Recent advances on polymer based separators for lithium-ion batteries

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Abstract:

Lithium-ion batteries stand out among the different energy storage systems, increasingly important in modern society. The separator membrane is one of the main components of battery systems, it is placed between the electrodes, represents the medium for the transfer of lithium ions and it is typically based on a polymeric membrane soaked with the electrolyte solution.

This chapter focuses on the recent advances on polymer-based separators for lithium-ion batteries. It is divided by the processing techniques of the membranes, such as, solvent casting, electrospinning, surface modification and coating process. In addition, the recent advances based on natural and biopolymers are presented. Finally, the main conclusions for each membrane are presented, as well as the future trends in the area.

Keywords: battery separators; polymer membranes; processing techniques; lithium-ion batteries

1. Introduction

The development of environmental friendlier and efficient energy storage systems for portable electronic devices and electric vehicles is an increasing need in a technological society heavily dependent on both mobility and energy [1]. The most used energy storage systems are lithium-ion batteries with a global market growth of 8.5% [2]. Despite this success, further developments are needed to improve the properties and characteristics of their different components: electrodes and separator/electrolyte.

The electrodes are the anode (negative electrode) that should show low potential to provide a high cell voltage, and the cathode (positive electrode) which determines the battery capacity [3]. In relation to the separator, it is placed between both electrodes and serves as the medium for transfer of lithium ions during the charge and discharge processes [4].

Typically, the separator membrane is soaked with a conventional electrolyte solution or ionic liquid (IL), and has a strong influence in the performance of the battery [5, 6].

A conventional electrolyte solution is composed by a lithium salt, lithium hexafluorophospate ($LiPF_6$), lithium hexafluoroarsenate ($LiAsF_6$), lithium perchlorate ($LiClO_4$) or lithium bistrifluoromethanesulfonimidate (LiTFSI), in a mixture of one or more solvents, typically ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC). The main requirements of the electrolyte are a large electrochemical stability, low viscosity, high thermal stability, low vapor pressure and high ionic conductivity [7]. Ionic liquids (IL) are also being used for lithium-ion battery applications. These are typically formed by an inorganic/organic anion ($TFSI^-$, PF_6^-, BF_4^-, FSI^-, and etc) and quaternary ammonium cation (imidazolium, pyrrolidinium and piperidinium) [8]. In addition to the conventional electrolyte solution or ionic liquid, the main characteristics/parameters that affect the performance of a separator are permeability, porosity/pore size, electrolyte absorption and retention, chemical, mechanical and thermal stability [6, 9]. Among the different parameters affecting battery separators, a key factor is their morphology (porosity and pore size), as it not only affects the battery performance but also the efficiency of assembling through the mechanical properties [10]. The main processing techniques used for tailoring porous membranes for this application are dry and wet processes [11, 12],

electrospinning [13], pre-irradiation grafting [14] and solvent casting with thermally induced phase separation (TIPS) [15, 16].

The most common polymers used for battery separators are poly(ethylene) (PE) [17], poly(propylene) (PP) [18], poly(ethylene oxide) (PEO) [19, 20], poly(acrylonitrile) (PAN) [19, 21], poly(vinylidene fluoride) and its copolymers (PVDF-co-trifluoroethylene, PVDF-TrFE and PVDF-co-hexafluoropropene, PVDF-HFP) [22-26], poly(tetrafluoroethylene) (PTFE) [27], poly(vinyl chloride) (PVC) [28] and poly(methyl methacrylate) (PMMA) [29], among others.

Further, synthetic and natural polymers such as polyimide [30], cellulose [31], lignin [32] and silk fibroin [33] have recently been used for separator membranes in lithium ion batteries.

In this chapter, the current status in separator membranes for lithium-ion batteries is presented and the future trends in the area are discussed.

2. Polymer types and characteristics

Separator membranes can be produced from different polymers, and the main properties of the most common polymers used for this application are shown in Table 1.

Typically, commercial separator membranes are based on thermoplastic polymers (PP and PE) due to their excellent chemical and mechanical properties, and the possibility of preparing porous membranes through different processing techniques [34].

The values for each property in table 1 are indicative, as they depend on the processing method of the polymer, polymerization conditions and additives used in their production. In particular, it is essential to know the glass transition and melting temperature values of the polymers since the ion transport within polymer chain is affected by the glass transition temperature [35] and the safety of the lithium-ion batteries is related to the melting temperature [36].

The mechanical properties of the separators are also a subject of intense research interest as they have an impact on battery performance, assembly and stability [37-42].

Table 1 – Values of some relevant properties of polymers used as battery separators.

Polymer	Glass temperature / ºC	Melting temperature / ºC	Tensile strength / MPa	Dielectric constant at 1 MHz
PE	-125 (LDPE) and -110 (HDPE)	115 – 135	12-15	2.3
PP	6	160	31-41	2.2-2.6
PEO	-51	66-75	12-30	10
PAN	80-145	322	150-450	4.2
PVC	~70	170-190	20	5
PTFE	-110	330	10	2.0
PMMA	85 - 165	160	70	3.3
PVDF	-40	160-175	45-55	8-10
P(VDF-HFP)	-35	130-140	30-35	8-10

The physical properties (thickness, porosity, pore size and distribution, tortuosity) of the separators affects their electrochemical performance and the normalized Gurley number and ionic conductance are strongly related to the electrochemical performance and, in particular, with the rate capability [43]. For the same thickness of the separator, the electrochemical performance increases with increasing the degree of porosity, which is related with the wettability of the membrane [43, 44].

Finally, the electrical properties (dielectric constant and ionic conductivity) of the polymer matrix are very relevant as they support ionization of lithium salts and improve their diffusion (table 1) [4].

3. Separator types

The separator is a key component of the batteries. Typically, it is a porous membrane, that allows the ion flow between the two electrodes (anode and cathode), while avoiding physical contact between them, preventing the occurrence of short circuits [9]. A good separator must have high electrochemical and thermal stability, mechanical strength, high ionic conductivity and must be a good electrical insulator [45]. In this chapter, the recent advances on battery separators for lithium-ion battery applications will be classified into five major types, four of them related to their processing technique (solvent casting, electrospinning, surface modified membranes and coating) and the latter related with environmental issues

For each separator type, the polymer matrix and electrolyte solutions will be presented as well as the ionic conductivity value and electrochemical performance.

3.1. Solvent casting

Solution casting and its variations are among the most used techniques in the production of separators due to their simplicity, no need for complex equipment and low production costs [46]. Table 2 shows the most recent advances in battery separator membranes produced by solvent casting technique for lithium-ion batteries. It is to notice that some membranes are formed by a single polymer, while other are based on polymer blends or particle reinforced polymers to improve specific characteristics of the separators.

Table 2 - Battery separator membranes prepared by solvent casting and their main characteristics.

Materials	**Fillers**	**Processing technique**	**Electrolyte**	**Porosity and Uptake (%)**	**Conductivity (S/cm) and capacity (mAhg)**	**Ref.**
PVDF-HFP/ PEGMEMA/ MMA/OVPOSS	ZnO	doctor blade	$LiPF_6$ EC/DEC (1:1 v/v)	30/182	1.4×10^{-3}/145	[47]

PVDF-TrFE	ZnO	doctor blade	$LiPF_6$ EC/DMC (1:1 v/v)	70/-	1.6×10^{-3}/137 (C/10)	[48]
PVDF	Silica nanospheres	Doctor blade and NIPS (non-solvent induced phase separation)	$LiPF_6$ EC/DMC (1:1 v/v)	65/214	9×10^{-4}/118 (2C)	[49]
PVDF-HFP	Al_2O_3	Doctor blade	$LiPF_6$ EC/DMC/EMC	-/372	7×10^{-4} (20°C)/140 (C)	[50]
PVDF-HFP	Poly($IDANa_2$)	NIPS	$LiPF_6$ EC/DMC (1:1 v/v)	-/-	-/50 (C)	[51]
PE	SnO_2	Doctor blade	-	-/-	7.2×10^{-4}/126.2 (C)	[52]
PVDF	SiO_2	Doctor blade and phase inversion method	$LiPF_6$ EC/DMC (1:1 v/v)	43/340	1×10^{-3} (25°C)/176 (C/10)	[53]
PSA	SiO_2	NIPS	$LiPF_6$ EC/DMC (1:1 v/v)	83/430	7.48×10^{-4}/130.5 (C/2)	[54]
PVDF-HFP	TiO_2	Doctor blade	$LiPF_6$ DEC/EMC/DMC/EC (20:35:15:30 v/v/v/v)	-/164.5	4.9×10^{-4} (20°C)/156.95 (C/10)	[55]
PVDF	ZrO_2	Papermaking process	$LiPF_6$ EC/EMC/DMC (1:1:1 w/w/w)	77.69/523.3	9.6×10^{-4}/134 (C/2)	[56]
PVDF	TEOS	NIPS	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	-/200	1.22×10^{-3} (25°C)/148.6 (C)	[57]

6FAPB/ODPA	-	NIPS	$LiPF_6$ EC/EMC/DMC (1:1:1 v/v/v)	67/420	9.2×10^{-4}/150.6 (C/5)	[58]
SII	-	Doctor blade	$LiPF_6$ EC/DEC/EMC (4:3:3 v/v/v)	-/30	1.45×10^{-4} (25°C)/-	[59]
HTPB-g-MPEG/PVDF	-	NIPS	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	56/390	3.2×10^{-3}/122 (C)	[60]
PEI/PVP	-	Doctor blade	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	80.0/332.0	6.53×10^{-4}/143.6	[61]
PVDF-HFP	LiTFSI, EC	Doctor blade	-	65.05/-	5.21×10^{-4}/110	[62]
PVDF-HFP	-		$LiPF_6$ EC/DMC (1:1 v/v)	-/-	2.3×10^{-3} (25°C)/-	[63]

The effect of ZnO nanoparticle size and concentration in a complex blend of PVDF-HFP, PEGMEMA, MMA and OVPOSS was studied, proving that 30 nm is the optimal diameter for forming a microporous structure [47]. High concentration of ZnO nanoparticles in PVDF-TrFE structure also presented good ionic conductivity and cycling performance [48]. PVDF/silica nanospheres composite membranes showed potential for application in LIBs [49]. The inclusion of different fillers into a PVDF matrix proved to increase the ionic conductivity of the membrane, its thermal and mechanical stability, as well as the rate performance of the batteries. Al_2O_3 [50], Poly($IDANa_2$) [51], SnO_2 [52], SiO_2 [53, 54], TiO_2 [55], ZrO_2 [56] and TEOS [57] are some successfully used fillers for this purpose. Complex membranes of blended polymers as 6FAPB/ODPA [58], SII [59], HTPB-g-MPEG/PVDF [60] and PEI/PVP [61] can also be processed by solvent casting, combining the merits of different polymers and improving the properties of the separator. Gel polymer electrolytes of PVDF-HFP, LiTFSI and EC prepared by solution casting methods result in enhanced battery performance and high cycle life [62, 63].

