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

João C. Barbosa¹, José P. Dias¹, Senentxu Lanceros-Méndez²,³*, and Carlos M. Costa¹

¹ Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal; joaocpbarbosa@live.com.pt (J.C.B.);
jmpedrodias@gmail.com (J.P.D.), cmscosta@fisica.uminho.pt (C.M.C.)
² BCMaterials, Basque Center Centre for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain;
³ IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain
⁴ Centro de Química, Universidade do Minho, 4710-057 Braga, Portugal

* Correspondence: senentxu.lanceros@bcmaterials.net; Tel.: +34-94-612-8811

Received: date; Accepted: date; Published: date

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

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

1. Introduction

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

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

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

Further, the global market of lithium ion batteries is currently growing, being expected that in 2022, the market value will reach $46.21 billion, with an annual growth rate of 10.8% [6].
The first commercial lithium ion battery entered the market in 1991 by Sony, with the fundamental contribution of John Goodenough, in the development of LiCoO2 as active material for the cathode [7].

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

![Figure 1 - Schematic representation of a lithium ion battery and its working operation.](image)

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

2. Battery separator: function, characteristics and types

Separators play a key role in the operation of electrochemical devices. The main purpose of the separator membranes is to separate the cathode from the anode, avoiding the occurrence of short circuits and controlling the mobility of lithium ions between electrodes. The performance of a separator in a lithium ion battery is determined by some requirements such as porosity, chemical and thermal stability, electrical insulator, wettability, dimensional stability and resistance to degradation by chemical reagents and electrolytes (Figure 2) [9]. Figure 2 shows the 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                                                               |
The most commonly used materials as matrix for lithium ion battery separators are polymers, or polymer composites. Some of the most used polymers are poly(propylene) (PP), poly(ethylene) (PE), poly(vinylidene fluoride) (PVDF) and its copolymers, poly(ethylene oxide) (PEO), and poly(acrylonitrile) (PAN) [11]. Some separators are developed by blending two different polymers to improve the characteristics of the membrane. In some cases, nanoparticles are added to the matrix as fillers to increase its mechanical stability or ionic conductivity. In composites separators, the most widely used fillers are oxide ceramics (ZrO$_2$ [12,13], Al$_2$O$_3$ [14,15], SiO$_2$ [16,17]), carbonaceous fillers (graphene [18], carbon black [19], carbon nanofiber [20]) and ionic liquids [21], among others.

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

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

Considering the different polymer matrices used for battery separators, PVDF and its copolymers (poly(vinylidene fluoride-co-trifluoroethylene), PVDF-TrFE, poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP, and poly(vinylidene fluoride-co-chlorotrifluoroethylene), PVDF-CTFE) show exceptional properties and characteristics for the development of battery separators, highlighting high polarity, excellent thermal and mechanical properties, wettability by organic solvents, being chemically inert and stable in the cathodic environment and tailorable porosity through binary and ternary solvent/non-solvent systems [22,23].

The main properties of these polymers are presented in table 2 [11].

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

| Polymer electrolyte | Simultaneously separator and electrolyte; High chemical and mechanical integrity; |
|---------------------|----------------------------------------------------------------------------------|
| Solid ion conductor | Simultaneously separator and electrolyte |

| 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                 |

| Table 2 – Main properties of PVDF and its copolymers [26-28]. |
PVDF copolymers have drawn increasing attention for battery separator due that the addition of another monomers to the VDF blocks increase the fluorine content and decrease the degree of crystallinity (table 2), which is particularly relevant once the uptake of the electrode solution occurs in the amorphous region through a swelling process for accommodating the electrolyte and, as a result, increasing the ionic conductivity [29]. The recent literature on PVDF and its battery separator copolymers is structured into four sections dedicated to single polymers, surface modification, composites and polymer blends, respectively.

