

Polymers for advanced lithium-ion batteries: state of the art and future needs on polymers for the different battery components

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Abstract

Polymers have been successfully used as electrode compounds and separator / electrolyte materials for lithium ion batteries (LiBs) due to their inherent outstanding properties such as low-density, easy of processing, excellent thermal, mechanical and electrical properties and easily tailored functional performance matching the final device requirements. Battery performance strongly depends on the polymer type used. The physico-chemical properties of the polymers that are being used as different battery components need to be further improved to boost the development of the next generation of batteries for the electric vehicle industry, where increased energy density and safety are required. Considering its role in LIBs, this review summarizes the latest advances in the field of polymers applied as electrode compounds and separator/electrolytes. For each battery component, the state-of-art is divided by polymer type. Current bottlenecks and challenges that face polymers in LIBs are shown, and possible strategies to face them are provided.

Keywords: Polymers; electrodes; separator/electrolytes; lithium-ion batteries

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1. Introduction

There is an increasing and needed trend towards a reduction of the consumption of fossil fuels mainly due to environmental impact as well as an increasing need of highly efficient energy storage systems as energy heads the list of top global problems for the next 50 years [1]. In fact, the use of efficient energy storage devices for portable electronics and electric vehicles is continuously growing and for the near future, novel materials and devices with improved energy density and safety will be needed. In this framework, Fig. 1 presents the Ragone plot (Energy density vs Power density) for the different energy storage systems [2, 3].

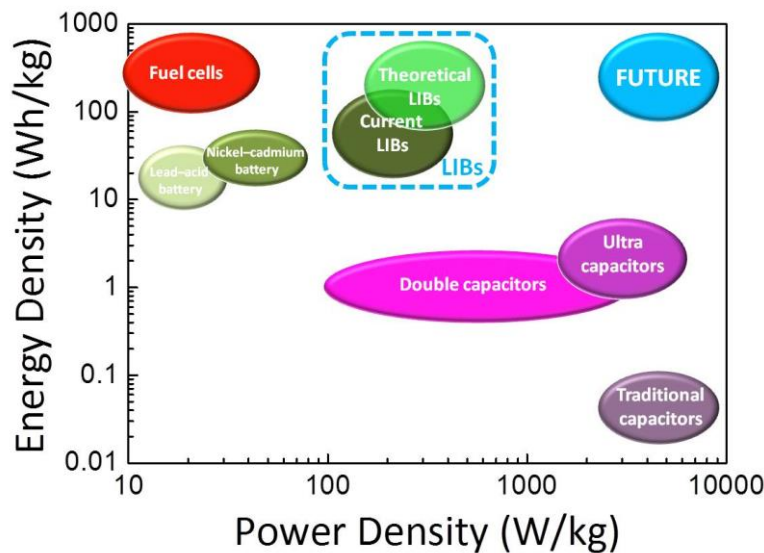


Fig. 1. Ragone plot for energy storage systems.

Currently, lithium-ion batteries (LIBs) represent one of the most prominent energy storage systems when compared to other energy storage systems (Fig. 1), with a compound annual growth rate (CAGR) of 17.0% and an expected global value of US \$ 93.1 billion by 2025 [4]. When compared to other battery technologies, LIBs are lighter, cheaper, show higher energy density with lower lost load (self-discharge), no memory effect, prolonged service life and larger number of charge / discharge cycles [5, 6]. As a matter of fact, specific energy, power, safety and reliability are key issues for improving the performance of lithium-ion batteries, which are typically composed of two electrodes (anode and cathode, negative and positive electrodes, respectively) and a separator / electrolyte as shown in Fig. 2[7, 8].

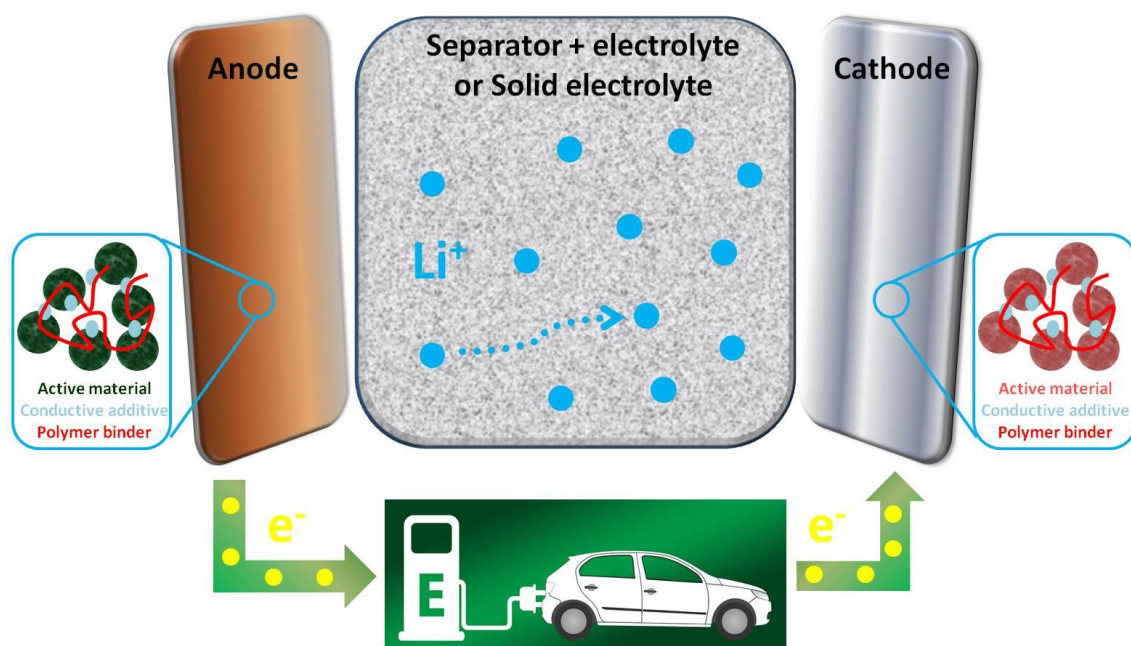


Fig. 2. Typical components of lithium-ion batteries.

Both electrodes are typically composed of a polymer binder, a conductive additive and an active material as represented in Fig. 2 [9]. Each component of the electrode has a specific function, where the polymer binder holds together the other components (active material and conductive additive) at the same time that improves the mechanical stability and flexibility of the electrode [10, 11]. The separator / electrolyte, as the other component of the battery, have the function of electrically separating the anode and the cathode while ensuring lithium ion mobility [12]. Polymeric materials are particularly relevant in LIBs since they are used within the electrodes as binders and also in the separator/electrolytes. Overall, polymers can be used in all of the components thanks to their unique properties such as mechanical flexibility, chemical resistance, excellent processability and lightweight. Accordingly, Fig. 3 shows the different polymer types used for both components of LIBs [12].

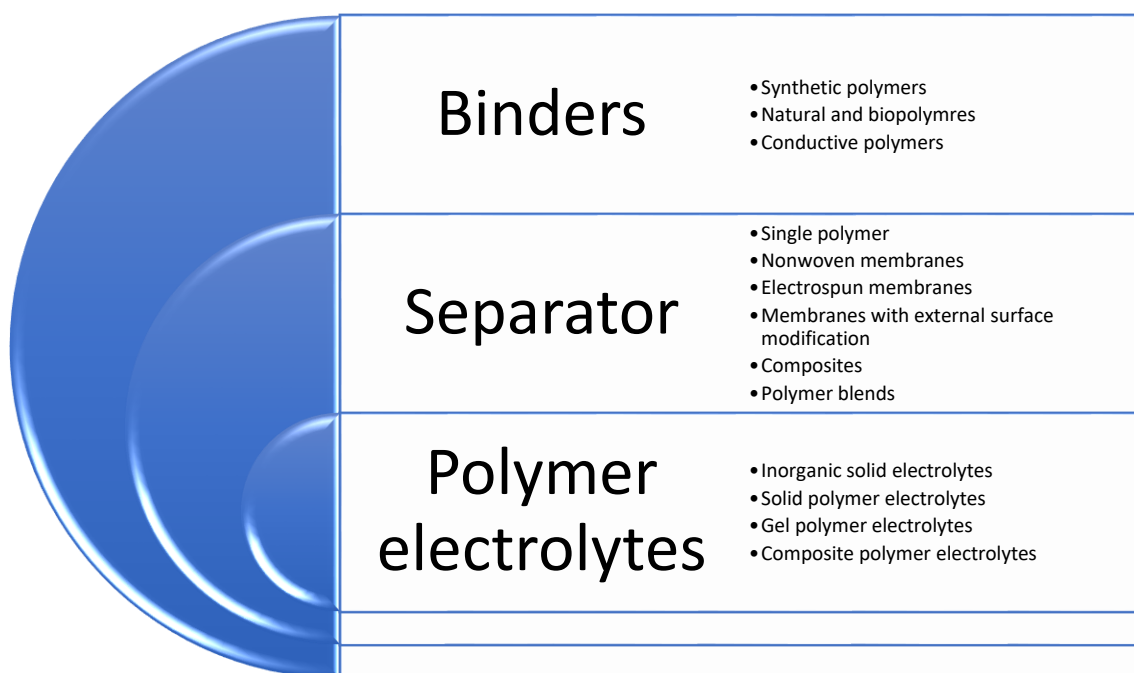


Fig. 3. Polymer types used in electrodes and separator/electrolytes.

This review analyzes the wide variety of polymer materials used in lithium ion batteries, considering the different types presented in Fig. 3. Special emphasis is placed in the role, function and properties of the different polymeric materials. Due to the critical role of polymers in the separator/electrolyte when compared to polymer binders for electrodes, stronger research efforts have been carried out in aspect related to the separator/electrolyte, as it is shown in this review.

2. Polymers for electrodes: polymer binder

2.1. Function of the polymer binder and main desired characteristics

Fig. 4 shows the typical structure of the electrode showing the main function of the polymer binder which acts as a cohesion element between the active material, the conductive additive and the current collector.

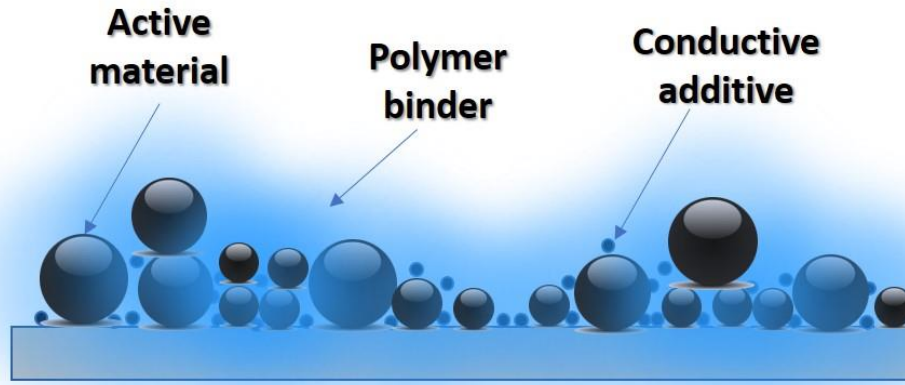


Fig. 4.– Schematic representation of the battery electrode.

Thus, the polymer binder affects the bonding between active material and conductive additive, processing parameters, morphology within electrode, and electrical and mechanical properties of the electrode, as well as the electrochemical performance as it is illustrated in the Fig. 5 [13]. An absence or deterioration of the binder results in decreased electronic conductivity and electrochemical properties of the electrode due to a non-efficient physical contact between the particles of the electrode [10].

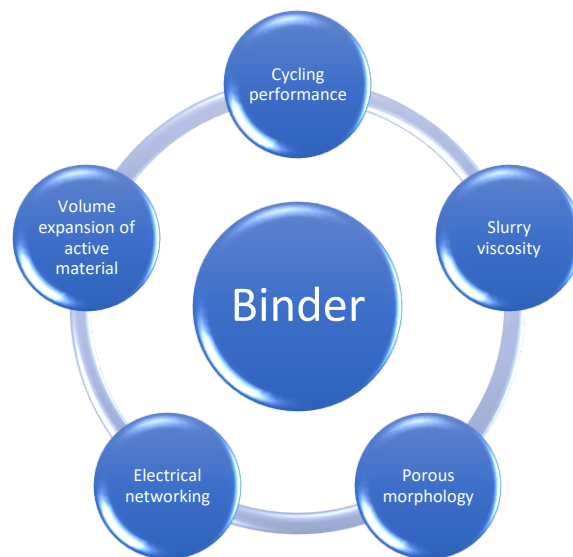


Fig. 5. Main properties affected by the polymer binder

Properties such as molecular type of polymer and molecular weight, mechanical properties and the used solvent [14] affect the resulting rheological properties of the electrode material and consequently, their electrochemical properties [15]. Similarly, the polymer binder affects the rheological behavior of the slurries, determining the binder

preparation method, slurry stability and hence the battery performance [16]. In fact, the microstructure of the slurry, i.e, dispersion of the particles, can be estimated by the rheological measurements [17].

The polymer distribution on filler particles depends on the surface area and surface chemistry, different types of polymers or even different batches of similar materials leading to different surface chemistry properties, being therefore critical the electrode optimization for each polymer in order to obtain an optimum performance [18]. For example, an unsuitable binder distribution would reduce the adhesion strength to the current collector, increase surface resistance of the electrode plates and reduce the overall electrochemical properties [19]. Accordingly, the role of the polymer binder can be described at the macroscopic and microscopic levels, as represented in Fig. 6.

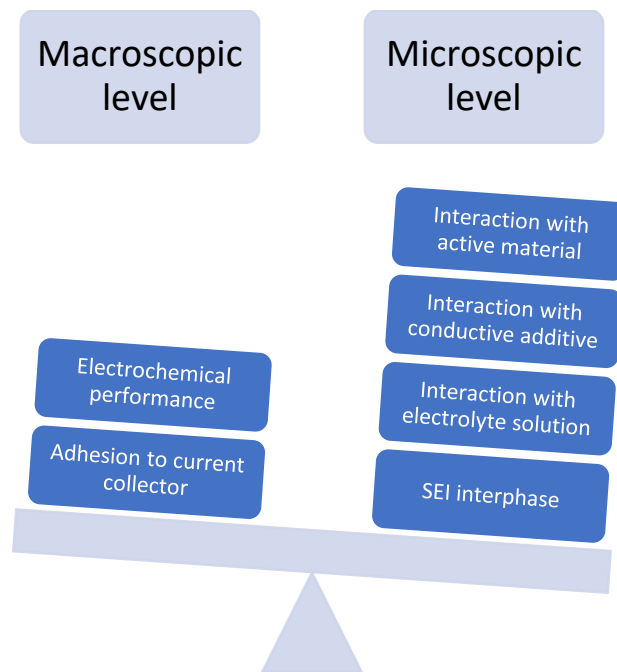


Fig. 6. Polymer binder influence on battery properties at the macroscopic and microscopic levels.

The macroscopic level is associated with the electrochemical performance, i.e., electronic / ionic conductivity and cycling performance (cycle life and rate performance). On the contrary, the microscopic level is associated with the following issues:

- a) cohesion between active material and conductive additive – binding bridges;
- b) distribution of binder on the active material surface;

- c) interaction of binder with active material (nature of chemical bonding: hydrogen bonds and Van der Waals forces);
- d) contribution of the binder to the formation of a stable solid electrolyte interface (SEI) layer (mainly onto anode electrodes);
- e) interaction/absorption (electrolyte wettability) of the electrolyte by the binder allowing a facile Li transport to the active material's surface.

2.2. Polymer binder types

Different polymer binder types are used in electrode materials from fluorinated polymers such as poly(vinylidene fluoride) (PVDF) or carboxymethyl cellulose (CMC) biopolymers. Therefore, the state of the art on polymer binders for the electrodes is organized into three sections dedicated to synthetic polymers, natural/biopolymers and conductive polymers, respectively.

2.2.1. Synthetic polymers

Polymer binders are an essential component of electrodes, affecting cycling performance of lithium-ion batteries. Some characteristics such as high adhesion, suitable mechanical properties, high electrolyte absorption, high thermal stability and chemical resistance need to be fulfilled by the polymer binders [9]. In that sense, Table 1 shows the most common polymer used as binder for electrodes. Although there are several synthetic polymer binders optimized for different active materials, taking into account their size and surface area, among others, PVDF emerges as the most widely used polymer for various active materials, independently of being the anode or the cathode due to its electrochemical stability from 0 to 5 V, high adhesion to the current collector and excellent mechanical properties [20].

Table 1. Typical synthetic polymers used as binders for electrodes.