3.2. Electrospun separator membranes

Electrospinning technique consists in the application of a high voltage in a polymer solution to form nonwoven fibers [64, 65]. It is a simple, cheap, efficient and high reproducible technique for the development of separators for LIBs applications. Table 3 shows the most recent advances in separator membranes produced by electrospinning for lithium-ion batteries.

Table 3 - Battery separator membranes prepared by electrospinning and their main characteristics.

Materials	**Fillers**	**Electrolyte**	**Porosity and Uptake (%)**	**Conductivity (S/cm) and capacity (mAhg)**	**Ref.**
PI	AlOOH	$LiPF_6$ EC/DEC (1:1 w/w)	65.8 / 337.5	2.18×10^{-3}/157 (C)	[66]
PMIA	OPS	$LiPF_6$ EC/DMC (1:1 v/v)	90.27/1171	1.93×10^{-3}/122 (2C)	[67]
PVDF-HFP/PMIA	-	-	93.75/~900	1.27×10^{-3}/153.8 (C/2)	[68]
PMIA/PVDF	-	$LiPF_6$ EC/DEC/EMC (1:1:1 v/v/v)	72.9/753	1.7×10^{-3}/143.6 (C/2)	[69]
PVDF-CTFE	Sb_2O_3	$LiPF_6$ EC/DEC (1:1 w/w)	72/356	2.88×10^{-3}/172	[70]
PVDF-TrFE	Al_2O_3	$LiPF_6$ EC/DMC (1:1 v/v)	81/375	5.8×10^{-3} (25°C)/154	[71]
PVDF	ZSM-5	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	80/378	1.72×10^{-3} (25°C)/128 (C)	[72]
PVDF-HFP	SQ-T10	-	80.17/406	3.97×10^{-3}/~140 (C)	[73]
PVA	SiO_2	$LiPF_6$ DMC/EC/DEC (1:1:1 v/v/v)	80/633	1.58×10^{-3}/110 (C/2)	[74]

PVDF-HFP	Al_2O_3	$LiPF_6$ EC/DMC (1:1 v/v)	-/~230	1.24×10^{-3}/~140	[75]
PET/PP	-	$LiPF_6$ EC/DMC/DEC (1:1:1 v/v/v)	-/293	7.82×10^{-4} (25°C)/161 (C/10)	[76]
PI	-	$LiPF_6$ EC/DMC (3:7 v/v)	69.8/138.5	8.29×10^{-4}/~100(C/2)	[77]
PAN	-	$LiPF_6$ EC/DMC (3:7 v/v)	83/650	2.95×10^{-3}/130 (C/10)	[78]
PVDF/PMMA	-	$LiPF_6$ EC/DMC (1:1 v/v)	87/290	1.5×10^{-4} (25°C)/150.3	[79]
PU	GO	$LiPF_6$ EC/EMC/DMC (1:1:1 w/w/w)	90.7/733	3.73×10^{-3}/130 (C)	[80]
PEEK	-	$LiPF_6$ DMC/DEC/EC (1:1:1 v/v/v)	-/215.8	1.3×10^{-3} (30°C)/~170 (C)	[81]
PEEK	-	$LiPF_6$ EMC/DMC/EC (1:1:1 v/v/v)	88/524	3.81×10^{-3}/160.9 (C/10)	[82]
PTFE	-	$LiPF_6$ EC/DMC (1:1 v/v)	80/320	1.87×10^{-3}/142	[83]
FPI	-	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	81.3/711.8	1.50×10^{-3}/132	[84]
PEI	-	$LiPF_6$ EC/DMC/DEC (1:1:1 v/v/v)	84.5/343.9	3.41×10^{-3}/143.4 (C)	[85]
PVA	SiO_2	-	73/405	1.81×10^{-3}/137.8	[86]
PVDF/PS	-	$LiPF_6$ EC/DEC/EMC (1:1:1 w/w/w)	71.8/333.9	1.58×10^{-3}/159.9 (C/5)	[87]
PEEK/PMMA	-	$LiPF_6$ EC/DMC/DEC (1:1:1 v/v/v)	64.1/172.8	1.03×10^{-3} (30°C)/~190 (C/10)	[76]
PPESK/PVDF	-	-	75/650	1.69×10^{-3}/157.6 (C/5)	[88]
PEI/PVDF	-	-	89/475	-/-	[89]
PVDF/PMMA	SiO_2	$LiPF_6$	77/406	4×10^{-3} (25°C)/158 (C/5)	[90]

FPEEK	-	$LiPF_6$ EMC/DMC/EC (1:1:1 v/v/v)	88/559	3.12×10^{-3}/150.3	[91]
PI	-	$LiPF_6$ EC/DEC/EMC (1:1:1 w/w/w)	87.9/479.1	1.74×10^{-3}/122.1 (C)	[92]
PAN/PU	SiO_2	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	90.4/767.8	-/147.3	[93]
PI	SiO_2	$LiPF_6$ EC/DMC/DEC (1:1:1 v/v/v)	73/296	1.67×10^{-3}/164.5 (C/10)	[94]
PAN/PVDF-HFP	-	$LiPF_6$ EC/EMC/DEC (1:1:1 v/v/v)	-/420	1.74×10^{-3}/144.1 (C)	[95]
PVP	TiO_2	$LiPF_6$ EC/DEC/DMC (1:1:1 v/v/v)	71/252	1.41×10^{-3}/~145 (C/5)	[96]
PVDF-HFP	-	$LiPF_6$ EC/DMC (1:1 v/v)	-/-	2.3×10^{-3} (25°C)/-	[63]

A membrane with a PI matrix and an AlOOH coating was produced by electrospinning techniques. This membrane presented high thermal stability and flame retardant capacity [66]. Electrospun separators synthesized with a PMIA matrix and OPS nanoparticles also showed high ionic conductivity, mechanical strength and improved battery performance [67]. A PVDF-HFP/PMIA composite electrospun membranes revealed potential for gel polymer electrolytes, with high porosity and electrolyte uptake [68]. The use of PVDF [69] and its copolymers [70, 71] (Figure 1) has been extensively explored, presenting suitable results in terms of battery performance. The addiction of zeolites [72] and silesquioxanes [73] into the PVDF matrix also improves the thermal and electrochemical characteristics of the membrane. SiO_2 porous fiber membranes with high thermal safety and excellent electrolyte uptake can also be produced using electrospinning [74].

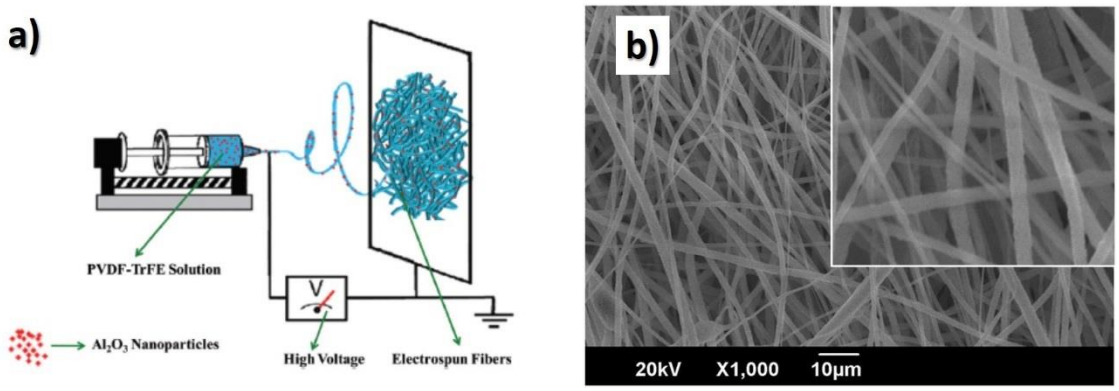

Figure 1 – a) Preparation of PVDF-TrFE/ Al_2O_3 electrospun membranes and SEM image of PVDF-TrFE/Al_2O_3 electrospun fibers with 10% Al_2O_3 [71].

Al_2O_3 fillers were added to electrospun PVDF-HFP nanofibers by atomic layer deposition. The obtained membrane showed fire resistant properties and high electrochemical performance [75]. The coating of a PP membranes with electrospun PET fibers resulted in a separator with improved electrochemical properties and a shutdown function [76]. PI [77], PAN [78], PMMA [79], PU [80], PEEK [81, 82], PTFE [83], FPI [84], PEI [85] and PVA [86] can be also successfully used in the fabrication of electrospun membranes. Polymer blends, as PVDF/PS [87], PEEK/PMMA [76], PPESK/PVDF [88], PEI/PVDF [89] and PAN/PVDF are also effective options for the production of functional electrospun membranes for LIBs. The crystallinity of a PVDF electrospun membrane can be limited by adding PMMA and SiO_2, which increases thermal stability and electrolyte uptake, and consequently improving the cell performance [90]. The inclusion of fluorinated groups into the PEEk structure, proved to effectively increase the battery performance [91]. A variation of electrospinning, called solution blow spinning proved to be an efficient method to produce nanofibers, without the need of high-voltage equipment, when compared to the conventional electrospinning. This technique was successfully used with PI membranes [92]. SiO_2/PAN layers were applied in electrospun PAN/PU membranes using sequential electrospraying, leading to improved electrochemical properties [93]. A SiO_2@(PVDF/SiO_2) hybrid structure (Figure 2) was produced by combining electrospinning and inverse in-situ hydrolysis, presenting improved mechanical and thermal stability, and a high battery capacity [94].

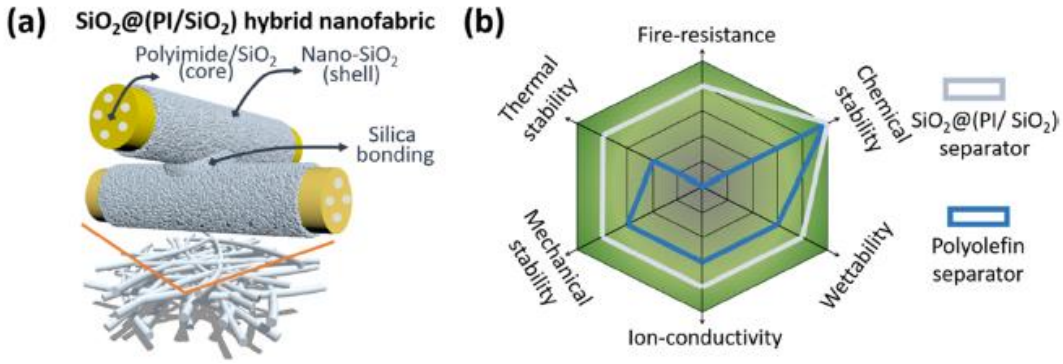

Figure 2 - Schematic representation of the (SiO_2@PVDF/SiO_2) structure (a); comparison between the (SiO_2@PVDF/SiO_2) separator and a conventional polyolefin separator (b) [94].

