

1 Review

## 2 Recent advances in poly(vinylidene fluoride) and its 3 copolymers for lithium-ion battery separators

4 João C. Barbosa<sup>1,†</sup>, José P. Dias<sup>1,†</sup>, Senentxu Lanceros-Méndez<sup>2,3,\*</sup> and Carlos M. Costa<sup>1,4</sup>

5 <sup>1</sup> Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal; [joaocpbarbosa@live.com.pt](mailto:joaocpbarbosa@live.com.pt) (J.C.B.);  
6 [jmpedrodias@gmail.com](mailto:jmpedrodias@gmail.com) (J.P.D.), [cmscosta@fisica.uminho.pt](mailto:cmscosta@fisica.uminho.pt) (C.M.C.)

7 <sup>2</sup> BCMaterials, Basque Center Centre for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940  
8 Leioa, Spain;

9 <sup>3</sup> IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

10 <sup>4</sup> Centro de Química, Universidade do Minho, 4710-057 Braga, Portugal

11 <sup>†</sup> Equal contribution

12 <sup>\*</sup> Correspondence: [senentxu.lanceros@bcmaterials.net](mailto:senentxu.lanceros@bcmaterials.net); Tel.: +34-94-612-8811

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14 **Abstract:** The separator membrane is an essential component of lithium-ion batteries, separating the  
15 anode and cathode and controlling the number and mobility of the lithium ions. Among the  
16 polymer matrices most investigated for battery separators are poly(vinylidene fluoride) (PVDF) and  
17 its copolymers poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), poly(vinylidene  
18 fluoride-co-hexafluoropropylene) (PVDF-HFP), and poly(vinylidene fluoride-  
19 cochlorotrifluoroethylene) (PVDF-CTFE), due to their excellent properties such as high polarity  
20 and the possibility of controlling the porosity of the materials through binary and ternary  
21 polymer/solvent systems, among others. This review presents the recent advances on battery  
22 separators based on PVDF and its copolymers for lithium-ion batteries. It is divided in the following  
23 sections: single polymer and co-polymers, surface modification, composites and polymer blends.  
24 Further, a critical comparison between those membranes and other separator membranes is  
25 presented, as well as the future trends on this area.

26 **Keywords:** PVDF; copolymers; battery separator; lithium-ion batteries

27

### 28 1. Introduction

29 In the field of mobile applications, the efficient storage of energy is one of the most critical issues,  
30 since there is a fundamental need to maximize the amount of energy stored. This issue can be  
31 accomplished by increasing the gravimetric and volumetric energy density of the batteries [1].

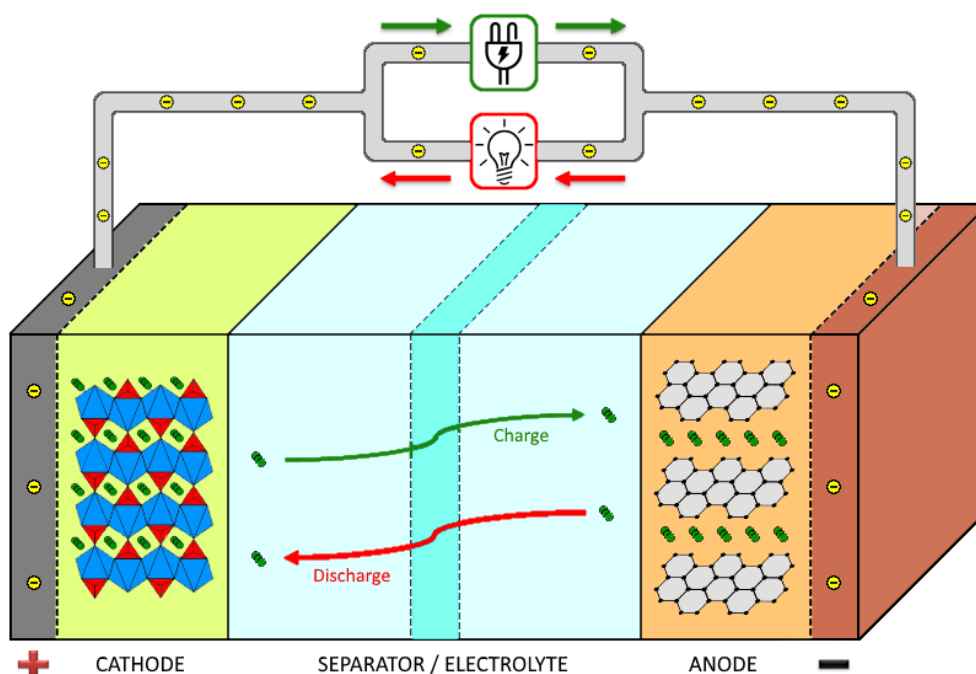
32 The electrochemical lithium ion battery is used to provide power to a large variety of mobile  
33 appliances, such as smartphones, tablets and laptops, as well as an increasing number of sensors and  
34 actuators, which will have a fundamental role in the shaping of the Internet of Things and Industry  
35 4.0 concepts, main trend of the nowadays technological evolution [2]. Lithium ion batteries can also  
36 power electric and hybrid vehicles and take part in the management of the renewable energy  
37 production, being essential in a more sustainable energy paradigm. As some renewable resources,  
38 such as solar and wind, are intermittent over time, storing energy for their use in periods of lack of  
39 resources is a critical issue for lithium ion batteries [3,4].

40 Lithium ion batteries are very suitable for the aforementioned applications due to their  
41 advantages with respect to other battery types, as they are lighter, cheaper, show higher energy density  
42 (250 Wh·kg<sup>-1</sup>, 650 Wh·L<sup>-1</sup>), lower charge loss, no memory effect, prolonged service-life and higher  
43 number of charge/discharge cycles [5].

44 Further, the global market of lithium ion batteries is currently growing, being expected that in  
45 2022, the market value will reach \$ 46.21 billion, with an annual growth rate of 10.8% [6].

46 The first commercial lithium ion battery entered the market in 1991 by Sony, with the  
 47 fundamental contribution of John Goodenough, in the development of  $\text{LiCoO}_2$  as active material for  
 48 the cathode [7].

49 The main components of a battery are the anode, the cathode and the separator, which are  
 50 represented in Figure 1, together with the working principle of a lithium ion battery.  
 51



52 **Figure 1** - Schematic representation of a lithium ion battery and its working operation.

53

54 During the discharge process of the battery, the cathode acts as an oxidizing element, receiving  
 55 electrons from the external electric circuit and being reduced. The anode is the reducing element,  
 56 releasing electrons to the external electrical circuit, being oxidized during the electrochemical reaction  
 57 [8].

58

## 59 2. Battery separator: function, characteristics and types

60 Separators play a key role in the operation of electrochemical devices. The main purpose of the  
 61 separator membranes is to separate the cathode from the anode, avoiding the occurrence of short  
 62 circuits and controlling the mobility of lithium ions between electrodes. The performance of a  
 63 separator in a lithium ion battery is determined by some requirements such as porosity, chemical and  
 64 thermal stability, electrical insulator, wettability, dimensional stability and resistance to degradation  
 65 by chemical reagents and electrolytes (Figure 2) [9]. Figure 2 shows the ideal values for the main  
 66 requirements of a separator membrane.



Figure 2 – Ideal values for the main requirements of a separator membrane.

There are different types of separators, but the most widely used consist on a polymer matrix embedded by the electrolyte solution, i.e., a liquid electrolyte where salts are dissolved in solvents, water or organic molecules. The main types of separators are shown in Table 1 [10].

Table 1 - Types and characteristics of different separators adapted from [10].

Separator	Characteristics	Typical materials
Microporous	Operates at low temperatures (<100°C); Pore size = 50-100 Å	Nonwoven fibers (cotton, nylon, polyester, glass), polymers (PP, PE, PVC, PTFE), rubber, asbestos, wood
Nonwoven	Resistance to degradation by electrolytes; Thickness>25 µm; Pore size = 1-100 µm	Polyolefins (PE, PP, PA, PTFE; PVDF; PVC
Ion exchange membrane	High chemical resistance; Impervious to electrolytes, Pore size < 20 Å	PE, PP, Teflon-based films
Supported liquid membrane	Solid matrix with a liquid phase; Insolubility in electrolyte; High chemical stability	PP, PSU, PTFE, CA

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Polymer electrolyte	Simultaneously separator and electrolyte; High chemical and mechanical integrity;	Polyethers, PEO, PPO; Lithium salts
Solid ion conductor	Simultaneously separator and electrolyte	

75

76 The most commonly used materials as matrix for lithium ion battery separators are polymers,  
 77 or polymer composites. Some of the most used polymers are poly(propylene) (PP), poly(ethylene)  
 78 (PE), poly(vinylidene fluoride) (PVDF) and its copolymers, poly(ethylene oxide) (PEO), and  
 79 poly(acrylonitrile) (PAN) [11]. Some separators are developed by blending two different polymers to  
 80 improve the characteristics of the membrane. In some cases, nanoparticles are added to the matrix as  
 81 fillers to increase its mechanical stability or ionic conductivity. In composites separators, the most  
 82 widely used fillers are oxide ceramics (ZrO<sub>2</sub> [12,13], Al<sub>2</sub>O<sub>3</sub> [14,15], SiO<sub>2</sub> [16,17]), carbonaceous fillers  
 83 (graphene [18], carbon black [19], carbon nanofiber [20]) and ionic liquids [21], among others.

84 The solvents must attend some requirements to ensure proper battery operation. The properties  
 85 of a good solvent are high dielectric constant, low viscosity, high chemical stability and to be liquid  
 86 in a wide temperature range. For this application, solvents of ethylene carbonate (EC), propylene  
 87 carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate  
 88 (EMC) are the most commonly used [11].

89

### 90 3. Poly(vinylidene fluoride) and its copolymers

91 Considering the different polymer matrices used for battery separators, PVDF and its  
 92 copolymers (poly(vinylidene fluoride-co-trifluoroethylene), PVDF-TrFE, poly(vinylidene fluoride-  
 93 co-hexafluoropropylene), PVDF-HFP, and poly(vinylidene fluoride  
 94 co-chlorotrifluoroethylene), PVDF-CTFE) show exceptional properties and characteristics for the  
 95 development of battery separators, highlighting high polarity, excellent thermal and mechanical  
 96 properties, wettability by organic solvents, being chemically inert and stable in the cathodic  
 97 environment and tailorable porosity through binary and ternary solvent/non-solvent systems [22,23].  
 98 The main properties of these polymers are presented in table 2 [11].

