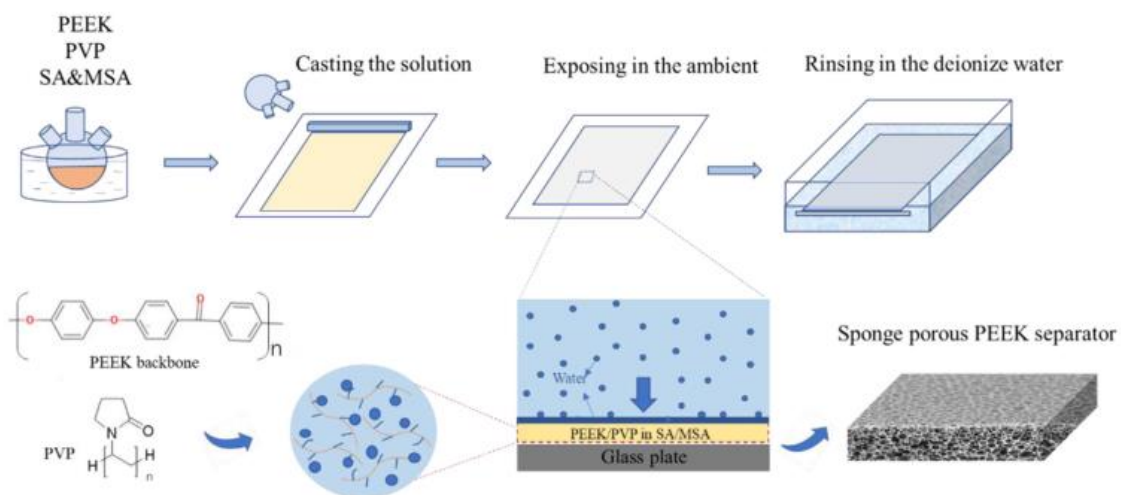
Figure 5.12 - Membrane preparation process of PEEK [133].

Through this method, it is possible to control pore size and porosity and these membranes in order to improve electrolyte uptake, porosity, ionic conductivity and electrochemical stability [133]. Polyacrylonitrile (PAN) nanofibrous membranes were prepared by electrospinning technique confirming that the porosity of the separators is essential to tailor the electrochemical performance of batteries, and that the tensile strength plays a key role in the winding operation during battery assembly [134].

PAN nanofibrous membranes were produced in one step by electrospinning of the ternary system of PAN/DMF/H_2O with phase separation mechanism, leading to fibers with an average diameter of 700–800 nm [142]. This separator membrane shows a higher air permeability value than the Celgard PP separators, leading also to hihgler porosity, interconnected pores and ionic conductivity [142].

In summary, synthetic polymers are widely used for battery separators, the most prominent being PVDF and its copolymers and polyolefins (PP and PE). Typically, the further work on those polymers in focus on improving processing techniques for morphology control and surface treatment / modification.

6.   Conclusions

In recent years, and due to society continuous technological development, battery systems have been increasingly being used in portable devices and electric vehicles. From the global battery market, lithium-ion batteries stand out from other systems as they are lighter, cheaper, show higher energy density, no memory effect and low less charge lost (self-discharge). The battery separator is essential in lithium-ion batteries. It is typically composed by a porous membrane and an electrolyte, separating the anode and cathode, and controlling the number and mobility of the lithium ions, affecting, therefore, cycling behavior of the battery. Basically, the porous membranes for the battery separator are based on synthetic polymers and the most commonly used are PVDF and its copolymers and polyolefins (PP and PE). Recently, research work on these polymers has been focusing on the use of new processing techniques to control morphology and surface treatment / modification. In addition, novel polymers are being investigated to improve thermal resistance in order to solve thermal leakage. Considering the relevant role of battery separators in lithium-ion battery systems, many scientific efforts are still needed for the development of new multifuntional porous membranes based on synthetic polymers with improved high ionic conductivity value, excellent thermal and mechanical properties and, consequently, high cycling behavior at high C-rates.

References

[1] S. Rajendran, M. Naushad, K. Raju, R. Boukherroub, Emerging Nanostructured Materials for Energy and Environmental Science, Springer International Publishing2019.

[2] J.P. Holdren, Energy and Sustainability, Science, 315 (2007) 737-737.

[3] J. Gubbi, R. Buyya, S. Marusic, M. Palaniswami, Internet of Things (IoT): A vision, architectural elements, and future directions, Future Generation Computer Systems, 29 (2013) 1645-1660.

[4] B. Scrosati, J. Hassoun, Y.-K. Sun, Lithium-ion batteries. A look into the future, Energy & Environmental Science, 4 (2011) 3287-3295.

[5] M.M. Thackeray, C. Wolverton, E.D. Isaacs, Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries, Energy & Environmental Science, 5 (2012) 7854-7863.

[6] J.-M. Tarascon, Key challenges in future Li-battery research, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 368 (2010) 3227-3241.