3.3. Surface modification

Surface modification was performed by modifying the surface of the porous membrane in order to improve the specific properties for the separator, such as wettability, mechanical stability, ionic conductivity and etc. Table 4 shows the most recent advances on surface modified battery separators.

Table 4 – Surface modified battery separator membranes and their main characteristics.

Materials	Fillers	Processing technique	Electrolyte	Porosity and Uptake (%)	Conductivity (S/cm) and capacity (mAhg)	Ref.
PVDF-HFP	SiO_2	Hot-pressing	-	-/-	1.22×10^{-3} (25°C)/-	[97]
PP	TMB-5	Melt blending	$LiPF_6$ EC/DMC (1:1 v/v)	45.1/-	1.58×10^{-4}/141 (C/10)	[98]
PP	-	photo-induced functionalization	$LiPF_6$ EC/EMC/DMC (1:1:1 v/v/v)	-/-	7.3×10^{-4}/110 (C)	[99]
PVDF-HFP	BN	3D printing	$LiPF_6$ EC/DEC (1:1 v/v)	-/-	-/147.3 (C/5)	[100]

PVDF-HFP	-	Doctor blade	$LiPF_6$ EC/DMC/EMC/DEC (30:15:35:20 w/w/w/w)	-/114	3.27×10^{-3} (25°C)/104.8 (5C)	[101]
PP/PE	-	Multilayer coextrusion	$LiPF_6$ EMC/EC/DMC (1:1:1 v/v/v)	46.8/148	1.35×10^{-3}/135	[102]
PEEK	-	Novel vapor induced demixing method	$LiPF_6$ EC/EMC/DMC (1:1:1 w/w/w)	84/340	1.68×10^{-3}/145.6	[103]
PE	-	Chemical treatment	$LiPF_6$ EC/EMC (3:7 v/v)	-/~85	8.9×10^{-4}/-	[104]
PP	Cotton	Wet nonwoven papermaking method	$LiPF_6$ EC/DMC (1:1 v/v)	65/180	1.76×10^{-3}/169.9	[86]
NFC/PSA/NBSK	-	Wet-laid process	$LiPF_6$ EC/DMC (1:1 v/v)	63.8/333	1.58×10^{-3}/118.2 (C/2)	[105]
PI	PAA	Hot-press treatment	$LiPF_6$ EC/DMC/DEC (1:1:1 v/v/v)	41.5/61.2	-/~120 (C)	[106]

PVDF-HFP/SiO_2 nanoparticles membranes were produced by hot pressing in which SiO_2 increases the ionic conductivity. The presence of the nanoparticles improves the electrochemical performance of the cell, specially at high charge/discharge rates [97]. The presence of the nucleating agent TMB-5 in a PP structure presented a high cycling stability performance [98]. Photo-induced functionalization was used in PP membranes to improve their electrolyte affinity, leading to an increase in the electrochemical performance of the separator [99]. 3D printing techniques can be successfully used in the production of composite PVDF-HFP/BN membranes [100]. Hierarchically-constructed PVDF-HFP separators were developed by adding a warm PVDF-HFP solution into a

partially dissolved PVDF-HFP skeleton. The obtained porous structure showed good wettability, electrolyte uptake and ionic conductivity [101]. Multi-layered PP and PE separators produced using multilayer coextrusion and $CaCO_3$ template methods exhibited an interconnected spherical submicron porous structure that improves their electrochemical properties [102]. The use of vapour induced demixing methods to prepare PEEK separators allowed a better control on the por size and structure, leading to improved wettability, uptake and electrochemical properties [103]. The introduction of oxygen containing functional groups in the PE structure via chemical treatment with benzoyl peroxide proved to enhance the wettability and ionic conductivity of the separator [104]. Wet nonwoven papermaking methods were used to prepare PP/cotton separators with high wettability and uptake and improved ionic conductivity and cycling performance when compared with commercial PP separators [86]. These methods were also successfully used in the synthesis of a PSA/NBSK/NFC composite membrane [105]. Imidazation of PAA nanofiber sheets to PI membranes leads to a performance comparable to that of the commercial separators, using simple and cheap methods [106].

3.4. Coating process

The coating process of a previously fabricated membrane can significantly improve its thermal, mechanical and electrochemical characteristics. Table 5 shows the most recent advances in coated separator membranes for lithium-ion batteries

Table 5 - Battery separator membranes modified after a coating process and their main characteristics.

Materials	Coating	Electrolyte	Porosity and Uptake (%)	Conductivity (S/cm) and capacity (mAhg)	Ref.
PVDF/ Ethyl cellulose/ PE	A-SiO2	$LiPF_6$ EC/EMC (1:3 v/v)	-/-	7.9×10^{-4}/131.6 (C/5)	[107]
PP	SiO_2	$LiPF_6$ EC/DMC (1:1 v/v)	37.25/438.29	4.33×10^{-3}/135 (C/2)	[72]
PG/PEI/PP	Ethylsilicate	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	-/165	6.6×10^{-4}/125.4 (C)	[108]
PE	SiO_2	$LiPF_6$ EC/DEC/EMC (1:1:1 v/v/v)	-/-	8.52×10^{-4}/146.25 (2C)	[109]
PVDF-HFP/EC/PE	PA	$LiPF_6$ EC/DMC (1:1 v/v)	-/130	9.6×10^{-4}/-	[110]
PTFE/PE	-	$LiPF_6$ EC/DEC (1:1 v/v)	66/190.6	9.6×10^{-4}/141.9 (C/2)	[111]
PP	SiO_2/PVA	-	50.5/201.2	1.26×10^{-3}/125.5 (C/2)	[112]
PEI/PP	TA	$LiPF_6$ EC/DMC/EMC (1:1:1 w/w/w)	61.6/140.4	9.5×10^{-4} (25°C)/~100	[113]
PP	TA, $NaIO_4$	$LiPF_6$ EC/DMC/EMC (1:1:1 w/w/w)	-/187	9.1×10^{-4}/125.3 (C)	[114]
PE	TA, PEPA	$LiPF_6$ EC/DMC/EMC (1:1:1 w/w/w)	-/128	4.2×10^{-4}/133.7 (C/5)	[115]
PP	Boehmite	$LiPF_6$ EC/DMC (1:1 v/v)	-/454	7.2×10^{-4}/133.1 (C)	[116]
PET/PMPI	-	$LiPF_6$ EC/DEC (1:1 v/v)	55/-	1.35×10^{-3}/154	[117]
SBR/ PEG	Al_2O_3	$LiPF_6$ EC/DEC (1:1 w/w)	56/-	1.64×10^{-3}/152 (C)	[99]

PP	SiO_2	-	-/130	5.5×10^{-4}/-	[118]
PP	AA	$LiPF_6$ EC/DMC/EMC (1:1:1 w/w/w)	-/300	-/139.3	[119]
$PEI(PAA/PEO)_3/PE$	-	$LiPF_6$ EC/EMC/DMC (1:1:1 v/v/v)	56.4/201	4.5×10^{-4} (25°C)/~120 (C)	[120]
PPS/ PVDF-HFP	SiO_2	$LiPF_6$ EC/DEC (1:1 v/v)	57.3/230.1	1.02×10^{-3}/~145 (C/2)	[121]
PE	$SiO_xC_yH_z$	$LiPF_6$ EC/DEC/DMC (1:1:1 v/v/v)	-/103.1	3.61×10^{-4}/143.2 (C)	[122]
PE	SiO_2	$LiPF_6$ EC/DEC (1:1 v/v)	-/-	8.4×10^{-4} (25°C)/156 (C/10)	[123]
PE	Al_2O_3, PDA	$LiPF_6$ EC/DEC (1:1 v/v)	-/~450	-/90.1 (5C)	[124]
PE	SiO_2 / Organic components	$LiPF_6$ EC/DMC/EMC (1:1:1 v/v/v)	-/269	4.5×10^{-4} (25°C)/~110 (C)	[125]
PE/PVDF-HFP/ePOSS	Al_2O_3	$LiPF_6$ EC/EMC (3:7 v/v)	-/-	8.55×10^{-4}/145.3	[126]
PP/PPTA	-	$LiPF_6$ EC/EMC/DMC (1:1:1 v/v/v)	-/-	1×10^{-3}/~130 (C)	[127]
PP/silicone	-	-	-/96	-/137.6	[128]
PP/PVDF	SAC	$LiPF_6$ EC/DMC (1:1 v/v)	-/346	6.3×10^{-4}/154	[129]
PI	TiO_2	$LiPF_6$ EC/DEC (1:1 v/v)	86.2/455	1.47×10^{-3}/~160 (C/2)	[130]
PVDF/PET	-	-/-	-/259.7	9.8×10^{-4} (25°C)/150 (C/5)	[131]
PE/PVDF-HFP	BN	$LiPF_6$ DEC/EMC/DMC/EC (20:35:15:30 v/v/v/v)	50.8/348	4.4×10^{-4} (25°C)/120 (2C)	[132]
Cellulose	PPy	$LiPF_6$ EC/DEC (1:1 v/v)	59/-	8×10^{-4}/257	[133]
PI/PE/EtC	SiO_2	$LiPF_6$ EC/DEC (1:1 v/v)	78/575	9.41×10^{-4}/162.4	[134]

Different coatings were studied, including PVDF-ethyl cellulose composite filled with SiO_2 nanoparticles [72, 107-109], PA [110] and PTFE [111], PVA [112], PEI/TA [113], $NaIO_2$ [114], PEPA [115], boehmite [116], PMPI [117] and Al_2O_3 [99]. The coated structures are usually commercial membranes of PE [107, 110, 111] or PP [112, 113, 118] and coating can be successfully applied using atmospheric glow discharge plasma jet [119]. The coating of PE with a polymer multilayer $PEI(PAA/PEO)_3$ improved the separator/electrolyte interface, increasing the ionic conductivity, Li^+ transference number and electrolyte uptake [120]. PVDF-HFP coating in a nonwoven PPS matrix is also reported [121]. Roll-to-roll methods were used to fabricate a $SiO_xC_yH_z$ coating to a PE membrane, using a reactive atmospheric pressure plasma. The polar groups present in the coating caused an increase in the separator's thermal stability and electrolyte uptake [122]. Silica nanoparticles were chemically grafted in PE membranes, improving their adhesion strength, thermal stability and electrochemical performance [123]. Dual coating of PE membranes was applied using atomic layer deposition of Al_2O_3 followed by PDA coating (Figure 3). The obtained separator presented increased safety and higher capacity than the typical PE separators [124].