99 PVDF and its copolymers are partially fluorinated semi-crystalline polymers where the  
 100 amorphous phase is located between the crystalline lamellae arranged in spherulites. It can crystallize  
 101 in different crystalline phase depending on the temperature and processing conditions [24,25]. In  
 102 relation to the crystalline phases of PVDF and its copolymers, the most important phases are the  $\beta$ -  
 103 phase, since it presents ferroelectric, piezoelectric and pyroelectric properties, and the  $\alpha$ -phase, which  
 104 is the most stable thermodynamically, when material is obtained directly from the melt [24]. As  
 105 illustrated in table 2, PVDF and its polymers are characterized by excellent mechanical properties,  
 106 good thermal stability up to 100°C and a high dielectric constant which is essential for assisting  
 107 ionization of lithium salts.

108

109 **Table 2** – Main properties of PVDF and its copolymers [26-28].

Polymer	Melting temp. / °C	Degree of Crystallinity / %	Young modulus / MPa	Dielectric constant
PVDF	~170	40-60	1500-3000	6-12
PVDF-TrFE	~120	20-30	1600-2200	18
PVDF-HFP	130-140	15-35	500-1000	11
PVDF-CTFE	~165	15-25	155-200	13

110

111 PVDF copolymers have drawn increasing attention for battery separator due that the addition  
 112 of another monomers to the VDF blocks increase the fluorine content and decrease the degree of  
 113 crystallinity (table 2), which is particularly relevant once the uptake of the electrode solution occurs  
 114 in the amorphous region through a swelling process for accommodating the electrolyte and, as a  
 115 result, increasing the ionic conductivity [29]. The recent literature on PVDF and its battery separator  
 116 copolymers is structured into four sections dedicated to single polymers, surface modification,  
 117 composites and polymer blends, respectively.

118 The main achievement is PVDF and co-polymers as battery separators were thoroughly  
 119 reviewed in [11]. Since that, important contributions have been achieved, which are the subject of the  
 120 present review.

121

### 122 3.1. Single polymer and co-polymers

123 As already mentioned, one of the main characteristics of PVDF and its co-polymers is their high  
 124 dielectric permittivity, providing large affinity with polar electrolytes when compared to other  
 125 polymers [11]. The main characteristics of the developed PVDF and copolymers membranes are  
 126 shown in Table 3.

127

128 **Table 3** - Separator membranes based on PVDF and co-polymers, indicating also the main properties,  
 129 and the main goal/ achievement of the investigation.

Materials	Electrolyte solution	Porosity and uptake (%)	Conductivity (S·cm <sup>-1</sup> ) and capacity (mAh·g <sup>-1</sup> )	Main goal/achievement	Ref
PVDF	1 M (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> CH <sub>3</sub> NBF <sub>4</sub> + AN	- / -	- / -	Study of multistep electrospinning technique on the fabrication of PVDF composite membranes; High specific power.	[30]
PVDF	1 M LiPF <sub>6</sub> in EC:DEC (1:1, wt:wt)	- / 816	6.83×10 <sup>-4</sup> / 101.1 (0.5C)	Performance comparison with a PVDF-PDA separator; Enhanced cycling performance. Analysis of the migration mechanism of cation and anions	[31]
PVDF	1 M LiPF <sub>6</sub> in EC:DEC (1:1, v/v)	7 / -	- / -	trough the separator; The separator allows controlling structural stability and ion mobility.	[32]

PVDF	1 M LiPF <sub>6</sub> in EC/DMC/EMCC (1/1/1, w/w/w)	- / -	- / 95 (0.2C)	Production of a PVDF membrane; Good capacity retention.	[33]
PVDF	1 M TEABF <sub>4</sub> in AN/PC and 1 M LiPF <sub>6</sub> in EC/DEC	80 / -	1.8×10 <sup>-2</sup> (25 °C) / -	Manufacturing of a PVDF separator; Favorable mechanical properties.	[34]
PVDF	1 M LiBF <sub>4</sub> in EC/DMC (50:50 wt. %)	- / -	4.17×10 <sup>-3</sup> (20 °C) / -	Comparison of PVDF membranes performance with Nafigate separators.	[35]
PVDF	1 M LiPF <sub>6</sub> in EC/DMC/DEC (1:1:1)	78.9 / 427	1.72×10 <sup>-3</sup> / 164.3 (C/5)	Synthesis of dual asymmetric structure separators; Improved electrolyte uptake and ionic conductivity.	[36]
PVDF	1 M LiPF <sub>6</sub> in EC/DMC/DEC (1:1:1)	- / -	- / 447.36 (0.3C)	Production of a solid state SCPC with a PVDF separator; High storage capacity and stability.	[37]
PVDF	-	- / -	- / -	Assembly of a PVDF separator for air-cathode as application in microbial fuel cells; Improved electricity generation.	[38]
PVDF	PVA/H <sub>2</sub> SO <sub>4</sub>	- / -	- / -	Production of a PVDF separator for piezoelectric supercapacitors; High mechanical strength and elevated capacitance.	[39]
PVDF	1 M NaClO <sub>4</sub> in EC/DEC (1:1)	81 / 34	7.38×10 <sup>-4</sup> (29 °C) / 153	Production of an electroactive electrospun PVDF separator for sodium ion batteries.	[40]

PVDF	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	70 / 66	1.5×10 <sup>-3</sup> / 102 (2C)	Study of the effect of different PVDF copolymers as lithium ion battery separator.	[41]
PVDF-TrFE	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	72 / 84	1.1×10 <sup>-3</sup> / 118 (2C)		
PVDF-HFP	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	56 / 79	1.3×10 <sup>-1</sup> / 107 (2C)		
PVDF-CTFE	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	59 / 80	1.5×10 <sup>-3</sup> / 85 (2C)	Demonstration of the relevance of β-phase content. Preparation of PVDF separators using a green solvent and ionic liquid as electrolyte.	[9]
PVDF	[C <sub>2</sub> mim][NTf <sub>2</sub> ]	20 / 98	2.3×10 <sup>-4</sup> (25 °C) / 74.6 (C/5)		
PVDF-HFP	LiTFSI	48 / 248	5.2×10 <sup>-5</sup> (20 °C) / -	Application of disiloxane-based electrolytes on PVDF-HFP for the production of gel electrolyte separators; Good thermal and mechanical stability. Production of ionic liquid gel polymer electrolytes; High ionic conductivity.	[42]
PVDF-HFP	LiNfO/BMIImNfO	- / -	2.61×10 <sup>-2</sup> / (100 °C) 138.1 (C/4)	Evaluation of the performance of PVDF-HFP, as a single polymer membrane.	[43]
PVDF-HFP	1 M LiPF <sub>6</sub> in EC/DMC (1:2)	70 / 247	3.2×10 <sup>-3</sup> (25 °C) / -	Understanding on the way to avoid the formation of beads in the nanofibers of PVDF-HFP; Good electrolyte uptake.	[44]
PVDF-HFP	1 M LiPF <sub>6</sub> in EC:DMC (1:1)	78 / 86.2	1.03×10 <sup>-3</sup> / 145 (0.2C)	Development of a PVDF-HFP gel polymer electrolyte membrane with honeycomb type porous structure;	[45]

PVDF-HFP	1 M LiPF <sub>6</sub> in EC/DEC/EMC (1:1:1)	- / -	- / -	Excellent electrochemical performance. Production of separators with controlled pore structure; Improved rates and cycling performances. Preparation of a nanofiber-coated composite separator by electrospinning; High discharge capacity and good cycling stability.	[46]
PVDF-CTFE	1 M LiPF <sub>6</sub> in EC:DMC:EMC (1:1:1, v:v)	74 / -	7.51×10 <sup>-4</sup> (25 °C) / 147 (0.2C)		[47]

130

131 Table 3 shows that the electrospinning technique is widely used to produce functional  
 132 membranes. Thus, electrospun separators have been developed for PVDF-PDA [31], PVDF-HFP  
 133 [44] and PVDF-CTFE [47].

134 For the PVDF-CTFE membrane, the cell assembly considered for the battery performance tests  
 135 is represented in Figure 3.

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137 **Membrane preparation**

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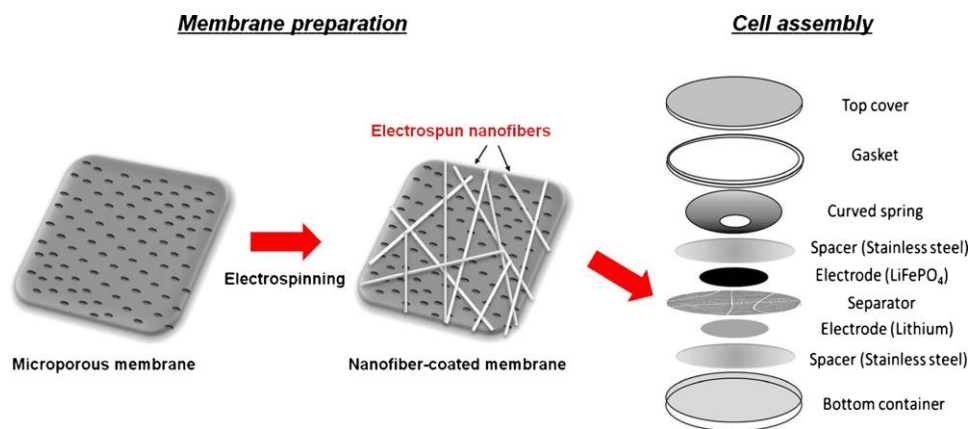
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148 **Figure 3** - Manufacturing of a testing cell based on PVDF-CTFE separators [47].

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150 For PVDF-HFP electrospun membranes it has been demonstrated that a single layer membrane  
 151 shows good porosity and uptake value but that the mechanical stability is negatively affected, the  
 152 viscosity of the solution playing an important role [44]. Also a novel gel electrolyte was developed  
 153 based on PVDF-HFP by the addition of disiloxane into the electrolyte solution [42], leading to a  
 154 thermally stable and not flammable separator, thus contributing to safer lithium ion batteries [45]. It  
 155 this sense, also ionic liquids have been used in the electrolyte solutions improving both safety and  
 156 ionic conductivity of the membranes [43].

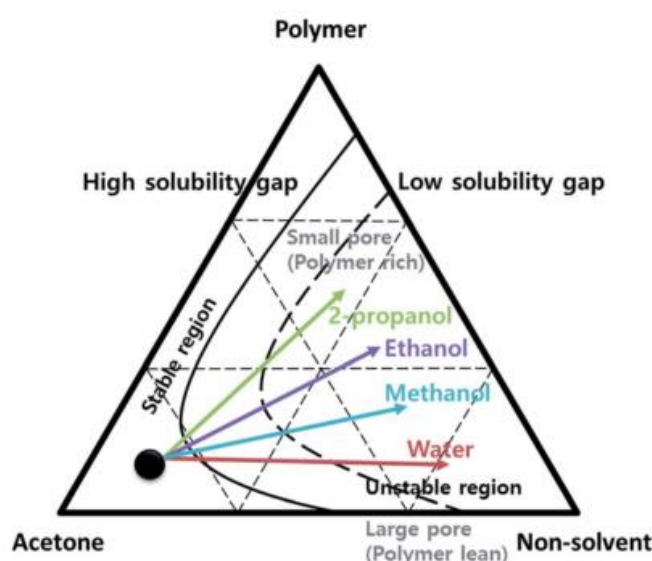
157 A multistep electrospinning technique for the production of PVDF membranes for electrical  
 158 double-layer capacitors has been proposed, allowing the manufacture of thinner and denser packed  
 159 separators [30].