Name of binder	Solvent	Main properties	Most used Active Material		Ref
			Cathode	Anode	
Lithium polyacrylate (Li-	Water	- improves the adhesion strength,	$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$	$\text{Sn}_{30}\text{Co}_{30}\text{C}_{40}$	[21]

PAA)		<ul style="list-style-type: none"> - improves slurry dispersion, - rate capability 		Si/graphite	[22]
Nafion	NMP	<ul style="list-style-type: none"> - high ionic conductivity, - high thermal stability 	LiMn ₂ O ₄		[23]
Poly(acrylic acid) (PAA)	NMP + water	<ul style="list-style-type: none"> - without the co-intercalation and decomposition of propylene carbonate (PC) molecules, - functional groups - improve reversibility of lithium intercalation 	LiFePO ₄ LiCoO ₂ LiMn ₂ O ₄	Graphite Si Sulfur SnSb/ Graphene Li ₁₅ Si ₄ ZnMoO ₄ Si-alloy SiO Fe ₃ O ₄ SnO ₂	[25] [26] [27] [28] [29] [30] [31] [32] [33] [34]
PAmA	DMAc	<ul style="list-style-type: none"> - highly adhesive, - good binding, - excellent mechanical properties 		Si-Ni-SiC	[35]
PAN	Toluene NMP	<ul style="list-style-type: none"> - excellent chemistry stability, - strong adhesion 		Si Li ₄ Ti ₅ O ₁₂ Graphite	[36] [37] [38] [39]
PBI	NMP	<ul style="list-style-type: none"> - - excellent electrochemical windows 		Graphene oxide	[40]
Polyethylene	----	<ul style="list-style-type: none"> - excellent mechanical properties, - side group 		Li _x SiO ₂	[41]
PEG	DMF	<ul style="list-style-type: none"> - excellent mechanical behavior, - electrode integrity, - chemical interaction with the electrolyte 		Sulfur Si	[42] [43]
PEI	DMF	<ul style="list-style-type: none"> - strong affinity with the electrolyte 		Sulfur	[44]

		<ul style="list-style-type: none"> - hyperbranched network structures, - excellent mechanical properties 			
Poly(ethylene oxide) (PEO)	Water	<ul style="list-style-type: none"> - effective transfer of lithium ions 		Sulfur	[45]
PEO:PVP	water	<ul style="list-style-type: none"> - water soluble, - mechanical integrity, - facilitates adsorption of polysulfides 		Sulfur	[46]
Poly(ionic liquid)	----	<ul style="list-style-type: none"> - high thermal and chemical stability, - ionic conductivity 	LiFePO ₄		[47] [48]
PIMA	water	<ul style="list-style-type: none"> - reduces electrolyte decomposition, - stable passivating layer 		Graphite	[49]
Polyimide	NMP	<ul style="list-style-type: none"> - mechanical and thermal stability, - high adhesion 	LiCoO ₂ $x\text{Li}_2\text{MnO}_3 \cdot (1-x)$ LiMn _{1-y-z} Ni _y Co _z O ₂ LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	Si Si/C Graphite	[50] [51] [52] [53] [54] [55] [56]
Poly(methacrylic acid) (PMA)				Graphite	[57]
Poly(vinyl alcohol) (PVA)			LiFePO ₄	Graphite Si	[57] [58] [59]
PMMA	Toluene	<ul style="list-style-type: none"> - excellent mechanical properties, high thermal stability 		Si ₆ H ₁₂	[60]
PVDF	NMP	<ul style="list-style-type: none"> - good absorbing electrolyte capability, - bondability - excellent mechanical properties 	LiCoO ₂ Li(Ni _{0.5} Mn _{0.3} Co _{0.2})O ₂ Li ₂ MnO ₃ -	Si MoO ₃ Graphite Cu/SnO ₂	[61] [62] [57] [63]

		and electrochemical stability	LiCo _{1/3} Ni _{1/3} Mn _{1/3} O ₂	Li ₄ Ti ₅ O ₁₂	[64]
			LiNi _{0.6} Mn _{0.2} Co _{0.2} O ₂	SnO ₂	[65]
			LiMn ₂ O ₄	CuFe ₂ O ₄	[66]
			LiFePO ₄	Li ₂ S ₂ / Li ₂ S	[67]
			LiNi _{0.5} Mn _{1.5} O ₄	Sulfur	[16]
					[68]
					[69]
					[70]
					[71]
					[72]
					[73]
PVDF-HFP	NMP	- large amount of amorphous phase, - excellent mechanical properties	NCM LiFePO ₄	graphite	[74] [75] [76]
PVTES-NaPAA	Water	- excellent flexibility, - adhesive properties		Si	[77]
Polystyrene spheres	Water	- decreases inactive interfaces, - reduces the diffusion length of Li ⁺ ,		Cu ₂ O	[78]
Styrene butadiene block co-polymer (SBR)	Ethyl acetate	- high adhesion, - excellent mechanical properties		Graphite Si ZnFe ₂ O ₄	[79] [68] [80] [81]
SEBS	CPME	- mechanical stability, - high adhesion to current collector, - bonding properties	LiFePO ₄	graphite	[82]
TBA-TEVS	NMP	- 3D-interconnected structure, - high thermal stability		Si	[83]

Although neat PVDF is widely used to develop LIBs, its properties can be further upgraded by grafting it with maleic anhydride [84], grafting of poly(tert -butylacrylate)

(PtBA) for increasing its mechanical properties [73], or addition of rosin biopolymer to decrease its crystallinity [85, 86] in order to improve overall electrode properties. Also, PVDF with lithium manganese oxide (LiMn_2O_4) active material leads to reduced Mn dissolution and consequently improves rate capability [87]. Similarly, PVDF latex [88], styrene butadiene block co-polymer (SBR) composites [89], polymethylmethacrylate-poly(lithium methacrylate) (PMMA-PMALi) composites [90], polyethylene oxide (PEO) composites [91], polyethylene-block-poly(ethylene glycol) (PE-PEG) co-polymer and poly(propylene carbonates) (PPCs) [92] and epoxy resin (ionized oligomer) [93] were developed to improve rate capability and overall properties of the electrode.

A new poly (styrene-butene/ethylene-styrene) polymer binder (SEBS) has been recently proposed for both electrodes (anode and cathode) in printed batteries, in order to provide better mechanical stability and a more effective electronic conductive network [82].

A work dealing with the effect of different binders for lithium iron phosphate (LiFePO_4) cathode active material demonstrated that poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) presents remarkable advantages due to the decrease of the charge-transfer resistance and the increase electronic conductivity in comparison of PVDF and PMMA polymers [94]. In order to further improve the properties of PVDF-HFP, lithium sulfonate-grafts were synthesized through covalent attachment of taurine, leading to a better cycling performance [76]. Typically, these common polymers are prepared with N-methyl-2-pyrrolidone (NMP) solvent within the slurry for casting the cathode and anode of lithium-ion batteries. This solvent needs to be replaced by a green and environmentally friendlier solvents in order to decrease the environmental impacts associated with the fabrication of batteries for electric vehicles [95]. A suitable strategy to avoid solvent use in the electrode slurry is to use a photocurable binder such as isosorbide dimethacrylate (ISDM) [96]. An essential property in the polymer binder is the flexibility and, considering this fact, a new binder based on polymethacrylic acid (PMAA) containing triethylene glycol monomethyl ether (TEG) was proposed for lithium-ion batteries with high flexibility [97].

Optimized processing conditions are critical for adequate binder performance. Thus, surface and interfacial cutting analysis system (SAICAS) was used to evaluate the PVDF binder distribution on the cathode and it was verified that upon high drying

temperatures of about 230 °C lead to electrodes with uniform adhesion properties and higher interfacial adhesion strength [64].

Poly(acrylic acid) (PAA) is a widely used polymer binder due to the high concentration of carbonyl groups and good mechanical elasticity, which improves the bonding properties of the active material. Different particle surfaces such as prepolymerizing dopamine [28], grafting of 1-(bromoethyl)benzene initiator groups [27], rosin embedded [98], grafting with polyvinyl alcohol [99, 100], composites with poly(butyl acrylate)-based (PBA) [101], cyanoethyl polymer (PVA-CN) [102], composites with CMC [103] and adding a photoreactive benzophenone group [104] have been used to improve its properties and it has been found that the adequate molecular weight ranges between 24 and 150 kDa [105].

Considering the marked thermal variations during the cycling performance of lithium-ion batteries, polyimide (PI) has been used as a binder due to its high thermal resistance. It has been found that this polymer enhances battery performance and also improves the adhesive/cohesive strength within the electrode composite [50]. Poly(acrylonitrile-butylacrylate) (P(AN-BA)) has been also used for graphite electrodes [37].

Lithium polyacrylate (Li-PAA) was used as a binder for $\text{Sn}_{30}\text{Co}_{30}\text{C}_{40}$ and its electrochemical performance was compared in sodium carboxymethyl cellulose (CMC) and PVDF binders, exhibiting an excellent capacity retention capacity [21].

For Si anodes, a polymer binder based on cross-linking of PVA and poly(ethylene imine) (PEI) precursor was developed, showing strong adhesion to silicon particles and improved electrochemical performance [106]. Similarly, a polymer binder based on vinyltriethoxysilane crosslinked poly(acrylic acid sodium) (PVTES-NaPAA) has shown to improve the Si electrode stability, which results in excellent cycling performance and high coulombic efficiency [77]. Poly(*tert*butyl acrylate —co— triethoxyvinylsilane) (TBA-TEVS) [83], polyimide with PEG [107], PEG with poly(fluorene phenylene) [108] and conductive graphene nano-carbon coatings on silica glass by pyrolysis of linear low-density polyethylene [109] have been also proposed as binders as they promote increased performance for this anode.

Some traditional binders are based on reactive polymers which allow different chemical modifications through the addition of diverse functional groups. This fact

opens the possibility to improve specific properties, such as binding properties to the solid material, mechanical properties, and adhesion to current collector, among others.

The effect of the surface modification of graphite particles by poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA) and poly(vinyl alcohol) (PVA) polymer binders was analysed. These binders have functional groups containing oxygen atoms and it was demonstrated that the surface modification affects the electrochemical lithium alloying and conversion reactions, improving battery properties with respect to PVDF as a binder [57].

The role of functional groups attached to the polymer binder on the structural stability of Li_xSiO_2 was investigated using molecular dynamics simulations. It was observed that polar groups work more effectively to suppress the volume expansion of Li_xSiO_2 from lithiation [41].

The stability of the different polymer binders in the presence of lithium peroxide was studied, in which the presence of electron withdrawing groups (-CN, -Cl, -F) adjacent to hydrogen atoms results in an atom electron-deficient hydrogen. As a consequence, it becomes more susceptible to lithium peroxide attack.

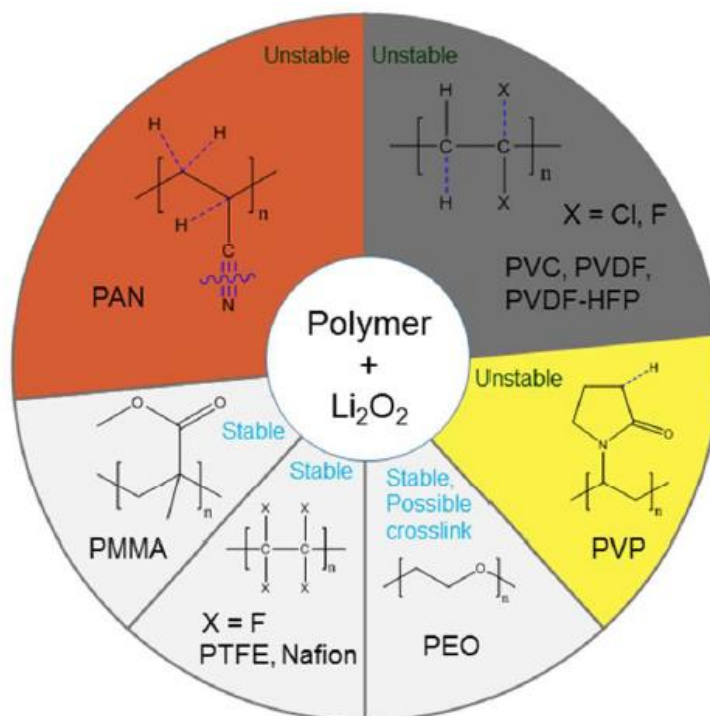


Fig. 7. Stability of the different polymer binder for Li_2O_2 active material. Reproduced with permission [110]. Copyright 2015, American Chemical Society.

Accordingly, as shown in Fig. 7, poly(tetrafluoroethylene) (PTFE), Nafion, poly(methyl methacrylate) (PMMA) and PEO have been found to be the most suitable polymers for Li_2O_2 active material [110].

For Li-S batteries, binders based on polyimide-poly(ethylene oxide) [106], hexamethylene diisocyanate (HDI) polymerized with polyethylenimine (PEI) have been developed as the amino groups can effectively reduce the polysulfide dissolution [44]. For this battery type also a binder based on sulfur-poly(acrylonitrile) was developed, as the interaction between the electrochemically active backbone, the covalently bound sulfur and the S_8 that forms during recharging, allow to obtain both high capacity and good cycling stability [36]. Another binder for Li-S batteries has been developed through the use of a high fluid ionic liquid carbon source for the carbon coating of nano- Li_2S under pyrolysis conditions [111].

The π -stacked perylene bisimide (PBI) polymer was used as a binder in Li-S batteries reducing the Li-S cell impedance with respect to PVDF and exhibiting excellent durability [40] [112]. Poly(isobutylene-alt-maleic anhydride) binders containing lithium have been developed for lithium-ion batteries in which the functional group ($-\text{COOLi}$) acts as a SEI component, reducing the electrolyte decomposition and providing a stable passivating layer for the favorable penetration of lithium ions [49]. In order to enhance the rate cyclability of Li-S batteries, a new binder based on SiO_2 -impregnated polymer blend of Li^+ -Nafion with PVP was developed to successfully regulate tetrasulfide movement [113].

A highly adhesive poly(amic acid) (PAmA) binder containing carboxylic acid and pyrenyl chains was produced for Si-Ni-SiC electrodes for lithium-ion battery applications where the presence of the carboxylic acid and pyrenyl groups helps to strengthen the integrity of the film through pi-pi stacking interactions with the conductive carbons [35], epoxy binders (for Sn electrode) [114] and epoxy resin with PEI polymer (for Li-S batteries) [115]. Finally a bis-imino-acenaphthenequinone (BIAN)-fluorene copolymer binder was used for the fabrication of a graphite electrodes in lithium-ion batteries, improving significantly the cycling performance of the battery with respect to PVDF as a binder [116].

Considering the function of the polymer binder in the electrode, different synthetic binders have been used as shown in Table 1. Most of the works include PVDF, PAA, PVA, or SBR, although new specific binders, such as PBI, PAmA, or SEBS, are being

investigated. The main advantage of these polymers is their large-scale production ability and the possibility of easy tuning their functional groups, which gives room to further improve their properties for the specific role as polymer binder. Unfortunately, the main disadvantage of synthetic binders is to use of toxic solvents. PVDF stands out as polymer binder in comparison to the other binders due to its chemical properties, stability and the improvements realized within the different research works. In any case, the development of a multifunctional binder with upgraded thermal, mechanical and electrochemical properties and good binding properties to the solid phase becomes of paramount relevance towards the fabrication of LIBs with improved performance.

2.2.2. *Natural polymers and biopolymers*

Considering the environmental issues associated with the use of traditional binders derived from fossil fuels, natural polymers and biopolymers are beginning to be widely used as binders for battery electrodes.

Table 2 shows the most commonly found natural polymer and biopolymers used as polymer binders for LIBs. The attempt to replace PVDF as a the most used conventional binder is being based on natural and biopolymers as such carboxymethyl cellulose (CMC) [117], gelatine [118], glycol chitosan [119], lignin [120], guar gum [121], and water-dispersible sulfopolyester [122], among others. This would allow the fabrication of environmentally friendlier electrodes with polymer binders produced through biomass or by microbial production and living organisms [123]. For these polymer binders, the study of their rheological properties is very important as it affects the network structure of the different electrode components, the development of a homogeneous electrode film becoming of paramount relevance [124, 125].

Carboxymethyl cellulose (CMC) is the most widely used biopolymer for LIB electrodes. Several works have been devoted for the improvement of its properties, such as crosslinkers with acid citric to improve the electrode stability [126], crosslinked with PAA polymer [127] [128], composites with SBR binder [129], doped with lithium ions [130] and crosslinking with sodium borate [131]. Cellulose nanocrystals (CNCs) with peroxotitanate have been used to obtain freestanding mesoporous films of TiO₂ and chiral nematic TiC structures [132], as well as on the fabrication of mesoporous black

titanium dioxide (TiO_{2-x}) with a chiral nematic organization [133] for application as lithium-ion battery anodes.

A base on gelatin-polyethylenimine composite (gelatin-PEI) was developed for Li-S batteries, in which the dispersion and adhesion ability of gelatin keeps the cathode homogeneous and stable during the electrochemical reaction, and the adsorption capability of PEI for polysulfide suppresses the “shuttling effect” [134].

Table 2. Typical common natural and biopolymers used as polymer binder for battery electrodes.

Name of binder	Solvent	Main properties	Most used active material		Ref
			Cathode	Anode	
Agarose	DMSO	<ul style="list-style-type: none"> - very abundant - strong adhesion 	LiMn_2O_4	Si	[135]
Carboxymethyl cellulose (CMC)	Water	<ul style="list-style-type: none"> - low cost - environmentally friendly - easy processability 	$\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ LiFePO_4 Li_2MnO_3 – LiMO_2 $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$	SnO_2	[117]
				Si	[136]
				Graphite	[68]
				Graphene	[137]
				Nano-Sn	[138]
				MCMBs	[139]
				ZnMoO ₄	[140]
				SnO_2	[30]
				CuFe_2O_4	[71]
				SiO	[72]
				ZnCo ₂ O ₄	[141]
				Sulfur	[142]
				TiO ₂	[31]
				NiO	[143]
				SnS	[144]
				α -MoO ₃	[145]
				MgH ₂	[146]
					[147]
					[148]
					[149]
					[150]
					[151]

					[152]
Carbonyl and β -Cyclodextrin		<ul style="list-style-type: none"> - hyperbranched network structure, - simple synthesis 		Si Sulfur	[153] [154] [155] [156]
Cellulose	Water	<ul style="list-style-type: none"> - low cost, - simple processing, - chemical stability 	LiFePO ₄		[157] [158]
Chitosan	Water	<ul style="list-style-type: none"> - positive amine groups, - water-soluble, - strong chemical bonding, - low cost fabrication 	LiFePO ₄	Si Fe ₃ O ₄ Li ₂ ZnTi ₃ O ₈	[159] [160] [161] [162]
DNA	Water	<ul style="list-style-type: none"> - excelente adhesion, - facilitates the distribution of particles 		Si Graphite	[163]
galactomannans	Water	<ul style="list-style-type: none"> - low-cost, - swelling properties, - fast Li transport 		Si	[164]
GC-g-LiPAA	Water	<ul style="list-style-type: none"> - environmental friendly, - bonding properties 		Graphite Si	[119]
Gelatin-PEI composites	Water	<ul style="list-style-type: none"> - good adhesion, - dispersion ability, - robust network structure 		Sulfur	[134]
Glucomannan	Water	<ul style="list-style-type: none"> - high adhesion, - superior mechanical properties 		SiO ₂	[165]
LA132 (new acrylic family)	Water	<ul style="list-style-type: none"> - moderate adhesive properties, - low cost 		Li ₄ Ti ₅ O ₁₂ Sulfur	[166] [167]
Lignin	DMF	<ul style="list-style-type: none"> - low cost, - flexibility, - thermal stability 	NMC	Si Carbon fibers	[120] [168]
PAAm	Water	<ul style="list-style-type: none"> - fast penetration of electrolyte, - high thermal stability, - formation of a more conductive 		Si Grafite Carbon	[169]

		solid electrolyte interface (SEI), - strong adhesion		nanotubes	
PAH	Water	- reduces the damage induced by volume expansion, - chemical interaction		Silicon graphite	[170]
Polyelectrolyte binder (PEB)	Water	- good Li ⁺ conductivity - flexibility, - good compatibility with the electrolyte		Sulfur	[171]
Sodium alginate	Water	- good battery stability - mechanical stability	MnO ₂ -graphene Li _{1.14} Ni _{0.18} Mn _{0.62} O ₂	Si Graphene oxide CoFe ₂ O ₄ TiO ₂ Si/C α -Fe ₂ O ₃	[172] [173] [174] [175] [176] [177] [178] [179] [180]
Starch	Water	- simplicity of the production process, - structural stability, - mechanical strength		Sulfur Si	[181] [182]
Xanthan and guar gum	Water	- higher affinity to the electrolyte,	NMC LiFePO ₄	Graphite Sulfur Si Co ₃ O ₄	[183] [184] [185] [186] [187] [188] [189] [190]

A multigrafting block copolymer based on glycol chitosan (GC) and lithium polyacrylate (LiPAA) was developed as binder for silicon electrodes. It was demonstrated that this binder improves the initial discharge capacity, long-term retaining capacity, and coulombic efficiency [119]. Seven different hydrocolloids (sodium carboxymethyl cellulose (Na-CMC), sodium alginate (Na-Alg), gum arabic

(GA), xanthan gum (XG), guar gum (GG), agar-agar (AA) and carrageenan (CAR)) were tested as water-soluble binders for synthetic graphite (SG)- based electrodes for LIBs and compared with the standard PVDF binder in which SG/GA, SG/CAR and SG/AA electrodes show poorer electrochemical performances in comparison with other binders [184]. However, to improve the properties of sodium alginate (SA), a crosslinker with Cu^{2+} ions was added for Li-S batteries and it was demonstrated that these modifications immobilize polysulfide anions and consequently improve battery performance [191]. Poly- γ -glutamate, a slimy constituent in the Japanese food Natto, consisting of fermented soybeans has also been studied as binder for silicon and graphite electrodes [192]. As depicted in Fig. 8, a low-cost and widely available biopolymer such as lignin has been mixed with silicon nanoparticles to use it as a binder with exceptional electrochemical performance [120].