[7] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature, 414 (2001) 359-367.

[8] W.A. Van Schalkwijk, B. Scrosati, Advances in Lithium-Ion Batteries, Kluwer Academic/Plenum Publishers2002.

[9] M. Wakihara, O. Yamamoto, Lithium Ion Batteries: Fundamentals and Performance, John Wiley & Sons2008.

[10] K.E. Aifantis, S.A. Hackney, R.V. Kumar, High Energy Density Lithium Batteries: Materials, Engineering, Applications, John Wiley & Sons2010.

[11] N. Nitta, F. Wu, J.T. Lee, G. Yushin, Li-ion battery materials: present and future, Materials Today, 18 (2015) 252-264.

[12] P.B. Balbuena, Y. Wang, Lithium-Ion Batteries: Solid-Electrolyte Interphase, Imperial College Press2004.

[13] K.H.J. Buschow, Encyclopedia of materials: science and technology, Elsevier2001.

[14] L.-L. Zhang, Z.-L. Wang, D. Xu, X.-B. Zhang, L.-M. Wang, The development and challenges of rechargeable non-aqueous lithium–air batteries, International Journal of Smart and Nano Materials, (2012) 1-20.

[15] P. Arora, Z. Zhang, Battery separators, Chemical Reviews, 104 (2004) 4419-4462.

[16] K. Xu, Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries, Chemical Reviews, 104 (2004) 4303-4418.

[17] G.J. Janz, R.P.T. Tomkins, Nonaqueous Electrolytes Handbook, Academic Press1972.

[18] Q. Xiao, Z. Li, D. Gao, H. Zhang, A novel sandwiched membrane as polymer electrolyte for application in lithium-ion battery, Journal of Membrane Science, 326 (2009) 260-264.

[19] M. Wachtler, D. Ostrovskii, P. Jacobsson, B. Scrosati, A study on PVdF-based SiO2-containing composite gel-type polymer electrolytes for lithium batteries, Electrochimica Acta, 50 (2004) 357-361.

[20] K. Gao, X. Hu, C. Dai, T. Yi, Crystal structures of electrospun PVDF membranes and its separator application for rechargeable lithium metal cells, Materials Science and Engineering: B, 131 (2006) 100-105.

[21] Y.J. Shen, M.J. Reddy, P.P. Chu, Porous PVDF with LiClO4 complex as 'solid' and 'wet' polymer electrolyte, Solid State Ionics, 175 (2004) 747-750.

[22] J. Saunier, F. Alloin, J.Y. Sanchez, L. Maniguet, Plasticized microporous poly(vinylidene fluoride) separators for lithium-ion batteries. III. Gel properties and irreversible modifications of poly(vinylidene fluoride) membranes under swelling in liquid electrolytes, Journal of Polymer Science Part B: Polymer Physics, 42 (2004) 2308-2317.

[23] C.M. Costa, Y.-H. Lee, J.-H. Kim, S.-Y. Lee, S. Lanceros-Méndez, Recent advances on separator membranes for lithium-ion battery applications: From porous membranes to solid electrolytes, Energy Storage Materials, (2019).

[24] J.C. Barbosa, J.P. Dias, S. Lanceros-Méndez, C.M. Costa, Recent Advances in Poly(vinylidene fluoride) and Its Copolymers for Lithium-Ion Battery Separators, Membranes, 8 (2018) 45.

[25] X. Huang, Separator technologies for lithium-ion batteries, Journal of Solid State Electrochemistry, 15 (2011) 649-662.

[26] R.F.P. Pereira, R. Brito-Pereira, R. Gonçalves, M.P. Silva, C.M. Costa, M.M. Silva, V. de Zea Bermudez, S. Lanceros-Méndez, Silk Fibroin Separators: A Step Toward Lithium-Ion Batteries with Enhanced Sustainability, ACS Applied Materials & Interfaces, 10 (2018) 5385-5394.

[27] W. Xiao, K. Zhang, J. Liu, C. Yan, Preparation of poly(vinyl alcohol)-based separator with pore-forming additive for lithium-ion batteries, Journal of Materials Science: Materials in Electronics, 28 (2017) 17516-17525.

[28] L. Ma, R. Chen, Y. Hu, W. Zhang, G. Zhu, P. Zhao, T. Chen, C. Wang, W. Yan, Y. Wang, L. Wang, Z. Tie, J. Liu, Z. Jin, Nanoporous and lyophilic battery separator from regenerated eggshell membrane with effective suppression of dendritic lithium growth, Energy Storage Materials, 14 (2018) 258-266.

[29] J.-K. Kim, D.H. Kim, S.H. Joo, B. Choi, A. Cha, K.M. Kim, T.-H. Kwon, S.K. Kwak, S.J. Kang, J. Jin, Hierarchical Chitin Fibers with Aligned Nanofibrillar Architectures: A Nonwoven-Mat Separator for Lithium Metal Batteries, ACS Nano, 11 (2017) 6114-6121.