160 Further, membranes have been developed based on PVDF for air-cathode in microbial fuel cells  
 161 [38] and piezo-supercapacitors [39]. Dual asymmetric PVDF separators were produced by a  
 162 thermally induced phase separation method in which the large and interconnected pores in the bulk  
 163 structure ensures an improved electrolyte uptake and ionic conductivity, while the small pores in the  
 164 surfaces prevent the loss of electrolyte and the lithium dendrite grow. It is indicated that those  
 165 separators ensure safer batteries with high discharge capacity and long cycle life [36].

166 A step further in the development of environmental friendlier PVDF separator membranes was  
 167 proposed by using DMPU as solvent for PVDF and the IL [C2mim][NTf2] as electrolyte. The use of  
 168 the IL allowed to increase the ionic conductivity and discharge capacity of the membrane, when  
 169 compared with separators using conventional electrolytes [9].

170 Porous PVDF-HFP membranes were prepared with non-solvents using the phase inversion  
 171 technique. When selecting different types of non-solvents, such as water, methanol, ethanol and  
 172 propanol, and their content in acetone, it was possible to control the size of the pores (Figure 4) [46].  
 173



174 **Figure 4** - Phase diagram of the ternary mixture -PVdF-HFP, acetone, and non-solvent-in order to control  
 175 PVdF-HFP membrane morphology [46].  
 176

177 Finally, a correlation between the  $\beta$ -phase content of the separators and the rate capability and  
 178 cyclability of the batteries was demonstrated for different PVDF co-polymers, showing the PVDF-  
 179 TrFE membrane the best battery performance for the highest  $\beta$ -phase content (100%) [41].

180 Thus, it is observed that for single (co)polymer membranes, the main focus is to tailor  
 181 morphology to obtain good uptake without mechanical deterioration and to improve the interaction  
 182 between the electrolyte solution and the separator membrane  
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## 193 3.2. Surface modification of the separator membranes

194 Typically, surface modification of the membranes is carried out to improve specific properties  
 195 such as wettability, thermal and mechanical stability. PVDF membranes have been prepared after  
 196 different surface modifications, but also have been used to modify the properties of other polymer  
 197 membranes, as presented in table 4.

198 **Table 4** - Surface modifications on PVDF and co-polymers, indicating also the main properties, goal  
 199 and achievement.

Materials	Electrolyte solution	Porosity and uptake (%)	Conductivity ( $S \cdot cm^{-1}$ ) and capacity ( $mAh \cdot g^{-1}$ )	Main goal/achievement	Ref
PVDF (plasma treated)	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	- / 1200	- / -	Study of the effect of plasma treatment in PVDF separators; Improved electrolyte uptake and mechanical properties.	[48]
PE/PVDF	1 M LiPF <sub>6</sub> in EC:EMC:DEC (1:1:1, wt:wt:wt)	- / -	$0.89 \times 10^{-3}$ (25 °C) / -	Investigation on the pore formation process in a coating layer for separators; Enhanced ionic conductivity.	[49]
PE/PVDF	1.10 M LiPF <sub>6</sub> in EC/PC/EP (3:1:6, v:v:v)	- / -	- / 1436 (0.2C)	Study of the electrochemical performance of PE/PVDF separators; Enhanced cycling performance.	[50]
PVDF/PP	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	58 / 140	$5.9 \times 10^{-4}$ / 145 (0.5C)	Coating of PVDF particles in the surface of a PP membrane; Increased electrolyte uptake.	[51]
PET/PVDF	1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1, w/w/w)	- / -	$8.36 \times 10^{-3}$ / -	Investigation of the performance of a hot-pressed PET/PVDF separator; Excellent mechanical behavior.	[52]
PVDF/HEC	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	- / 135.4	$8.8 \times 10^{-4}$ (25 °C) / 140	Preparation of a PVDF/HEC/PVDF membrane with a sandwich structure; High electrolyte uptake and ionic conductivity.	[53]
PVDF/PMMA	1 M LiTFSI in DME/DOL (1:1)	- / 294	$1.95 \times 10^{-3}$ (25 °C) / 1711.8	Preparation of a sandwiched GPE based on PVDF and PMMA for Lithium-Sulfur batteries;	[54]

PDA/PVDF	1 M LiPF <sub>6</sub> in EC:DEC (1:1, wt:wt)	- / 1160	9.62×10 <sup>-4</sup> / 104.5 (0.5C)	High discharge capacity and cycle stability. Prove that the PDA coating can be promising for manufacturing electrospun nanofiber separators; Better cycling performance and elevated power capability.	[31]
PE/(PVDF/Al <sub>2</sub> O <sub>3</sub> )	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	60.3 / 125, 314	1.14-1.23×10 <sup>-3</sup> / -	Development of a multilayer coating for separators; Improvement of the thermal stability and electrolyte wetting.	[55]
PI/PVDF/PI	1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1)	83 / 476	3.46×10 <sup>-3</sup> / 114.8 (0.5C)	Production of a electrospun sandwich type separator; Superior porosity, electrolyte uptake and ionic conductivity.	[56]
PVDF-HFP	1 M NaClO <sub>4</sub> in EC/PC (1:1)	- / -	3.8×10 <sup>-3</sup> / 291.1 (0.2C)	Development of a PVDF-HFP coated GF separator for sodium ion batteries; Good cycling performance.	[57]
PVDF-HFP	1 M LiPF <sub>6</sub> in DMC/EMC/EC (1:1:1)	53.5 / 106.9	8.34×10 <sup>-4</sup> / 131.33 (5C)	Study of the effect of the drying temperature on the performance of the separator.	[58]
PP/(PVDF-HFP/SiO <sub>2</sub> )	1 M LiPF <sub>6</sub> in DEC/EC (1/1, v/v)	- / -	7.2×10 <sup>-4</sup> / -	Analysis on the effect of a PVDF-HFP/SiO <sub>2</sub> coating layer for PP separators; Better electrolyte uptake and ionic conductivity.	[59]
PMMA/PVDF-HFP	1 M LiPF <sub>6</sub> in EC:DMC (1:1)	- / 342	1.31×10 <sup>-3</sup> / 143 (0.2C)	Investigation and analysis on a produced PMMA/PVDF-HFP electrolyte membrane; Exceptional thermal and electrochemical stability.	[60]
PVDF-HFP/PDA	LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1)	72.8 / 254	1.40×10 <sup>-3</sup> (20 °C) / -	Production of a PVDF-HFP/PDA separator by a dip-coating method.	[12]
PVDF-HFP/PET	1 M LiClO <sub>4</sub> in DMSO	- / 282	6.39×10 <sup>-3</sup> (25 °C) / 158 (0.1C)	Combination of PVDF-HFP with SiO <sub>2</sub> nanoparticles modified PET matrix; Improved thermal stability, electrolyte uptake and ionic conductivity.	[61]

PP/(AlO <sub>2</sub> /PVDF-HFP)	1 M LiPF <sub>6</sub> in EC/DEC (1/1, v/v)	- / -	7.95×10 <sup>-4</sup> / 98.6 (0.2C)	Inspection of the performance of a separator for PP membrane coating; Improved thermal stability.	[62]
γ-Al <sub>2</sub> O <sub>3</sub> /PVDF-HFP/TTT	1 M LiClO <sub>4</sub> in EC/DEC (1:1)	- / 157	1.3×10 <sup>-3</sup> / ~100 (0.5C)	Dip coating of a PE separator with a γ-Al <sub>2</sub> O <sub>3</sub> /PVDF-HFP/TTT; Increased electrolyte uptake and ionic conductivity.	[13]
PP/PE/PP /PVDF-co-CTFE	1 M LiPF <sub>6</sub> in EC/DMC/DEC (1:1:1, v:v:v)	- / -	- / -	Fabrication of PVDF-co-CTFE nanofiber coatings for improving the performance of polyolefin separators; High electrolyte uptake and good wettability.	[63]

200

201 The most commonly used surface modification is the use of PVDF and its copolymers for the  
 202 coating of other polymers such as polyethylene porous separators. Thus, the coating of PE with a  
 203 Al<sub>2</sub>O<sub>3</sub> ceramic layer and a PVDF electrospun nanofiber layer leads to enhanced electrolyte uptake,  
 204 improving capacity discharge and cycle life [55]. Similarly, PDA coating on PVDF improves  
 205 hydrophilicity, enhancing electrolyte uptake and ionic conductivity of the separator [31].

206 A typical surface modification technique, such as plasma treatment, allows to significantly  
 207 improve the electrolyte uptake of PVDF electrospun membranes [48].

208 A hot-pressing technique was proposed to develop PET/PVDF separators, with improved  
 209 mechanical behavior properties [52].

210 The preparation of a PVDF/PMMA/PVDF separator showed a great potential for its use in  
 211 Lithium-Sulfur batteries, showing high initial discharge capacity and cycle stability, reducing also  
 212 cell polarization and suppressing the shuttle effect described as the transport of soluble polysulfides  
 213 between both electrodes and the associated charge [54].

214 A composite membrane with a PVDF/HEC/PVDF sandwich structure was developed, leading  
 215 to higher electrolyte uptake, ionic conductivity and cycling performance. It is also greener and safer  
 216 because of the fire-retardant behaviour of its components [58].

217 For PVDF-HFP membranes several coatings have been applied such as ZrO<sub>2</sub> nanoparticles [64],  
 218 PP polymer [59], PMMA polymer [60], PDA layer [12] and SiO<sub>2</sub> modified PET [61], leading mainly  
 219 to improved electrolyte uptake.

220 Surface modifications are achieved also by modifying drying temperature of PVDF-HFP/PET  
 221 separators prepared by dip-coating, the drying temperature of 80°C improving cycle and rate  
 222 performances with respect to batteries with conventional PP separator [58].

223 The dip-coating of a PE separator with γ-Al<sub>2</sub>O<sub>3</sub>/PVDF-HFP/TTT, proved to increase electrolyte  
 224 uptake and ionic conductivity, when compared with the conventional membranes as it is shown in  
 225 Figure 5 where its microstructure and cycling performance are presented. The discharge performance  
 226 was also enhanced as well as the thermal resistance [13].