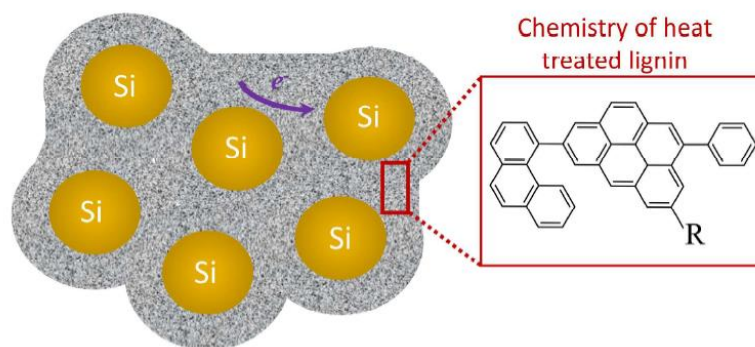


Fig. 8. Schematic structure of the silicon-lignin composite used as a binder. Reproduced with permission [120]. Copyright 2016, American Chemical Society.

A polymer binder based on polyacrylamide (PAAm) was developed through the dual-crosslinking with grafted alginate, where an improved lithium ion kinetics in the Si/C electrode with good reversibility of lithium ions insertion/desertion was observed [169]. A systematic analysis of different polysaccharide binders was performed for the Si electrode and it was found that the superior performance of native-xanthan gum (XG) originates from its ion-dipole interactions that are properly positioned on the side chains within the superstructure of native-XG [193]. This natural polysaccharide also acts as a microporous binder to obtain improved electrochemical properties [194]. A binder consisting on a natural rubber / chitosan blend was developed to improve the properties of each individual constituent to provide a proper elastic performance which accommodates the large volume Si expansion during cycling[195].

These novel binders derived from renewable resources such as polysaccharides and proteins emerge as key materials for electrodes in the near future, although their mechanical, electrochemical and binding properties need to be further improved. The improvement of these properties is essential to replace traditional binders by these renewable binders which apart from being environmentally friendlier and cheap, can be processes without the use of toxic solvents.

2.2.3. Conductive polymers

The use of conductive polymers on electrodes for LIBs has the advantage of replacing the conductive additive at the same time that acts as polymer binder, supporting the reduction of the amount of non-active material used for the electrode. Different conductive polymers are used, including polyaniline (PANI) [196], polypyrrole (PPy) [197], poly(3,4-ethylenedioxythiophene) (PEDOT) [198], sodium poly-(9,9-bis(3-propanoate) fluorene) (PF-COONa) [199], poly(3-hexylthiophene) [200], poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) [201], poly(2,7-9,9-dioctylfluorene) (PFO) [202], poly[3-(lithium acetate) thiophene-2,5-diyl] (PT-3-LiA) [203], poly[3-(lithium-4-butanoate) thiophene-2,5-diyl] (PT-3-LiB) [203], Poly(1-pyrenemethyl methacrylate-co-methacrylic acid) (PPyMAA) [204] and poly(3,4-propylenedioxythiophene-2,5-dicarboxylic acid) (ProDOT) [205]. PFPQ-COONa was tested as conductive binder for Si anode and presents an excellent cycling stability and satisfactory rate performance with relatively high area loading, which outperforms currently reported single component conductive binders [199]. Also for this anode, polymer binders based on graphite/polyaniline [206] and polyaniline nanocomposites [207] were developed.

Table 3. Conductive polymers most commonly used as polymer binders in battery electrodes.

Name of binder	Solvent	Main properties	Most used Active Material		Ref
			Cathode	Anode	
P3HT/PEO	Water	- mechanical flexibility,	V ₂ O ₅		[200]

		- suitable electronic properties			
PANI	hydrochloric acid	<ul style="list-style-type: none"> - simple synthesis, - high environmental stability, - tailorable conductivity by doping, 	LiFePO ₄	Sulfur	[196] [208]
PEDOT	----	<ul style="list-style-type: none"> - high electrical conductivity, - good thermal and - chemical stability 	LiCoO ₂		[198] [209]
PEDOT:PSS	---	<ul style="list-style-type: none"> - high electronic conductivity, - high solubility 	LiFePO ₄ Li ₄ DTT	Si Graphene oxide	[201] [210] [211] [212] [213]
(PF-COONa)	tetrahydrofuran (THF)	<ul style="list-style-type: none"> - good adhesive properties, - high electrolyte uptake, - electric conductivity 		Si	[199]
PPy	N,N-dimethylformamide (DMF)	<ul style="list-style-type: none"> - high conductivity 		CNF	[197]

An electrode consisting of two-component slurries of PEDOT:PSS binder and LiFePO₄ active material in the absence of conductive carbon additives was fabricated. A better adhesion, higher electrical conductivity and improved electrochemical performance of the resulting positive electrodes was observed when using a solid loading of 40% [201]. This conductive polymer was latter used in silicon anodes produced by inkjet-printing as shown Fig. 9 [211].

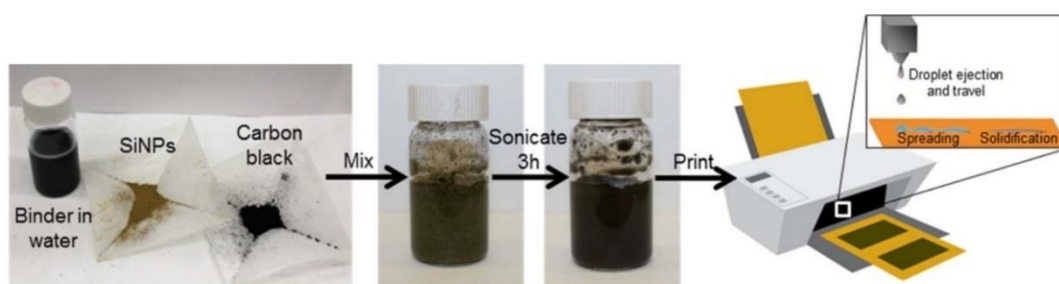


Fig. 9. Schematic representation of conductive electrodes based on the PEDOT:PSS binder produced by inkjet-printing technique. Reproduced with permission [211]. Copyright 2017, Elsevier.

A novel binder based on the mixture of PAA and PEDOT:PSS was developed to significantly improve the specific capacity and cycling stability of Li-S batteries. While PEDOT:PSS facilitates the electron transfer and prevents the polysulfide dissolution, PAA improves the solvent system for sulfur cathodes and promotes the lithium-ion transfer [214]. Also composite materials consisting on PEDOT:PSS with CMC and PEDOT:PSS with PEO and PEI [215] were developed for Si anodes [216], while composites of PEDOT:PSS with carboxymethyl chitosan were proposed for LiFePO_4 cathode [217] of lithium-ion batteries.

Conductive polymers have been used as a binder in order to improve the electrical conductivity of the electrodes through their backbone or side chains. Diverse works demonstrate the applicability of these binders to improve battery performance, but their use is limited taking into account their mechanical and electrochemical properties. Importantly, the binding and adhesion properties to current collectors are issues that need to be faced in order to spread the use of conductive polymers in LIBs.

Overall, PVDF, cellulose and PEDOT:PSS are the most commonly used polymer binders in the areas of traditional, natural and conductive binders, respectively. Independently of the polymer binder used, its function results essential in the development of suitable electrodes towards high battery performance. The development of a universal binder based on natural polymers that can be used in small amounts and possess excellent properties such as high adhesion to current collector would be needed in the coming years. Moreover, such binder must also present a combination of high thermal, mechanical and electrical properties with a wide electrochemical window up to 6.0V that can disable the SEI formation and improve Li^+ transference.

3. Polymers for battery separators and solid electrolytes

Conventional rechargeable LIBs are typically composed by solid electrodes and a liquid solution which impregnates a solid membrane known as separator [218]. In LIBs, electrolytes are lithium salts dissolved in a mixture of one or more solvents and are responsible for the Li^+ ion diffusion between both electrodes. The separator acts as an interlayer to physically isolate the positive and negative electrodes to prevent electrical contact between anode and cathode at the same time that allows an efficient ionic diffusion between electrodes. Consequently, separators should be electronic insulators

and must display high ionic conductivity either by intrinsic ionic conduction or by soaking an electrolyte. Separators should ideally be highly resistant to the electrochemical interaction from electrodes and electrolyte and protect against short circuit, thermal runaway and overcharge [219].

Although classified as an inactive cell component, the separator is a critical component in LIBs as its properties affect the cell performance (energy-density, power-density), cycle-life and most importantly, its safety, especially considering the burnings and explosions of consumer electronics powered by LIBs that happened, for example, in 2016 [218, 220]. Different factors need to be taken into account when selecting a separator for specific LIB applications. These factors have been classified into structural properties, physical/chemical properties, functional properties (which are determined by the structure and physico-chemical character) and additional desirable properties, as represented in Fig. 10.

Structural properties:

- **Thickness:** Current desirable thicknesses are around 20-25 μm [221]. The thicker the membrane, the better stability against puncture, which also implies a higher Li^+ diffusion resistance. High performance cells use 16 μm thick separators to obtain high volumetric energy density. Separators should be uniform to support many charging cycles and provide homogeneous Li^+ transfer which delays dendrite formation.
- **Porosity:** pores should be small enough to avoid dendrite penetration through the separator ($< 1\mu\text{m}$) but large enough to allow Li^+ ion diffusion (several nanometers). A non-uniform pore size results in non-uniform current densities, which in turn yield low-performance and faster dendrite growth. Porosity values in the range of 40-60 % are usually required to allow efficient and fast ion diffusion. An excessive porosity may hinder the ability of the separator to shut-down [222].
- **Tortuosity:** it describes the average pore conductivity of the separator and should present an intermediate value to allow low resistance to ion diffusion but high enough to avoid dendrite growth.
- **Structural stability:** the structure should be kept after electrolyte soaking (shrinkage, wrinkle, swell).

Physical/chemical properties:

- **Electrolyte wettability / absorption:** separators should be rapidly swollen when soaked with electrolyte and they should retain the absorbed electrolyte under operating conditions [223].
- **Mechanical properties:** soft separators are not stable against dendrite growth; a high puncture stress is required to avoid internal short-circuit by dendrite growth and penetration. On the contrary, too rigid separators may complicate the assembly process (especially in flexible batteries).
- **Thermal stability:** the separator should be stable against thermal shrinkage ($< 5\%$ after 60 minutes at $90\text{ }^{\circ}\text{C}$) [10]. It must also keep its integrity after shutdown to avoid direct contact between electrodes. Separators with stable mechanical properties at high temperatures provide a larger safety margin.
- **Chemical stability:** Inert to strong reducing and oxidizing conditions (on the negative and positive electrode sides respectively) under long-term cycling at high temperatures. They should be able to withstand electrolyte degradation, electrode reactants or impurities [223].

Functional properties:

- **Ionic conductivity:** it should be high to allow an efficient Li^+ diffusion. The ionic resistivity of an electrolyte wetting a separator is much higher than the resistivity of the free electrolyte. MacMullin number accounts for the change in separator/electrolyte ionic resistivity in comparison with that of the electrolyte, and needs to be kept under a value of 8 [222].
- **Electrical resistivity:** the separator should be electrically insulator to maintain electrical isolation between the cathode and anode and avoid short-circuit between electrodes. In practice, the electrical resistivity of commercial separators is 10^{12} - $10^{14}\text{ }\Omega\cdot\text{m}$.
- **Air permeability:** high permeability values ensure a good separator performance. It can be quantified by the Gurley number as it accounts for the time that a specific amount of air needs to pass across a specific area of separator under a specific

pressure. The Gurley number is inversely proportional to the ionic resistance of a given separator morphology [222].

- **Puncture stress:** It accounts for the maximum load that must be applied to a needle to puncture a given separator. A high puncture strength (> 300 g for $25\ \mu\text{m}$ separators) ensures that both electrodes are kept electrically isolated during cell-assembly (either spiral winding or stacked-plate process) and protects against dendritic penetration [224].
- **Auto-shutdown ability:** Auto-shutdown is an essential mechanism for preventing thermal runaway. The protection against short-circuit is induced by the controlled collapse of the ionically conducting porous membrane due to the partial melting of the separator to yield an ionically insulating non-porous protecting layer between both electrodes (a 1000-fold increase in impedance is required) [20]. As a consequence, the electrochemical activity in the cell is stopped, shutting the battery down.

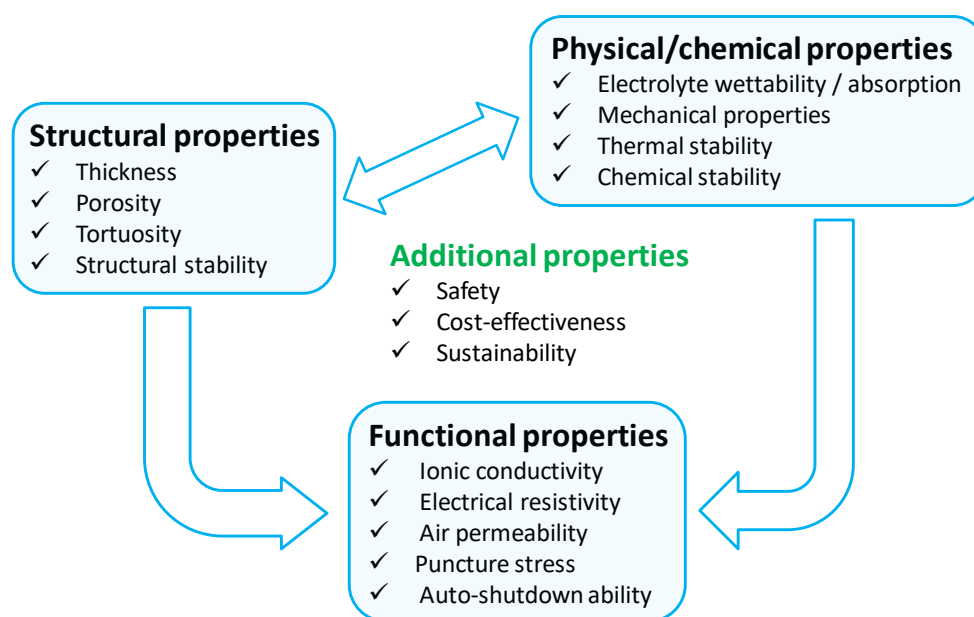


Fig. 10. General requirements for LIB separators.

Additional desirable properties that need to be taken into account when designing separators for LIBs are safety, cost-effectiveness and sustainability. Together with the above-mentioned dendrite growth resistance and dimensional stability at high temperatures, separators should present flame-retarding properties to avoid explosion events. Thermally-conductive membranes may help to reduce the temperature increase under operation conditions as they facilitate heat dissipation, reducing explosion risks.

As the cost of the separators can reach 20% of the total cost of a high-power LIB, designing novel materials and technologies for separators becomes of key relevance towards industrial applications. Separators based on renewable polymers such as biomass-based cellulose and its derivatives emerge as novel alternatives for traditional fossil-based polymer separators. Separators of high wettability, nanoporous structure, dimensional stability at temperatures up to 180 °C and the often disjoint mechanical flexibility and robustness can be obtained [225-227]. Accordingly, the fabrication of porous separator membranes via facile papermaking processes could pave the way towards the development of future cost-effective and sustainable separators.

Depending on the application area, the relevance of these criteria may change, although in most of the cases a compromise between all these characteristics (which often are mutually exclusive) must be taken. For instance, a thin separator may allow an easier Li^+ transport between electrodes, which would increase battery power and capacity on the one side but could lead to poor stability against dendrite growth and eventual failure *via* short-circuit from the other. Taking into account, that LIBs are finding many novel applications, there is an increasing demand to upgrade battery safety without limiting their cost and performance, which results in a renewed interest in separators from both industry and academia. As a result, the market for separators is expected to exceed \$ 3 billion by 2020 [228].

One of the main differences between the separator and the polymeric electrolyte is that, contrarily to the separator, which is a solid porous membrane, the polymeric electrolyte is defined as a polymeric matrix containing lithium salts, ionic liquids or other inorganic materials yielding a composite, together with non-aqueous solvents (dimethyl carbonate, DMC; diethyl carbonate, DEC; propylene carbonate, PC or ethylene carbonate, EC) [229]. Polymer electrolytes can be divided into solid polymer electrolyte (SPE) and gel polymer electrolyte (GPE). Table 4 shows the most used polymer types for battery separators and polymer electrolytes, highlighting their main properties for these applications.

Table 4. Most commonly used polymers in battery separators and polymer electrolytes in which S represent that is used and N that is not used.