[30] R. Gonçalves, E. Lizundia, M.M. Silva, C.M. Costa, S. Lanceros-Méndez, Mesoporous Cellulose Nanocrystal Membranes as Battery Separators for Environmentally Safer Lithium-Ion Batteries, ACS Applied Energy Materials, 2 (2019) 3749-3761.

[31] Y.S. Chung, S.H. Yoo, C.K. Kim, Enhancement of Meltdown Temperature of the Polyethylene Lithium-Ion Battery Separator via Surface Coating with Polymers Having High Thermal Resistance, Industrial & Engineering Chemistry Research, 48 (2009) 4346-4351.

[32] G. Venugopal, J. Moore, J. Howard, S. Pendalwar, Characterization of microporous separators for lithium-ion batteries, Journal of Power Sources, 77 (1999) 34-41.

[33] B.K. Choi, K.H. Shin, Y.W. Kim, Lithium ion conduction in PEO-salt electrolytes gelled with PAN, Solid State Ionics, 113-115 (1998) 123-127.

[34] Y. Kang, H.J. Kim, E. Kim, B. Oh, J.H. Cho, Photocured PEO-based solid polymer electrolyte and its application to lithium-polymer batteries, Journal of Power Sources, 92 (2001) 255-259.

[35] B. Huang, Z. Wang, G. Li, H. Huang, R. Xue, L. Chen, F. Wang, Lithium ion conduction in polymer electrolytes based on PAN, Solid State Ionics, 85 (1996) 79-84.

[36] D. Djian, F. Alloin, S. Martinet, H. Lignier, Macroporous poly(vinylidene fluoride) membrane as a separator for lithium-ion batteries with high charge rate capacity, Journal of Power Sources, 187 (2009) 575-580.

[37] C.M. Costa, A. California, V.F. Cardoso, V. Sencadas, L.C. Rodrigues, M.M. Silva, S. Lanceros-Méndez, Electroactive Poly(Vinylidene Fluoride-Trifluorethylene) (PVDF-TrFE) Microporous Membranes for Lithium-Ion Battery Applications, Ferroelectrics, 430 (2012) 103-107.

[38] C.M. Costa, L.C. Rodrigues, V. Sencadas, M.M. Silva, S. Lanceros-Méndez, Effect of the microsctructure and lithium-ion content in poly[(vinylidene fluoride)-co-trifluoroethylene]/lithium perchlorate trihydrate composite membranes for battery applications, Solid State Ionics, 217 (2012) 19-26.

[39] C.M. Costa, L.C. Rodrigues, V. Sencadas, M.M. Silva, G. Rocha, S. Lanceros-Méndez, Effect of degree of porosity on the properties of poly(vinylidene fluoride-trifluoroethylene) for Li-ion battery separators, Journal of Membrane Science, 407-408 (2012) 8.

[40] A. Maceiras, A. Gören, V. Sencadas, C.M. Costa, J.L. Vilas, S. Lanceros-Méndez, L.M. León, Effect of cyano dipolar groups on the performance of lithium-ion battery electrospun polyimide gel electrolyte membranes, Journal of Electroanalytical Chemistry, 778 (2016) 57-65.

[41] H. Li, B. Zhang, B. Lin, Y. Yang, Y. Zhao, L. Wang, Electrospun Poly(ether ether ketone) Nanofibrous Separator with Superior Performance for Lithium-Ion Batteries, Journal of The Electrochemical Society, 165 (2018) A939-A946.

[42] D. Li, H. Zhang, X. Li, Porous polyetherimide membranes with tunable morphology for lithium-ion battery, Journal of Membrane Science, 565 (2018) 42-49.

[43] G. Sun, L. Kong, B. Liu, H. Niu, M. Zhang, G. Tian, S. Qi, D. Wu, Ultrahigh-strength, nonflammable and high-wettability separators based on novel polyimide-core@polybenzimidazole-sheath nanofibers for advanced and safe lithium-ion batteries, Journal of Membrane Science, 582 (2019) 132-139.

[44] H. Zhang, Y. Zhang, T. Xu, A.E. John, Y. Li, W. Li, B. Zhu, Poly(m-phenylene isophthalamide) separator for improving the heat resistance and power density of lithium-ion batteries, Journal of Power Sources, 329 (2016) 8-16.

[45] X.Q. Yang, H.S. Lee, L. Hanson, J. McBreen, Y. Okamoto, Development of a new plasticizer for poly(ethylene oxide)-based polymer electrolyte and the investigation of their ion-pair dissociation effect, Journal of Power Sources, 54 (1995) 198-204.

[46] O. Nishikawa, T. Sugimoto, S. Nomura, K. Doyama, K. Miyatake, H. Uchida, M. Watanabe, Preparation of the electrode for high temperature PEFCs using novel polymer electrolytes based on organic/inorganic nanohybrids, Electrochimica Acta, 50 (2004) 667-672.