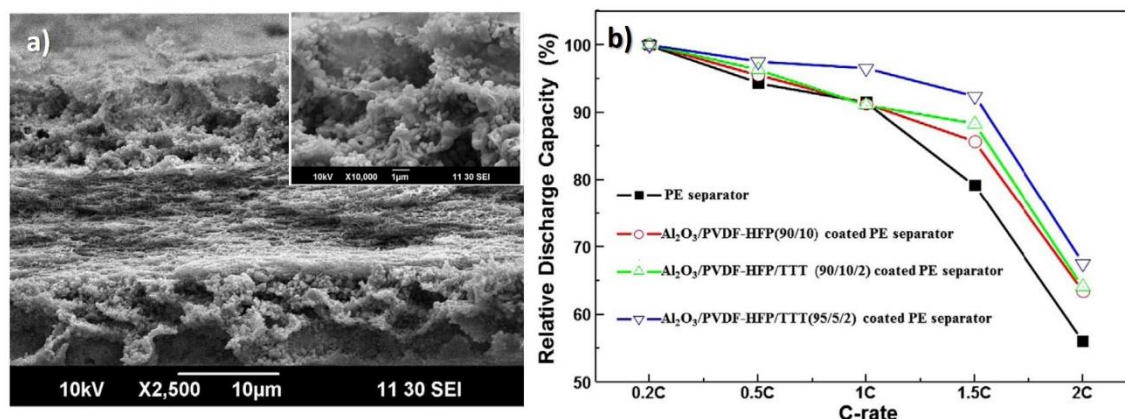


Figure 5 – a) cross-section SEM images of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/PVDF-HFP/TTT(95/5/2)- coated PE separator and b) relative discharge capacities as a function of the C-rate [13].

Basically, surface modifications are essential for improve the electrolyte wettability of the separators and is realized in several polymer membranes of single and multiple layers with many polymers (PP, PET, PMMA, etc) and filler nanoparticles.

### 3.3. Composite membranes

Polymer composites are used to improve battery performance by incorporating suitable fillers, such as oxides ceramic, zeolites and carbon nanotubes, among others, with the objective of increasing ionic conductivity, mechanical strength and thermal stability. The main properties of composite separator membranes based on PVDF and its copolymers are presented in Table 5.

Table 5 - Polymer composites based on PVDF and co-polymers with main properties, goal and achievement.

Materials	Fillers	Electrolyte solution	Porosity and uptake (%)	Conductivity (S·cm <sup>-1</sup> ) and capacity (mAh·g <sup>-1</sup> )	Main goal/achievement	Ref
PVDF	Al <sub>2</sub> O <sub>3</sub>	1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1)	55.8 / 153.5	2.23×10 <sup>-3</sup> (25 °C) / 114.2	Production of a composite PVDF/ Al <sub>2</sub> O <sub>3</sub> ; High thermal stability and ionic conductivity, low discharge capacity decay.	[15]
PVDF	Al <sub>2</sub> O <sub>3</sub>	EC/DMC (1:1)	- / 230	1.24×10 <sup>-3</sup> / 151.97 (C)	Core-shell composite nonwoven separator of PVDF-HFP@Al <sub>2</sub> O <sub>3</sub> ; high heat resistance up to 200 °C without any shrinkage,	[65]
PVDF	Al <sub>2</sub> O <sub>3</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1/1, v/v)	67 / 230	1.49×10 <sup>-3</sup> / 146.3 (0.2C)	Separator-cathode assembly with PVDF/Al <sub>2</sub> O <sub>3</sub> ; Good electrochemical performance.	[66]

PVDF	AlO(OH) nanoparticles	1 M LiPF <sub>6</sub> in EC/DEC (3:7)	- / 65	- / -	Ceramic separator based on boehmite nanoparticles; Improved safety and wettability.	[67]
PVDF	BC	1 M LiTFSI in EC/DEC (1:1)	- / -	4.2×10 <sup>-3</sup> (30 °C) / -	Preparation of GPEs based on cross-linkers; High ionic conductivity and thermal stability.	[68]
PVDF	Carbon	1 M LiTFSi and 0.1 M LiNO <sub>3</sub> in DOL/DME (1:1)	- / -	- / 827 (0.5C)	PVDF-C separator, by phase inversion technique; Superior rate performance and stability.	[69]
PVDF	CNF	1 M LiTFSI in DOL/DME (1:1)	- / 119	- / 1739.2 (C)	Production of CNF/PVDF Separators for Li-S batteries Great battery discharge capacity and cycling stability.	[20]
PVDF	Cellulose acetate/ Al(OH) <sub>3</sub>	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	68.6 / 403.9	2.85×10 <sup>-3</sup> / 151.97 (C)	Environmental friendly materials in a separator; High electrolyte uptake, ionic conductivity and cycling performance.	[70]
PVDF	DNA-CTMA	LiAsF <sub>6</sub> in EC/EMC/DMC	- / -	- / -	PVDF/DNA-CTMA membrane as solid polymer/gel electrolyte separator; Improved thermal and mechanical properties.	[71]
PVDF	LiPVAOB	1 M LiPF <sub>6</sub> in EC/DMC/EMCC (1/1/1, w/w/w)	- / 88.5	2.6×10 <sup>-4</sup> / 120 (0.2C)	Composite gel polymer electrolyte PVDF/LiPVAOB membrane; Good ionic conductivity.	[33]
PVDF	Nanoclays/PVP	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	87.4 / 553.3	- / -	Study of the influence of solvents in the separator High porosity and uptake.	[72]
PVDF	NCC	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	- / -	3.73×10 <sup>-3</sup> (25 °C) / -	Preparation of NCC-PVDF separators by phase inversion; Improved wettability and mechanical properties.	[73]
PVDF	MA groups	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	67.4 / -	1.48×10 <sup>-3</sup> / 136 (0.2C)	Study of the addition of MA groups to the PVDF structure; High ionic conductivity.	[74]

PVDF	MMT	1 M LiPF <sub>6</sub> in EC/EMC/DEC (1:1:1)	84.08 / 333	4.20×10 <sup>-3</sup> (25 °C) / 144	Effect of different contents of MMT filler in PVDF separators; High ionic conductivity and porosity.	[75]
PVDF	MOF-808	-	- / -	1.56×10 <sup>-4</sup> (65 °C) / -	Production of a MOF/polymer membrane; Good mechanical properties and durability.	[76]
PVDF	Octaphenyl-POSS	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	66.1 / 912	4.2×10 <sup>-3</sup> / 145.8 (0.5C)	Electrospun membrane with Octaphenyl-POSS particles; Increased uptake and porosity, high ionic conductivity.	[77]
PVDF	Polyether (PEGDA+PEG MEA)	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	- / 230	~1.4×10 <sup>-3</sup> (25 °C) / 93 (0.5C)	Preparation of GPEs with PVDF and polyethers.	[78]
PVDF	PMIA	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1/1/1, w/w/w)	- / -	8.1×10 <sup>-4</sup> / 135.29 (0.2C)	Composite sandwich type separator, by electrospinning; High capacity retention and good rate performance.	[79]
PVDF	P-PAEK	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	71.7 / 123.7	/ 141.6 (C/2)	Development of a P-PAEK/PVDF separator High wettability and electrolyte uptake.	[80]
PVDF	PFSA	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	- / -	1.53×10 <sup>-3</sup> / 137.9 (C)	PVDF/PFSA blend membrane; High stability and discharge capacity.	[81]
PVDF	rGO	1 M LiTFSI + 0.1 M LiNO <sub>3</sub> in DME/DOL (1:1)	71 / 380	/ 646	Double-layer PVDF/rGO membrane by electrospinning; High safety and cycling stability.	[82]
PVDF	SiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	54.1 / 279.5	- / 175.7	Synthesis of a composite separator with SiO <sub>2</sub> ; High wettability, uptake and thermal/mechanical stability.	[17]
PVDF	SiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/EMC (1:1 in volume)	70 / 370	2.6×10 <sup>-3</sup> / 132 (C)	Addition of SiO <sub>2</sub> nanoparticles on PVDF membranes; Improvement of wettability and ionic conductivity.	[83]
PVDF	SiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1/1, v/v)	85 / 646	7.47×10 <sup>-3</sup> / 159 (0.2C)	Electrospun PVDF/SiO <sub>2</sub> composite separator;	[84]

PVDF	SnO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DMC (1:1 w/w)	- / -	- / -	Excellent thermal stability and high ionic conductivity. Use of SnO <sub>2</sub> nanoparticles in a PVDF electrospun separator; Good cycling performance.	[85]
PVDF	ZnO	1 M LiPF <sub>6</sub> in EC/EMC (1:2)	- / -	- / -	Piezo-separator for integration on a self-charging power cell; Enhanced electrochemical performance.	[86]
PVDF	ZnO	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	- / -	- / -	Piezo-separator for self-charging power cells; Stable and efficient performance.	[87]
PVDF	ZrO <sub>2</sub> /PEO	1 M LiTFSI in DOL/DME (1:1)	- / 147.3	3.2×10 <sup>-4</sup> (25 °C) / 1429 (0.2C)	GPE for lithium-sulfur batteries; High discharge capacity and rate performance.	[88]
PVDF-HFP	Al <sub>2</sub> O <sub>3</sub>	0.5 M NaTf/EMITf	- / -	6.3–6.8×10 <sup>-3</sup> (25°C) / -	Introduction of Al <sub>2</sub> O <sub>3</sub> in a gel polymer electrolyte; Improved mechanical properties.	[14]
PVDF-HFP	Al <sub>2</sub> O <sub>3</sub>	1 M LiPF <sub>6</sub> in EC/DEC +2% VC	- / 372	1.3×10 <sup>-3</sup> / 155 (0.5C)	Colloidal Al <sub>2</sub> O <sub>3</sub> composite separator; enhance the mechanical strength of the PVDF-HFP separator.	[89]
PVDF-HFP	Al <sub>2</sub> O <sub>3</sub>	1 M LiPF <sub>6</sub> in EC/DMC/EMC (v/v/v = 1:1:1)	- / 420	4.7×10 <sup>-4</sup> / 109 (4C)	Production of a low cost membrane, with a simple and easy scalable manufacturing process; High electrolyte uptake and good electrochemical stability and performance.	[90]
PVDF-HFP	Al(OH) <sub>3</sub>	1.15 M LiPF <sub>6</sub> in EC/EMC (3:7, v:v)	84 / 127	10 <sup>-3</sup> / 81 (C/2)	Upgrading the battery safety operation by the addition of metal hydroxides in composite separators; Suitable electrolyte uptake.	[91]
PVDF-HFP	Al <sub>2</sub> O <sub>3</sub> /CMC	1 M LiPF <sub>6</sub> in EC/DEC/PC/EMC (2:3:1:3)	42.7 / -	9.3×10 <sup>-4</sup> (25 °C) / -	Composite separator with Al <sub>2</sub> O <sub>3</sub> /CMC; Safer and more stable separators.	[92]
PVDF-HFP	BN	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	- / -	- / 150 (0.2C)	3D separator; improved cycling stability	[93]