Polymer	Separator	Ref for separator	Polymer electrolytes	Ref for polymer	Main property
---------	-----------	-------------------	----------------------	-----------------	---------------

				electrolytes	
PE/PP	S	[230]	N	----	<ul style="list-style-type: none"> - Low cost - Easy processability - Good mechanical properties
PVDF and its copolymers	S	[231, 232]	S	[233, 234]	<ul style="list-style-type: none"> - Good mechanical properties - High chemical resistance - High polarity - Interaction with lithium ions
PAN	S	[235]	S	[236]	<ul style="list-style-type: none"> - Good processability - Thermal stability - Wettability
PET	S	[237]	N	----	<ul style="list-style-type: none"> - Excellent electronic insulation - Good mechanical and thermal properties
PI	S	[238]	N	----	<ul style="list-style-type: none"> - High thermal stability and mechanical properties - Chemical resistance - Good wettability
PAEK	S	[239]	N	----	<ul style="list-style-type: none"> - Excellent thermal oxidative and chemical stability - Good mechanical properties
PTFE	S	[240]	S	[241]	<ul style="list-style-type: none"> - Chemically inert - Excellent thermal and electrochemical stability
PU	S	[242]	N	----	<ul style="list-style-type: none"> - Low cost - Good mechanical properties
PDA	S	[243]	N	----	<ul style="list-style-type: none"> - Excellent wettability - Without shrinkage - Good adhesion to electrodes
PMMA	S	[244]	S	[245]	<ul style="list-style-type: none"> - Good thermal and electrochemical stability - Excellent affinity to

					electrolytes solutions
Cellulose	S	[246]	S	[247]	<ul style="list-style-type: none"> - Good wettability - Easy processability
PEO	N	----	S	[248]	<ul style="list-style-type: none"> - High affinity to Li⁺ ions
Silicones	N	----	S	[249]	<ul style="list-style-type: none"> - Good thermal and chemical stability
Polycarbonates	N	----	S	[177]	<ul style="list-style-type: none"> - Good dissociation of the lithium salts - Good electrochemical stability
Nafion	N	----	S	[250]	<ul style="list-style-type: none"> - High ionic conductivity - Good thermal and chemical stability - Excellent mechanical properties

3.1. Separator/electrolyte and solid electrolytes

Traditional LIBs that operate using liquid electrolytes always present a latent risk that eventual mechanical stresses and successive charge/discharge cycles can yield to electrolyte leakages, resulting in serious malfunction. Liquid electrolytes used in commercial LIBs present ionic conductivities in the order of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and are nonaqueous electrolytes because of the reactivity of lithium to water. These organic solvent-based electrolytes should ensure a rapid Li⁺ diffusion across both the electrolyte and the electrode/electrolyte interface, should not react/degrade under normal operating conditions, should provide a stable electrolyte-electrode interface during cycling [251]. and are composed by Li salts (typically LiPF₆) dissolved in linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC) [252].

A main strategy to develop novel safer, lighter and non-flammable electrolyte systems and to provide LIBs with improved resistance against dendrite formation is the introduction of a mechanically resistant solid electrolyte sandwiched between both electrodes, the so-called solid polymer electrolyte. Solid polymer electrolytes are ionically conducting materials and have the peculiarity of functioning as both electrolyte and separator. The replacement of conventional liquid electrolytes by solid electrolytes also opens the path towards flexible LIBs capable of withstanding large

mechanical deformations with no leakage and short-circuit [253]. Although liquid electrolytes have been the preferred choice so far for the development of high-performance LIBs because of the lower ionic conductivity of solid electrolytes [254], current concerns on battery safety are boosting the development of solid electrolytes, which can be classified as:

- Solid polymer electrolytes (SPEs): SPEs are composed by lithium salts dissolved in polymeric matrices such as PEO, PMMA, PVDF, PVDF-HFP or PAN. Their mechanically flexible character enables a plethora of designs for batteries at the same time that alleviates drawbacks associated with the volume changes of electrodes as a consequence of cycling. SPEs are cheap, easy to produce, show low densities of nearly 1.2 g cm^{-3} and are compatible with cathode and anode [255].
- Gel polymer electrolytes (GPEs): they are obtained through the trapping of Li^+ containing solutions such as lithium hexafluorophosphate (LiPF_6) in carbonate solvent within a polymeric gel-type membrane based on PEO, PMMA, PVDF, PVC... They combine the advantages of liquid and solid polymer electrolytes, i.e., high ionic conductivity provided by the diffusive properties of liquids together with the proper mechanical stability arising from the cohesive properties of solids. GPEs would not be discussed here as they cannot be considered as “all-solid” electrolytes. For detailed information readers are directed to the recent review works [256, 257].
- Composite polymer electrolytes (CPEs): they are composed by SPEs or GPEs reinforced with nanoparticles to improve the ionic conductivity, thermal stability and mechanical strength of the hosting matrix. These particles could be either micrometer or nanometer in size and ceramic, metallic oxide or bio-based.

3.1.1. Separator types

Polymeric separators for LIBs are composed by microporous films, nonwoven fabrics or electrospun membranes. Celgard® separator is an example of microporous polymeric (Fig.s 11a and 11b) films which can be manufactured through “wet” or “dry” processes. Wet fabrication involves the extrusion of a plasticizer/polymer mixture at elevated temperatures followed by phase separation, biaxial stretching, and extraction of the pore former with a volatile solvent (elliptical pores with an overall porosity of 40-50% is obtained). Dry fabrication, on the contrary, is based on the extrusion of a thin

polymer sheet which is subjected to a rapid drawdown where after a thermal treatment below melting temperature, crystalline regions are obtained. Then, the sheet is rapidly stretched to achieve slit-like pores with an overall porosity of 35-45%. Nonwoven separators are membranes manufactured directly from fibres which can be directionally or randomly arranged. Despite to their easier fabrication with respect to microporous membranes, their application has been limited as it is difficult to obtain thin, uniform and mechanically stable films, which is a prerequisite for LIB separators. Separator membranes obtained by phase separation (Fig. 11c) or electrospinning (Fig. 11d) emerge as attractive candidates for high performance batteries as these techniques provide materials with porosities up to 90 % with interconnected structure, which when used in LIBs result in improved ionic conductivities [258]. Although it was first invented in 1934, the fabrication of one-dimensional nanofibers through electrospinning for separators has witness an increasing interest during the last years [258]. In spite of the desirable structure of nonwoven and electrospun separators, their fabrication process is somewhat slow, and their mechanical properties are still relatively weak, making their large-scale commercialization a challenging task.

One of the most pursued strategies to improve the performance of separators is the development of composite materials as the addition of micrometer or nanometer sized fillers into polymeric membranes results in improved mechanical strength, wettability with organic electrolyte, increased thermal stability and increased ionic conductivity of the separator by promoting the migration of lithium ions [259-261]. A reinforcing phase may also provide an improved resistance against pinhole formation and thus, preventing the penetration of Li dendrites and extending the life-cycle of LIBs [262]. Incorporated fillers can be either active or passive, i.e. they participate in the conduction process by modifying the ionic conductivity and Li transference number or they do not directly take part in the conduction process [263]. SiO₂ (silicon dioxide), Al₂O₃ (aluminium oxide) or TiO₂ (titanium dioxide) are the most representative inert ceramic oxides [260]. Their addition into polymer host matrices results in an increase of the ionic conductivity, which is associated to a concomitant decrease of the crystallinity of the hosting matrix and Lewis acid-base type interactions between inorganic nanoparticles and electrolyte solution [264]. Other fillers include ferroelectric ceramics with high dielectric constant such as barium titanate (BaTiO₃) which increase the Li transference number (and therefore the ionic conductivity) as a result of the filler polarization [265],

layered clays such as montmorillonite (MMT) which improve electrolyte wettability and thermal stability [266], carbonaceous fillers such as graphene, graphene oxide or carbon nanotubes (their concentration should be below percolation threshold to avoid electrical contact between electrodes) which serve as mechanical reinforcement and thermal stabilizers [260], and zeolites such as NaY which possess strong Lewis acid centres [267].

Obtaining a homogeneous distribution of fillers remains a challenging issue. Other approaches such as polymer blending and surface functionalization have also been pursued so far to upgrade the functional performance of separators, which include the use of a binder such as PVDF-HFP, although it usually brings undesired thickness increases and pore block up, decreasing the energy density of the battery. To overcome these drawbacks, a thin layer of inorganic phase could be coated in a controlled fashion onto organic supports by methods such as atomic layer deposition (ALD) [137], magnetron sputtering deposition (MSD) [268], or Direct Current (DC) sputtering [269]. With the goal of simplifying the list, in this section the most used LIB separators will be listed, which are classified according to the hosting matrix regardless of they consisting on a single polymer, nonwoven membranes, electrospun membranes, membranes with external surface modification, composites membranes and polymer blends [229].

3.1.1.1. Polyolefins

Based on their high mechanical strength, fair chemical and electrochemical stability and cost effectiveness, polyolefins such as polyethylene (PE) and polypropylene (PP) are currently the most widely used materials for LIB separators [270]. Commercial polyolefin monolayer separators with a pore sizes in the 0.03–0.5 μm range and a porosity of 30–50 % have been used in LIBs so far; where high pore volumes and large pore diameters support improving the ionic conductivity of polyolefin separators after being soaked with the electrolyte, increasing capacities at high C-rates [271]. On the contrary, low porosity and small pore sized membranes are more efficient in order to prevent internal shorts between electrodes [272]. As depicted in Fig. 11a, monolayer separators have been proven efficient for low-voltage LIBs, where PE separators are preferred as they show improved cyclic stability in comparison with PP separators due to their lower HOMO energy [273]. Microporous multilayer membranes composed by PP and PE, either as PE-PP bilayer or as PP-PE-PP trilayer, have been developed by

separator manufacturers as thermal shutdown strategy. In these trilayer systems (Fig. 11b) a temperature increase produces the partial melting of the PE layer, which collapses the pores and therefore prevents the migration of the Li^+ between electrodes. Most of the commercial separators use PE as a “shut-down” layer (at $\approx 130^\circ\text{C}$), while PP layer still retains the dimensional structure of the membrane [270]. Although the electrochemical reactions within the cell are stopped and the cell shuts down to protect against external short circuit or accidental overcharge, the marked thermal shrinkage suffered by polyolefins may result in internal short circuits when the temperature further increases [274].

One of the most representative examples of microporous commercial separators is Celgard® (Celgard LLC), which is a 25 μm thick trilayer microporous membrane (0.03–0.1 μm pores) composed of PP-PE-PP. Other commercial manufacturers of LIB separators are Asahi Kasei, which commercialises a single-layer PE membrane with a 0.05–0.5 μm pore range under the name of HiPore™, ENTEK Manufacturing LLC which provides three main membrane types for LIBS (EP, EPH and EPX lines), Mitsui Chemicals Inc., that produces a ultra high molecular weight polyethylene membrane under the name of HI-ZEX MILLION™ or Ube Industries, Ltd. which fabricates PE-PP separators under the name of UPORE®. Despite the low prices of the raw materials, the complex fabrication processes increase the cost of these separators.

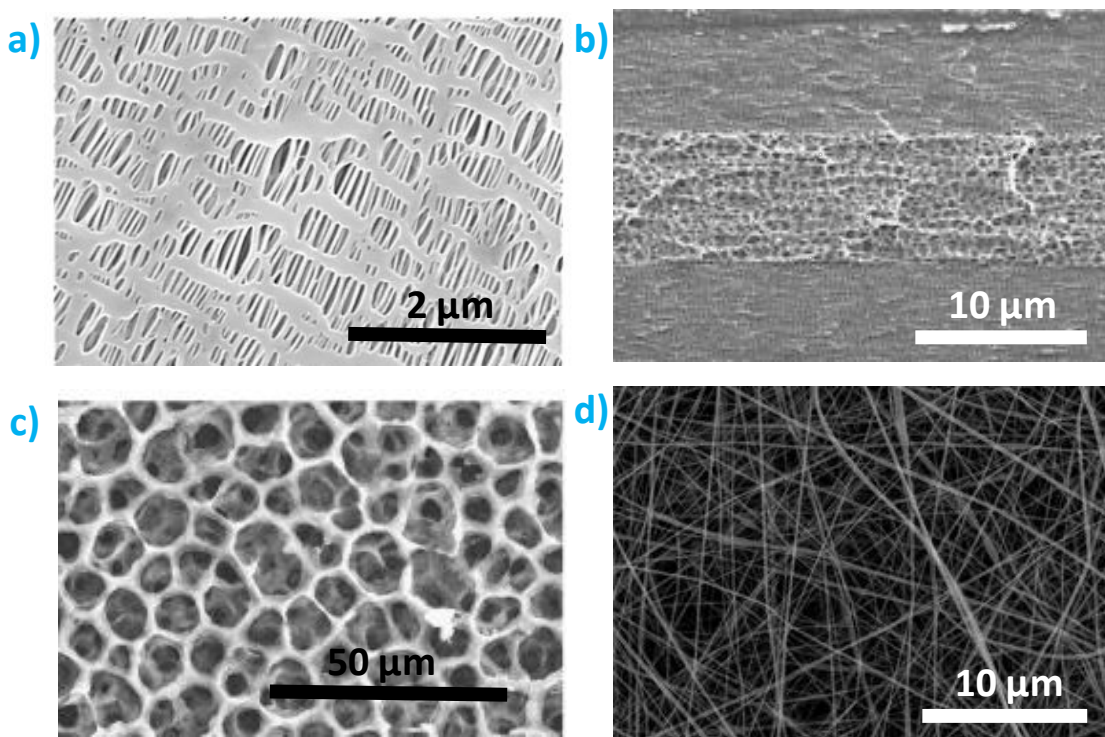


Fig. 11. SEM images of polymer separators with different morphologies: a) Surface of the Celgard commercial PP2075 monolayer separator with a porosity of 48%. Reproduced with permission [275]; b) Cross-section of the Celgard 2325 (PP/PE/PP) trilayer separator. Reproduced with permission [222]. Copyright 2004, American Chemical Society; c) PVdF-HFP separator obtained via phase inversion method. Reproduced with permission [276]. Copyright 2010, Elsevier and d) a PI electrospun polyimide nonwoven separator. Reproduced with permission [277]. Copyright 2013, Elsevier.

Many strategies have been pursued to improve the performance of polyolefin separators. High surface-area metal oxide particles including ZnO, SiO₂ and Al₂O₃ have been dispersed into PP membranes as they show the ability of adsorbing the impurities formed during cycling and, at the same time, enhance the wettability to liquid electrolyte and its retention, providing composite membranes with good capacity retention [278]. PE membranes have been coated by depositing SiO₂ nanoparticles via chemical vapour deposition (CVD) to obtain membranes with improved thermal and dimensional stability at high temperature and extended cycle life. Interestingly, the separator is highly stable at temperatures above the melting point of the PE. Satisfactory cell performance in terms of ion conductivity, C-rate and cycle life were obtained, introducing a new approach for LIB separators that can potentially limit unwanted explosion events [279]. Similarly, 6 nm thick Al₂O₃ has been grown on a commercial porous PP separator (Celgard 2500) by atomic layer deposition (ALD) in order to prevent the marked thermal shrinkage of neat PP and improve its wettability with extremely polar electrolytes such as pure propylene carbonate. Interestingly, such a thin layer does not increase, in a significant way, the overall thickness of the separator while keeps the electrochemical performance of the cell (capacity, rate capability, and cycle life) in extremely polar electrolytes [280]. A 9 nm thick boron-nitride (BN) nanosheet layer was coated onto one side of a commercial separator (Celgard 2325) by vacuum filtration [281]. When using a conventional organic carbonate-based electrolyte, the more homogeneous thermal distribution resulting from the BN coating and the smaller surface area of initial Li deposition results in a more uniform deposition/stripping of Li, decreasing the risk of dendritic Li growth and improving cycling performance. PP separators (Celgard 2400) were coated with a TiO₂ layer (up to 131 nm thick) by magnetron sputtering deposition (MSD) to yield membranes with an improved stability against thermal degradation of about 100 °C, a 2 to 4 fold reduced thermal shrinkage and an improved wettability with polar electrolytes as evidenced by the larger

electrolyte uptake and lower water contact angle values [268]. As a result, composite separators with improved safety and capacity retention (84.0 % after 100 cycles in comparison with 72.3 % for neat PP) were obtained. A separator membrane composed by PE-PP sheath-core fibres fabricated via air-laid method was reinforced with nanosilica particles to obtain improved wettability and better electrochemical performance than the bare separator [282]. More interestingly, the cells comprising nanosilica-reinforced PE-PP nonwovens were thermally stable at 150 °C, while the cell with the commercial Celgard membrane showed a short circuit as a result of the thermal shrinkage of the separator, which is about 37% in comparison with the 3% of the reinforced separator.

Overall, polyolefins display a poor thermal stability, are highly inflammable and their hydrophobic character results in poor wetting capability, leading to a significant decrease in ionic conductivity and ultimately to low power densities [222]. Considering these drawbacks and despite of their wide commercialization, recent efforts carried out regarding polyolefin separators are basically aimed to improve their wettability and thermal stability, which can be accomplished through plasma treatment [283], polymer grafting [284], and surface chemical modification [285]. Therefore, alternative materials with better thermal stability, mechanical robustness, proper wettability and easily controllable morphology are being developed.

3.1.1.2. Poly(vinylidene difluoride)

Poly(vinylidene difluoride) (PVDF) is a semicrystalline polymer which shows good mechanical properties, high chemical resistance and displays a high polarity and dielectric constant, which improves the ionization of lithium salts [228]. PVDF offers a wide variety of possibilities to control its morphology through binary and ternary polymer/solvent systems and it presents a high anodic stability thanks to the strong electron-withdrawing functional groups (-C-F-) [286]. As a result, PVDF has been proven as efficient battery separator when soaked with liquid electrolytes such as LiPF₆ or lithium bis(trifluoromethane sulfonyl)imide (LiTFSI), although the interaction between PVDF fluorine atoms and lithium ions could lead to the formation of lithium fluoride (LiF). As shown in Fig. 11c, microporous sponge-like PVDF membranes with good wettability, mechanical properties and electrochemical stability have been fabricated through thermally induced phase separation (TIPS) method [287]. The high

dielectric constant (ϵ) of 8.4 of PVDF allows its fabrication into the form of electrospun separators, where voltages in the range of 8 to 15 kV can control the diameter of the nanofibers from 884 to 514 nm respectively [288]. PVDF nonwoven mats were prepared as LIB separators, where the high porosity and large surface area of the membranes combined with the swelling ability of electrospun fibres resulted in high electrolyte uptake [289]. As a result of their 3D network formed by interconnected fibres, when soaked in liquid electrolyte the nonwoven mats kept their structural integrity and show good mechanical strength [290]. One advantage of preparing nonwoven PVDF mats is that although the fibres are composed by highly oriented chains, their degree of crystallinity is rather low, supporting the Li^+ diffusion process [288].

As the crystalline regions hinder Li^+ ion mobility in polymeric membranes, batteries with separators composed by semicrystalline polymers usually display low charge-discharge capacity and poor C-rates [10, 222]. Therefore, PVDF-based copolymers such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) and poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) have been used as LIB separators to obtain improved ionic conductivity, mechanical flexibility, compatibility with electrodes and low degree of crystallinity [291]. In this sense, Fig. 12 shows the correlation between the β phase content in membranes composed by PVDF and its copolymers (having the same degree of porosity and degree of crystallinity) and their cycling performance [292]. Overall, larger β -phase contents (a highly polar phase) facilitates faster lithium ion migration through the interaction between lithium ions and the fluorine atoms present into polymer chains.