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

### 3.1. Single polymer and co-polymers

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

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

| Materials | Electrolyte solution | Porosity and uptake (%) | Conductivity (S·cm\(^{-1}\)) and capacity (mAh·g\(^{-1}\)) | Main goal/achievement | Ref |
|-----------|----------------------|-------------------------|--------------------------------------------------------|-----------------------|-----|
| PVDF      | 1 M (C\(_2\)H\(_5\))CH\(_3\)NBF\(_4\) + AN | -/-                     | -/-                                                   | Study of multistep electrospinning technique on the fabrication of PVDF composite membranes; High specific power. Performance comparison with a PVDF-PDA separator; Enhanced cycling performance. Analysis of the migration mechanism of cation and anions through the separator; The separator allows controlling structural stability and ion mobility. | [30] |
| PVDF      | 1 M LiPF\(_6\) in EC:DEC (1:1, wt:wt) | -/816                   | 6.83×10\(^{-4}\)/101.1 (0.5C)                          | Performance comparison with a PVDF-PDA separator; Enhanced cycling performance. Analysis of the migration mechanism of cation and anions through the separator; The separator allows controlling structural stability and ion mobility. | [31] |
| PVDF      | 1 M LiPF\(_6\) in EC:DEC (1:1, v/v) | 7/-                     | -/-                                                   | Performance comparison with a PVDF-PDA separator; Enhanced cycling performance. Analysis of the migration mechanism of cation and anions through the separator; The separator allows controlling structural stability and ion mobility. | [32] |
| PVDF | 1 M LiPF$_6$ in EC/DMC/EMCC (1/1/1, w/w/w) | - / - | - / 95 (0.2C) | Production of a PVDF membrane; Good capacity retention. |
| PVDF | 1 M TEABF$_4$ in AN/PC and 1 M LiPF$_6$ in EC/DEC | 80 / - | 1.8x10$^2$ (25°C) / - | Manufacturing of a PVDF separator; Favorable mechanical properties. |
| PVDF | 1 M LiBF$_4$ in EC/DMC (50:50 wt. %) | - / - | 4.17x10$^3$ (20°C) / - | Comparison of PVDF membranes performance with Nafigate separators. |
| PVDF | 1 M LiPF$_6$ in EC/DMC/DEC (1:1:1) | 78.9 / 427 | 1.72x10$^3$ / 164.3 (C/5) | Synthesis of dual asymmetric structure separators; Improved electrolyte uptake and ionic conductivity. |
| PVDF | 1 M LiPF$_6$ 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. |
| PVDF | - | - / - | - / - | Assembly of a PVDF separator for air-cathode as application in microbial fuel cells; Improved electricity generation. |
| PVDF | PVA/H$_2$SO$_4$ | - / - | - / - | Production of an electroactive electrospun PVDF separator for sodium ion batteries. |
| PVDF | 1 M NaClO$_4$ in EC/DEC (1:1) | 81 / 34 | 7.38x10$^4$ (29°C) / 153 | Production of a PVDF separator for piezoelectric supercapacitors; High mechanical strength and elevated capacitance. |
PVDF 1 M LiPF$_6$ in EC/DEC (1:1) 70 / 66 1.5×10$^{-3}$ / 102 (2C) Study of the effect of different PVDF copolymers as lithium ion battery separator. Demonstration of the relevance of β-phase content. Preparation of PVDF separators using a green solvent and ionic liquid as electrolyte. 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. Evaluation of the performance of PVDF-HFP, as a single polymer membrane. Understanding on the way to avoid the formation of beads in the nanofibers of PVDF-HFP; Good electrolyte uptake. Development of a PVDF-HFP gel polymer electrolyte membrane with honeycomb type porous structure; 

PVDF-TrFE 1 M LiPF$_6$ in EC/DEC (1:1) 72 / 84 1.1×10$^{-3}$ / 118 (2C)

PVDF-HFP 1 M LiPF$_6$ in EC/DEC (1:1) 56 / 79 1.3×10$^{-1}$ / 107 (2C)

PVDF-CTFE 1 M LiPF$_6$ in EC/DEC (1:1) 59 / 80 1.5×10$^{-3}$ / 85 (2C)

PVDF [C$_m$im][NTf$_2$] 20 / 98 2.3×10$^4$ (25 °C) / 74.6 (C/5)

PVDF-HFP LiTFSI 48 / 248 5.2×10$^{-5}$ (20 °C) / -

PVDF-HFP LiNfO/BMImNfO - / - 2.61×10$^{-2}$ / (100 °C) 138.1 (C/4)

PVDF-HFP 1 M LiPF$_6$ in EC/DMC (1:2) 70 / 247 3.2×10$^{-3}$ (25 °C) / -

PVDF-HFP 1 M LiPF$_6$ in EC:DMC (1:1) 78 / 86.2 1.03×10$^{-3}$ / 145 (0.2C)
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.