[47] C.M. Costa, L.C. Rodrigues, V. Sencadas, M.M. Silva, J.G. Rocha, S. Lanceros-Méndez, Effect of degree of porosity on the properties of poly(vinylidene fluoride–trifluoroethylene) for Li-ion battery separators, Journal of Membrane Science, 407-408 (2012) 193-201.

[48] C.M. Costa, M. Kundu, V.F. Cardoso, A.V. Machado, M.M. Silva, S. Lanceros-Méndez, Silica/poly(vinylidene fluoride) porous composite membranes for lithium-ion battery separators, Journal of Membrane Science, 564 (2018) 842-851.

[49] J.R. Kim, S.W. Choi, S.M. Jo, W.S. Lee, B.C. Kim, Electrospun PVdF-based fibrous polymer electrolytes for lithium ion polymer batteries, Electrochimica Acta, 50 (2004) 69-75.

[50] C.M. Costa, M. Kundu, J.C. Dias, J. Nunes-Pereira, G. Botelho, M.M. Silva, S. Lanceros-Méndez, Mesoporous poly(vinylidene fluoride-co-trifluoroethylene) membranes for lithium-ion battery separators, Electrochimica Acta, 301 (2019) 97-106.

[51] V. Deimede, C. Elmasides, Separators for Lithium-Ion Batteries: A Review on the Production Processes and Recent Developments, Energy Technology, 3 (2015) 453-468.

[52] J.H. Ahn, H.-J. Shin, S. Abbas, K.-Y. Lee, H.Y. Ha, Plasma-functionalized carbon-layered separators for improved performance of lithium sulfur batteries, Journal of Materials Chemistry A, 7 (2019) 3772-3782.

[53] J.T. Jung, J.F. Kim, H.H. Wang, E. di Nicolo, E. Drioli, Y.M. Lee, Understanding the non-solvent induced phase separation (NIPS) effect during the fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS), Journal of Membrane Science, 514 (2016) 250-263.

[54] A.J. Castro, Methods for making microporous products, Google Patents, 1981.

[55] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes, Journal of Membrane Science, 375 (2011) 1-27.

[56] D.R. Lloyd, K.E. Kinzer, H.S. Tseng, Microporous membrane formation via thermally induced phase separation. I. Solid-liquid phase separation, Journal of Membrane Science, 52 (1990) 239-261.

[57] Z. Cui, E. Drioli, Y.M. Lee, Recent progress in fluoropolymers for membranes, Progress in Polymer Science, 39 (2014) 164-198.

[58] M. Zahid, A. Rashid, S. Akram, Z. Rehan, W. Razzaq, A Comprehensive Review on Polymeric Nano-Composite Membranes for Water Treatment, Journal of Membrane Science & Technology, 08 (2018).

[59] M. Gu, J. Zhang, X. Wang, H. Tao, L. Ge, Formation of poly(vinylidene fluoride) (PVDF) membranes via thermally induced phase separation, Desalination, 192 (2006) 160-167.

[60] J.L. Kim, Kent R. Kerley: Religious Faith in Correctional Contexts, Review of Religious Research, 57 (2015) 461-463.

[61] J.C.C. Ferreira, T.S. Monteiro, A.C. Lopes, C.M. Costa, M.M. Silva, A.V. Machado, S. Lanceros-Mendez, Variation of the physicochemical and morphological characteristics of solvent casted poly(vinylidene fluoride) along its binary phase diagram with dimethylformamide, Journal of Non-Crystalline Solids, 412 (2015) 16-23.

[62] H.H. Wang, J.T. Jung, J.F. Kim, S. Kim, E. Drioli, Y.M. Lee, A novel green solvent alternative for polymeric membrane preparation via nonsolvent-induced phase separation (NIPS), Journal of Membrane Science, 574 (2019) 44-54.

[63] G.-d. Kang, Y.-m. Cao, Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review, Journal of Membrane Science, 463 (2014) 145-165.

[64] X. Dong, A. Al-Jumaily, I.C. Escobar, Investigation of the Use of a Bio-Derived Solvent for Non-Solvent-Induced Phase Separation (NIPS) Fabrication of Polysulfone Membranes, Membranes, 8 (2018) 23.

[65] P. van de Witte, P.J. Dijkstra, J.W.A. van den Berg, J. Feijen, Phase separation processes in polymer solutions in relation to membrane formation, Journal of Membrane Science, 117 (1996) 1-31.

[66] J.F. Kim, J.T. Jung, H.H. Wang, S.Y. Lee, T. Moore, A. Sanguineti, E. Drioli, Y.M. Lee, Microporous PVDF membranes via thermally induced phase separation (TIPS) and stretching methods, Journal of Membrane Science, 509 (2016) 94-104.

[67] Z. Cui, N.T. Hassankiadeh, S.Y. Lee, K.T. Woo, J.M. Lee, A. Sanguineti, V. Arcella, Y.M. Lee, E. Drioli, Tailoring novel fibrillar morphologies in poly(vinylidene fluoride) membranes using a low toxic triethylene glycol diacetate (TEGDA) diluent, Journal of Membrane Science, 473 (2015) 128-136.