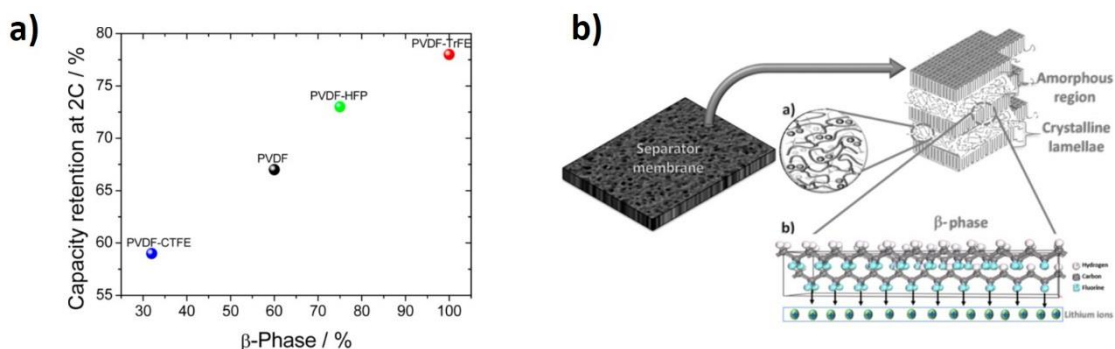


Fig. 12. a) Capacity retention as a function of β -phase content and b) Schematic representation of the interaction between lithium ions and the fluorine atoms for the different membranes. Reproduced with permission [292]. Copyright 2017, American Chemical Society.

In such copolymers, amorphous swollen regions, for example HFP in a PVDF-HFP copolymer, retain large amounts of liquid electrolyte, while the crystalline PVDF phase provides mechanical support [293] and PVDF-TrFE [294]. However, although Li intercalation and deintercalation process proceeds with low internal resistance, their low melting temperature together with their relatively poor mechanical strength remains a limitation for their practical use as separators. In this sense, PVDF has been reinforced with fillers, blended with other polymers or used as a multi-layered material in order to improve its ionic conductivity and thermo-mechanical properties.

PVDF/SiO₂ nanofibers with a nanoparticle concentration up to 24 wt.% were obtained by a combination of electrospinning and electrospraying. An increase in ionic conductivity up to 289 % and electrolyte uptake of 370 % was observed as a result of the high SiO₂ affinity with the electrolyte. A discharge capacity of 95 mA·h·g⁻¹ was observed at 8C, which contrast with the 67 mA·h·g⁻¹ obtained using a commercial PP separator [295]. PVDF composites with TiO₂/graphene oxide [296] and LiSnZr(PO₄)₃ [297] were developed as battery separators with the objective to increase the ionic conductivity. SiO₂, ZrO₂ and TiO₂ particles have been also incorporated into microporous PVDF-HFP membranes via phase inversion method using deionized water as a non-solvent and acetone as solvent. The obtained membranes showed a proper control over pore-morphology leading to increased wettability, ionic conductivity and electrochemical stability [298-300]. Al₂O₃ particles have been proven to effectively weaken the interaction between the fluorine atoms in PVDF and lithium ions, increasing the ionic conductivity and Li⁺ transference number when incorporated into PVDF and PVDF-HFP [301, 302]. The addition of Al₂O₃ into a PVDF-HFP matrix serves to increase the thermal conductivity of the membrane up to five times more than that of commercial polyolefins, which improves heat dissipation in the battery and reduces explosion risks [303]. Other PVDF-based composites with improved cell-performance have been obtained by incorporating montmorillonite (MMT) [304], NaY zeolites [305] [65], or barium titanate (BaTiO₃) [265].

Many PVDF blends were obtained for separator materials, including those with poly(methyl methacrylate) (PMMA) [306], polyacrylonitrile (PAN) [307], poly(ethylene oxide) (PEO) [308], poly(ethylene glycol) (PEG) [309], poly(methyl methacrylate-co-poly(ethylene glycol) methacrylate) (P(MMA-co-PEGMA) [310], and (poly(dimethyl siloxane) graft poly(propylene oxide)-block-poly(ethylene oxide) (PDMS-g-(PPO-PEO) [311]. These blends provide complementary properties in relation to PVDF, and are aimed to improve the ionic conductivity, mechanical stability, electrochemical stability window and cycling battery performance.

In addition, PVDF-TrFE has been reinforced with MMT, BaTiO₃, NaY and CNT in order to improve the performance of the hosting matrix as shown in Fig. 13 [312]. It is observed that PVDF-TrFE membranes reinforced with MMT show the best overall performance among the evaluated fillers [312]. For example, thanks to an improved anode-separator interface provided by the interaction between the oxide anode and the same oxide incorporated into the separator, a 4 wt.% addition of CuO nanoparticles (~350 nm) into a PVDF-HFP separator has been shown to increase the capacity by 13 % when a CuO anode is used in a LIB [313].

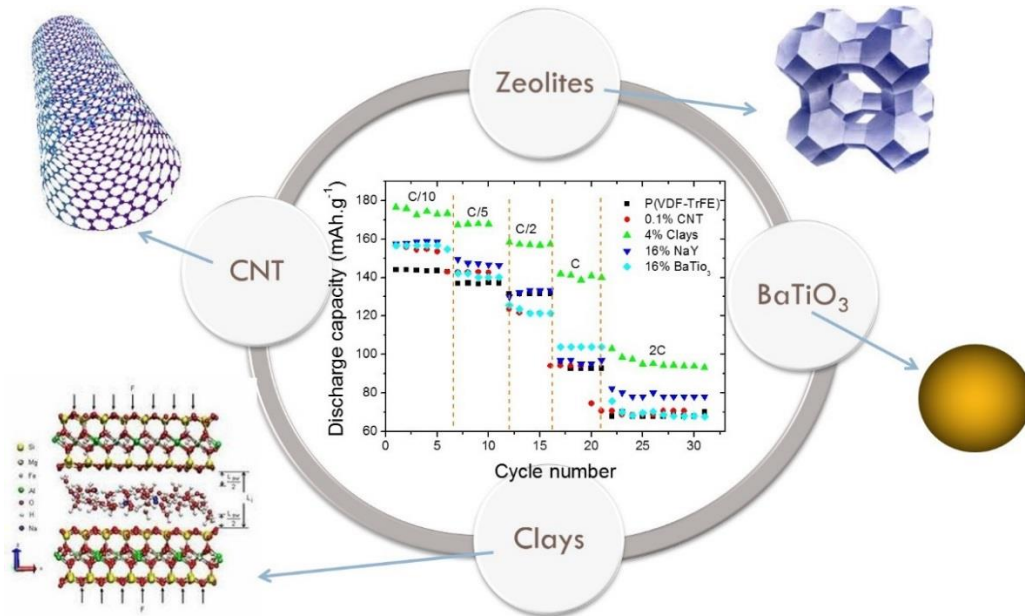


Fig. 13. Cycling performance of PVDF-TrFE membranes modified with different fillers. Reproduced with permission [312]. Copyright 2016, Elsevier.

Multilayered separators were obtained after the coating of PVDF onto commercial Celgard® membranes by electrospinning to improve electrolyte absorption and separator-electrode interface [314]. Zhu et al. showed the development of a flame retarding material upon the coating of a PVDF layer onto a nonwoven Celgard 2730 commercial separator consisting of PE and PP [315]. The ionic conductivity of the separator soaked with 1 M LiPF₆ solution in EC/DMC/EMC (1/1/1) electrolyte showed an ionic conductivity of 0.30 mS·cm⁻¹, which is above the corresponding commercial separator (0.21·mS·cm⁻¹). A doubled lithium ion transference number was also obtained upon PVDF coating, which together with the self-extinguishing behaviour of the separator make these membranes attractive for large-scale battery systems requiring high safety and low cost. The hydrogen bond network of poly(m-phenylene isophthalamide) (PMIA) layer when sandwiched between PVDF membranes provides an excellent mechanical performance to the system, limiting the thermal shrinkage at high temperatures (180 °C) and improving the rate performance in comparison with Celgard® commercial separator [316]. In order to improve separator wettability, ionic conductivity and mechanical/electrochemical stability, PVDF was coated onto PE, PP and PET porous membranes [258, 317, 318]. For example, a PVDF-HFP porous structure has been embedded together with a PET membrane to obtain superior cell performance as a result of the nanoporous structure that allows an easy ion transport [70].

Recently, a strategy aimed to improve the properties of dual-layers based on PET [319] and hydroxyl-terminated polybutadiene grafted methoxyl polyethylene glycol (HTPB-g-MPEG) [320] has been reported using a plasma treatment, resulting in improved electrolyte affinity through the incorporation of oxygen moieties on their surface [283].

3.1.1.3. Polyacrylonitrile

Polyacrylonitrile (PAN) is a semicrystalline polymer which apart from being compatible with many salts, exhibits good processability, small diffusion resistance, good thermal stability, proper wettability and excellent electrochemical stability [321]. The interaction between the C≡N nitrile groups of PAN with lithium ions in liquid electrolytes and the carbonyl groups in the solvent yields membranes with high ionic conductivities, making this material very useful for LIB separators. One of the

drawbacks associated with the use of PAN as LIB separator is that electrolyte leakage events may occur after long-term storage [322].

Electrospun nonwoven PAN mats show high electrolyte uptake, high ionic conductivity, good swelling capacity and are able to keep their original porous structure after prolonged charge-discharge cycles [323]. PAN nanofibre based nonwovens for LIB separators have been prepared [324], showing higher ionic conductivities than commercial ones in the -10 to 60°C temperature range, with better cycling performance, C-rate and a remarkable electrochemical stability in the voltage range of -0.5 to 4.5 V vs. Li^0/Li^+ . Hot-pressed electrospun PAN nanofibrous membranes also show larger electrolyte uptake, higher thermal stability, wider electrochemical potential window, higher ion permeability and better electrochemical performance than commercial PP membranes [325]. The performance of bare PAN membranes has been further improved through the fabrication of microporous PAN/PU nonwoven composites prepared by multi-needle electrospinning technique [326]. Non-flammable membranes when exposed to naked flame with ionic conductivities as high as $2.07\text{ S}\cdot\text{cm}^{-1}$ and with an anodic stability up to 5.1 V were obtained. PAN has been used in order to increase the ionic conductivity of other hosting matrices upon blending. With the aim of increasing cycling stability and compatibility with the liquid electrolyte solution, PAN electrospun nanofiber membranes were prepared and subsequently oxidized by varying the heat treatment time [327].

For example, increased ionic conductivity of microporous PVDF-HFP/PAN membranes upon increasing PAN fraction has been demonstrated, offering better electrochemical performance than membranes composed by PVDF-HFP and PAN [307]. Similarly, PAN has been blended with PVA [328], and PMMA [329], while composites with improved electrochemical performance have been obtained upon the addition of graphene nanoflakes [330], SiO_2 [331], or lignin [332].

3.1.1.4. Polyethylene terephthalate

Polyethylene terephthalate (PET) is one of the most common thermoplastics within the polyester family. It shows good mechanical properties, excellent electronic insulation and, more interestingly, its high melting temperature of about 255°C provides PET a remarkable ability of enduring high temperature exposure far superior to

that of other separators composed by polyolefins or PVDF [237]. PET nonwoven separators have been prepared via electrospinning technique with a 484 % electrolyte (1 M LiPF₆/EC-DMC) uptake in the first 10 minutes, the cells assembled using PET showing a better cycling capacity and higher discharge capacity than the ones using commercial Celgard separators [237].

A PVDF nanofiber layer deposited onto a PET microfiber support has been presented, where the PVDF layer improves the wettability of the membrane with increased porosity and surface area and PET provides enough mechanical support and dimensional stability at high temperatures [333]. A shutdown temperature of 131 °C was obtained as a result of the PVDF layer melting, while the meltdown temperature of 252 °C of PET can prevent the cell temperature from increasing before actually starting to cool down after cell shutdown. PET has been used in commercial separators although they are not as common as polyolefin separators. A series of Separion (trade name) separators composed by a nonwoven PET membrane coated with Al₂O₃/SiO₂ have been developed to provide membranes with dendrite penetration resistance, good thermal stability up to 220 °C and a dimensional shrinkage 3 times lower than commercial polyolefin membranes [223]. When working at 150 °C, cells with Separion separators showed no change while the cells with PE separators suffered short circuit events due to the marked shrinkage of the separator. In other work, a nonwoven PET layer was sandwiched between poly(vinyl alcohol-co-ethylene) membranes to obtain high electrolyte wettability and ionic conductivities comparable to commercial PP separators [334]. A nonwoven PET was used onto a PP separator to improve the electrolyte affinity, obtaining an excellent discharge capacity and superior thermal stability [335]. Other similar separator membranes have been also produced, such as a poly(vinyl alcohol-co-ethylene)/PET nanoporous membrane having a high porosity and low thermal shrinkage [334].

3.1.1.5. Polyimide

Polyimide (PI) is a high performance engineering polymer which shows a thermal stability up to 500 °C, proper chemical resistance, excellent mechanical performance and good electrolyte wettability thanks to its polar groups [336]. Considering its high thermal resistance, different separators were produced by non-solvent induced phase separation (NIPS) [337] and phase inversion methods using soluble polyimide (SPI)

containing trifluoromethyl substituent. This material is synthesized from 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) and 4,4'-oxydipthalic anhydride (ODPA) [338]. Electrospun PI membranes (see the morphology in Fig. 11d) with thicknesses ranging from 40 to 100 μm showed a better rate capability in comparison with Celgard® separator at current densities as high as 10 C [277]. Electrospun polyimide nonwovens have been developed by addition of trace plasticizer in order to enhance the mechanical properties [339]. Porous PI membranes were prepared using a wet phase inversion process, which showed an excellent thermal stability with glass transition temperature of 274 °C and a thermal shrinkage below 1% when stored at 200 °C [340]. PI (PMDA-ODA) nonwoven membranes obtained after the thermal imidization of poly(amic acid) exhibit capacity retention over the discharge rate of 0.2-10 C, making them suitable candidates for high-rate LIBs [277]. This was further confirmed by showing that a non-woven separator prepared via electrospinning with uniformly dispersed 491 nm diameter fibres and a porosity > 90% presents a capacity retention ratio of 33.6% at super high discharge rate of 28.8 C, while the capacity remains 99.66% after 320 cycles at 5 C rate [341]. PI separators prepared by electrospinning and subsequent thermal imidization result good candidates for high temperature operation (120 °C) owing to their high oxidative potential above 4.5 V, no thermal shrinkage, excellent lithium deposition-stripping performance and good ionic conductivity, which results in stable charge-discharge profiles with satisfactory cyclability [342].

The electrochemical performance of PI has been upgraded either by blending it with other polymers or through composite development. As depicted in Fig. 14, a thin Al_2O_3 layer was coated onto PI membranes to obtain separators with a markedly lower thermal shrinkage and bulk resistance than bare uncoated membranes, resulting in a dramatic improved rate capability in comparison with commercial PP membranes, especially at high rates [343]. Al_2O_3 coating also increases the ionic conductivity and alleviated the increase of cell impedance, resulting in separators with a rate capability of 78.9 % at 10 C in comparison 68.6 and 18.2 % for un-coated PI and commercial PP separators respectively. PI/glass microfiber membranes fabricated via dip-coating show a great potential for high-temperature applications as they show an excellent wettability, do not catch fire in the flame, do not display shrinkage at temperatures as high as 200 °C and show a stable cycling at 120 °C [344]. Hydrophilic SiO_2 has been incorporated within a

PI matrix to further upgrade electrolyte uptake and ionic conductivity [343, 345]. A trilayer PI/Cu/PI separator was prepared to obtain separators with efficient alarm response against Li penetration, opening up the opportunity for safer battery design by separator engineering [346].

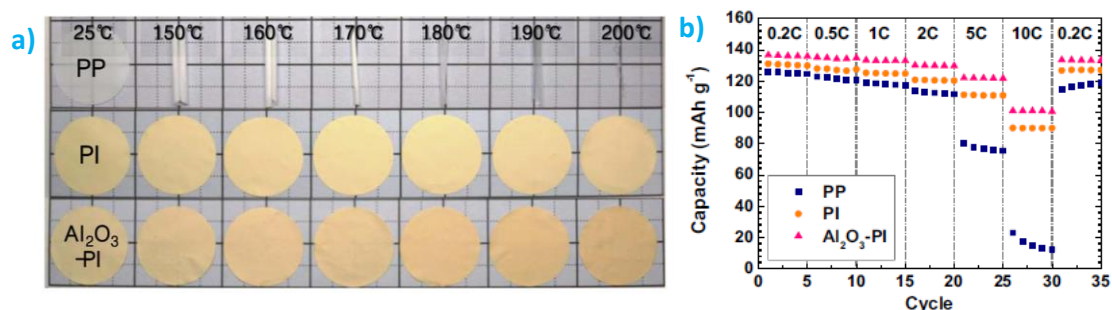


Fig. 14. High temperature separators based on PI with improved electrochemical performance. a) Photographs showing thermal shrinkage of the commercial PP, PI and Al₂O₃-coated PI separators as a function of exposure temperature and b) rate capability of cells with the PP, PI and Al₂O₃-PI separators at constant current charge/discharge rates. Reproduced with permission [343]. Copyright 2014, Elsevier.

Electrospun PI nanofibres were coated onto PET nonwovens to obtain improved electrolyte uptake, 2% dimensional shrinkage at 180 °C and a capacity retention of 87.5% after 50 cycles at 10 C [347]. Core-sheath PI@PVDF-HFP were fabricated to combine good mechanical/thermal properties and ionic conductivity [348]. PI membranes with a controllable shutdown function in the 120 - 200 °C range have been prepared by coating a PE layer onto electrospun PI fibers [349]. Similarly, sandwich-type PI/PVDF/PI membranes were synthesized through electrospinning to obtain shutdown function as the intermediate PVDF layer melts at 170 °C to fill the pores within PI. Electrolyte uptake up to 476%, an ionic conductivity of 3.46 mS·cm⁻¹ and a low specific capacity decay rate of 2.9% after 100 cycles under 0.5C-rate discharges were obtained [350].