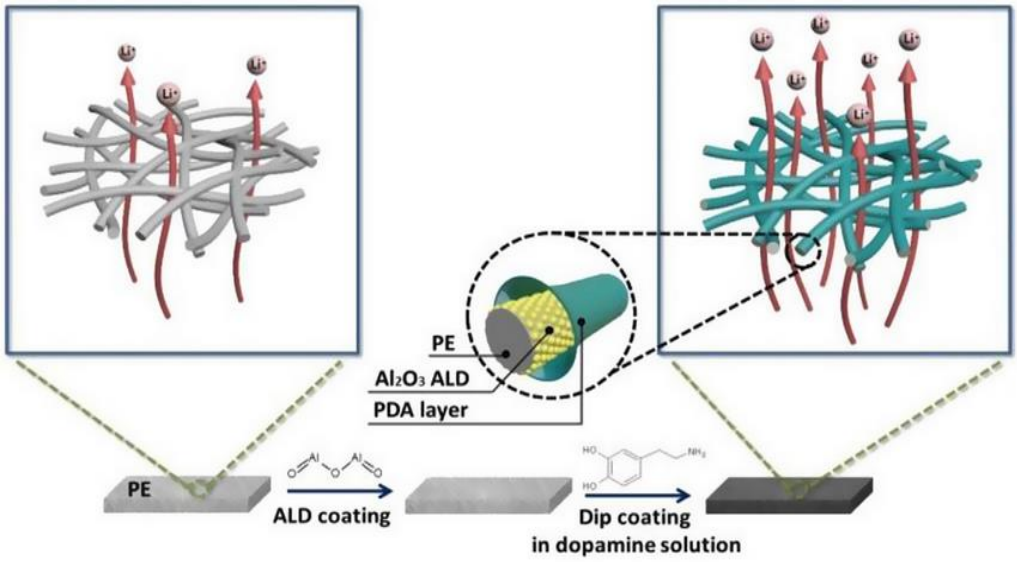

Figure 3 - Schematic representation of a dual coating process [124].

A hybrid coating of inorganic SiO_2 and different organic components was applied in a PE separator by UV curing techniques. The fabricated membrane showed improved uptake, ionic conductivity and battery performance [125]. The application of ePOSS as co-binder with PVDF for coating of PE membranes showed high electrochemical stability and cycling performance [126]. Coating layers of PPTA in PP substrates present performance comparable to those of commercial PP separators [127]. The coating of a PP membrane

with silicone lead to a better electrolyte affinity, which results in better battery performance [128]. Hydrophobic silica aerogel composite coating lead to high thermal stability and good electrochemical performance at high current densities [129]. TiO_2 coatings were applied in PI membranes using a green surface-alkaline-etching and in-situ complexation-hydrolysis technique. The produced separator presented improved ionic conductivity and cycling performance [130] (Figure 4).

Figure 4 - TiO_2 coating process by alkaline etching and complexation hydrolysis [130].

A multisided pore structure can be obtained by creating a sandwich membrane with PVDF and PET nonwoven fabrics using a nonuniform cooling process (Figure 5) [131]. A PVDF-HFP and PE-BN bilayer membrane with highly interconnected porous microstructure was created by wet chemistry methods. The separator was able to supress the formation and growing of lithium dendrites [132]. A bilayer cellulose separator was also fabricated, enhancing the capacity of the tested LIBs. The redox active layer, containing PPy can also work as cathode, increasing the theoretical capacity of the device [133]. A complex sandwich-like membrane was constructed using two layers of electrospun PI/SiO_2 and a conventional PE separator coated with ethyl cellulose. This separator presented superior mechanical properties and thermal shutdown at temperatures above 131°C [134].

Figure 5 - Schematic representation of a sandwich structure composite separator [131].

3.5. Natural and biopolymers

The increasing concern on environmental issues leads to a constant search for more sustainable and more environmentally friendly materials to replace the most used synthetic polymers. Table 6 shows the most recent advances on battery separators containing or based on natural and biopolymers.

Table 6 - Battery separator membranes based on natural and biopolymers and their main characteristics.

Materials	Fillers	Electrolyte	Porosity and Uptake (%)	Conductivity (S/cm) and capacity (mAhg)	Ref.
PVDF-HFP/cellulose	-	$LiPF_6$ EC/DMC (1:1 v/v)	80.03/310	1.89×10^{-3}/171.08 (C/5)	[135]
PVDF-HFP/CAP	-	$LiPF_6$ EC/EMC/DEC (3:5:2 w/w/w)	63/238	1.3×10^{-3}/166.2	[136]
PE/cellulose	-	$LiPF_6$ EC/DEC (1:1 v/v)	26/-	2.2×10^{-4}/~145	[137]
PE/PVDF(HEC)	-	$LiPF_6$ EC/DEC (1:3 v/v)	-/-	7.8×10^{-3} (25°C)/133	[138]
POM/CNF	-	$LiPF_6$ DMC/DEC/EC (1:1:1 v/v/v)	80/412	1.39×10^{-3}/161.9	[139]
Cellulose	Titania particles	$LiPF_6$ EC/DEC (1:1 v/v)	78/-	6.2×10^{-4}/120	[140]
SF	-	$LiPF_6$ EC/DMC (1:1 v/v)	68/1738	1×10^{-3} (20°C)/126 (C/2)	[141]
RESM	-	$LiPF_6$ EC/DEC (1:1 v/v)	48/340	-/138 (C/2)	[142]
pCSA	-	$LiPF_6$ EC/DMC (1:1 v/v)	58.43/385	1.34×10^{-3} (30°C)/104.1	[143]

Studies on the application of cellulose in LIB separators showed to be a good candidate to replace the most common polymers [144] The addiction of cellulose to PVDF-HFP [135, 136], PE [137, 138] and POM [139] membranes proved to enhance their porosity and electrolyte uptake, consequently leading to higher ionic conductivity. The addiction of titania particles to the cellulose matrix further improves battery performance [140]. The use of silk fibroin structures produced by electrospinning and lyophilization as separator membranes leads to membranes with high wettability, excellent thermal stability and good cycling performance [141]. Eggshell membrane is also a suitable

material for LIB applications with effective suppression of lithium dendrite growth. The regeneration process allows the production of large area and flat eggshell membranes [142] (figure 6).

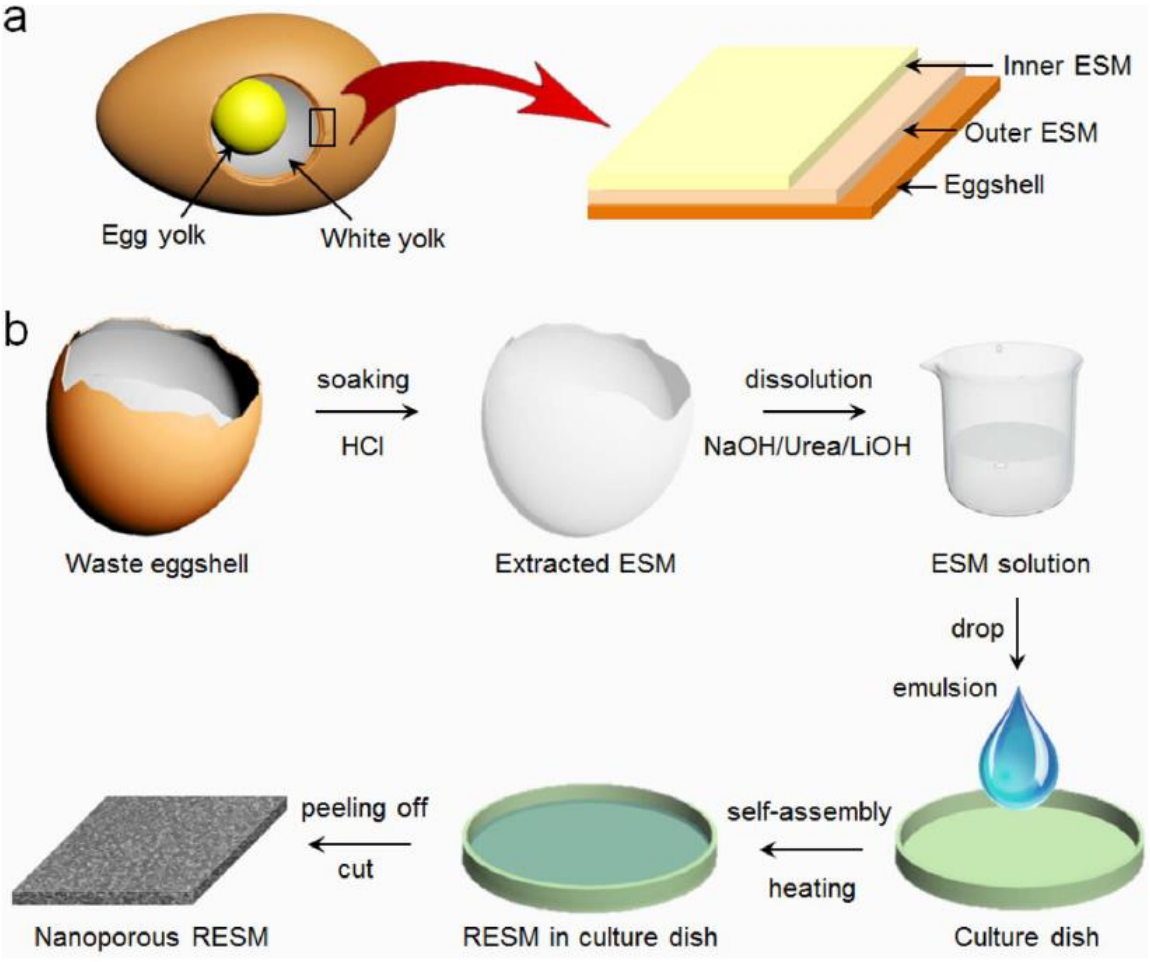

Figure 6 - Structure of an eggshell (a); extraction and regeneration processes [142].

PVA, cellulose and styrene-co-acrylate composite membranes were prepared by phase inversion methods in a simple and cost-effective process. This separator presented high thermal stability and good electrochemical properties [143].

4. Summary and outlook

This chapter summarizes the recent advances for the main types of polymer based lithium-ion battery separators. Each separator type produced with different processing technique shows advantages and disadvantages, being essential the separator to show excellent mechanical and thermal stability, high wettability and high ionic conductivity.