[68] P. Mallick, S. Tripathi, P. Srivastava, Advancement in Scaffolds for Bone Tissue Engineering: A Review, IOSR Journal of Pharmacy and Biological Sciences, 10 (2015) 37-54.

[69] U. Sampath, C. Yern Chee, C.H. Chuah, J. J. Sabariah, P.-C. Lin, Fabrication of Porous Materials from Natural/Synthetic Biopolymers and Their Composites, Materials, 9 (2016) 991.

[70] A.G. Mikos, A.J. Thorsen, L.A. Czerwonka, Y. Bao, R. Langer, D.N. Winslow, J.P. Vacanti, Preparation and characterization of poly(l-lactic acid) foams, Polymer, 35 (1994) 1068-1077.

[71] D.M. Correia, C. Ribeiro, V. Sencadas, L. Vikingsson, M. Oliver Gasch, J.L. Gómez Ribelles, G. Botelho, S. Lanceros-Méndez, Strategies for the development of three dimensional scaffolds from piezoelectric poly(vinylidene fluoride), Materials & Design, 92 (2016) 674-681.

[72] Y. Xia, G.M. Whitesides, Soft lithography, Annual review of materials science, 28 (1998) 153-184.

[73] D.B. Weibel, W.R. DiLuzio, G.M. Whitesides, Microfabrication meets microbiology, Nature Reviews Microbiology, 5 (2007) 209.

[74] C. Ribeiro, C.M. Costa, D.M. Correia, J. Nunes-Pereira, J. Oliveira, P. Martins, R. Gonçalves, V.F. Cardoso, S. Lanceros-Méndez, Electroactive poly(vinylidene fluoride)-based structures for advanced applications, Nature Protocols, 13 (2018) 681.

[75] T. Marques-Almeida, V.F. Cardoso, S. Ribeiro, F.M. Gama, C. Ribeiro, S. Lanceros-Mendez, Tuning Myoblast and Preosteoblast Cell Adhesion Site, Orientation, and Elongation through Electroactive Micropatterned Scaffolds, ACS Applied Bio Materials, 2 (2019) 1591-1602.

[76] V.F. Cardoso, A.R. Machado, V.C. Pinto, P.J. Sousa, G. Botelho, G. Minas, S. Lanceros-Méndez, From superhydrophobic- to superhydrophilic-patterned poly(vinylidene fluoride-co-chlorotrifluoroethylene) architectures as a novel platform for biotechnological applications, Journal of Polymer Science Part B: Polymer Physics, 54 (2016) 1802-1810.

[77] G.S. Fiorini, R.M. Lorenz, J.S. Kuo, D.T. Chiu, Rapid Prototyping of Thermoset Polyester Microfluidic Devices, Analytical Chemistry, 76 (2004) 4697-4704.

[78] D. Sticker, M. Rothbauer, S. Lechner, M.-T. Hehenberger, E. Peter, Multi-layered, membrane-integrated microfluidics based on replica molding of a thiol-ene epoxy thermoset for Organ-on-a-Chip applications, Lab on a chip, 15 (2015).

[79] C. Mu, Y. Su, M. Sun, W. Chen, Z. Jiang, Fabrication of microporous membranes by a feasible freeze method, Journal of Membrane Science, 361 (2010) 15-21.

[80] U. Soltmann, H. Böttcher, D. Koch, G. Grathwohl, Freeze gelation: a new option for the production of biological ceramic composites (biocers), Materials Letters, 57 (2003) 2861-2865.

[81] K. Whang, C.H. Thomas, K.E. Healy, G. Nuber, A novel method to fabricate bioabsorbable scaffolds, Polymer, 36 (1995) 837-842.

[82] M.-H. Ho, P.-Y. Kuo, H.-J. Hsieh, T.-Y. Hsien, L.-T. Hou, J.-Y. Lai, D.-M. Wang, Preparation of porous scaffolds by using freeze-extraction and freeze-gelation methods, Biomaterials, 25 (2004) 129-138.

[83] A. Kramschuster, L.-S. Turng, Fabrication of Tissue Engineering Scaffolds, 2013, pp. 427-446.

[84] A. Formhals, Process and apparatus for preparing artificial threads. US Patent, 1975504, vol, 1 (1934) 7.

[85] Z.-M. Huang, Y.Z. Zhang, M. Kotaki, S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocomposites, Composites Science and Technology, 63 (2003) 2223-2253.

[86] X. Shi, W. Zhou, D. Ma, Q. Ma, D. Bridges, Y. Ma, A. Hu, Electrospinning of Nanofibers and Their Applications for Energy Devices, Journal of Nanomaterials, 2015 (2015) 20.

[87] H. Zong, X. Xia, Y. Liang, S. Dai, A. Alsaedi, T. Hayat, F. Kong, J.H. Pan, Designing function-oriented artificial nanomaterials and membranes via electrospinning and electrospraying techniques, Materials Science and Engineering: C, 92 (2018) 1075-1091.