A PI-based mechanically flexible but strong non-flammable separator which withstands bending, cutting and nail penetration has been recently proposed [351]. The 8.6-μm-thick separator was obtained upon the filling of a nanoporous PI film with PEO/LiTFSI. The vertical nanochannels in the separator provide high ionic conductivities up to 2.3·10⁻⁴ S·cm⁻¹, opening new strategies to develop safe and flexible high energy density LIBs. Dual redox-active polyimides based on phenothiazine and naphthalene tetracarboxylic dianhydride show a great potential to be used

simultaneously as anode and cathode materials as they can deliver a high power density up to $1542 \text{ W} \cdot \text{kg}^{-1}$ with stable cycling for 1000 cycles at current densities as high as $800 \text{ mA} \cdot \text{g}^{-1}$, opening the path towards symmetric polymer batteries [352].

3.1.1.6. *Poly(aryl ether ketone)*

Poly(aryl ether ketone) (PAEK), a family of semi-crystalline thermoplastics that presents an excellent thermal oxidative stability, good mechanical properties and good chemical stability [353], has been used as separator material in LIBs [354, 355]. The aromatic main chains provide excellent thermal and mechanical stability, while the polar ether/ketone groups strongly interact with carbonate electrolytes, resulting in improved power densities. Novel porous separators based on PAEK were prepared by selective removal of poly(lactic acid) (PLA) chains on their structure [356]. One of the best known types of PAEK is the high-performance engineering semicrystalline poly(ether ether ketone) (PEEK). Its melting temperature is above 330°C , it shows a negligible thermally-induced shrinkage, it is highly chemically stable and it shows very low flammability. Despite these favourable characteristics, its poor solubility (usually H_2SO_4 needs to be used) has limited its used as LIB separator as membrane fabrication results somewhat dangerous. Porous PEEK membranes with symmetric sponge-like structure have been prepared by phase inversion method. The obtained membranes showed a 251% electrolyte uptake, high thermal stability and a discharge capacity of $124.1 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$ at 5°C [355].

In an attempt to improve its performance as separator material, PEEK has been modified to obtain the so-called sulfonated poly(ether ether ketone) (SPEEK), which is a low cost non-fluorinated ionomer membrane with adequate ionic conductivity, good thermal and mechanical stability and low cost [357]. SPEEK can be obtained upon sulfonation of raw PEEK, where large sulfonation results in an increased ionic conductivity at expenses of mechanical strength [358]. Typically, 6g of PEEK are poured into 100 mL concentrated sulphuric acid at 50°C . The sulfonation reaction can proceed for different times and could be quenched by precipitating the resulting mixture iced water.

3.1.1.7. *Polytetrafluoroethylene*

In an attempt to look for cheap high-performance separators, polytetrafluoroethylene (PTFE) has emerged as a novel material as it is chemically inert, it shows a zero-static discharge, it has a high dielectric breakdown voltage and possess good mechanical properties. Electrospun PTFE nanofiber membranes with thermal stability, electrochemical stability (up to 5.5 V versus Li/Li⁺) and rate performance better than that of the conventional polyolefin separators were obtained, providing enhanced safety to the cell [240].

PTFE blends have also been used for LIB separators. A PTFE/PVDF-HFP separator was designed to absorb large amounts of liquid electrolyte at the same time that the mechanical stability of the membrane is maintained [359]. PVDF-HFP enhances the wettability and acts as shutdown element, while PTFE provides good mechanical stability even at elevated temperatures. Similarly, calcium carbonate (CaCO₃) has been incorporated into a PTFE matrix to obtain composite films with good dimensional stability at high temperatures, excellent wettability and able to suppress the formation of hydrogen fluoride (HF) [360]. In LIBs, HF develops as a consequence of the LiPF₆ hydrolysis, resulting in one of the most relevant causes for capacity fade. The obtained membranes show an ionic conductivity of 2.4 mS·cm⁻¹ at 20 °C after being soaked with liquid electrolyte (in comparison with 8.0 mS·cm⁻¹ of the liquid electrolyte) and show a superior cycling performance as a result of the ability of alkaline CaCO₃ to scavenge acidic impurities

3.1.1.8. Polyurethanes

Polyurethanes (PU) are a group of thermoplastic materials composed of phase separated hard and soft domains; whereas the soft segments (polyether or polyester) have the ability of dissolve alkali metals, the hard segments (diisocyanates) act as physical cross-link sites, providing good mechanical performance to the system [361]. As a result of their low cost, stretchy character, high thermal stability and proper electrolyte wettability, PUs have been used as separator membranes to build full-cells in the form of clothes and watchstraps which show comparable electrochemical performance to those of conventional cells even under severe folding–unfolding motions, opening the path towards flexible energy storage systems [362]. A porous PU/PVDF membrane has been reported as a separator that sticks to the electrodes, a key aspect for the development of cost-effective wavy battery with high stretchability [189].

Other separators using PUs include electrospun PAN/PU separators [326], and high performance SiO₂/PEI-PU membranes [363].

3.1.1.9. Polydopamine

Thanks to its hydroxyl and amino groups, polydopamine (PDA) can be used as a coating to increase the surface energy of the membranes and therefore, their wettability with the electrolyte. It also protects against dimensional shrinkage when used at high temperatures at the same time that protects active materials from unwanted side reactions with electrolytes. Its catechol groups adhere to the electrodes, increasing the life cycle of LIBs [364]. As shown in Fig. 15, a PDA surface coating has been applied onto PE separators to modify the surface properties; i.e., electrolyte wettability and uptake was improved while porosity and Gurley number remained intact, yielding to increased ionic conductivities, enhanced cycle life and improved C-rate [365]. A mussel-inspired PDA coating has been applied onto a PEG-coated PP separators to obtain enhanced cell performance as a result of improved affinity of the separator membrane with the liquid electrolyte [366]. PDA-coated PVDF electrospun nonwoven membranes display an improved cycling performance and power capability than the uncoated PVDF as a result of the combined effects of an increased electrolyte affinity provided by the PDA layer, enhanced ionic conductivity and catechol adhesion between electrodes and the separator [367]. PDA has been coated onto other porous structures such as PP [368], cellulose microfibrillated membrane [369], poly(ether sulfone) (PES) membranes [369], or PP-PE-PP separators [370].

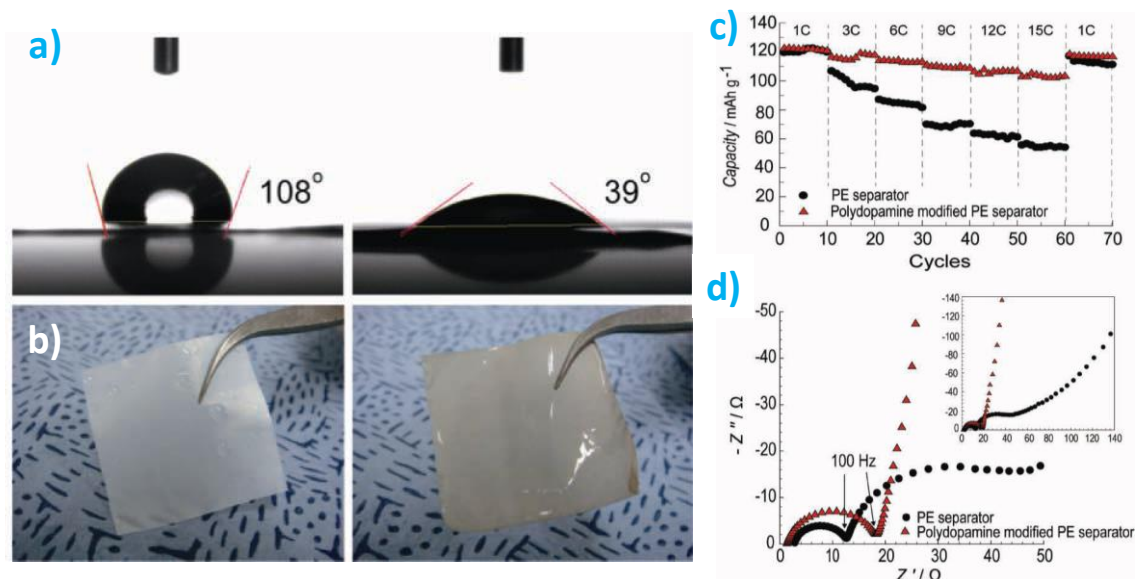


Fig. 15. A mussel-inspired polydopamine surface treatment of polyethylene via simple dip-coating in aqueous solution at pH 8.5 yield hydrophilic surfaces with improved electrochemical properties. a) Contact angle images of PE separators before (left) and after (right) the polydopamine coating.; b) wetting test of the corresponding separators in 1 M LiPF₆ in EC/DEC/PC; c) discharge capacities for coated and uncoated PE separators in the 3.0-4.5 V range and d) Nyquist plots measured after the 70 cycles. Reproduced with permission [365]. Copyright 2011, Wiley.

3.1.1.10. Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is a transparent amorphous thermoplastic material that presents a high affinity towards liquid electrolytes. PMMA membranes have shown high ionic conductivity, good thermal and electrochemical stability and remarkable adhesion with electrodes as it forms a gel when soaked with liquid electrolyte, although its poor mechanical performance has limited its used as LIB separators. In spite of this, the inherent electrolyte affinity of PMMA has been used to upgrade the electrochemical performance of other polymer membranes. Grafting a PMMA layer onto PE membranes by electron beam irradiation has been proven as an efficient approach to improve electrolyte uptake and retention, increasing cell performance [371]. Similarly, the PMMA phase in PAN/PMMA nonwoven mats prepared by electrospinning provides a good compatibility with the liquid electrolyte to yield an ionic conductivity of 3.6 mS·cm⁻¹ [372]. PMMA has been blended with PVDF and PVC microporous membranes to obtain separators where blends having 60 wt.% of PMMA showed a favourable ionic conductivity and lithium self-diffusion thanks to the gel-forming capability of PMMA upon being soaked with the liquid electrolyte [373,

374]. Multilayer membranes with unique structures have been prepared upon the preparation of a close-packed PMMA nanoparticle arrays onto a PE [244]. A highly ordered porous structure with well-connected interstitial voids was obtained by PMMA nanoparticle coating, facilitating the electrolyte wettability and uptake. As a consequence of the well-developed ordered morphology, the ionic conductivity of the PMMA nanoparticle arrays-coated separator increased up to $0.52 \text{ mS}\cdot\text{cm}^{-1}$ in comparison with the $0.31 \text{ mS}\cdot\text{cm}^{-1}$ obtained for the separator coated with a dense PMMA layer. Composites having PMMA were also reported. A thin Al_2O_3 coating on both sides of a PMMA membrane was applied by dip coating method using PVDF-HFP as a binder at a 9:1 ratio (Al_2O_3 to PVDF-HFP) to obtain a tri-layer separator with a remarkable thermal stability thanks to the inorganic layers and good capacity retention at high rates [375]. In other work, PMMA-coated SiO_2 microspheres were deposited onto a PE separator to improve electrolyte absorption, while the cycle performance and C-rate capability are increased by the presence of SiO_2 [376].

3.1.1.11. *Cellulose and derivatives*

Cellulose, as the most abundant biopolymer on the biosphere, is a promising material to develop environmentally benign LIBs [377]. Cellulose has been traditionally used in the form of wood for construction purposes, as fibre for textile applications, as paper or as reinforcing element for polymers. The use of cellulose-derived separators by common papermaking approaches results a suitable solution to the expensive fabrication methods and disposal issues associated with traditional microporous polymer membranes. Although paper-sheets have been used in alkaline batteries provided their wettability, porosity, low density and easy of processing [378], their application in LIBs has been limited due to its hygroscopic character as water contents below 20-50 ppm are required to avoid LiPF_6 hydrolysis and HF formation [379].

Several cellulose derivatives have been used so far as LIB separators. For example, ethyl cellulose (EC) was coated onto monolayer PE and trilayer PP-PE-PP separators by simple dipping process, leading to increased electrolyte capacity retention from 28 to 99% and a decrease in the thermal shrinkage from 20 to 9% at shutdown temperature [380]. A porous cellulose diacetate (CDA)- SiO_2 composite was coated onto a PE membrane to obtain increased ionic conductivity, electrolyte wettability and thermo-mechanical properties. More interestingly, CDA- SiO_2 layer successfully suppresses

dendrite growth and promotes the formation of a stable SEI, resulting in a plausible approach towards safer LIBs [381]. Using electrospinning technique, a non-woven mat of cellulose acetate (CA) was coated onto a PVDF-HFP film to obtain improved capacity retention and rate capability in comparison with commercial PP separators [382]. Remarkable ionic conductivity of $4 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at room temperature (higher than the $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ of the original 1M LiFP₆ electrolyte in 1:1 EC:PC) was obtained by blending a cyanoethylated cellulose derivative with PVDF-HFP and subsequently dissolving the mixture in dimethylformamide to obtain microporous membranes [383].

Membranes composed by cellulosic fibres have also been demonstrated efficient as LIB separators. It was already shown in 1996 that after being soaked in an aprotic solvent, membranes based of fibrilliform cellulosic fibres (diameters 0.5 to 5.0 μm) embedded in a microporous cellulosic matrix display a complex impedance lower than conventional polyolefin separators while being “pinhole-free” and maintaining proper mechanical properties [270]. Rice paper consisting on large fibres of 5 to 40 μm in diameter has been also proven to be electrochemically stable when used as separators for LIBs [384]. Currently, nanocelluloses, either cellulose nanofibers (CNFs), cellulose nanocrystals (CNCs) or bacterial cellulose (BC) have attracted an increasing interest for the development of novel LIBs separators thanks to their inherent strength, surface chemistry, and biodegradability. Interestingly, the low coefficient of thermal expansion (CTE) of about $10^{-7}\cdot\text{K}^{-1}$ of cellulose-based nanopapers make them interesting candidates for high-temperature environment applications [385]. In this line, non-woven membranes composed by CNFs fabricated by high pressure homogenization showed improved thermal and mechanical resistance in comparison with Celgard® membranes [386]. Similarly, in comparison with PP separators, cellulose-based composite nonwoven (FCCN) separators present improved shrinkage resistance, combustion behaviour, rate capability at room temperature and more interestingly, cycle performance at high temperatures (120 °C) [219] as shown in Fig. 16. Covalently linked bacterial cellulose nanofiber separators display high-strength and excellent thermal and dimensional stabilities, having better cycling performance and rate capability to Celgard® separators [227]. The characteristic nanoscale labyrinth morphology of bacterial cellulose nanofiber separators results in enhanced electrolyte wettabilities, increased ionic conductivity and reduced thermal shrinkage in comparison with commercial polyolefin separators [226]. High specific surface area ($172 \text{ m}^2\cdot\text{g}^{-1}$)

mesoporous membranes consisting on CNCs show a good electrolyte affinity with both conventional 1 M LiPF₆ in EC-DMC and ionic liquids, resulting in ionic conductivities as high as 2.7 mS·cm⁻¹ [246]. It has been shown that mesopores provide efficient paths for Li⁺ ion migration through the membrane, delivering a specific capacity of 122 mAh·g⁻¹ at a C/2 rate. Moreover, a single ion conductor behaviour of such membranes can be obtained upon lithiation of the -OSO₃H groups on the surface of the CNCs. The obtained impressive high Li⁺ transference number of = 0.9 enables a smooth Li metal deposition and stable cycling of Li- LiFePO₄ cells [387].

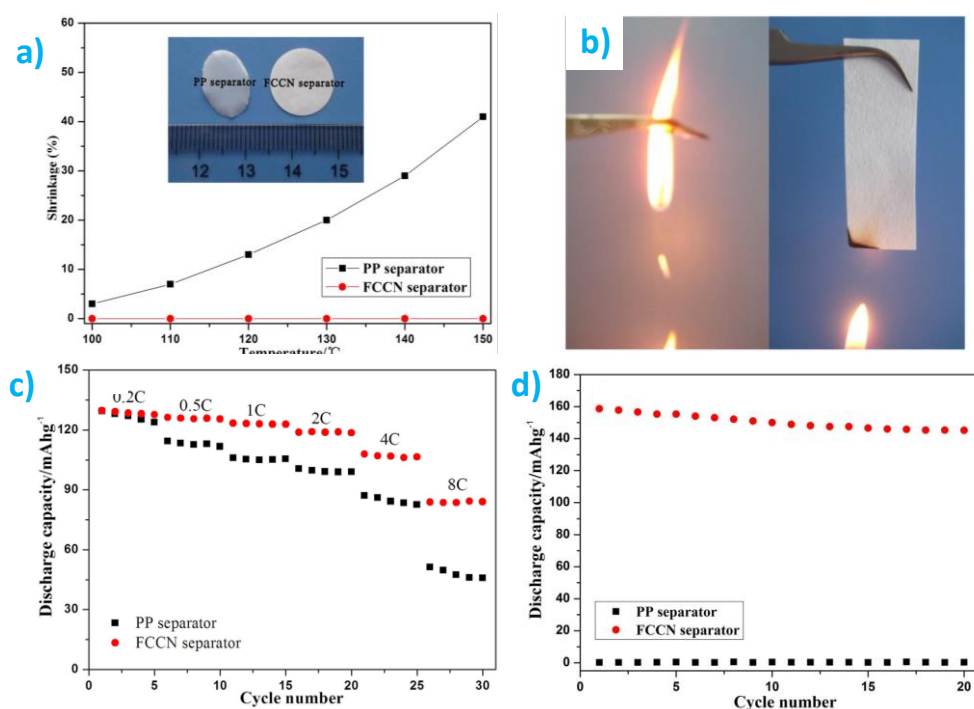


Fig. 16. a) Thermal shrinkage rate of PP separators and cellulose-based composite nonwoven (FCCN) separators (the inset shows both separators after thermal treatment at 150 °C for 30 mins; b) combustion behavior of PP and FCCN separators; c) rate capability of the LiCoO₂/graphite cells using PP and FCCN separators and d) cycle performance for LiFePO₄/Li cells using PP separator and FCCN separator at 120 °C. Reproduced with permission [219]. Copyright 2014, Springer Nature.

A 35 μm thick mesoporous separators from nanometric cellulose fibres showed good mechanical properties, wettability, thermal stability at 150 °C, ionic conductivity of 0.4 mS·cm⁻¹ and electrochemically inertness in the potential range between 0 and 5 V vs. Li/Li⁺ [388]. The performance nanocellulose-based separators could be further upgraded through mussel-inspired PDA coating [369], or through the incorporation of inorganic nanoparticles such as SiO₂ [389], or Al₂O₃ [390]. Nanocelluloses are also being used as a reinforcing phase in polymer separators with the main aim of improving

the mechanical response of the membrane. In this line, CNCs were incorporated into a PVDF and PVDF-HFP matrices to obtain porous separators with a remarkable thermal stabilization at temperatures higher than the melting temperature of the PVDF as a result of the rigid percolating network formed by CNCs [391, 392]. Recently, electrospun cellulose nanofiber membranes have been produced as separators with flame resistance properties [393]. Also, zeolitic imidazolate framework-8 (ZIF8)-CNF nanocomposite membranes have been synthesized and used as separators, allowing to improve the thermal, mechanical and surface wetting properties of battery separator membranes [394].