The main advantages of separators produced by solvent casting are the low cost and simplicity, the main challenges in this battery separator type are the control of relevant properties such as the degree of porosity and pore size in natural and hydrophilic polymers, as well as in thermally resistant polymers.

Electrospinning is an emergent technique that allies its low cost and simplicity to the ability of producing nonwoven fibers with high controllable and easily reproducible conditions. Future applications in battery separators consist in the search for new composite materials to be used in electrospinning, allowing an improvement in their properties.

Surface modification techniques allows the alteration of the properties of a membrane by modifying the structure and composition of its surface, leading to an improvement of the performance. The main challenges in this area are the precise determination of the conditions to improve properties as ionic conductivity, or thermal/mechanical stability.

The coating process of a previously fabricated membrane allows a wide range of available processing techniques and materials with variable costs and efficiencies. Its main advantage is the ability to combine the properties of different materials in one multilayered membrane. Research is focused in study the interface between different layers in order to optimize the performance of the separators.

All the above-techniques must take into account the environmental issues. The use of natural polymers or fillers and less hazardous solvents will lead to increasing the sustainability of the membrane. However, most of the available natural materials do not have the adequate performance when compared with the synthetic ones, and therefore research must be carried out to reduce the environmental impacts without compromising the performance of the separator.

Beyond these specific issued for each battery separator, it is essential that the separator presents excellent compatibility with the electrodes. For proper comparison of the electrochemical performance of different works it is important that electrodes also show a similar degree of porosity, active mass loading and thickness. Also, for each type of separator it is essential a relation between cost/benefit considering its applicability.

Considering the relevance of the separator membranes in the battery systems, important scientific and technological advances are needed and expected in the next years.

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List of symbols and abbreviations

6FAPB	1,4-Bis(4amino-2-trifluoromethylphenoxy)benzene
AA	Acrylic acid
A-SiO_2	Amino-functionalized nano-SiO_2
BN	Boron nitride
CAP	Cellulose acetate phthalate
CNF	Cellulose nanofibers
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EMC	Ethylmethyl carbonate
ePOSS	Polyhedral oligomeric silsesquioxane with epoxy functional groups
EtC	Ethylcellulose
FPEEK	Fluorinated poly(ether ether ketone)
FPI	Fluorinated polyimide

GO	Graphene oxide
HEC	Hydroxyethyl cellulose
HMDSO	Hexamethyldisiloxane
HTPB-g-MPEG	Hydroxyl-terminated polybutadiene grafted methoxyl polyethylene glycol
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
MMA	Methyl methacrylate
NBSK	Northern bleached softwood kraft
NFC	Nano-fibrillated cellulose
NIPS	Non-solvent induced phase separation
ODPA	4,4′-Oxydiphthalic anhydride
OPS	Octaphenyl- Polyhedral oligomeric silsesquioxane
OVPOSS	Octavinyl-T8-silsesquioxane
PA	Polyacrylate
PAA	Poly(acrylic acid)
PAA	Polyamic acid
PAN	Polyacrylonitrile
pCSA	Polyvinyl alcohol modified cellulose/ styrene-co-acrylate
PDA	Polydopamine
PE	Polyethylene
PEEK	Poly(ether ether ketone)
PEG	Polyethylene glycol
PEGMEMA	Poly(ethylene glycol methyl ether methacrylate)
PEI	Polyetherimide
PEO	Poly(ethylene oxide)
PEPA	Polyethylene polyamine
PET	Polyethylene terephthalate
PG	Pyrogallic acid
PI	Polyimide
PLT	Polyester
PMIA	Poly-m-phenyleneisophthalamide
PMMA	Poly(methyl methacrylate)
PMPI	Poly(m-phenylene isophthalamide)

Poly($IDANa_2$)	Disodium iminodiacetate
POM	Polyformaldehyde
PP	Polypropilene
PPESK	Poly(phthalazinone ether sulfone ketone)
PPR	Polypropilene copolymer
PPS	Plastic polyphenylene sulfide
PPTA	Poly-*p*-phenylene terephthamide
PPy	Polypyrrole
PS	Polystyrene
PSA	Polysulfonamide
PTFE	Polytetrafluoroethylene
PU	Polyuretane
PVA	Poly(vinil alcohol)
PVDF	Poly(vinilidene fluoride)
PVDF-CTFE	Poly(vinylidene fluoride-co-chlorotrifluoroethylene)
PVDF-HFP	Poly(vinilidene fluoride)-hexafluoropropylene
PVDF-TrFE	Poly(vinylidene fluoride-trifluoroethylene)
PVP	Polyvinyl pyrrolidone
RESM	Regenerated eggshell membrane
SAC	Silica aerogel composite
SBR	Styrene-butadiene rubber
SF	Silk fibroin
SII	Poly(styrene-block-isoprene-block-sulfonated isoprene)
SQ-T10	Decakis(methacryloxypropyl) silsesquioxane
TA	Tannic acid
TEOS	Tetraethyl orthosilicate silane
ZIF-67	Zeolitic imidazolate framework-67
ZSM-5	Zeolite Socony Mobil–5

References

[1] Tarascon, J.-M. Key challenges in future Li-battery research2010.

[2] Harrop, P., Zervos, H. Batteries, Supercapacitors, Alternative Storage for Portable Devices 2009-2019. IDTechEx.

[3] Goodenough, J. B., Park, K.-S. The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.*, 135,1167-76, 2013.

[4] Costa, C. M., Silva, M. M., Lanceros-Mendez, S. Battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium ion battery applications. *RSC Advances*. 3,11404-17, 2013.

[5] Aurbach, D., Talyosef, Y., Markovsky, B., Markevich, E., Zinigrad, E., Asraf, L., Gnanaraj, J. S., Kim, H.-J. Design of electrolyte solutions for Li and Li-ion batteries: a review. *Electrochim. Acta*. 50,247-54, 2004.

[6] Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.*, 104,4303-418, 2004.

[7] Robinson, R. A., Stokes, R. H. Solutions of Electrolytes and Diffusion in Liquids. *Annu. Rev. Phys. Chem.*, 8,37-54, 1957.

[8] Giffin, G. A. Ionic liquid-based electrolytes for "beyond lithium" battery technologies. *Journal of Materials Chemistry A*. 4,13378-89, 2016.

[9] Arora, P., Zhang, Z. Battery Separators. *Chem. Rev.*, 104,4419-62, 2004.

[10] Huang, X. Separator technologies for lithium-ion batteries. *J. Solid State Electrochem.*, 15,649-62, 2011.

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

[12] Nishikawa, O., Sugimoto, T., Nomura, S., Doyama, K., Miyatake, K., Uchida, H., Watanabe, M. Preparation of the electrode for high temperature PEFCs using novel polymer electrolytes based on organic/inorganic nanohybrids. *Electrochim. Acta*. 50,667-72, 2004.

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

[14] Li, Z., Shan, F., Wei, J., Yang, J., Li, X., Wang, X. High ionic conductive PVDF-based fibrous electrolytes. *J. Solid State Electrochem.*, 12,1629-35, 2008.

[15] Abraham, K. M., Jiang, Z., Carroll, B. Highly Conductive PEO-like Polymer Electrolytes. *Chem. Mater.*, 9,1978-88, 1997.

[16] Sylla, S., Sanchez, J. Y., Armand, M. Electrochemical study of linear and crosslinked POE-based polymer electrolytes. *Electrochim. Acta*. 37,1699-701, 1992.

[17] Chung, Y. S., Yoo, S. H., Kim, C. K. Enhancement of Meltdown Temperature of the Polyethylene Lithium-Ion Battery Separator via Surface Coating with Polymers Having High Thermal Resistance. *Industrial & Engineering Chemistry Research*. 48,4346-51, 2009.

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

[19] Choi, B. K., Shin, K. H., Kim, Y. W. Lithium ion conduction in PEO-salt electrolytes gelled with PAN. *Solid State Ionics*. 113-115,123-7, 1998.

[20] Kang, Y., Kim, H. J., Kim, E., Oh, B., Cho, J. H. Photocured PEO-based solid polymer electrolyte and its application to lithium-polymer batteries. *J. Power Sources*. 92,255-9, 2001.

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

[22] Djian, D., Alloin, F., Martinet, S., Lignier, H. Macroporous poly(vinylidene fluoride) membrane as a separator for lithium-ion batteries with high charge rate capacity. *J. Power Sources*. 187,575-80, 2009.

[23] Costa, C. M., California, A., Cardoso, V. F., Sencadas, V., Rodrigues, L. C., Silva, M. M., Lanceros-Méndez, S. Electroactive Poly(Vinylidene Fluoride-Trifluorethylene) (PVDF-TrFE) Microporous Membranes for Lithium-Ion Battery Applications. *Ferroelectrics*. 430,103-7, 2012.

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

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

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

[27] Xiong, M., Tang, H., Wang, Y., Lin, Y., Sun, M., Yin, Z., Pan, M. Expanded polytetrafluoroethylene reinforced polyvinylidenefluoride–hexafluoropropylene separator with high thermal stability for lithium-ion batteries. *J. Power Sources*. 241,203-11, 2013.

[28] Wei, X., Nie, Z., Luo, Q., Li, B., Sprenkle, V., Wang, W. Polyvinyl Chloride/Silica Nanoporous Composite Separator for All-Vanadium Redox Flow Battery Applications. *J. Electrochem. Soc.*, 160,A1215-A8, 2013.

[29] Park, J.-H., Cho, J.-H., Park, W., Ryoo, D., Yoon, S.-J., Kim, J. H., Jeong, Y. U., Lee, S.-Y. Close-packed SiO2/poly(methyl methacrylate) binary nanoparticles-coated polyethylene separators for lithium-ion batteries. *J. Power Sources*. 195,8306-10, 2010.

[30] Park, S., Son, C. W., Lee, S., Kim, D. Y., Park, C., Eom, K. S., Fuller, T. F., Joh, H.-I., Jo, S. M. Multicore-shell nanofiber architecture of polyimide/polyvinylidene fluoride blend for thermal and long-term stability of lithium ion battery separator. *Scientific Reports*. 6,36977, 2016.

[31] Chen, W., Yu, H., Lee, S.-Y., Wei, T., Li, J., Fan, Z. Nanocellulose: a promising nanomaterial for advanced electrochemical energy storage. *Chem. Soc. Rev.*, 47,2837-72, 2018.

[32] Uddin, M.-J., Alaboina, P. K., Zhang, L., Cho, S.-J. A low-cost, environment-friendly lignin-polyvinyl alcohol nanofiber separator using a water-based method for safer and faster lithium-ion batteries. *Materials Science and Engineering: B*. 223,84-90, 2017.