[88] J. Anu Bhushani, C. Anandharamakrishnan, Electrospinning and electrospraying techniques: Potential food based applications, Trends in Food Science & Technology, 38 (2014) 21-33.

[89] K. Ghosal, A. Chandra, P. G, S. S, S. Roy, C. Agatemor, S. Thomas, I. Provaznik, Electrospinning over Solvent Casting: Tuning of Mechanical Properties of Membranes, Scientific Reports, 8 (2018) 5058.

[90] F.E. Ahmed, B.S. Lalia, R. Hashaikeh, A review on electrospinning for membrane fabrication: Challenges and applications, Desalination, 356 (2015) 15-30.

[91] N. Bhardwaj, S.C. Kundu, Electrospinning: A fascinating fiber fabrication technique, Biotechnology Advances, 28 (2010) 325-347.

[92] Z. Xue, Z. Zhang, S.S. Zhang, Microstructurally Composed and Surface Modification of Polyolefin Separator, in: Z. Zhang, S.S. Zhang (Eds.) Rechargeable Batteries: Materials, Technologies and New Trends, Springer International Publishing, Switzerland, 2015, pp. 353-392.

[93] S.S. Zhang, A review on the separators of liquid electrolyte Li-ion batteries, Journal of Power Sources, 164 (2007) 351-364.

[94] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, X. Zhang, A review of recent developments in membrane separators for rechargeable lithium-ion batteries, Energy and Environmental Science, 7 (2014) 3857-3886.

[95] ASTM D645 / D645M-97(2007), Standard Test Method for Thickness of Paper and Paperboard, ASTM International, West Conshohocken, 2007.

[96] ASTM E1294-89(1999), Standard Test Method for Pore Size Characteristics of Membrane Filters Using Automated Liquid Porosimeter, ASTM International, West Conshohocken, 1999.

[97] ASTM D2873-94(1999)e1, Standard Test Method for Interior Porosity of Poly(Vinyl Chloride) (PVC) Resins by Mercury Intrusion Porosimetry, ASTM International, West Conshohocken, 1999.

[98] J. Nunes-Pereira, C.M. Costa, R.E. Sousa, A.V. Machado, M.M. Silva, S. Lanceros-Méndez, Li-ion battery separator membranes based on barium titanate and poly(vinylidene fluoride-co-trifluoroethylene): Filler size and concentration effects, Electrochimica Acta, 117 (2014) 276-284.

[99] ASTM D726-94(2003), Standard Test Method for Resistance of Nonporous Paper to Passage of Air, ASTM International, West Conshohocken, 1994.

[100] ASTM D737-96, Test Method for Air Permeability of Textile Fabrics, ASTM International, West Conshohocken, 1996.

[101] ASTM D882-18, Standard Test Method for Tensile Properties of Thin Plastic Sheeting, ASTM International, West Conshohocken, 2018.

[102] ASTM D638-14, Standard Test Method for Tensile Properties of Plastics, ASTM International, West Conshohocken, 2014.

[103] ASTM D3763-18, Standard Test Method for High Speed Puncture Properties of Plastics Using Load and Displacement Sensors, ASTM International, West Conshohocken, 2018.

[104] R. Gonçalves, D. Miranda, A.M. Almeida, M.M. Silva, J.M. Meseguer-Dueñas, J.L.G. Ribelles, S. Lanceros-Méndez, C.M. Costa, Solid polymer electrolytes based on lithium bis(trifluoromethanesulfonyl)imide/poly(vinylidene fluoride -co-hexafluoropropylene) for safer rechargeable lithium-ion batteries, Sustainable Materials and Technologies, 21 (2019).

[105] D. Chen, Z. Zhou, C. Feng, W. Lv, Z. Wei, K.H.L. Zhang, B. Lin, S. Wu, T. Lei, X. Guo, G. Zhu, X. Jian, J. Xiong, E. Traversa, S.X. Dou, W. He, An Upgraded Lithium Ion Battery Based on a Polymeric Separator Incorporated with Anode Active Materials, Advanced Energy Materials, 9 (2019) 1803627.

[106] J. Liu, X. Shi, B. Boateng, Y. Han, D. Chen, W. He, A Highly Stable Separator from an Instantly Reformed Gel with Direct Post-Solidation for Long-Cycle High-Rate Lithium-Ion Batteries, ChemSusChem, 12 (2019) 908-914.

[107] X. Gui, L. Liu, S. Gao, L. Sun, K. Xu, M. Chen, A novel silsesquioxanes modified electrospun composite fibrous separator by in-situ crosslinking method for lithium-ion batteries, Materials Letters, 242 (2019) 66-70.

[108] X. Shi, Q. Sun, B. Boateng, Y. Niu, Y. Han, W. Lv, W. He, A quasi-solid composite separator with high ductility for safe and high-performance lithium-ion batteries, Journal of Power Sources, 414 (2019) 225-232.