3.1.1.12. *Other polymers*

New promising polymers for LIB separators are currently emerging. Although the most common applications of electroactive polymers are found in sensors and actuators, electroactive polymers show a bright future for “smart” separators. The fact that such materials exhibit a change in shape when stimulated by an electric field can be used to fabricate membranes that effectively shut down the batteries during overcharging. These materials can be reversibly doped and de-doped to yield electronically conductive/insulating phases depending on the applied potential so at overcharged voltage they can effectively protect the batteries from voltage runaway. Separators composed by redox-active polymers such as p-polyphenyl (PPP)/polyaniline (PAn) [395], poly(3-butylthiophene) (P3BT) [396], poly(3-decylthiophene) (P3DT) [397], or polytriphenylamine (PTPAn) [398], have been fabricated as they can be used as a potential-sensitive switch to maintain the charge voltage of LIBs at a safety value of few volts with no negative impact on the charge-discharge cycles.

Poly(p-phenylene benzobisoxazole (PBO), a rod-like aromatic heterocyclic polymer consisting of repeating units of benzobisoxazole and phenylene functional groups, has been used to fabricate flexible yet strong membrane separators through a simple blade casting process [399]. The obtained good electrolyte wettability and ionic conductivity together with its superior thermal stability up to 600 °C and mechanical properties (ultimate strengths of 525 MPa and Young’s modulus up to 20 GPa) make PBO-nanofiber separators suitable for lithium dendrite-proof LIBs.

Considering the enormous relevance of the environmental issues in this area of application, separator membranes based on silk fibroin have been recently developed

[400]. In addition, the effect of pore size on silk fibroin separators has been studied, demonstrating that a higher discharge capacity value is obtained for average pore sizes in the range 250–106 μm [401]. It has been proven that *Bombyx mori* silkworm cocoons can be used as resources to develop separators for the development of more sustainable lithium-ion batteries to improve environmental friendliness and safety in the next generation of energy storage devices [402].

Overall, separator membranes have been developed using different polymer types where each system shows advantages and disadvantages. Independently of the used polymer type, separator membranes should be highly porous with excellent mechanical and thermal properties, must show good wettability by the electrolyte solution and high ionic conductivity values. The development of separators based on natural polymers with high thermal stability and compatibility with electrolyte and electrodes emerges as a new research area. The proper control of porosity and pore size becomes an essential issue, where scalable production techniques that allow the fabrication of separators at low cost need to be evaluated. Further, the transition from the separator/electrolyte pair to solid electrolytes results critical for the fabrication of the next generation solid-state batteries.

3.1.2. Solid electrolytes

An ideal solid electrolyte needs to fulfil partly antagonistic requirements, making its development a challenging task. They should be mechanically flexible to allow as easy fabrication and optimal solid electrolyte-electrode interface at the same time that they should present a proper stiffness and strength in order to limit dendrite growth. More importantly, their ionic conductivity should be high enough to ensure a proper Li^+ ion diffusion through the membrane between the negative and positive electrodes. Limiting the charge-transfer resistance barrier at the solid/solid electrode/electrolyte interface is one of the most challenging issues that face nowadays solid electrolytes. Contrarily to liquid electrolytes which easily penetrate into the electrodes, solid electrolytes cannot form a continuous contact with the active material; i.e., the electrochemical interface is not continuous. Since charge transfer could only occur at such contact points, a continuous electrode/electrolyte interface is required for high energy density LIBs as this ensures an even current distribution through the electrode material, avoiding large current density areas and successfully suppressing dendrite formation [403]. Similarly,

successive cycling leads to electrode volume changes, modifying electrode/electrolyte interface and weakening the connection between them. In this framework, malleable solid electrolytes are required as their shape may be adapted to fill the voids between electrodes at the same time that a soft SPE may accommodate volume changes occurring during charge/discharge, alleviating interfacial strain as shown in Fig. 17.

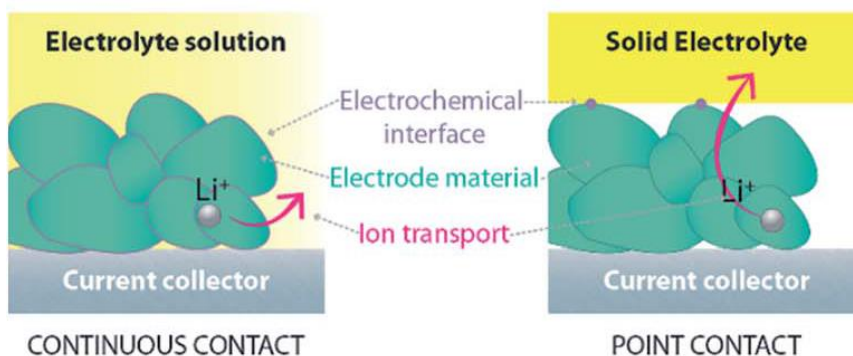


Fig. 17. Influence of electrolytes on the establishment of proper electrode/electrolyte interfaces. Reproduced with permission [404]. Copyright 2016, Royal Chemical Society.

Due to their mechanically soft nature in comparison with solid inorganic electrolytes (SIE), solid polymer electrolytes (SPEs) are attractive materials, which successfully face most of the above-mentioned issues, where SPE can be classified as a gel polymer electrolyte (GPE) containing high amount of lithium salts or liquid ionic forming an ion-conducting solution with a suitable mechanical stability [263]. Thanks to the pioneering works of Fenton et al. in 1973, [405] who suggested ion conductivity in a PEO-alkaline metal ion complex, and Armand in 1978 [406], who used PEO in batteries for the first time, polymer based ion conducting materials have generated an increasing scientific and industrial interest in the field of LIBs. SPEs are obtained after the dissolution of a lithium salt within a polymeric matrix. In spite of the advances made on SPEs, the vast majority of SPEs are bi-ionic systems where both anions and cations are mobile, which results in Li-ion transference numbers (LTN) lower than 0.5 [407]. To increase the ionic conductivity of traditional dual-ion conducting electrolytes, in which both cations and anions are mobile and cause polarization concentration, more recently single lithium-ion conducting SPEs (SLIC-SPEs) have been synthesized [408]. They consist on carboxylated or sulfonated anions covalently bonded to the polymeric matrix in combination with mobile cations, where the high LTN results in improved performances [409].

Modern LIBs require solid electrolytes capable of withstanding strong thermal and mechanical solicitations. Quite often, SPEs fail to provide an efficient protection against short-circuit events as their inherent mechanically soft nature allows a relatively easy penetration of lithium dendrites through the membrane [410]. In 1982 Weston and Steele reported a pioneering work to provide SPEs with increased mechanical properties as they showed a concomitant improvement on both the ionic conductivity and mechanical stability with the addition of α -Al₂O₃ inorganic particles into PEO, opening the path for the development of composite polymer electrolytes (CPEs) [411]. Since then, many efforts have been made in the understanding of the impact of different kind of fillers on the electrochemical, thermal and mechanical properties of CPEs [251, 412].

3.1.2.1. Poly(ethylene oxide)

Poly(ethylene oxide) (PEO) is a semicrystalline polymer which has been extensively used as SPE after its complexation with a lithium salt (LiX, where X=ClO₄⁻, PF₆⁻, BF₄⁻, N(SO₂CF₃)₂⁻...) [406]. It shows a glass transition temperature (T_g) and melting temperature (T_m) of -60 and 65 °C, respectively and its ether groups show a high affinity to Li⁺ ions, allowing the mixing of lithium salts within the polymer matrix. PEO-based solid electrolytes have been highly appealing option thanks to their proper compatibility with electrodes, mitigating Li dendrite growth characteristic of LIBs having liquid electrolytes. In any case, recent studies have shown that such systems are not completely thermodynamically stable with lithium metal, yielding the formation of an intermediate passivation layer [413]. As depicted in Fig. 18, Li⁺ ions are complexed to PEO through five ether oxygen atoms within the PEO chain, where the cation mobility is decreased as a consequence of their complexation [410]. Therefore, the cation transport is defined as the motion of the Li⁺ between complexation sites assisted by the segmental motion of the PEO matrix. The success of PEO-LiX SPEs is evidenced by the lithium batteries that power Bluecar, a small four-seat electric car supplied by the Bolloré Group. The car provides an electric range of 250 km in urban use and its battery includes a lithium anode, a PEO-lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) solid electrolyte and a FePO₄ cathode [155]. As a semicrystalline polymer, the ionic conductivity of PEO markedly drops when large crystalline areas are found as ionic conductivities are generally associated with the amorphous phase. This conductivity decrease is of paramount relevance when SPEs are used below their glass transition

temperature (T_g), where the segmental chain mobility is drastically reduced. As a result, the ion motion in PEO-LiX SPEs is severely hampered, yielding ionic conductivities of $\sim 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ when used at room temperature [414]. This fact obligates the battery to operate above 60 °C, where all the polymer remains in a viscous liquid state and acceptable conductivity values of $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ can be reached. The anion mobility along the chain is larger than that of the cation, resulting in low lithium transport numbers which can be improved by properly selecting salts with larger organic anions and huge electron delocalization such as TFSI⁻ [415].

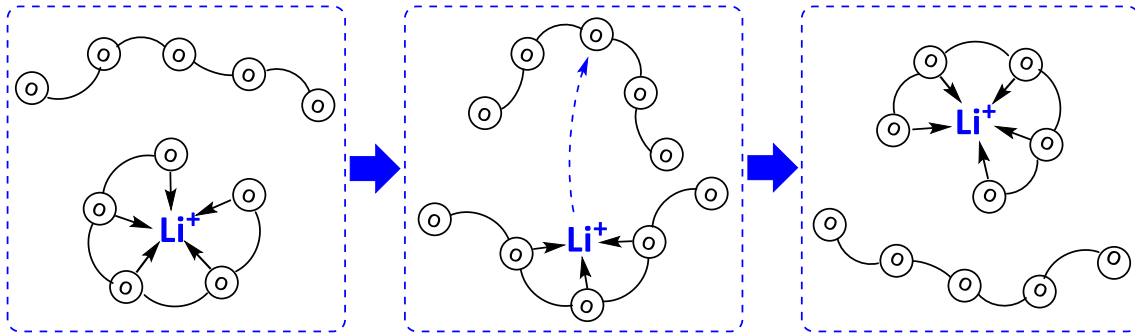


Fig. 18. Schematic representation of the Li^+ transport in PEO matrix where an oxygen-assisted hopping mechanism of Li^+ takes place. Reproduced with permission [410]. Copyright 1999, Wiley. Li^+ ions are complexed through five ether oxygen atoms of a PEO chain (represented as closed circles).

Therefore, an ideal SPE should present a low T_g to perverse high lithium ion conductivity at the same time that its rubbery state ensures a good stability with both electrodes and preserves a wide electrochemical stability. In this sense, a plasticizer with high salt dissociation level such as lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) can be added to PEO to increase its ionic conductivity [416]. The incorporation of plasticizers or copolymers into PEO-LiX can offer strategies to reduce both the crystallinity and T_g , increasing the electrochemical stability and inhibiting lithium dendrite formation [417, 418]. For instance, PEO/PEI blends with LiClO_4 lithium salt show an ionic conductivity as high as $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 30 °C [419], while PEO/PAA blends present increased ionic conductivity by blocking the anion and increasing the lithium transport number [420], and PEO-PAN copolymer complexed with LiClO_4 display an ionic conductivity of $6.79 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C [421]. Many PEO-LiX based systems incorporating diblock and triblock copolymers have been developed so far [422-424]. Interestingly, the combination of the single-ion conducting block poly(lithium methacrylate-co-oligoethylene glycol methacrylate) (P(MALi-co-

OEGMA)) together with a PS block allows to achieve a remarkable ionic conductivity at room temperature of $0.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ [424]. Other viable approach is the dispersion of solid plasticizing elements to form hybrid SPEs. Homogeneously dispersed reinforcing phases such as TiO_2 , Al_2O_3 , SiO_2 , zeolites or BaTiO_3 , called passive fillers as they do not directly participate in the conduction process, serve to prevent dendrite penetration through the SPE while increasing the ionic conductivity, to limit undesired matrix crystallization, to increase the thermal stability and to improve the mechanical and thermal properties of SPEs. Other fillers such as graphene [425] or super acid oxides [426] are also used in SPEs. Beyond to the inert fillers, several lithium fillers (such as $\text{Li}_{0.3}\text{La}_{0.557}\text{TiO}_3$, LLTO [427]; $\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$, LLZO [428], among others), have been also used as reinforcing elements. Those fillers are identified as active fillers as they contribute to the conduction process.

The low electrochemical stability of PEO does not allow the use of high energy density cathode materials such as LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, limiting most of the works to LiFePO_4 cathodes [429]. Additionally, its relatively low ionic conductivity at room temperature does not allow the development of commercial high performance LIBs. Therefore, industry and research are making notable efforts in order to upgrade the performance of SPEs. An optimal SPE should, in principle, comprise a lithium salt having a low lattice energy dissolved into a polymer host with a high dielectric constant to enable the dissociation and prospective transport of ions [410]. In this line, salts ensure a maximum ionization, while polar polymers are preferred as they can form coordination bonds with cations and anions [430].

Other strategy for increasing the ionic conductivity rely on lowering the T_g value. Accordingly, different methods have been proposed, such as a cross-linking step via photopolymerization of poly(ethylene glycol) methyl ether acrylate (PEGMEA, monomer) and poly(ethylene glycol) diacrylate (PEGDA, cross-linker) [431], using a cross-linking agent by nano- SiO_2 [432], or using bisphenol a ethoxylate diacrylates (BPAEDA) [433], tetra(ethylene glycol)dimethyl ether (G4) [434] or a copper(I)-catalyzed azide–alkyne cyclo-addition [435].

The incorporation of copper oxide powders within a PEO matrix resulted in interesting ionic conductivity at room temperature ($0.1 \text{ mS}\cdot\text{cm}^{-1}$), although low discharge capacity was obtained upon battery assembly ($51 \text{ mAh}\cdot\text{g}^{-1}$ at C/10) [436]. The effect of different shapes of BaTiO_3 nanoparticles in a PEO structure doped with

LiTFSI has also been studied, concluding that nanospheres lead to the highest ionic conductivity ($1.8 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$) and discharge capacity ($135.6 \text{ mAh}\cdot\text{g}^{-1}$ at C/10) [437].

A double composite membrane consisting on lithium salts and SiO_2 ceramic particles into a PEO/PPO blend was prepared using electrospinning. Such membranes showed a promising ionic conductivity and an excellent discharge capacity, presenting a low and stable interface resistance between the separator and the metal anode [438]. Additionally, a SPE based on PEO and glass fibres effectively suppresses Li dendrite growth, improving the cycling stability and battery life by an order of magnitude in comparison with pure PEO electrolytes [439].

Polysiloxanes, also known as silicones, are polymers made up of repeating units of siloxane (alternating silicons and oxygen atoms) that are highly flexible, show good thermal and chemical stability and tuneable properties as they can have a wide range of substituents bound to the silicon and are added to PEO polymer [440]. When polar units are introduced, the achieved low T_g values (-123°C for poly (dimethyl siloxane), for example) and high free volumes result very interesting for the fabrication of SPEs [441]. For example, poly (dimethyl siloxane-co-ethylene oxide) with 5 wt.% LiClO_4 shows ionic conductivities of 3.0×10^{-5} and $2.6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at -30 and 25°C respectively, which together with the wide electrochemical stability of 5.0 V Li/Li^+ make this material useful for many practical applications [442]. Further polysiloxanes have been developed so far as SPE for LIBs, which include cross-linked poly (siloxane-g-ethylene oxide)-LiTFSI as a strategy to upgrade the poor mechanical stability of silicones at high temperatures (ionic conductivity at RT of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$, electrochemical window above 4.5 V Li/Li^+) [443], cross-linked polysiloxanes with pendant oligo (ethylene glycol) as plasticizing and doped with LiTFSI (ionic conductivity at RT of $1.33 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$) [441], or a mixture of polysiloxane with PVDF and LiTFSI to improve the mechanical properties and electrode compatibility while keeping the ionic conductivity at $7.9 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ and an electrochemical window up to 5.17 V Li/Li^+ at 25°C [444].

3.1.2.2. Polycarbonates

Thanks to its relatively small dielectric constant value, PEO-based SPEs do not allow an effective dissociation of lithium salts, yielding a large amount of ion aggregates

[445]. Polycarbonates emerge as a possible solution that faces this issue as it is shown that the polar carbonate groups ($-\text{O}-(\text{C}=\text{O})-\text{O}-$) are able to suppress the crystallization ability of the hosting matrix and are also able to increase the dissociation of lithium salts [446]. The aliphatic amorphous polyethylene carbonate (PEC) mixed with LiFSI has been shown to reduce the coordinate bonding of polymer chains and lithium ions to yield a conductivity of $2.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which is increased up to $4.3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ upon the incorporation of 1 wt.% of TiO_2 nanoparticles [447]. PEC-LITFSI SPE displays a lithium ion transference number of 0.4, which is 4 times larger than that obtained for PEO-based SPEs [448]. As a result, a good electrochemical stability up to 4.5 V Li/Li^+ and ionic conductivities as high as $4.7 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ can be obtained upon the introduction of 0.2 M of LiTFSI [448]. Poly (vinyl carbonate) (PVCA) has been used to develop SPEs with an electrochemical window of 4.5 V Li^+/KLi and a ionic conductivity of $9.82 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 50 °C [449]. Free standing poly(propylene carbonate) (PPC) based composites with a ionic conductivity of $5.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 20 °C, an electrochemical window of 4.6 V Li/Li^+ , a transference number of 0.75 and which can operate in the temperature range of 0-160 °C [450]. Cyclic carbonates such as poly(trimethylene carbonate) (PTMC) containing LiTFSI with ionic conductivity of $10^{-7} \text{ S}\cdot\text{cm}^{-1}$ at high temperatures and good electrochemical stability up to 5.0 V Li/Li^+ where synthesized [177]. The biodegradable character of poly (ϵ -caprolactone) (PCL) and poly (propylene carbonate) (PPC) polycarbonates may be used to develop biodegradable batteries. Recent works have shown good electrochemical stabilities, high ion transference numbers, good interfacial compatibility, high Coulombic efficiency, extended cycle-life and ionic conductivities in the range of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ for SPEs based on PCL and PPC [451, 452].