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

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

![Figure 3](image_url) - Manufacturing of a testing cell based on PVDF-CTFE separators [47].

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

A multistep electrospinning technique for the production of PVDF membranes for electrical double-layer capacitors has been proposed, allowing the manufacture of thinner and denser packed separators [30].
Further, membranes have been developed based on PVDF for air-cathode in microbial fuel cells [38] and piezo-supercapacitors [39]. Dual asymmetric PVDF separators were produced by a thermally induced phase separation method in which the large and interconnected pores in the bulk structure ensures an improved electrolyte uptake and ionic conductivity, while the small pores in the surfaces prevent the loss of electrolyte and the lithium dendrite grow. It is indicated that those separators ensure safer batteries with high discharge capacity and long cycle life [36].

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

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

![Phase diagram of the ternary mixture -PVdF–HFP, acetone, and non-solvent- in order to control PVdF-HFP membrane morphology] (Figure 4)

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

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

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

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

| Materials           | Electrolyte solution                  | Porosity and uptake (%) | Conductivity (S·cm⁻¹) and capacity (mAh·g⁻¹) | Main goal/achievement                                                                 | Ref |
|---------------------|--------------------------------------|-------------------------|-----------------------------------------------|-------------------------------------------------------------------------------------|-----|
| PVDF (plasma treated) | 1 M LiPF₆ 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 LiPF₆ in EC:EMC:DEC (1:1:1, wt:wt:wt) | - / -                   | 0.89×10⁻³ (25 °C) / -                         | Investigation on the pore formation process in a coating layer for separators; Enhanced ionic conductivity. | [49] |
| PE/PVDF             | 1.10 M LiPF₆ 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 LiPF₆ in EC/DMC (1:1)             | 58 / 140                | 5.9×10⁻⁴ / 145 (0.5C)                         | Coating of PVDF particles in the surface of a PP membrane; Increased electrolyte uptake. | [51] |
| PET/PVDF            | 1 M LiPF₆ in EC/DEC/DMC (1:1:1, w/w/w) | - / -                   | 8.36×10⁻³ / -                                | Investigation of the performance of a hot-pressed PET/PVDF separator; Excellent mechanical behavior. | [52] |
| PVDF/HEC            | 1 M LiPF₆ in EC/DMC/EMC (1:1:1)       | - / 135.4               | 8.8×10⁻⁴ (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                 | 1.95×10⁻³ (25 °C) / 1711.8                    | Preparation of a sandwiched GPE based on PVDF and PMMA for Lithium-Sulfur batteries; | [54] |
| Membrane System | LiPF₆/EC/DEC (wt:wt) | Cycles | Cycle Efficiency | Electrolyte | Notes |
|-----------------|----------------------|--------|-----------------|-------------|-------|
| PDA/PVDF | 1 M LiPF₆ in EC:DEC (1:1, wt:wt) | - / 1160 | 9.62×10⁻⁴ / 104.5 (0.5C) | High discharge capacity and cycle stability. Prove that the PDA coating can be promising for manufacturing electrosyn nanofiber separators; Better cycling performance and elevated power capability. |
| PE/(PVDF/Al₂O₃) | 1 M LiPF₆ in EC:DEC (1:1) | 60.3 / 125, 314 | 1.14-1.23×10⁻³ / - | Development of a multilayer coating for separators; Improvement of the thermal stability and electrolyte wetting. |
| PI/PVDF/PI | 1 M LiPF₆ in EC/DEC/DMC (1:1:1) | 83 / 476 | 3.46×10⁻³ / 114.8 (0.5C) | Production of an electrosyn sandwich type separator; Superior porosity, electrolyte uptake and ionic conductivity. |
| PVDF-HFP | 1 M NaClO₄ in EC/PC (1:1) | - / - | 3.8×10⁻³ / 291.1 (0.2C) | Development of a PVDF-HFP coated GF separator for sodium ion batteries; Good cycling performance. |
| PVDF-HFP | 1 M LiPF₆ in DMC/EMC/EC (1:1:1) | 53.5 / 106.9 | 8.34×10⁻⁴ / 131.33 (5C) | Study of the effect of the drying temperature on the performance of the separator. |
| PP/(PVDF-HFP/SiO₂) | 1 M LiPF₆ in DEC/EC (1:1, v/v) | - / - | 7.2×10⁻⁴ / - | Analysis on the effect of a PVDF-HFP/SiO₂ coating layer for PP separators; Better electrolyte uptake and ionic conductivity. |
| PMMA/PVDF-HFP | 1 M LiPF₆ in EC:DMC (1:1) | - / 342 | 1.31×10⁻³ / 143 (0.2C) | Investigation and analysis on a produced PMMA/PVDF-HFP electrolyte membrane; Exceptional thermal and electrochemical stability. |
| PVDF-HFP/PDA | LiPF₆ in EC/DEC/DMC (1:1:1) | 72.8 / 254 | 1.40×10⁻³ (20 °C) / - | Production of a PVDF-HFP/PDA separator by a dip-coating method. |
| PVDF-HFP/PET | 1 M LiClO₄ in DMSO | - / 282 | 6.39×10⁻³ (25 °C) / 158 (0.1C) | Combination of PVDF-HFP with SiO₂ nanoparticles modified PET matrix; Improved thermal stability, electrolyte uptake and ionic conductivity. |
The most commonly used surface modification is the use of PVDF and its copolymers for the coating of other polymers such as polyethylene porous separators. Thus, the coating of PE with a Al2O3 ceramic layer and a PVDF electrospun nanofiber layer leads to enhanced electrolyte uptake, improving capacity discharge and cycle life [55]. Similarly, PDA coating on PVDF improves hydrophilicity, enhancing electrolyte uptake and ionic conductivity of the separator [31].