PVDF-HFP	CA	1 M LiPF <sub>6</sub> in EC/DMC	85 / 310	1.89×10 <sup>-3</sup> / 136 (8C)	with lower voltage polarization Porous and honeycomb-structured membrane; higher lithium-ion transference number and improved rate performance	[94]
PVDF-HFP	Clay	1 M LiPF <sub>6</sub> in EC/DEC/EMC (1:1:1, v/v/v)	- / -	1.49×10 <sup>-3</sup> / -	New technique to incorporate clay sheets in a PVDF-HFP matrix, as separator; Thermal stability and higher ionic conductivity.	[95]
PVDF-HFP	EMImNfO-LiNfO	-	- / -	3.92×10 <sup>-4</sup> / (20°C) 57 (C)	Introduction of anion based IL and lithium salt in a GPE; High thermal stability, good electrochemical properties.	[96]
PVDF-HFP	GO	1 M LiPF <sub>6</sub> in EC/DEC/EMC (1:1:1)	- / 71	1.115×10 <sup>-3</sup> (25°C) / -	Addition of GO in separators to increase thermal properties; improved electrochemical and mechanical properties.	[97]
PVDF-HFP	Graphene	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	88 / 470	3.61×10 <sup>-3</sup> / 149 (C)	PVDF-HFP/graphene GPE by NIPS; Increased porosity, uptake and ionic conductivity.	[18]
PVDF-HFP	HMSS	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	~70 / 285	2.57×10 <sup>-3</sup> (25°C) / -	Development of PVDF-HFP with HMSS separators; Increased wettability and porosity.	[98]
PVDF-HFP	Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>	1 M LiTFSI + 0.25 M LiNO <sub>3</sub> in DME/DOL (1:1)	34 / 143.9	8.8×10 <sup>-4</sup> (25 °C) / 1614	Ceramic/polymer membrane for lithium-sulfur cells; High ionic conductivity and discharge capacity.	[99]
PVDF-HFP	LiTFSI/SN	-	- / -	1.97×10 <sup>-3</sup> (20°C) / -	Production of supercapacitors with GO electrodes and GPE; High ionic conductivity.	[100]
PVDF-HFP	LLTO	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	69.8 / 497	13.897×10 <sup>-3</sup> (25°C) / 155.56	Incorporation of LLTO in a PVDF-HFP separator; Improved ionic conductivity.	[101]
PVDF-HFP	PI	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	73 / 350	1.46×10 <sup>-3</sup> / -	Evaluation of a bicomponent	[102]

PVDF-HFP	PET/SiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1/1)	60 / -	9.3×10 <sup>-4</sup> / -	electrospinning method to produce the separator, Good physical properties and improved electrochemical stability. Separator with an organized porous structure, with benefits for cell operation at high C-rates; Excellent cell performance.	[103]
PVDF-HFP	MgAl <sub>2</sub> O <sub>4</sub>	1 M LiPF <sub>6</sub> in EC:DEC (1:1, v/v)	- / -	2.80×10 <sup>-3</sup> / 140 (0.1C)	Influence of different quantities of the MgAl <sub>2</sub> O <sub>4</sub> filler in the membrane; Good ionic conductivity.	[104]
PVDF-HFP	MgAl <sub>2</sub> O <sub>4</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1:1, w/w)	60 / 81	10 <sup>-3</sup> (30 °C) / 140 (C/10)	MgAl <sub>2</sub> O <sub>4</sub> as filler of thin and flexible separator; Good thermal stability and stable cycling performance.	[105]
PVDF-HFP	Mg(OH) <sub>2</sub>	1.15 M LiPF <sub>6</sub> in EC/EMC (3:7, v:v)	64 / 115	8.08×10 <sup>-4</sup> / 105 (C/2)	Upgrading the battery safety operation by the addition of metal hydroxides in composite separators; High thermal stability and good capacity retention.	[106]
PVDF-HFP	MMT	1 M LiPF <sub>6</sub> in EC/DEC (1/1, v/v)	40 / 251	9.01×10 <sup>-4</sup> / 105 (0.1C)	Use of montmorillonite as filler; High thermal stability and stable cycling performance.	[107]
PVDF-HFP	NaA	1 M LiPF <sub>6</sub> in EC/DEC (1/1, v/v)	65 / 194	2.1×10 <sup>-3</sup> / -	Separator with incorporation of NaA zeolite; Excellent thermal stability and wettability.	[108]
PVDF-HFP	NaAlO <sub>2</sub>	0.5 M NaTf/EMITf	- / -	5.5–6.5×10 <sup>-3</sup> (25°C) / -	Introduction of NaAlO <sub>2</sub> in a gel polymer electrolyte; Improved ionic conductivity.	[14]
PVDF-HFP	m-SBA15	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	- / 82.83	3.23×10 <sup>-3</sup> / 156 (0.1C)	A PVDF-HFP composite membrane with m-SBA15 as filler; High coulomb efficiency.	[109]
PVDF-HFP	m-SBA15	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	- / 85.36	3.78×10 <sup>-3</sup> / 198.6 (0.1C)	Effect of the addition of a silica filler on a PVDF-	[110]

PVDF-HFP	OIL	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	- / 13	2×10 <sup>-3</sup> (25°C) / 141 (C)	HFP composite matrix separator; High coulomb efficiency. Synthesis of the OIL from a phenolic epoxy resin; Non-flammability, good cell performance.	[111]
PVDF-HFP	SiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DMC (1:2)	65.41 / 217	- / 124.5 (C)	Synthesis of dual asymmetric structure separators with SiO <sub>2</sub> particles; High thermal stability and electrolyte uptake.	[16]
PVDF-HFP	SiO <sub>2</sub>	1 M LiPF <sub>6</sub> in DMC/EMC/DC/VC (46.08:22.91:27.22:3.79)	26.7 / 202	8.47×10 <sup>-4</sup> (25 °C) / 154.4	Composite separator with SiO <sub>2</sub> ; Improved thermal stability and cycling performance.	[112]
PVDF-HFP	TiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1, v:v:v)	58 / 330	3.45×10 <sup>-3</sup> / 122 (10C)	Evaluation of the performance of a nanocomposite polymer membrane with addition of TiO <sub>2</sub> ; Excellent electrochemical performance.	[85]
PVDF-HFP	ZrO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1:1)	71 / 182	1.48×10 <sup>-3</sup> Scm <sup>-1</sup> (25°C) / 126.8 mAhg <sup>-1</sup> (0.5C)	Preparation of ZrO <sub>2</sub> /PVDF-HFP by the dip-coating method High wettability, ionic conductivity and thermal resistance.	[113]
PVDF-HFP	ZrO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/EMC (1:3)	- / -	2.06×10 <sup>-3</sup> (25°C) / 149.7	Improvement of the electrochemical properties of a electrospun membrane High uptake and ionic conductivity.	[114]
PVDF-HFP	ZrO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1)	87.53 / 351.2	3.2×10 <sup>-4</sup> / 646 (0.2C)	Inorganic fibers as substrates to separators; High thermal stability and good mechanical properties.	[115]
PVDF-HFP	ZrO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	60 / 160	10 <sup>-3</sup> (25°C) / 75 (C)	Development of thin and flexible ZrO <sub>2</sub> separators High porosity and thermal stability.	[116]
PVDF-HFP	ZrO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	95.7 / 481	2.695×10 <sup>-3</sup> (25 °C) / -	Incorporation of ZrO <sub>2</sub> in PVDF-HFP electrospun membranes;	[117]

PVP/PVDF	Carbon Black nanoparticles	6 M KOH	- / -	- / -	High ionic conductivity and cycling stability. Production of separators for supercapacitor applications Improved thermal and mechanical properties.	[19]
PP/PVDF-HFP	PMMA	1 M LiPF <sub>6</sub> in EC/DMC (1/1, v:v)	77.9 / 212	1.57×10 <sup>-3</sup> / 138 (0.2C)	Physical and electrochemical performances of a PP/PVDF-HFP/PMMA composite separator; Enhanced thermal stability and electrolyte uptake.	[52]
PP/PVDF-HFP	SiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1:1, v/v)	- / 290	1.76×10 <sup>-3</sup> / 150 (0.2C)	PP/PVDF-HFP separator, with the inclusion of SiO <sub>2</sub> nanoparticles; Favorable chemical stability and discharge capacity.	[118]
PI/PVDF-HFP	TiO <sub>2</sub>	1 M LiPF <sub>6</sub> in EC/DEC (1/1, v/v)	- / -	1.88×10 <sup>-3</sup> / 161 (0.5C)	Electrospun PI/PVDF-HFP membrane, with addition of TiO <sub>2</sub> nanoparticles; Excellent electrochemical properties.	[119]

244

245 Several fillers such as n-butanol [90], SiO<sub>2</sub> [103], ZnO [86] MgAl<sub>2</sub>O<sub>4</sub> [105] and MMT [107] particles  
246 were used into PVDF and its copolymers composites in order to improve thermal and mechanical  
247 stability as well as the ionic conductivity value.

248 Mechanical improvement of separators has been achieved by developing sandwich type  
249 composite separators, by a successive electrospinning method and based on PMIA [79].

250 The addition of DNA-CTMA in a PVDF matrix allows the development of flexible membranes,  
251 with interesting mechanical properties, highlighting its favorable stretch property, allowing foldable  
252 separators with elevated elasticity [71].

253 The addition of cellulose nanoparticles in the separator structure proved to increase  
254 significantly the mechanical strength of the membrane. It also improves the wettability and induces  
255 the β-phase formation in PVDF. However, the presence of NCC reduces the ionic conductivity of the  
256 membrane [73].

257 The use of SnO<sub>2</sub> nanoparticles in a PVDF electrospun separator can raise the mechanical strength  
258 of the membrane, thus leading to a more tough and durable battery [106].

259 Improved security operation for lithium ion batteries, due to suitable flammability resistance,  
260 has been addressed by developing PVDF/LiPVAOB composites membranes [33].

261 The direct application of a ceramic suspension of PVDF/Al<sub>2</sub>O<sub>3</sub> in the electrode, resulting in a  
262 separator-cathode assembly, enhances the adhesion between these structures, and improves  
263 electrochemical cell performance [66].

264 PVP/PVDF membranes incorporated with carbon black nanoparticles were produced for  
265 supercapacitor applications. The separators showed improvements in mechanical properties and  
266 dielectric constant values [19].

267 GPEs based on boron-containing cross-linker proved to have high thermal resistance,  
 268 maintaining their dimensional stability up to 150°C, due to their stable PVDF matrix. Also, the ionic  
 269 conductivity and electrochemical stability were improved when compared to commercial separators  
 270 [68].

271 Studies on the influence of solvents in nanoclay/PVDF separators showed that using DMAc as  
 272 solvent improves the porosity and electrolyte uptake of the membrane when compared with most  
 273 used solvents such as NMP or DMF. Further, the addition of PVP to the separator structure  
 274 contributes to increase the pore size and to reduce the degree of crystallinity [72].