CO_2 -sourced polycarbonates are interesting candidates to be used as raw materials for SPEs. Polymer electrolytes containing no solvent can be fabricated by simple UV cross-linking approach, displaying an ionic conductivity up to $3.75 \cdot 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ when loaded with 30 wt.% LiTFSI [453]. A SPE based on a poly(ethylene oxide carbonate) copolymer having PEO segments linked by carbonate groups with cross-linkable methacrylic pendant groups showed improved ionic conductivity and mechanical stability in comparison with bare polycarbonates. A maximum of $3.2 \cdot 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ with a lithium transference number of 0.59 was obtained at 30 wt.% LiTFSI [454]. When compared to analogous conventional salt in polymer electrolytes containing equal molar

lithium cation and free TFSI anions, poly(ethylene oxide carbonate) copolymer electrolytes present an improved performance during lithium plating and stripping steps [455]. Moreover, the introduction of cyclic carbonate linkages within a polycarbonate/polyether backbone loaded with LiTFSI has been proven as a successful strategy to surpass by up to 150% the ionic conductivity of polymer electrolytes containing linear carbonate linkages [456].

3.1.2.3. Other common synthetic polymers used for SPE development

Its amorphous character and polar functional groups that present a high affinity for Li ions and plasticizing solvents make PMMA an interesting candidate to develop SPEs. For example, it has been shown that PMMA with LiTFSI and 4.wt% of silica nanoparticles prepared by solution casting showed a maximum ionic conductivity of $2.44 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ at room temperature [245]. Thanks to its good compatibility with other polymers, PMMA has been blended with different counterparts to obtain solid electrolytes for LIBs. SPEs comprising PVA and PMMA blends with LiBF_4 and EC have been prepared by solvent-casting to obtain materials with a maximum ionic conductivity of $1.29 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at a 8 wt.% LiBF_4 [457]. Similarly, PVDF-HFP/PMMA blends plasticized with the BMIPF₆ ionic liquid showed an electrochemical window of 4.43 V Li-/Li and a remarkable ionic conductivity of $0.45 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C and $1.73 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 75 °C, approaching to that of liquid electrolyte [458].

The incorporation of LLZN nanowires into a PMMA/ LiClO_4 matrix promoted the decrease of the polymer crystallinity, significantly improving the ionic conductivity and allowing the battery operation in the range of 60-70°C [459]. Considering the large amorphous fraction of PVDF-HFP, it is being used in SPE applications, where thanks to the active lithium ion conductor character of LLZTO, its addition leads to an increase in ionic conductivity up to $8.80 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ [460].

Poly(vinyl chloride) (PVC) has been used as a host polymer of polymer electrolytes, either by directly incorporating lithium salts or by forming polymer blends with PMMA and incorporating then different lithium salts [457, 461]. Similarly, PAN-based polymer electrolytes have been intensively studied upon the addition of different lithium salts such as LiTFSI [462], LiClO_4 [463], or a liquid-plasticizer-containing gel type [464,

465]. It is observed that the addition of butadiene [466] and nitrile [467] monomers into PAN increases the lithium solvation when salts such as LiTFSI, LiAsF₆, LiCF₃SO₃ and LiClO₄ are incorporated. Indeed, these monomers improve the Li transport number [466].

3.1.2.4. Plastic crystals

Plastic crystal electrolytes are plastic crystalline substances, i.e, solutions of lithium-containing salts incorporated into plastic crystals that are able to melt above a certain temperature. A fast Li⁺ transport is achieved thanks to their rotational disorder and the presence of vacancies in their lattice [468]. The mechanical malleability of plastic crystals allows their use as SPEs for flexible batteries. Solid state electrolytes based on plastic crystalline solvents were prepared and it was proven that SPEs containing plastic crystals and lithium salts show unusual room temperature ionic conductivities and thermal stabilities [469]. An example of plastic crystals are nitrile materials, which apart from presenting high diffusivity values in the -40 to +60 °C temperature range, also display excellent electrochemical stability and thermomechanical properties [470]. Li ions interact favourably with nitrile groups (-C≡N), contributing to enhance the resulting ionic conductivity. Among all nitrile materials, the highly polar succinonitrile (SN) is one of the most interesting candidates to develop SPEs as it shows a single plastic-crystalline phase in the temperature range of -35 to +62 °C [471]. Further, after dissolving 5 wt.% of LiTFSI within a plastic-crystal form of SN, a remarkable ionic conductivity up to $3 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ is obtained [472]. Unfortunately, these developed materials could not be used as self-standing films. As a strategy to upgrade such issue, a SPE consisting on SN-LiTFSi reinforced with UV-cured ETPTA macromer/Al₂O₃ nanoparticles yielded mechanically robust and self-standing materials with stable cycling performance [473]. More recently, a hierarchical SPE based on nitrile was developed by *in situ* polymerizing the cyanoethyl polyvinyl alcohol (PVA-CN) in succinonitrile (SN)-based solid electrolyte filled in the network of PAN-based electrospun fibre membrane. Good mechanical stability and flexibility together with a remarkable room temperature ionic conductivity up to $2.32 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and a lithium ion transference number of 0.57 were achieved [470].

3.1.2.5. Cellulose derivatives

The high crystallinity of natural polymers has limited their potential as SPEs because the ion conduction is restricted by crystalline domains. An effective approach to increase the room temperature ionic conductivity of biopolymers is the concomitant reduction of their crystallinity by incorporating plasticizing agents together with the introduction of suitable chemical moieties that provide free mobile ions. Accordingly, it has been shown that the incorporation of Ionic Liquids (a mixture of LiTFSI and deep eutectic solvent (DES) with CA or 1-allyl-3-methylimidazolium chloride) into cellulose acetate (CA) increases the ionic conductivity of CA by six order of magnitude, up to $2.61 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ while retaining its mechanical integrity over the storage time [474, 475]. The used ILs show a high mobility of carrier ions, which are able to break the extensive hydrogen bonding network and allows the polar oxygen atom in the CA to form coordination with the free mobile ions [476]. The increase in ionic conductivity was ascribed to the strong hydrogen bond-forming abilities of CA, which after plasticization increases the structural disorder to show an enhancement in free conducting ion transport as observed through the shifting of loss tangent peaks toward higher frequencies in impedance spectroscopy measurements. Glycerol has been proven to be an effective plasticizing agent for cellulose and its derivatives, as it also results in materials with remarkable film-forming and adherent properties to glass and steel surfaces, which may help towards achieving stable electrolyte-electrode interfaces [477]. Accordingly, SPEs based on hydroxyethylcellulose (HEC) with lithium trifluoromethane sulfonate (LiCF_3SO_3) salt and different amounts of glycerol as plasticizer have been developed. As a consequence of the extensive solvation of HEC, maximum ionic conductivity values up to $1.07 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ and $1.06 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 30 and 83 °C respectively were obtained for samples containing lithium salt concentration of $[\text{O}]/[\text{Li}] = 6$. The effect of molecular interactions on the resulting ionic conductivity of a SPE composed by cellulose phthalate (CP) and LiClO_4 [478] has been analyzed. CP was obtained after the substitution of $-\text{OH}$ groups of the cellulose with phthalic anhydride and the maximum ionic conductivity was obtained at intermediate Li^+ cation concentration. This effect was explained by the fact that at low concentrations Li^+ coordinates with carbonyl and ether groups and also forms ionic bonds with carboxyl groups of CP, while only ionic bonds are obtained at high concentrations.

Cellulose and its derivatives offer a plethora of novel opportunities to develop SPEs for LIBs. Accordingly, other SPEs based on cellulose include those formed by cellulose

triacetate (CTA) and lithium salts [479], oligo(ethylene oxide) grafted hydroxypropylcellulose (HPC) (ionic conductivity of $2.5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and proper mechanical stability at temperatures up to 100°C) [480]. Cellulose in the form of microfibrils and whiskers can be used to reinforce PEO-LiTFSI [481]. A remarkable increase in mechanical stability was found at temperatures above the melting temperature of PEO (65°C) as the percolated network with strong hydrogen bonds formed by cellulosic fillers is able to hold the PEO-LiTFSI matrix. It was found that although sisal-whisker reinforced counterpart showed a slight ionic conductivity decrease at 60°C from $4 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ for PEO-LiTFSI to $3.1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, the presence of microfibrils decreases the ionic conduction by a factor of 3 as a result of the more restricted PEO mobility due to the addition of long and entangled fibrils.

3.1.2.6. Single lithium-ion conducting SPEs

Contrarily to traditional SPEs, which are dual-ion conductors where both Li^+ cations and its counter anions are mobile, single lithium-ion conducting SPEs (SLIC-SPEs) have immobilized anions, offering a very relevant advantages for LIBs such as high lithium ion transference numbers, low rate of dendrite growth as indicated by Chazalviel model and absence of anion polarization effects [408]. Bannister et al. proposed in 1984 two methods to obtain SLIC-SPEs; the anion can be chemically attached to a polymer side chain or the mobility of the anion is suppressed using a lithium salt of a dibasic acid such as dilithium hexafluoroglutarate which acts as a trapping agents for anions [482]. In both cases, only Li^+ cation will contribute to a permanent flow of charge. Many polymer based SLIC-SPEs show carboxylate ($-\text{CO}_2^-$), sulfonate ($-\text{SO}_3^-$), sulfonylimide ($-\text{SO}_2\text{N}^-(\text{SO}_2^-)$) as a counterpart of the Li^+ cation. While carboxylate anions were firstly developed in the 1980s, sulfonate anions were introduced in the 1990s as an attempt to obtain SLIC-SPEs with higher ionic conductivities, as $-\text{SO}_3^-$ has a higher degree of negative charge delocalization. SLIC-SPEs comprising sulfonylimide anions have been later developed to improve the performance of solid polymer electrolytes. More recently, boron and phosphorous have been used as center atoms to develop SLIC-SPEs [210, 483]. Regarding the electrochemical performance of SLIC-SPEs, it is interesting to note that single-ion BAB triblock copolymers based on PEO (LiPSTFSI-b-PEO-b-LiPSTFSI) are highly efficient solid electrolyte for lithium-metal batteries. A lithium-ion transport number close to 1,

excellent mechanical properties, no capacity fade when working at 60-80 °C temperature range and a good electrochemical stability up to 5 V versus Li⁺/Li were obtained, outperforming a conventional battery based on traditional SPEs [484]. The remarkable capacity retention obtained by SLIC-SPEs, ascribed to the prevention of concentration gradients and dendrite formation, which is a characteristic feature of dual-ion conducting SPEs, results a strong proof-of-concept for the advantages of such materials for the next generation LIBs. In any case, the low ionic conductivities obtained so far for many SLIC-SPEs in comparison with traditional SPEs such as those based on PEO is a matter that needs to be solved. In this line, it is believed that rather than any specific polymer+matrix, anions with super delocalized negative charge distribution are required in order to obtain highly conductive SLIC-SPEs.

A gel-type fluorinated polysulfonamide-based single ion conducting polymer electrolyte blended with PVDF-HFP showed a high ionic conductivity of 0.52 mS·cm⁻¹ and a lithium ion transference number of 0.9, where the presence of -C(CF₃)₂ functional groups play a pivotal role during the lithiation process [485]. When mixed with bis(4-carbonyl benzene sulfonyl)imide) (LiPSI), an electrospun PVDF-HFP mat (0.68 mS·cm⁻¹) showed an excellent long cycle life performance while facing the poor thermal stability and moisture sensitivity of LiPF₆ salt, at the same time that suppresses lithium dendrite growth [486].

Nafion™ is among the best-known ion conducting polymers and can be found commercialized by DuPont Co. (Wilmington, DE, USA). Nafion™ has a polytetrafluoroethylene backbone and a perfluorovinylether side chain where sulfonic acid groups (-SO₃H) are covalently immobilized, which provides a high ionic conductivity and good thermal, chemical and mechanical stability [487]. This ionomer is extremely resistant to chemical attack and is thermally stable up to 160 °C. Although it is primarily used as an ion exchange membrane in the chlorine– caustic soda industries thanks to its good stability and high proton conductivity [488, 489], this perfluorosulfonic acid emerges as an alternative SPE material with good performance. It can be purchased in H⁺ form (H-Nafion) with different thicknesses (25 to 100 μm). It is usually referred to its protonated form, but this proton can be ion-exchanged to Li or Na ions to increase its ionic conductivity (it is easily lithiated in a Li⁺ containing electrolyte) [487, 490]. After ion exchange of H⁺ to Li⁺, the lithiated Nafion (Li-Nafion) soaked in PC displays a remarkable room temperature ionic conductivity of 8.18 × 10⁻⁵

$\text{S}\cdot\text{cm}^{-1}$ [491], which is larger than that of many single-ion conducting polymer electrolytes [417]. Indeed, the Li^+ transport number can reach almost the unity after using Li-NafionTM and codissolving it with copolymer poly-(vinylidene fluoride)-hexafluoropropylene [409]. The flexibility and light weight of lithiated NafionTM membrane swollen in PC has been used as SPE, which offers an ionic conductivity of $2.1\times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 70 °C, an electrochemical window of 0 to + 4.1 V vs. Li/Li^+ and a Li-ion transference number is 0.928 [250]. Similarly, Li-NafionTM membranes were used as SPE in Li-ion cells using LiFePO_4 as cathode and Li as anode, where the cell displayed a reversible specific capacity of $126.6 \text{ mAh}\cdot\text{g}^{-1}$ at 60 °C [492]. It has been also shown that the use of Li-NafionTM as both separator and electrolyte prevents the dissolution of Mn^{2+} from the LiMn_2O_4 cathode as there is no HF generation from the LiPF_6 salt dissolved in the organic liquid electrolyte [493].

Following a poly(ionic liquid)-in-salt approach, a strategy towards obtaining safer batteries was reported, where a liquid-free SPE was obtained using poly(diallyldimethylammonium) bis(fluorosulfonyl)imide (PDADMA FSI) with a high LiFSI salt content. Thanks to the co-coordination of the FSI anion with both the Li^+ and the polymer backbone, a Li^+ ion transference number of 0.56 was obtained, providing a long-term stable Li-metal symmetrical cycling [494].

Solid polymer electrolytes are likely to become an essential component for the next generation of solid-state batteries. Such polymers must display a high ionic conductivity, an excellent electrochemical stability window and enough mechanical and thermal stability. Each polymer type has advantages and disadvantages and, at the moment, the most widely used candidate for solid electrolytes is PEO. Currently, there is a trend towards the use of natural polymers, but these still show low ionic conductivity, which represents the major limitation for their implementation in actual battery systems. The future trends in solid polymer electrolytes include increasing the ionic conductivity values at room temperature, reducing the contact resistance solid polymer electrolyte/electrodes (anode and cathode) and improving the electrochemical windows.

4. Conclusions and future perspectives

Polymeric materials have become essential components in electrodes and separator / electrolyte systems of high-performance lithium-ion batteries. Regarding the electrodes, the polymer binder plays an important role in maintaining the mechanical and structural

integrity, improving adhesion to the current collector, and binding together the active material and conductive additive. Several types of polymers are currently being applied as polymer binders, where the most commonly used ones are PVDF and CMC. PVDF is the dominant binder so far in the battery industry due to its high electrochemical stability, excellent mechanical properties, thermal stability, good interaction with the electrolyte solution and its proven ability to allow the transport of Li^+ . The main disadvantages of using PVDF are the use of toxic solvents during its processing and the typically low adhesion/cohesion to the current collector.

Most of the efforts regarding polymer binder are focusing on the improvement of the adhesion/cohesion to current collector and in the development of binders that successfully cover essential characteristics such as enhanced mechanical, electrical, and electrochemical performance. The search for binders having a high conductivity is emerging as a suitable strategy to eliminate the need of a conductive additive to the electrodes. Moreover, it becomes essential to design new environmentally friendlier binders that remain easily recyclable. Providing additional functions such as stretchability, self-healing properties and low resistance may yield to improved rate capability and cycle life of LIBs.

Regarding the separator membranes, their main function is to provide a medium to effectively transfer ions between the electrodes, preventing electrical contact between the anode and the cathode, regulating cell kinetics and ensuring a safe charge/discharge process. The most used materials for separator membranes are polyolefins and PVDF-based polymers. Commercially available separators based on polyolefins show low thermal and mechanical stability, are highly inflammable and have low wettability. On the contrary, PVDF has excellent mechanical properties, good thermal stability and can allow the control of morphology through the binary and ternary polymer/solvent systems. The future trends in this field include the use of natural polymers with proper control over the microstructure (large porosities of 80% and small pore sizes below 1 μm), good mechanical performance, sufficient thermal stability, an obtaining an increased compatibility with electrodes. These new separators should be produced using scalable and safe methods, where fillers of different nature can be incorporated in order to upgrade ionic conductivity values. Solid polymer electrolytes are essential for the next generation of solid-state batteries as they may improve the safety of the LIBs, where PEO results the most used material. Unfortunately, the ionic conductivity at room

temperature of solid electrolytes still remains below the desired level, limiting their use in commercial LIBs. In this sense, diverse polysaccharides including cellulose derivatives and carrageenan show interesting characteristics to develop solid polymer electrolytes as their inherently amorphous character facilitates lithium salt incorporation into the solid structure.

Although generally speaking LIBs are safe, with millions of consumers using energy-storage devices based on lithium, failures are bound to happen. In this sense, battery safety is one of the most relevant issues that need to be overcome in the near future in order to allow the use of LIBs in electric cars. Different approaches have been carried out so far for the effective suppression of lithium dendrite growth in LIBs using polymeric separators, where future works will address the use of coatings to improve electrochemical stability and safety.

The use of water-processable biosourced polymers also should be taken into account. In this framework, cellulose and their derivatives emerge as potential materials for the development of sustainable all solid-state LIBs as they provide the opportunity to use papermaking processes during their fabrication, offering an easy, efficient, cost-effective scale-up method. The fabrication of SPEs could boost the development of novel strategies towards the improvement of conventional LIBs. Besides of the associated safety increase, SPEs with high Li^+ conductivity could help in the design of novel batteries consisting on lithium anode and a liquid or gaseous cathode reactant. Such configuration may help to increase cell voltage at the same time that both anode and cathode capacity is increased. Similarly, the field of flexible LIBs offers a plethora of novel opportunities, where the use of solid electrolytes is a hot research topic.

Overall, this review demonstrates the relevant role of polymeric materials for different components in LIBs, where further research efforts are needed in order to boost their performance. Obtaining low-cost, safer, longer lasting and sustainable LIBs will certainly remain among the key objectives in the research on energy storage materials and devices.

Declaration of competing interest

We declare that this manuscript entitled “Polymers for advanced lithium-ion batteries: state of the art and future needs on polymers for the different battery

components” is original, has not been published before and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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