[33] Pereira, R. F. P., Brito-Pereira, R., Gonçalves, R., Silva, M. P., Costa, C. M., Silva, M. M., de Zea Bermudez, V., Lanceros-Méndez, S. Silk Fibroin Separators: A Step Toward Lithium-Ion Batteries with Enhanced Sustainability. *ACS Applied Materials & Interfaces*. 10,5385-94, 2018.

[34] Deimede, V., Elmasides, C. Separators for Lithium-Ion Batteries: A Review on the Production Processes and Recent Developments. *Energy Technology*. 3,453-68, 2015.

[35] Golodnitsky, D., Strauss, E., Peled, E., Greenbaum, S. Review—On Order and Disorder in Polymer Electrolytes. *J. Electrochem. Soc.*, 162,A2551-A66, 2015.

[36] J Orendorff, C. The Role of Separators in Lithium-Ion Cell Safety2012.

[37] Xu, J., Wang, L., Guan, J., Yin, S. Coupled effect of strain rate and solvent on dynamic mechanical behaviors of separators in lithium ion batteries. *Materials & Design*. 95,319-28, 2016.

[38] Plaimer, M., Breitfuß, C., Sinz, W., Heindl, S. F., Ellersdorfer, C., Steffan, H., Wilkening, M., Hennige, V., Tatschl, R., Geier, A., Schramm, C., Freunberger, S. A. Evaluating the trade-off between mechanical and electrochemical performance of separators for lithium-ion batteries: Methodology and application. *J. Power Sources*. 306,702-10, 2016.

[39] Zhang, X., Sahraei, E., Wang, K. Deformation and failure characteristics of four types of lithium-ion battery separators. *J. Power Sources*. 327,693-701, 2016.

[40] Xu, H., Zhu, M., Marcicki, J., Yang, X. G. Mechanical modeling of battery separator based on microstructure image analysis and stochastic characterization. *J. Power Sources*. 345,137-45, 2017.

[41] Kalnaus, S., Wang, Y., Turner, J. A. Mechanical behavior and failure mechanisms of Li-ion battery separators. *J. Power Sources*. 348,255-63, 2017.

[42] Zhang, X., Sahraei, E., Wang, K. Li-ion Battery Separators, Mechanical Integrity and Failure Mechanisms Leading to Soft and Hard Internal Shorts. *Scientific Reports*. 6,32578, 2016.

[43] Lee, Y., Park, J., Jeon, H., Yeon, D., Kim, B.-H., Cho, K. Y., Ryou, M.-H., Lee, Y. M. In-depth correlation of separator pore structure and electrochemical performance in lithium-ion batteries. *J. Power Sources*. 325,732-8, 2016.

[44] Xie, Y., Zou, H., Xiang, H., Xia, R., Liang, D., Shi, P., Dai, S., Wang, H. Enhancement on the wettability of lithium battery separator toward nonaqueous electrolytes. *Journal of Membrane Science*. 503,25-30, 2016.

[45] Zhang, S. S. A review on the separators of liquid electrolyte Li-ion batteries. *J. Power Sources*. 164,351-64, 2007.

[46] Ribeiro, C., Costa, C. M., Correia, D. M., Nunes-Pereira, J., Oliveira, J., Martins, P., Goncalves, R., Cardoso, V. F., Lanceros-Mendez, S. Electroactive poly(vinylidene fluoride)-based structures for advanced applications. *Nat Protoc*. 13,681-704, 2018.

[47] Gu, L., Zhang, M., He, J., Ni, P. A porous cross-linked gel polymer electrolyte separator for lithium-ion batteries prepared by using zinc oxide nanoparticle as a foaming agent and filler. *Electrochim. Acta*. 292,769-78, 2018.

[48] Costa, C. M., Kundu, M., Dias, J. C., Nunes-Pereira, J., Botelho, G., Silva, M. M., Lanceros-Méndez, S. Mesoporous poly(vinylidene fluoride-co-trifluoroethylene) membranes for lithium-ion battery separators. *Electrochim. Acta*. 301,97-106, 2019.
[49] Costa, C. M., Kundu, M., Cardoso, V. F., Machado, A. V., Silva, M. M., Lanceros-Méndez, S. Silica/poly(vinylidene fluoride) porous composite membranes for lithium-ion battery separators. *Journal of Membrane Science*. 564,842-51, 2018.
[50] Ali, S., Tan, C., Waqas, M., Lv, W., Wei, Z., Wu, S., Boateng, B., Liu, J., Ahmed, J., Xiong, J., Goodenough, J. B., He, W. Highly Efficient PVDF-HFP/Colloidal Alumina Composite Separator for High-Temperature Lithium-Ion Batteries. *Advanced Materials Interfaces*. 5,1701147, 2018.
[51] Anjan Banerjee, B. Z. S. L., Doron Aurbach, Ion C. Halalay. The Effectiveness of Multifunctional Li-Ion Battery Separators past Their Saturation with Transition Metal Ions. *Journal ofThe Electrochemical Society*. 165,A2096-A101, 2018.
[52] Xiang, Y., Zhu, W., Qiu, W., Guo, W., Lei, J., Liu, D., Qu, D., Xie, Z., Tang, H., Li, J. SnO_2 Functionalized Polyethylene Separator with Enhanced Thermal Stability for High Performance Lithium Ion Battery. *ChemistrySelect*. 3,911-6, 2018.
[53] Xia, Y., Li, J., Wang, H., Ye, Z., Zhou, X., Huang, H., Gan, Y., Liang, C., Zhang, J., Zhang, W. Synthesis and electrochemical performance of poly(vinylidene fluoride)/SiO2 hybrid membrane for lithium-ion batteries. *J. Solid State Electrochem.*, 23,519-27, 2018.
[54] Wang, X., Xu, G., Wang, Q., Lu, C., Zong, C., Zhang, J., Yue, L., Cui, G. A phase inversion based sponge-like polysulfonamide/SiO 2 composite separator for high performance lithium-ion batteries. *Chin. J. Chem. Eng.*, 26,1292-9, 2018.
[55] Waqas, M., Tan, C., Lv, W., Ali, S., Boateng, B., Chen, W., Wei, Z., Feng, C., Ahmed, J., Goodenough, J. B., He, W. A Highly-Efficient Composite Separator with Strong Ligand Interaction for High-Temperature Lithium-Ion Batteries. *ChemElectroChem*. 5,2722-8, 2018.
[56] Wang, Z., Xie, Y., Xu, C., Shi, S., Wang, L., Zhang, G., Wang, X., Zhu, L., Xu, D. Zirconia fiber membranes based on PVDF as high-safety separators for lithium-ion batteries using a papermaking method. *J. Solid State Electrochem.*, 23,269-76, 2018.
[57] Liu, J., Wang, C., Wu, X., Zhu, F., Liu, M., Xi, Y. An enhanced poly(vinylidene fluoride) matrix separator with TEOS for good performance lithium-ion batteries. *J. Solid State Electrochem.*, 23,277-84, 2018.

[58] Tan, J., Kong, L., Qiu, Z., Yan, Y. Flexible, high-wettability and thermostable separator based on fluorinated polyimide for lithium-ion battery. *J. Solid State Electrochem.*, 22,3363-73, 2018.

[59] Liu, K.-L., Chao, C.-H., Lee, H.-C., Tsao, C.-S., Fang, J., Wu, N.-L., Chao, C.-Y. A novel non-porous separator based on single-ion conducting triblock copolymer for stable lithium electrodeposition. *J. Power Sources*. 419,58-64, 2019.

[60] Li, H., Niu, D.-H., Zhou, H., Chao, C.-Y., Wu, L.-J., Han, P.-L. Preparation and characterization of PVDF separators for lithium ion cells using hydroxyl-terminated polybutadiene grafted methoxyl polyethylene glycol (HTPB-g-MPEG) as additive. *Appl. Surf. Sci.*, 440,186-92, 2018.

[61] Li, D., Zhang, H., Li, X. Porous polyetherimide membranes with tunable morphology for lithium-ion battery. *Journal of Membrane Science*. 565,42-9, 2018.

[62] Shin, Y.-K., Kim, M.-C., Moon, S.-H., Kim, E.-S., Lee, J.-E., Choi, S., Kim, H., Park, K.-W. Pore-controlled polymer membrane with Mn (II) ion trapping effect for high-rate performance LiMn2O4 cathode. *J. Solid State Electrochem.*, 23,475-84, 2018.

[63] Kim, I., Kim, B. S., Nam, S., Lee, H. J., Chung, H. K., Cho, S. M., Luu, T. H. T., Hyun, S., Kang, C. Cross-Linked Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-co-HFP) Gel Polymer Electrolyte for Flexible Li-Ion Battery Integrated with Organic Light Emitting Diode (OLED). *Materials (Basel)*. 11, 2018.

[64] Li, L., Peng, S., Lee, J. K. Y., Ji, D., Srinivasan, M., Ramakrishna, S. Electrospun hollow nanofibers for advanced secondary batteries. *Nano Energy*. 39,111-39, 2017.

[65] Wang, S.-X., Yap, C. C., He, J., Chen, C., Wong, S. Y., Li, X. Electrospinning: a facile technique for fabricating functional nanofibers for environmental applications. *Nanotechnology Reviews*. 5, 2016.

[66] Zhong, G., Wang, Y., Wang, C., Wang, Z., Guo, S., Wang, L., Liang, X., Xiang, H. An AlOOH-coated polyimide electrospun fibrous membrane as a high-safety lithium-ion battery separator. *Ionics*. 2018.

[67] Zhao, H., Deng, N., Yan, J., Kang, W., Ju, J., Wang, L., Li, Z., Cheng, B. Effect of OctaphenylPolyhedral oligomeric silsesquioxane on the electrospun Poly-m-phenylene isophthalamid separators for lithium-ion batteries with high safety and excellent electrochemical performance. *Chem. Eng. J.*, 356,11-21, 2019.

[68] Zhao, H., Deng, N., Ju, J., Li, Z., Kang, W., Cheng, B. Novel configuration of heat-resistant gel polymer electrolyte with electrospun poly (vinylidene fluoride-co-

hexafluoropropylene) and poly-m-phenyleneisophthalamide composite separator for high-safety lithium-ion battery. *Mater. Lett.*, 236,101-5, 2019.

[69] Wang, L., Deng, N., Ju, J., Wang, G., Cheng, B., Kang, W. A novel core-shell structured poly-m-phenyleneisophthalamide@polyvinylidene fluoride nanofiber membrane for lithium ion batteries with high-safety and stable electrochemical performance. *Electrochim. Acta*. 300,263-73, 2019.

[70] Wang, L., Wang, Z., Sun, Y., Liang, X., Xiang, H. Sb_2O_3 modified PVDF-CTFE electrospun fibrous membrane as a safe lithium-ion battery separator. *Journal of Membrane Science*. 572,512-9, 2019.