275 The addition of a metal-organic framework to a polymer structure proved to increase the  
 276 conductivity of the produced membrane without needing electrolyte. The membrane also showed  
 277 high durability and good mechanical properties [76].

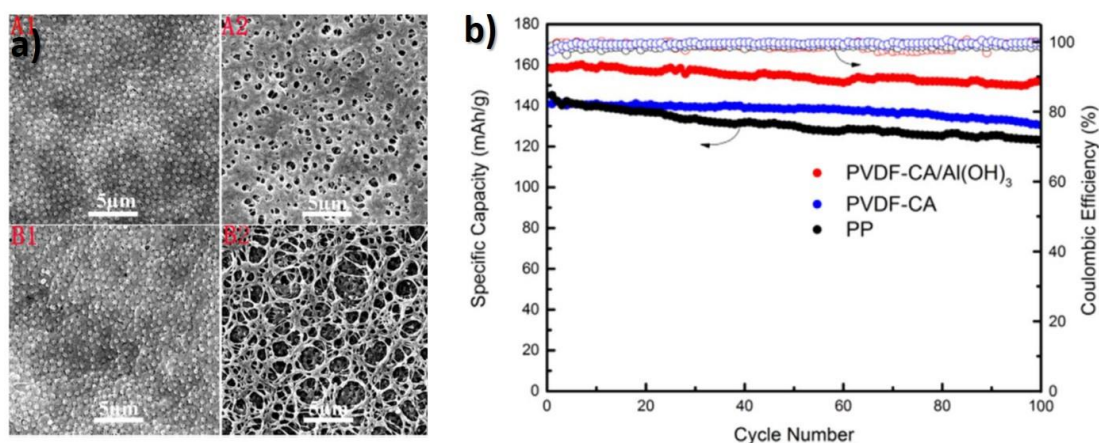
278 The dipping of PVDF nanofiber membranes into Al<sub>2</sub>O<sub>3</sub> proved to improve the thermal stability  
 279 of the produced separator and its ionic conductivity. It also shows a low discharge capacity decay,  
 280 even at high discharge rates [111].

281 A double-layer separator was prepared with PVDF and reduced graphene oxide, for lithium-  
 282 sulfur batteries. It is shown that the two layers combined properties enhance the thermal stability of  
 283 the membrane and the cycling performance of the cells [82].

284 The use of inorganic fibers as substrate for separators lead to improved thermal and mechanical  
 285 stability when compared to commercial membranes. It was also proven the enhancement of the  
 286 electrochemical performance of lithium ion cells [115].

287 CNF/PVDF composite membranes showed great performance when applied in Li-S batteries,  
 288 with enhanced cycling stability. The produced batteries retained a capacity of 768.6 mAhg<sup>-1</sup> after 200  
 289 cycles at a 0.5C rate [20]. The development of PVDF-C separators by the phase-inversion method for  
 290 Li-S batteries also leads to outstanding electrochemical performance results, associated to the  
 291 presence of the conductive carbon network in the polymer matrix [69].

292 In the search for more environmental friendly materials, a separator with PVDF, cellulose acetate  
 293 and Al(OH)<sub>3</sub> particles was developed by non-solvent induced phase separation (NIPS), the  
 294 microstructure being presented in Figure 6a). This membrane exhibited high porosity, electrolyte  
 295 uptake and ionic conductivity, as well as good cycling capacity, even at high C-rates as demonstrated  
 296 in Figure 6b) [70].



297  
 298 **Figure 6** - a) SEM images of separators microstructure and b) cycle performance of cells assembled [70].  
 299

300 PVDF was also used in the study of the potential of zeolitic imidazolate framework-4 in  
 301 separators. The prepared membranes showed high thermal stability, porosity, ionic conductivity, and  
 302 cycling performance when compared with conventional separators [120].

303 The incorporation of Meldrum's acid groups in the PVDF structure proved to increase the ionic  
 304 conductivity of the membrane, as well as the cycling performance, in particular at high C-rates [74].

305 PVDF/PFSA electrospun nanofibers allow the development of membrane with high mechanical  
306 stability and ionic conductivity with high discharge capacity and cycling stability [81].

307 A GPE membrane was developed by blending PVDF with PEO and ZrO<sub>2</sub>. This membrane  
308 showed high electrolyte uptake, excellent rate performance and discharge capacity for application in  
309 lithium-sulfur batteries [88].

310 Electrospun membranes with Octaphenyl-POSS nanoparticles showed a significant  
311 improvement in porosity and electrolyte uptake. For a ratio of 2:100 (w:w), the separator proved to  
312 have high mechanical stability, ionic conductivity and thermal stability [77].

313 A nonaflate anion-based IL and lithium salt was introduced on a GPE, allowing the development  
314 of membrane with high thermal stability and electrochemical properties. When used alongside with  
315 a LiCoO<sub>2</sub> cathode, this separator also showed good discharge capacity and capacity of retention [96].

316 The addition of MgAl<sub>2</sub>O<sub>4</sub> as filler in electrospun fibrous PVDF-HFP separator, contributes to  
317 improve the electrochemical performance, with high discharge capacity and excellent cycle life  
318 results [104].

319 The integration of m-SBA15 as filler in a polymer matrix, on the other hand, is advantageous as  
320 it decreases the degree of crystallinity of PVDF-HFP, increasing electrolyte uptake and enhancing the  
321 ionic conductivity [109,110].

322 The enhancement of the electrochemical performance has been extensively addressed by  
323 composites membranes with TiO<sub>2</sub> nanoparticles [119], and clay nanosheets [95], the later improving  
324 interfacial areal connection between the polymer structure and clay, facilitating the ion transport.

325 The NaA zeolite is considered a very interesting material for incorporation as filler, in lithium  
326 ion battery separators. It allows the formation of voids in the composite separator structure, which  
327 are filled with electrolyte, substantially increasing the ionic conductivity [108].

328 The safety operation of lithium ion batteries can be upgraded by the addition of metal  
329 hydroxides, such as Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub>, in PVDF-HFP composite separators. These metal  
330 hydroxides endow a fire-retardant behavior in the cells, due to their natural thermal stability [91].

331 Kuo et al. synthesized an oligomeric ionic liquid from a phenolic epoxy resin. By blending this  
332 ionic liquid with PVDF-HFP, a high performance, non-flammable gel polymer membrane was  
333 obtained. This membrane exhibits high ionic conductivity, although with a low liquid electrolyte  
334 uptake (<50%) [111].

335 The addition of ZrO<sub>2</sub> filler increases the porosity, ionic conductivity and thermal resistance of  
336 the PVDF membranes. The presence of polar constituents and high connected interstitial voids  
337 facilitate electrolyte absorption, increasing the ionic conductivity and the performance of the  
338 membranes [113]. When a layer of ZrO<sub>2</sub> was added between two layers of PVDF-HFP, the obtained  
339 separator presents even better electrochemical properties [114].

340 Graphene oxide nanosheets incorporated during the phase inversion of PVDF-HFP, improve  
341 electrochemical battery performances of the produced separators, as well as thermal stability and the  
342 mechanical properties of the membrane [97].

343 HMSS/PVDF-HFP composite separators with improved porosity were developed, the presence  
344 of SiO<sub>2</sub> spheres created a well-developed microporous structure, leading to higher wettability and  
345 ionic conductivity [98].

346 The incorporation of a superfine LLTO in a PVDF-HFP separator enhanced the ionic  
347 conductivity of the membrane. It was also been shown that a cell with a this type of separator presents  
348 improved discharge capacity and rate performance [101].

349 Bohemite composite separators were produced exhibiting cycling performances comparable to  
350 the conventional ones. These membranes are also safer because of the limitation to Li dendrites  
351 formation, preventing the occurrence of short circuits [67].

352 A comparative study of Al<sub>2</sub>O<sub>3</sub> and NaAlO<sub>2</sub> particles in a gel polymer electrolyte proved that  
353 NaAlO<sub>2</sub> membranes presents higher ionic conductivity than Al<sub>2</sub>O<sub>3</sub>, as well as improved mechanical  
354 properties [14].

355 ZrO<sub>2</sub> membranes with PVDF-HFP as binder were produced by solvent casting methods. These  
 356 separators present high porosity and thermal stability, but show lower mechanical strength than  
 357 commercial available membranes [116].

358 A GPE produced by thermal crosslinking of PEGDA and PEGMEA proved to be compatible  
 359 with lithium ion batteries, with a high coulombic efficiency of 94% after 100 cycles [78].

360 Liu et al. produced a GPE with PVDF-HFP and graphene via NIPS. The addition of a small  
 361 concentration of graphene (0.002 wt%) proved to significantly improve the properties of the  
 362 membrane by increasing porosity, electrolyte uptake, ionic conductivity and cycling performance,  
 363 when compared to commercial separators [18].

364 Regardless of the fillers type used, Table 5 shows that most of the work is devoted to increase  
 365 ionic conductivity and electrochemical performance compared to pure matrix. In particular, inert  
 366 oxide ceramics (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>) reduce the degree of crystallinity, enhance mechanical  
 367 properties and ionic conductivity value. Carbon materials (CNF, Graphene, rGO) improve safety and  
 368 interfacial stability between electrodes and separator membranes and lithium fillers as  
 369 Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub>, LiTSFI and LLTO increase ionic conductivity value of the separators.

370 In addition, there are other fillers types such as zeolites and clays are being intensely used for  
 371 the development of separators, allowing to improve electrochemical behavior.

372  
 373

374 *3.4. Polymer blend separator membranes*

375 Finally, another type of separator membranes are polymer blends where two different polymers  
 376 with complementary properties are used, for example one showing excellent mechanical properties  
 377 and the other with a hydrophilic character. The main properties of polymer blends based on PVDF  
 378 and its copolymer are presented in Table 6.

379

380 **Table 6** - Polymer blends based on PVDF and co-polymers with main properties, goal and  
 381 achievement.