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

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

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

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

For PVDF-HFP membranes several coatings have been applied such as ZrO2 nanoparticles [64], PP polymer [59], PMMA polymer [60], PDA layer [12] and SiO2 modified PET [61], leading mainly to improved electrolyte uptake.

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

The dip-coating of a PE separator with γ-Al2O3/PVDF-HFP/TTT, proved to increase electrolyte uptake and ionic conductivity, when compared with the conventional membranes as it is shown in Figure 5 where its microstructure and cycling performance are presented. The discharge performance was also enhanced as well as the thermal resistance [13].

| Membrane | Electrolyte Composition | Performance Parameters | Remarks |
|-----------|-------------------------|------------------------|---------|
| PP/(AlO2/PVDF-HFP) | 1 M LiPF6 in EC/DEC (1/1, v/v) | 7.95×10^-4 / 98.6 (0.2C) | Inspection of the performance of a separator for PP membrane coating; Improved thermal stability. |
| γ-Al2O3/PVDF-HFP/TTT | 1 M LiClO4 in EC/DEC (1:1) | 1.3×10^-3 / -100 (0.5C) | Dip coating of a PE separator with a γ-Al2O3/PVDF-HFP/TTT; Increased electrolyte uptake and ionic conductivity. |
| PP/PE/PP/PVDF-co-CTFE | 1 M LiPF6 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. |
Figure 5 – a) cross-section SEM images of the γ-Al2O3/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⁻¹) and capacity (mAh·g⁻¹) | Main goal/achievement | Ref |
|-----------|---------|----------------------|-------------------------|-----------------------------------|-----------------------|-----|
| PVDF      | Al₂O₃   | 1 M LiPF₆ in EC/DEC/DMC (1:1:1) | 55.8 / 153.5 | 2.23×10⁻³ (25 °C) / 114.2 | Production of a composite PVDF/Al₂O₃; High thermal stability and ionic conductivity, low discharge capacity decay. | [15] |
| PVDF      | Al₂O₃   | EC/DMC (1:1)         | - / 230             | 1.24×10⁻³ / 151.97 (C)       | Core-shell composite nonwoven separator of PVDF-HFP@Al₂O₃; high heat resistance up to 200 °C without any shrinkage, | [65] |
| PVDF      | Al₂O₃   | 1 M LiPF₆ in EC/DEC (1/1, v/v) | 67 / 230           | 1.49×10⁻³ / 146.3 (0.2C)    | Separator-cathode assembly with PVDF/Al₂O₃; Good electrochemical performance. | [66] |
PVDF AIO(OH) nanoparticles 1 M LiPF6 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) -/- 4.2x10^-3 (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 LiNO3 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) -/- -/ 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)3 1 M LiPF6 in EC/DMC/EMC (1:1:1) 68.6 / 2.85x10^-3 / 403.9 / 151.97 (C) Environmental friendly materials in a separator; High electrolyte uptake, ionic conductivity and cycling performance. [70]