[71] K, B., Suriyakumar, S., P, A. P., A. S, A., Kalarikkal, N., Stephen, A. M., G, G. V., Rouxel, D., Thomas, S. Highly lithium ion conductive, Al_2O_3 decorated electrospun P(VDF-TrFE) membranes for lithium ion battery separators. *New J. Chem.*, 42,19505-20, 2018.

[72] Zhang, J., Xiang, Y., Jamil, M. I., Lu, J., Zhang, Q., Zhan, X., Chen, F. Polymers/zeolite nanocomposite membranes with enhanced thermal and electrochemical performances for lithium-ion batteries. *Journal of Membrane Science*. 564,753-61, 2018.

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

[74] Shi, C., Zhu, J., Shen, X., Chen, F., Ning, F., Zhang, H., Long, Y.-Z., Ning, X., Zhao, J. Flexible inorganic membranes used as a high thermal safety separator for the lithium-ion battery. *RSC Advances*. 8,4072-7, 2018.

[75] Shen, X., Li, C., Shi, C., Yang, C., Deng, L., Zhang, W., Peng, L., Dai, J., Wu, D., Zhang, P., Zhao, J. Core-shell structured ceramic nonwoven separators by atomic layer deposition for safe lithium-ion batteries. *Appl. Surf. Sci.*, 441,165-73, 2018.

[76] Cai, H., Tong, X., Chen, K., Shen, Y., Wu, J., Xiang, Y., Wang, Z., Li, J. Electrospun Polyethylene Terephthalate Nonwoven Reinforced Polypropylene Separator: Scalable Synthesis and Its Lithium Ion Battery Performance. *Polymers*. 10,574, 2018.

[77] Byun, S., Lee, S. H., Song, D., Ryou, M.-H., Lee, Y. M., Park, W. H. A crosslinked nonwoven separator based on an organosoluble polyimide for high-performance lithium-ion batteries. *Journal of Industrial and Engineering Chemistry*. 72,390-9, 2019.

[78] Sabetzadeh, N., Gharehaghaji, A. A., Javanbakht, M. Porous PAN micro/nanofiber separators for enhanced lithium-ion battery performance. *Solid State Ionics*. 325,251-7, 2018.

[79] Mahant, Y. P., Kondawar, S. B., Nandanwar, D. V., Koinkar, P. Poly(methyl methacrylate) reinforced poly(vinylidene fluoride) composites electrospun nanofibrous polymer electrolytes as potential separator for lithium ion batteries. *Materials for Renewable and Sustainable Energy*. 7, 2018.

[80] Liu, X., Song, K., Lu, C., Huang, Y., Duan, X., Li, S., Ding, Y. Electrospun PU@GO separators for advanced lithium ion batteries. *Journal of Membrane Science*. 555,1-6, 2018.

[81] Li, Z., Wang, W., Han, Y., Zhang, L., Li, S., Tang, B., Xu, S., Xu, Z. Ether modified poly(ether ether ketone) nonwoven membrane with excellent wettability and stability as a lithium ion battery separator. *J. Power Sources*. 378,176-83, 2018.

[82] Hai Li, B. Z., Bin Lin, Yanzhang Yang, Yang Zhao, Lei Wang. Electrospun Poly(ether ether ketone) Nanofibrous Separator with Superior Performance for Lithium-Ion Batteries. *Journal ofThe Electrochemical Society*. 165,A939-A46, 2018.

[83] Li, J., Zhong, Q., Yao, Y., Bi, S., Zhou, T., Guo, X., Wu, M., Feng, T., Xiang, R. Electrochemical performance and thermal stability of the electrospun PTFE nanofiber separator for lithium-ion batteries. *J. Appl. Polym. Sci.*, 135,46508, 2018.

[84] Kong, L., Yan, Y., Qiu, Z., Zhou, Z., Hu, J. Robust fluorinated polyimide nanofibers membrane for high-performance lithium-ion batteries. *Journal of Membrane Science*. 549,321-31, 2018.

[85] Kong, L., Liu, B., Ding, J., Yan, X., Tian, G., Qi, S., Wu, D. Robust polyetherimide fibrous membrane with crosslinked topographies fabricated via in-situ micro-melting and its application as superior Lithium-ion battery separator with shutdown function. *Journal of Membrane Science*. 549,244-50, 2018.

[86] Jiang, L., Zhang, X., Chen, Y., Qiao, L., Lu, X., Tian, X. Modified polypropylene/cotton fiber composite nonwoven as lithium-ion battery separator. *Mater. Chem. Phys.*, 219,368-75, 2018.

[87] Liu, H., Wang, X., Kuang, C., Li, L., Zhai, Y. Polyvinylidene fluoride/polystyrene hybrid fibers with high ionic conductivity and enhanced mechanical strength as lithium-ion battery separators. *J. Solid State Electrochem.*, 22,3579-87, 2018.

[88] Gong, W., Wei, S., Ruan, S., Shen, C. Electrospun coaxial PPESK/PVDF fibrous membranes with thermal shutdown property used for lithium-ion batteries. *Mater. Lett.*, 244,126-9, 2019.

[89] Chae, J., Park, S., Kim, D., Joh, H.-I., Kim, J., Lee, S., Jo, S. Reinforced PEI/PVdF Multicore-Shell Structure Composite Membranes by Phase Prediction on a Ternary Solution. *Polymers*. 10,436, 2018.

[90] Fu, Q., Lin, G., Chen, X., Yu, Z., Yang, R., Li, M., Zeng, X., Chen, J. Mechanically Reinforced PVdF/PMMA/SiO2

Composite Membrane and Its Electrochemical Properties as a Separator in Lithium-Ion Batteries. *Energy Technology*. 6,144-52, 2018.

[91] Li, H., Zhang, B., Liu, W., Lin, B., Ou, Q., Wang, H., Fang, M., Liu, D., Neelakandan, S., Wang, L. Effects of an electrospun fluorinated poly(ether ether ketone) separator on the enhanced safety and electrochemical properties of lithium ion batteries. *Electrochim. Acta*. 290,150-64, 2018.

[92] Li, J., Luo, K., Yu, J., Wang, Y., Zhu, J., Hu, Z. Promising Free-Standing Polyimide Membrane via Solution Blow Spinning for High Performance Lithium-Ion Batteries. *Industrial & Engineering Chemistry Research*. 57,12296-305, 2018.

[93] Chen, Y., Gao, Y., Jian, J., Lu, Y., Zhang, B., Liu, H., Li, L., Wang, X., Kuang, C., Zhai, Y. A dual-layer micro/nanostructured fibrous membrane with enhanced ionic conductivity for lithium-ion battery. *Electrochim. Acta*. 292,357-63, 2018.

[94] Kong, L., Wang, Y., Yu, H., Liu, B., Qi, S., Wu, D., Zhong, W. H., Tian, G., Wang, J. In-Situ Armoring: A Robust, High-Wettability and Fire-Resistant Hybrid Separator for Advanced and Safe Batteries. *ACS Appl Mater Interfaces*. 2018.

[95] Yang, S., Ma, W., Wang, A., Gu, J., Yin, Y. A core–shell structured polyacrylonitrile@poly(vinylidene fluoride-hexafluoro propylene) microfiber complex membrane as a separator by co-axial electrospinning. *RSC Advances*. 8,23390-6, 2018.

[96] Jiang, Y., Ding, Y., Zhang, P., Li, F., Yang, Z. Temperature-dependent on/off PVP@TiO_2 separator for safe Li-storage. *Journal of Membrane Science*. 565,33-41, 2018.

[97] Caimi, S., Klaue, A., Wu, H., Morbidelli, M. Effect of SiO_2 Nanoparticles on the Performance of PVdF-HFP/Ionic Liquid Separator for Lithium-Ion Batteries. *Nanomaterials (Basel)*. 8, 2018.

[98] Yang, S., Gu, J., Yin, Y. A biaxial stretched β-isotactic polypropylene microporous membrane for lithium-ion batteries. *J. Appl. Polym. Sci.*, 135,45825, 2018.

[99] Wenyi Zhu, Z. W., Weijian Qiu, Yinyu Xiang, Yue Du, Dan Liu, Deyu Qu, Zhizhong Xie, Haolin Tang, Junsheng Li. Improving the Electrochemical Performance of

Polypropylene Separator through Instantaneous Photo-Induced Functionalization. *Journal ofThe Electrochemical Society*. 165,A1909-A14 2018.

[100] Liu, Y., Qiao, Y., Zhang, Y., Yang, Z., Gao, T., Kirsch, D., Liu, B., Song, J., Yang, B., Hu, L. 3D printed separator for the thermal management of high-performance Li metal anodes. *Energy Storage Materials*. 12,197-203, 2018.

[101] Liu, J., Shi, X., Boateng, B., Han, Y., Chen, D., He, W. A Highly Stable Separator from an Instantly Reformed Gel with Direct Post-Solidation for Long-Cycle High-Rate Lithium-Ion Batteries. *ChemSusChem*. 12,908-14, 2019.

[102] Li, Y., Pu, H., Wei, Y. Polypropylene/polyethylene multilayer separators with enhanced thermal stability for lithium-ion battery via multilayer coextrusion. *Electrochim. Acta*. 264,140-9, 2018.

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

[104] Kim, K. J., Kwon, Y. K., Yim, T., Choi, W. Functional separator with lower resistance toward lithium ion transport for enhancing the electrochemical performance of lithium ion batteries. *Journal of Industrial and Engineering Chemistry*. 71,228-33, 2019.

[105] Hao Zhang, J. L., Min Guan, Zhen Shang, Yiwei Sun, Zonghong Lu, Hailong Li, Xingye An, and Hongbin Liu. Nano-fibrillated cellulose (NFC) as a pore size mediator in the preparation of thermal resistant separators for lithium ion batteries. *ACS Sustainable Chemistry Engineering*. 2018.

[106] Hou, J., Jang, W., Kim, S., Kim, J.-H., Byun, H. Rapid formation of polyimide nanofiber membranes via hot-press treatment and their performance as Li-ion battery separators. *RSC Advances*. 8,14958-66, 2018.

[107] Zuo, X., Wu, J., Ma, X., Deng, X., Cai, J., Chen, Q., Liu, J., Nan, J. A poly(vinylidene fluoride)/ethyl cellulose and amino-functionalized nano-SiO2 composite coated separator for 5 V high-voltage lithium-ion batteries with enhanced performance. *J. Power Sources*. 407,44-52, 2018.