Materials	Blends	Electrolyte solution	Porosity and uptake (%)	Conductivity (S·cm <sup>-1</sup> ) and capacity (mAh·g <sup>-1</sup> )	Main goal/achievement	Ref
PVDF	HDPE	1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1)	58 /260	2.54×10 <sup>-3</sup> Scm <sup>-1</sup> (25°C) / 156.1 mAhg <sup>-1</sup> (0.1C)	Production of a sponge like PVDF/HDPE film; High ionic conductivity and cycling performance.	[121]
PVDF	HTPB-g-MPEG	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	56 / 350	3.1×10 <sup>-3</sup> / 116 (C)	Enhance the stability of entrapped liquid electrolyte and corresponding ion conductivity.	[122]
PVDF	MC	1 M LiPF <sub>6</sub> in EC/DEM/EMC (1/1/1, w/w/w)	- / 138.6	1.5×10 <sup>-3</sup> / 110 (C)	PVDF composite separator with cellulose material;	[123]

PVDF	MEP	1 M TEABF <sub>4</sub> in AN/PC and 1 M LiPF <sub>6</sub> in EC/DEC	77 / -	1.3×10 <sup>-2</sup> / -	Excellent electrochemical performance. Manufacturing by phase inversion, with MEP as cross-linking agent; Good mechanical strength.	[34]
PVDF	NCC	1 M LiFAP in EC/DMC (1:1)	- / -	- / -	Separators with application in hybrid electric vehicles; Favorable performance at high-voltage cells.	[124]
PVDF	NCC	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	- / -	- / 108 (1C)	Separators with application in hybrid electric vehicles; Influence on high-rate cell working.	[125]
PVDF	PAN	1 M LiPF <sub>6</sub> in EC/DMC/DEC (1:1:1)	77.7 / 414.5	2.9×10 <sup>-3</sup> (25°C) / -	Improved thermal and mechanical properties; High cycling stability.	[126]
PVDF	PAN	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	- / 320	1.45×10 <sup>-3</sup> / 145.71 (0.2C)	Production of an electrospun blend membrane; High thermal and mechanical stability.	[127]
PVDF	PBA	1 M LiPF <sub>6</sub> in EC/DEC/DMC (1:1:1)	- / 120	8.1×10 <sup>-4</sup> (25°C) / 95 (0.1C)	Preparation of a cross-linked PBA/PVDF GPE; Good cycling stability.	[128]
PVDF	PDMS-g-(PPO-PEO)	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1/1/1, w/w/w)	80.1 / 512	4.5×10 <sup>-3</sup> / 120 (1C)	Porous separator; Good electrochemical stability.	[129]
PVDF	PEGDA	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	- / -	3.3×10 <sup>-3</sup> / 117 (0.1C)	Separator produced by thermal polymerization; High capacity retention.	[130]
PVDF	PEO	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	/ 530	- / -	Production of blend membranes by electrospinning; improved conductivity and uptake.	[131]



PVDF	PEO	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	- / 527	- / -	Development of electrospun membranes; High electrolyte uptake, low shutdown temperature.	[132]
PVDF	PET	-	80 / 270	- / -	Synthesis of a hybrid separator; High wettability and electrolyte uptake.	[133]
PVDF	PI	1 M LiPF <sub>6</sub> in EC/PC/DEC/VC (35.4:17.2:45.1:2.3)	- / -	1.3×10 <sup>-3</sup> / 141	Preparation of the separator by electrospinning; Improved thermal stability and mechanical properties.	[134]
PVDF	PMMA/CA	1 M LiPF <sub>6</sub> in EC/DMC (1:1, w/w)	99.1 / 323	- / -	Elevated porosity and electrolyte uptake.	[135]
PVDF	P(MMA-co-PEGMA)	1 M LiPF <sub>6</sub> in EC/EMC/DMC (1/1/1, w/w/w)	- / 372	3.01×10 <sup>-3</sup> / -	Porous separator; Improved capacity retention.	[136]
PVDF	PMMA/SiO <sub>2</sub>	-	80.1 / 293.2	1.97×10 <sup>-3</sup> / -	Evaluation of the effect of PMMA and SiO <sub>2</sub> blend on a PVDF electrospun membrane, as separator; High electrolyte uptake and improved ionic conductivity.	[137]
PVDF	PVP	1 M Et <sub>4</sub> N-BF <sub>4</sub> / PC	- / 360	1.8×10 <sup>-3</sup> (25°C) / -	Separators for supercapacitors; High uptake and power density.	[138]
PVDF	TAIC	1 M TEABF <sub>4</sub> in AN/PC and 1 M LiPF <sub>6</sub> in EC/DEC	75 / -	1.4×10 <sup>-2</sup> / -	Manufacturing of separator by phase inversion, with TAIC as cross-linking agent. High ionic conductivity.	[34]
PVDF-TrFE	PEO	1 M LiTFSI in PC	44.5 / 107	5.4×10 <sup>-4</sup> / 124 (C/5)	Research about the physical and chemical properties of a PVDF-TrFE/PEO blend	[139]

PVDF-HFP	CA	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1, v/v/v)	66.36 / 355	6.16×10 <sup>-3</sup> / 138 (0.2C)	Favorable cycling performance. Investigation of the use of CA from waste cigarette filters, in PVDF-HFP membranes; Good electrochemical performance, and excellent thermal stability.	[140]
PVDF-HFP	HDPE	-	71 / 300	2.97×10 <sup>-3</sup> (25°C) / 140.5 (C)	Preparation of the separator by non-solvent induced phase separation; High ionic conductivity.	[141]
PVDF-HFP	PANI	1 M LiPF <sub>6</sub> in EC/DMC (1:1)	83 / 270	1.96×10 <sup>-3</sup> / -	High thermal stability, electrolyte uptake and ionic conductivity	[142]
PVDF-HFP	PEG/PEGDMA	1 M LiClO <sub>4</sub> in EC/DEC (1:1, v/v)	71 / 212	1.70×10 <sup>-3</sup> / -	Investigation about a strengthened electrospun nanofiber membrane separator; High porosity and electrolyte uptake.	[143]
PVDF-HFP	PLTB	1 M LiPF <sub>6</sub> in EC/DMC (1/1, v/v)	70 / 260	1.78×10 <sup>-3</sup> / 138 (0.5C)	Excellent electrochemical performance.	[144]
PVDF-HFP	PSx-PEO3	1 M LiTFSI in EC/DMC (1:1, w:w)	- / 520	4.2×10 <sup>-4</sup> (20 °C) / 123 (C)	Production of a safe PVDF-HFP blended membrane, which can be sprayed; Elevated electrolyte uptake.	[145]
PVDF-HFP	PVSK	1 M LiTFSI + 0.25 M LiNO <sub>3</sub> in DME/DOL (1:1)	27 / -	- / 1220	Improved cycling performance.	[146]
PVDF-HFP	PVC	1 M LiPF <sub>6</sub> in EC/DMC (1:2)	62 / 230	1.58×10 <sup>-3</sup> / 125 (0.1 C)	Tri-layer polymer membrane; Good mechanical and thermal stability.	[44]
PEI/PVDF	x-PEGDA	1 M LiPF <sub>6</sub> in EC/DMC/EMC (1:1:1)	64.6 / 235.6	1.38×10 <sup>-3</sup> (25°C) / 160.3 (0.2C)	Production of x-PEGDA coated PEI/PVDF membranes; high	[147]

wettability,  
porosity and ionic  
conductivity.

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PVDF composite separators with methyl cellulose as host of gel polymer electrolyte allows the development of low cost and environmental friendlier separators with excellent mechanical, thermal and electrochemical performances [123].

384

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A trilayer porous membrane of PVDF-HFP with PVC as middle layer was developed. It was shown that a good porosity and uptake value can be achieved, though the mechanical stability is negatively affected [44].

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Cells produced with PVDF-NCC separators present a good battery performance at high C-rates, very critical to meet the minimum and maximum power assist requirements for integration in hybrid electric vehicles [124,125].

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A mechanically strengthened electrospun composite PVDF-HFP/PEG/PEGDMA separator was developed. PEG and PEGDMA allow to improve the mechanical strength of the composite membrane, which is confirmed by the existence of physical bonded structures [143].

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P(MMA-co-PEGMA) and PDMS-g-(PPO-PEO) copolymers within PVDF allow reducing the crystallinity of the PVDF matrix, and gently improve the electrolyte uptake, thus leading to an enhanced ionic conductivity [129,136].

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PLTB can be successful used in a PVDF-HFP composite separator. In comparison with a typical PP separator, it is more safe and efficient, due to its thermal and electrochemical stability. This separator is very promising in terms of security operation, because of the flame retardant characteristics [144].

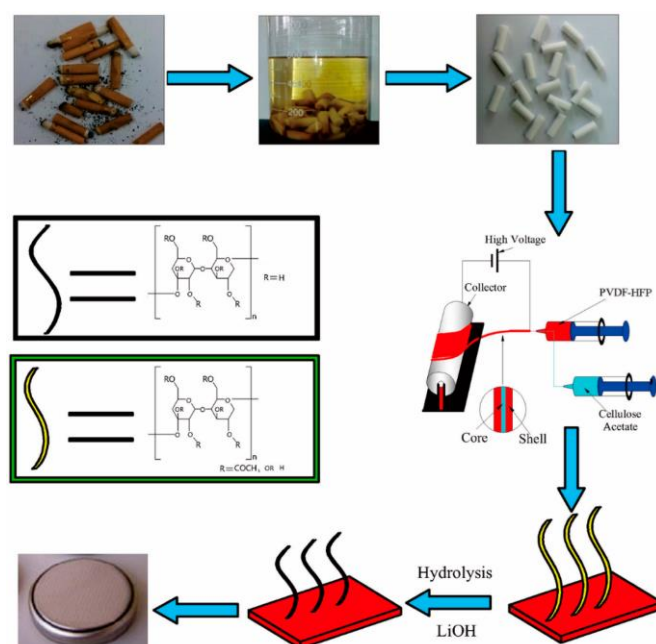
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An eco-friendly technique to recover cellulose acetate from wasted cigarette filters (Figure 7) was developed and the material can be integrated in a PVDF/CA membrane for lithium ion batteries, which presents a good performance [140].

396

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**Figure 7** - Preparation of PVDF-HFP/CA nanofiber separators for lithium ion batteries [140].

407

408 PVDF separators were manufactured by phase inversion technique, with two different cross-  
409 linking agents (TAIC and MEP) and with the application of gamma radiation. The produced  
410 membranes are characterized by good mechanical behavior and low electrical resistance [34].

411 Electrospun PVDF membranes blended with PMMA/SiO<sub>2</sub> show good porosity and elevated  
412 electrolyte uptake [137]. Blended with PI further enhance their thermal and mechanical properties,  
413 ensuring a better battery performance than commercial PE separators [134].

414 PVDF/PEO blend membranes show an increase of the ionic conductivity and electrolyte uptake  
415 when compared with PVDF membranes. The improved wettability and porosity in  $\alpha$ -PEGDA coated  
416 PEI/PVDF membranes has been also reported [147].

417 PVDF-HFP/HDPE membranes were prepared by non-solvent induced phase separation. This  
418 separator presents good cycling performance in lithium ion batteries and a high ionic conductivity  
419 [141]. Further studies showed an increased discharge capacity of these membranes, by decreasing the  
420 size of the HDPE fillers [121].

421 PVDF/PAN blend separators were produced by TIPS [126] and electrospinning [127] with  
422 improved thermal and mechanical properties. The best PVDF/PAN ratio was 90:10. Despite the lower  
423 ionic conductivity when compared with conventional separators, these membranes showed higher  
424 cycle and C-rate performance [126].