[109] N. Wei, J. Hu, M. Zhang, J. He, P. Ni, Cross-linked porous polymer separator using vinyl-modified aluminum oxide nanoparticles as cross-linker for lithium-ion batteries, Electrochimica Acta, 307 (2019) 495-502.

[110] Y. Han, L. Ye, B. Boateng, Q. Sun, C. Zhen, N. Chen, X. Shi, J.H. Dickerson, X. Li, W. He, Direct electrophoretic deposition of an ultra-strong separator on an anode in a surfactant-free colloidal system for lithium ion batteries, Journal of Materials Chemistry A, 7 (2019) 1410-1417.

[111] M. Waqas, S. Ali, W. Lv, D. Chen, B. Boateng, W. He, High-Performance PE-BN/PVDF-HFP Bilayer Separator for Lithium-Ion Batteries, Advanced Materials Interfaces, 6 (2019) 1801330.

[112] R. Gonçalves, T. Marques-Almeida, D. Miranda, M.M. Silva, V.F. Cardoso, C.M. Costa, S. Lanceros-Méndez, Enhanced performance of fluorinated separator membranes for lithium ion batteries through surface micropatterning, Energy Storage Materials, (2019).

[113] L. Wang, Z. Wang, Y. Sun, X. Liang, H. Xiang, Sb2O3 modified PVDF-CTFE electrospun fibrous membrane as a safe lithium-ion battery separator, Journal of Membrane Science, 572 (2019) 512-519.

[114] J. Liu, C. Wang, X. Wu, F. Zhu, M. Liu, Y. Xi, An enhanced poly(vinylidene fluoride) matrix separator with TEOS for good performance lithium-ion batteries, Journal of Solid State Electrochemistry, (2018).

[115] L. Wang, N. Deng, J. Ju, G. Wang, B. Cheng, W. Kang, A novel core-shell structured poly-m-phenyleneisophthalamide@polyvinylidene fluoride nanofiber membrane for lithium ion batteries with high-safety and stable electrochemical performance, Electrochimica Acta, 300 (2019) 263-273.

[116] M.V. Bhute, S.B. Kondawar, Electrospun poly(vinylidene fluoride)/cellulose acetate/AgTiO2 nanofibers polymer electrolyte membrane for lithium ion battery, Solid State Ionics, 333 (2019) 38-44.

[117] Y. Xia, J. Li, H. Wang, Z. Ye, X. Zhou, H. Huang, Y. Gan, C. Liang, J. Zhang, W. Zhang, Synthesis and electrochemical performance of poly(vinylidene fluoride)/SiO2 hybrid membrane for lithium-ion batteries, Journal of Solid State Electrochemistry, 23 (2019) 519-527.

[118] Z. Wang, Y. Xie, C. Xu, S. Shi, L. Wang, G. Zhang, X. Wang, L. Zhu, D. Xu, Zirconia fiber membranes based on PVDF as high-safety separators for lithium-ion batteries using a papermaking method, Journal of Solid State Electrochemistry, 23 (2019) 269-276.

[119] G. Dong, G. Sun, G. Tian, S. Qi, D. Wu, Robust Polyimide Nanofibrous Membrane with Bonding Microstructures Fabricated via Dipping Process for Lithium-Ion Battery Separators, Energy Technology, 7 (2019) 1801072.

[120] G. Dong, B. Liu, G. Sun, G. Tian, S. Qi, D. Wu, TiO2 nanoshell@polyimide nanofiber membrane prepared via a surface-alkaline-etching and in-situ complexation-hydrolysis strategy for advanced and safe LIB separator, Journal of Membrane Science, 577 (2019) 249-257.

[121] L. Li, P. Liu, Q.S. Fu, Y. Gong, S.R. Zhang, H.J. He, J. Chen, Study on preparation of polyacrylonitrile/polyimide composite lithium-ion battery separator by electrospinning, Journal of Materials Research, 34 (2019) 642-651.

[122] S. Byun, S.H. Lee, D. Song, M.-H. Ryou, Y.M. Lee, W.H. Park, A crosslinked nonwoven separator based on an organosoluble polyimide for high-performance lithium-ion batteries, Journal of Industrial and Engineering Chemistry, 72 (2019) 390-399.

[123] G. Zhong, Y. Wang, C. Wang, Z. Wang, S. Guo, L. Wang, X. Liang, H. Xiang, An AlOOH-coated polyimide electrospun fibrous membrane as a high-safety lithium-ion battery separator, Ionics, 25 (2019) 2677-2684.

[124] W. Gong, J. Gu, S. Ruan, C. Shen, A high-strength electrospun PPESK fibrous membrane for lithium-ion battery separator, Polymer Bulletin, (2019).