[108] Yuan, J.-J., Song, Y.-Z., Zhang, Y., Qiu, Z.-L., Sun, C.-C., Yin, X., Zhu, L.-P., Zhu, B.-K. Polyphenols assisted silica coating on polypropylene separators with improved wettability and heat-resistance for lithium-ion batteries. *J. Appl. Polym. Sci.*, 136,47277, 2019.

[109] Choi, Y., Kim, J. I., Moon, J., Jeong, J., Park, J. H. Electron beam induced strong organic/inorganic grafting for thermally stable lithium-ion battery separators. *Appl. Surf. Sci.*, 444,339-44, 2018.

[110] Zhao, J., Hu, Q., Wang, J., Zhang, P., Zhu, Y., Wu, G., Lv, Y., Lv, L., Zhao, Y., Yang, M. Effects of Island-Coated PVdF-HFP Composite Separator on the Performance of Commercial Lithium-ion Batteries. *Coatings*. 8,437, 2018.

[111] Zhang, K., Xiao, W., Liu, J., Yan, C. A Novel Self-Binding Composite Separator Based on Poly(tetrafluoroethylene) Coating for Li-Ion Batteries. *Polymers*. 10,1409, 2018.

[112] Zhang, Z., Yuan, W., Li, L. Enhanced wettability and thermal stability of nano-SiO 2 /poly(vinyl alcohol)-coated polypropylene composite separators for lithium-ion batteries. *Particuology*. 37,91-8, 2018.

[113] Zhang, Y., Yuan, J.-J., Song, Y.-Z., Yin, X., Sun, C.-C., Zhu, L.-P., Zhu, B.-K. Tannic acid/polyethyleneimine-decorated polypropylene separators for Li-Ion batteries and the role of the interfaces between separator and electrolyte. *Electrochim. Acta*. 275,25-31, 2018.

[114] Song, Y.-Z., Zhang, Y., Yuan, J.-J., Lin, C.-E., Yin, X., Sun, C.-C., Zhu, B., Zhu, L.-P. Fast assemble of polyphenol derived coatings on polypropylene separator for high performance lithium-ion batteries. *J. Electroanal. Chem.*, 808,252-8, 2018.

[115] Song, Y.-Z., Yuan, J.-J., Yin, X., Zhang, Y., Lin, C.-E., Sun, C.-c., Fang, L.-F., Zhu, B., Zhu, L.-P. Effect of polyphenol-polyamine treated polyethylene separator on the ionic conduction and interface properties for lithium-metal anode batteries. *J. Electroanal. Chem.*, 816,68-74, 2018.

[116] Xu, R., Lin, X., Huang, X., Xie, J., Jiang, C., Lei, C. Boehmite-coated microporous membrane for enhanced electrochemical performance and dimensional stability of lithium-ion batteries. *J. Solid State Electrochem.*, 22,739-47, 2017.

[117] Huang, X., Ellison, N. Fabricating a high performance composite separator with a small thickness for lithium ion batteries. *Compos. Sci. Technol.*, 168,346-52, 2018.

[118] Chao, C.-Y., Feng, Y.-F., Hua, K., Li, H., Wu, L.-J., Zhou, Y.-S., Dong, Z.-W. Enhanced wettability and thermal stability of polypropylene separators by organic-inorganic coating layer for lithium-ion batteries. *J. Appl. Polym. Sci.*, 135,46478, 2018.

[119] Yin, M., Huang, J., Yu, J., Chen, G., Qu, S., Wang, X., Li, C. The polypropylene membrane modified by an atmospheric pressure plasma jet as a separator for lithium-ion button battery. *Electrochim. Acta*. 260,489-97, 2018.

[120] Rui Jin, L. F., Hualan Zhou, Zhuyi Wang, Zhengfu Qiu, Liyi Shi, Jiefang Zhu, and Shuai Yuan. High Li+ ionic flux separator enhancing cycling stability of lithium metal anode. *ACS Sustainable Chemistry & Engineering* 2018.

[121] Luo, D., Chen, M., Xu, J., Yin, X., Wu, J., Chen, S., Wang, L., Wang, H. Polyphenylene sulfide nonwoven-based composite separator with superior heat-resistance and flame retardancy for high power lithium ion battery. *Compos. Sci. Technol.*, 157,119-25, 2018.

[122] Qin, S., Wang, M., Wang, C., Jin, Y., Yuan, N., Wu, Z., Zhang, J. Binder-Free Nanoparticulate Coating of a Polyethylene Separator via a Reactive Atmospheric Pressure Plasma for Lithium-Ion Batteries with Improved Performances. *Advanced Materials Interfaces*. 5,1800579, 2018.

[123] Na, W., Koh, K. H., Lee, A. S., Cho, S., Ok, B., Hwang, S.-W., Lee, J. H., Koo, C. M. Binder-less chemical grafting of SiO_2 nanoparticles onto polyethylene separators for lithium-ion batteries. *Journal of Membrane Science*. 573,621-7, 2019.

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

[125] Zhi, Y., Sun, X., Li, N., Yuan, S., Wang, Z., Jin, L., Hang, J., Shi, L. UV curable organic-inorganic hybrid coatings on microporous polyethylene separator for enhancing mechanical and electrochemical performance. *J. Alloys Compd.*, 743,756-62, 2018.

[126] Jeon, H., Roh, Y., Jin, D., Ryou, M.-H., Jeong, Y.-C., Lee, Y. M. Crosslinkable polyhedral silsesquioxane-based ceramic-coated separators for Li-ion batteries. *Journal of Industrial and Engineering Chemistry*. 71,277-83, 2019.

[127] Schadeck, U., Kyrgyzbaev, K., Zettl, H., Gerdes, T., Moos, R. Flexible, Heat-Resistant, and Flame-Retardant Glass Fiber Nonwoven/Glass Platelet Composite Separator for Lithium-Ion Batteries. *Energies*. 11,999, 2018.

[128] Gao, H., Chen, Y., Sun, H., Zhao, A., Wang, L., Liu, N. Silicone modified polypropylene separator for high temperature lithium ion battery applications. *Materials Research Express*. 5,065512, 2018.

[129] Feng, G., Li, Z., Mi, L., Zheng, J., Feng, X., Chen, W. Polypropylene/hydrophobic-silica-aerogel-composite separator induced enhanced safety and low polarization for lithium-ion batteries. *J. Power Sources*. 376,177-83, 2018.

[130] Dong, G., Liu, B., Sun, G., Tian, G., Qi, S., Wu, D. TiO_2 nanoshell@polyimide nanofiber membrane prepared via a surface-alkaline-etching and in-situ complexation-

hydrolysis strategy for advanced and safe LIB separator. *Journal of Membrane Science*. 577,249-57, 2019.

[131] Zhou, Y.-T., Yang, J., Liang, H.-Q., Pi, J.-K., Zhang, C., Xu, Z.-K. Sandwich-structured composite separators with an anisotropic pore architecture for highly safe Li-ion batteries. *Composites Communications*. 8,46-51, 2018.

[132] Waqas, M., Ali, S., Lv, W., Chen, D., Boateng, B., He, W. High-Performance PE-BN/PVDF-HFP Bilayer Separator for Lithium-Ion Batteries. *Advanced Materials Interfaces*. 6,1801330, 2018.

[133] Wang, Z., Pan, R., Ruan, C., Edstrom, K., Stromme, M., Nyholm, L. Redox-Active Separators for Lithium-Ion Batteries. *Adv Sci (Weinh)*. 5,1700663, 2018.

[134] Liu, J., Liu, Y., Yang, W., Ren, Q., Li, F., Huang, Z. Lithium ion battery separator with high performance and high safety enabled by tri-layered SiO 2 @PI/m-PE/SiO 2 @PI nanofiber composite membrane. *J. Power Sources*. 396,265-75, 2018.

[135] Asghar, M. R., Zhang, Y., Wu, A., Yan, X., Shen, S., Ke, C., Zhang, J. Preparation of microporous Cellulose/Poly(vinylidene fluoride-hexafluoropropylene) membrane for lithium ion batteries by phase inversion method. *J. Power Sources*. 379,197-205, 2018.

[136] Fangbin Chen, Y. L., Minsui Li, Jinhong Huang, Qiming Huang, Weishan Li. Application of Low Cost Non-Woven Fabric in 4.4 V LiCoO2 Based Lithium Ion Battery by Simple Coating Blended Polymer. *J. Electrochem. Soc.*, 165,A206-A14, 2018.

[137] Pan, R., Xu, X., Sun, R., Wang, Z., Lindh, J., Edstrom, K., Stromme, M., Nyholm, L. Nanocellulose Modified Polyethylene Separators for Lithium Metal Batteries. *Small*. 14,e1704371, 2018.

[138] Ma, X., Zuo, X., Wu, J., Deng, X., Xiao, X., Liu, J., Nan, J. Polyethylene-supported ultra-thin polyvinylidene fluoride/hydroxyethyl cellulose blended polymer electrolyte for 5 V high voltage lithium ion batteries. *Journal of Materials Chemistry A*. 6,1496-503, 2018.

[139] Liu, J., Yang, K., Mo, Y., Wang, S., Han, D., Xiao, M., Meng, Y. Highly safe lithium-ion batteries: High strength separator from polyformaldehyde/cellulose nanofibers blend. *J. Power Sources*. 400,502-10, 2018.

[140] Boriboon, D., Vongsetskul, T., Limthongkul, P., Kobsiriphat, W., Tammawat, P. Cellulose ultrafine fibers embedded with titania particles as a high performance and eco-friendly separator for lithium-ion batteries. *Carbohydr. Polym.*, 189,145-51, 2018.

[141] Pereira, R. F. P., Brito-Pereira, R., Goncalves, R., Silva, M. P., Costa, C. M., Silva, M. M., de Zea Bermudez, V., Lanceros-Mendez, S. Silk Fibroin Separators: A Step

Toward Lithium-Ion Batteries with Enhanced Sustainability. *ACS Appl Mater Interfaces*. 10,5385-94, 2018.

[142] Ma, L., Chen, R., Hu, Y., Zhang, W., Zhu, G., Zhao, P., Chen, T., Wang, C., Yan, W., Wang, Y., Wang, L., Tie, Z., Liu, J., Jin, Z. Nanoporous and lyophilic battery separator from regenerated eggshell membrane with effective suppression of dendritic lithium growth. *Energy Storage Materials*. 14,258-66, 2018.

[143] Guo, T., Song, J., Jin, Y., Sun, Z., Li, L. Thermally stable and green cellulose-based composites strengthened by styrene-co-acrylate latex for lithium-ion battery separators. *Carbohydr. Polym.*, 206,801-10, 2019.

[144] Sheng, J., Wang, R., Yang, R. Physicochemical Properties of Cellulose Separators for Lithium Ion Battery: Comparison with Celgard2325. *Materials (Basel)*. 12, 2018.