425 PVDF/PAN electrospun membrane have excellent dimensional stability even at high  
426 temperatures, high electrolyte uptake and ionic conductivity and superior discharge capacity [127].

427 The blending of PVDF and PEO in an electrospun membrane proved to increase significantly  
428 the electrolyte uptake of the separator, while decreasing the shutdown temperature [132]

429 Cross-linked PBA/PVDF GPE were prepared by soaking semi-interpenetrating polymer  
430 networks with liquid electrolyte. For a PBA/PVDF ratio of 1:0.5, the best results of electrolyte uptake,  
431 ionic conductivity and cycling stability were obtained [128].

432 A PVDF/PET hybrid separator was produced via mechanically pressing process. The obtained  
433 membrane presented high wettability and electrolyte uptake, while maintaining good thermal  
434 stability [133].

435 The introduction of PANI in a PVDF separator by the breath figure method proved to increase  
436 the electrolyte uptake and ionic conductivity of the membrane. The best results were obtained for  
437 30% of PANI, with a uniform pore structure and excellent thermal stability [142].

438 The use of PVDF-HFP/PVSK membranes in lithium-sulfur batteries has been reported. It has  
439 been proved that even small amounts of PVSK (5 wt%) increase the discharge capacity of the cell and  
440 reduce the capacity decay [146].

441 An increase of the use of natural polymers and biopolymers is observed for the preparation of  
442 PVDF and copolymer blends, considering the environmental issues. It is demonstrated in table 6 that  
443 they allow to improve mechanical properties, wettability and consequently the battery performance.  
444 In addition, the use of conductive polymers such as PANI in polymer blends has acquired special  
445 attention in recent years, considering that the electrical properties are improved without mechanical  
446 deterioration. Typically, the most commonly used PVDF and PVDF-HFP blends are developed with  
447 PAN and PEO polymers, allowing to improve thermal and mechanical stability, as well as wettability  
448 and ionic conductivity value, respectively.

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#### 455 4. Conclusions and future trends

456 In this review, the latest advances in PVDF-based battery separators for lithium-ion battery  
457 applications are presented.

458 Considering the excellent properties of PVDF and its copolymers as a separation membrane and  
459 the importance / role of the battery separator in battery applications, this review was divided into  
460 four different sections, that is, single polymers, surface modification, polymer composites and blends  
461 where for each category the improvement of the main properties of the separators -degree of porosity,  
462 uptake value, mechanical and thermal properties, ionic conductivity and cycling performance, as  
463 well as safety and environmental impact- by the different developed materials was presented.

464 In the single polymer category, PVDF and PVDF-HFP stands out as the most applied polymers  
465 produced by various processing techniques, being TIPS and electrospinning methods the most used  
466 to tailor microstructure (degree of porosity and pore size) to improve battery performance.

467 The number of research papers on surface modifications of the membranes has increased in  
468 recent years, as the surface of the polymer membrane strongly affects the uptake process. Surface  
469 modification is accomplished by coating hydrophilic polymers or plasma treatment to increase the  
470 interaction between the polymer membrane and the electrolytic solution

471 Generally, the addition of fillers increases battery performance through the improvement of  
472 ionic conductivity in polymer composites but has not yet demonstrated the best filler for PVDF and  
473 its copolymer membranes. The most commonly used fillers are inert oxide ceramics, carbon materials  
474 and lithium fillers. The most improved properties are mechanical properties, interfacial stability  
475 between electrodes and separator membranes and ionic conductivity value, respectively.

476 In relation to the polymer blends, the appearance of new blends based on natural and conductive  
477 polymers within PVDF for battery separator has been observed.

478 The blends of PVDF and its copolymers widely used are with PAN and PEO polymers, allowing  
479 to improve mechanical properties and wettability and electric properties, respectively.

480 The future trends for single polymer separators are to obtain single polymers with porosity  
481 above 50% but smaller pore size below 500 nm to prevent dendrite growth. Further, it is expected an  
482 increase in the use of ionic liquids as electrolytic solution. In relation to surface modifications, the use  
483 of poly (ionic liquids) and natural polymers as a surface modification coating of PVDF polymer  
484 membranes will be interesting, considering environmental issues.

485 With respect to polymer composites, future perspectives are related to improving the interaction  
486 between polymer matrix and fillers in order to optimize filler content without decreasing electrical  
487 properties or hindering mechanical stability. Also, the use of more than one filler with  
488 complementary properties may be the way for improving cycling performance.

489 The progress with respect to polymer blends is related to the scalability of the fabrication process  
490 and with increasing the interaction and compatibilization of the two polymers.

491 In summary, PVDF-based battery separators allow to tailor all the properties/characteristics  
492 required for a new generation of separator membranes for lithium-ion batteries with high power and  
493 excellent cycling performance.

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## 501 List of symbols and abbreviations

$(C_2H_5)_3CH_3NBF_4$ [C2mim][NTf2]	Triethylmethylammonium Tetrafluoroborate 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
Al(OH) <sub>3</sub>	Aluminum Hydroxide
Al <sub>2</sub> O <sub>3</sub>	Aluminum Oxide
AlO(OH)	Bohemite
AN	Acetonitrile
BC	Boron-containing cross-linker
CA	Cellulose acetate
CMC	carboxymethyl cellulose
CNF	Carbon nanofiber
DEC	Diethyl Carbonate
DEM	Diethoxymethane
DMAc	Dimethyl acetamide
DMC	Dimethyl Carbonate
DME	1,2-dimethoxyethane
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DNA-CTMA	Deoxyribonucleic acid- cetyltrimethylammonium
DOL	1,3-dioxolane
EC	Ethylene Carbonate
EMC	Ethyl Methyl Carbonate
EMImNfO-LiNfO	1-ethyl-3- methylimidazolium nonafluoro-1- butanesulfonate/ lithium nonafluoro-1- butanesulfonate
EMITf	1-ethyl 3-methyl imidazolium trifluoromethane sulfonate
EMITFSI	1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl) imide
EP	Ethyl Propionate
Et <sub>4</sub> N-BF <sub>4</sub>	Tetraethylammonium tetrafluoroboratein
GF	Glass fiber
GO	Graphene oxides
GPE	Gel polymer electrolyte
H <sub>2</sub> SO <sub>4</sub>	Sulfuric Acid
HDPE	High density polyethylene
HEC	Hydroxyethyl cellulose
HMSS	Hollow mesoporous silica spheres
HTPB-g-MPEG	Hydroxyl-terminated polybutadiene grafted methoxyl polyethylene glycol
KOH	Potassium hydroxide
LiClO <sub>4</sub>	Lithium Perchlorate
LiCoO <sub>2</sub>	Lithium cobalt oxide
LiFAP	Lithium Tris(pentafluoroethane)- trifluorophosphate
LiNfO/BMImNfO	Lithium nonafluorobutanesulfonate/1-butyl-3- me-thylimidazolium nonafluorobutanesulfonate
LiNO <sub>3</sub>	Lithium Nitrate
LiPF <sub>6</sub>	Lithium Hexafluorophosphate
LiPVAOB	Lithium Polyvinyl Alcohol Oxalate Borate
Li-S	Lithium-sulfur
LiTFSI	lithium bis(trifluoromethanesulfonyl) imide

LLTO	Li <sub>0.33</sub> La <sub>0.557</sub> TiO <sub>3</sub>
MA	Meldrum's acid
MC	Methyl Cellulose
MEP	Ethylene Oxide-propylene Oxide
Mg(OH) <sub>2</sub>	Magnesium Hydroxide
MgAl <sub>2</sub> O <sub>4</sub>	Magnesium Aluminate
MMT	Montmorillonite
MOF-808	Zirconium (IV) metal-organic framework
m-SBA 15	Mesoporous Silica
NaA	NaA Zeolite
NaClO <sub>4</sub>	Sodium Perchlorate
NaTf	Sodium trifluoromethane sulfonate
NCC	Nanocrystalline Cellulose
NIPS	Non-solvent induced phase separation
NMP	N-methyl-2-pyrrolidone
OIL	Oligomeric Ionic Liquid (Bromide Bis(tri-fluoromethane)sulfonimide)
P(MMA-co-PEGMA)	Poly(methyl methacrylate-co-poly(ethylene glycol) methacrylate)
PAN	Polyacrylonitrile
PANI	Polyaniline
PBA	Poly(butyl acrylate)
PC	Propylene Carbonate
PDA	Polydopamine
PDMS-g-(PPO-PEO)	Poly(dimethylsiloxane) graft poly(propylene oxide)-block-poly(ethylene oxide)
PE	Polyethylene
PEG	Polyethylene glycol
PEGDA	Poly(ethylene glycol)diacrylate
PEGDMA	Polyethylene glycol dimethacrylate
PEGMEA	Poly(ethylene glycol) methyl ether acrylate
PEI	Polyetherimide
PEO	Polyethylene Oxide
PET	Polyethylene terephthalate
PFSA	Perfluorosulfonic acid
PI	Polyimide
PLTB	Polimeric Lithium Tartaric Acid Borate
PMIA	Poly(m-phenylene isophthalamide)
PMMA	Polymethyl methacrylate
POSS	Polyhedral oligomeric silsesquioxane
PP	Polypropylene
P-PAEK	Phenolphthaleine-poly(aryl ether ketone)
PS <sub>x</sub> -PEO <sub>3</sub>	Polysiloxane-comb-propyl(triethylene oxide)
PSU	Poly(sulfone)
PTFE	Poly(tetrafluoroethylene)
PVA	Polyvinyl Alcohol
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
PVDF-co-CTFE	Polyvinylidene fluoride-co-chlorotrifluoroethylene
PVDF-co-HFP	Poly(vinylidene fluoride -co-hexafluoropropylene)
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropene)
	Poly(vinylidene fluoride-hexafluoropropylene)

PVDF-PE	Polyvinylidene difluoride-coated polyethylene
PVDF-TrFE	Poly(vinylidene fluoride-trifluoroethylene)
PVP	Polyvinylpyrrolidone
PVSK	Polyvinylsulfate potassium salt
rGO	Reduced graphene oxide
SCPC	Self-charging power cell
SiO <sub>2</sub>	Silicon Dioxide
SN	Succinonitrile
SnO <sub>2</sub>	Tin Oxide
TAIC	Triallyl Isocyanurate
TEABF <sub>4</sub>	Tetraethyl Ammonium Tetrafluoroborate
TiO <sub>2</sub>	Titanium Dioxide
TIPS	Thermal induced phase separation
TTT	1,3,5-triallyl- 1,3,5-triazine-2,4,6(1 H,3 H,5 H)-trione
VC	Vinylene carbonate
x-PEGDA	x-polyethylene glycol diacrylate
ZnO	Zinc Oxide
ZrO <sub>2</sub>	Zirconium Dioxide

502

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