[125] Y. Fan, D. Liu, M.M. Rahman, T. Tao, W. Lei, S. Mateti, B. Yu, J. Wang, C. Yang, Y. Chen, Repelling Polysulfide Ions by Boron Nitride Nanosheet Coated Separators in Lithium–Sulfur Batteries, ACS Applied Energy Materials, 2 (2019) 2620-2628.

[126] M.M. Rahman, S. Mateti, Q. Cai, I. Sultana, Y. Fan, X. Wang, C. Hou, Y. Chen, High temperature and high rate lithium-ion batteries with boron nitride nanotubes coated polypropylene separators, Energy Storage Materials, 19 (2019) 352-359.

[127] J. Moon, J.Y. Jeong, J.I. Kim, S. Kim, J.H. Park, An ultrathin inorganic-organic hybrid layer on commercial polymer separators for advanced lithium-ion batteries, Journal of Power Sources, 416 (2019) 89-94.

[128] H. Jeon, Y. Roh, D. Jin, M.-H. Ryou, Y.-C. Jeong, Y.M. Lee, Crosslinkable polyhedral silsesquioxane-based ceramic-coated separators for Li-ion batteries, Journal of Industrial and Engineering Chemistry, 71 (2019) 277-283.

[129] K.J. Kim, Y.K. Kwon, T. Yim, W. Choi, Functional separator with lower resistance toward lithium ion transport for enhancing the electrochemical performance of lithium ion batteries, Journal of Industrial and Engineering Chemistry, 71 (2019) 228-233.

[130] J.Y. Kim, D.O. Shin, K.M. Kim, J. Oh, J. Kim, S.H. Kang, M.J. Lee, Y.-G. Lee, Graphene Oxide Induced Surface Modification for Functional Separators in Lithium Secondary Batteries, Scientific Reports, 9 (2019) 2464.

[131] L. Shen, H.B. Wu, F. Liu, C. Zhang, S. Ma, Z. Le, Y. Lu, Anchoring anions with metal–organic framework-functionalized separators for advanced lithium batteries, Nanoscale Horizons, 4 (2019) 705-711.

[132] T. Zhang, H. Qu, K. Sun, Development of polydopamine coated electrospun PAN/PMMA nanofibrous membrane as composite separator for Lithium-ion batteries, Materials Letters, 245 (2019) 10-13.

[133] J. Li, X. Niu, J. Song, Y. Li, X. Li, W. Hao, J. Fang, T. He, Harvesting vapor by hygroscopic acid to create pore: Morphology, crystallinity and performance of poly (ether ether ketone) lithium ion battery separator, Journal of Membrane Science, 577 (2019) 1-11.

[134] W.U. Arifeen, M. Kim, J. Choi, K. Yoo, R. Kurniawan, T.J. Ko, Optimization of porosity and tensile strength of electrospun polyacrylonitrile nanofibrous membranes, Materials Chemistry and Physics, 229 (2019) 310-318.

[135] F. Zeng, R. Xu, L. Ye, B. Xiong, J. Kang, M. Xiang, L. Li, X. Sheng, Z. Hao, Effects of Heat Setting on the Morphology and Performance of Polypropylene Separator for Lithium Ion Batteries, Industrial & Engineering Chemistry Research, 58 (2019) 2217-2224.

[136] L. Ding, R. Xu, L. Pu, F. Yang, T. Wu, M. Xiang, Pore formation and evolution mechanism during biaxial stretching of β-iPP used for lithium-ion batteries separator, Materials & Design, 179 (2019) 107880.

[137] E. Shekarian, M.R. Jafari Nasr, T. Mohammadi, O. Bakhtiari, M. Javanbakht, Preparation of 4A zeolite coated polypropylene membrane for lithium-ion batteries separator, Journal of Applied Polymer Science, 136 (2019) 47841.

[138] S.H. Lee, J. Kim, B.-H. Kim, S. Yoon, K.Y. Cho, Delamination-Free Multifunctional Separator for Long-Term Stability of Lithium-Ion Batteries, Small, 15 (2019) 1804980.

[139] X. Zhang, N. Li, Z. Hu, J. Yu, Y. Wang, J. Zhu, Poly(p-phenylene terephthalamide) modified PE separators for lithium ion batteries, Journal of Membrane Science, 581 (2019) 355-361.

[140] N. Kanhere, K. Rafiz, G. Sharma, Z. Sun, Y. Jin, Y.S. Lin, Electrode-coated alumina separators for lithium-ion batteries - effect of particle size and distribution of alumina powders, Powder Technology, 353 (2019) 230-237.

[141] C. Zhang, L. Shen, J. Shen, F. Liu, G. Chen, R. Tao, S. Ma, Y. Peng, Y. Lu, Anion-Sorbent Composite Separators for High-Rate Lithium-Ion Batteries, Advanced Materials, 31 (2019) 1808338.

[142] N. Sabetzadeh, A.A. Gharehaghaji, M. Javanbakht, Porous PAN micro/nanofiber membranes with potential application as Lithium-ion battery separators: physical, morphological and thermal properties, Journal of Polymer Research, 26 (2019) 20.