PVDF DNA-CTMA LiAsF6 in EC/EMC/DMC -/- -/- PVDF/DNA-CTMA membrane as solid polymer/gel electrolyte separator; Improved thermal and mechanical properties. [71]

PVDF LiPVAOB 1 M LiPF6 in EC/DMC/EMCC (1/1/1, w/w/w) / 2.6x10^-4 / 88.5 / 120 (0.2C) Composite gel polymer electrolyte PVDF/LiPVAOB membrane; Good ionic conductivity. Study of the influence of solvents in the separator High porosity and uptake. [33]

PVDF Nanoclays/PVP 1 M LiPF6 in EC/DMC (1:1) 87.4 / 553.3 -/- Good ionic conductivity. Study of the influence of solvents in the separator High porosity and uptake. [72]

PVDF NCC 1 M LiPF6 in EC/DMC (1:1) -/- 3.73x10^-3 (25 °C) / - Preparation of NCC-PVDF separators by phase inversion; Improved wettability and mechanical properties. [73]

PVDF MA groups 1 M LiPF6 in EC/DMC/EMC (1:1:1) 67.4 / 1.48x10^-3 / 136 (0.2C) Study of the addition of MA groups to the PVDF structure; High ionic conductivity. [74]
| Polymer | Filler | Electrolyte Composition | T | C | Effect |
|---------|--------|-------------------------|---|---|--------|
| PVDF   | MMT    | 1 M LiPF$_6$ in EC/EMC/DEC (1:1:1) | 84.08 | 4.20$\times$10$^{-3}$ (25°C) / 144 | Effect of different contents of MMT filler in PVDF separators; High ionic conductivity and porosity. |
| PVDF   | MOF-808| -                       | - / - | 1.56$\times$10$^{2}$ (65°C) / - | Production of a MOF/polymer membrane; Good mechanical properties and durability. |
| PVDF   | Octaphenyl-POSS | 1 M LiPF$_6$ in EC/DMC/EMC (1:1:1) | 66.1 / 912 | 4.2$\times$10$^{-3}$ / 145.8 (0.5C) | Electrospun membrane with Octaphenyl-POSS particles; Increased uptake and porosity, high ionic conductivity. |
| PVDF   | Polyether (PEGDA+PEG MEA) PMIA | 1 M LiPF$_6$ in EC/DMC/EMC (1:1:1) | - / - / 230 | -1.4$\times$10$^{-3}$ (25°C) / 93 (0.5C) | Preparation of GPEs with PVDF and polyethers. |
| PVDF   | P-PAEK | 1 M LiPF$_6$ 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. |
| PVDF   | PFSA   | 1 M LiPF$_6$ in EC/DMC/EMC (1:1:1) | - / - / - | 1.53$\times$10$^{-3}$ / 137.9 (C) | PVDF/PFSA blend membrane; High stability and discharge capacity. |
| PVDF   | rGO    | 1 M LiTFSI + 0.1 M LiNO$_3$ in DME/DOL (1:1) | 71 / 380 | / / 646 | Double-layer PVDF/rGO membrane by electrospinning; High safety and cycling stability. |
| PVDF   | SiO$_2$ | 1 M LiPF$_6$ in EC/DMC/EMC (1:1:1) | 54.1 / 279.5 | - / 175.7 | Synthesis of a composite separator with SiO$_2$; High wettability, uptake and thermal/mechanical stability. |
| PVDF   | SiO$_2$ | 1 M LiPF$_6$ in EC/EMC (1:1 in volume) | 70 / 370 | 2.6$\times$10$^{-3}$ / 132 (C) | Addition of SiO$_2$ nanoparticles on PVDF membranes; Improvement of wettability and ionic conductivity. |
| PVDF   | SiO$_2$ | 1 M LiPF$_6$ in EC/DEC (1/1, v/v) | 85 / 646 | 7.47$\times$10$^{-3}$ / 159 (0.2C) | Electrospun PVDF/SiO$_2$ composite separator; |
| Material Combination | Electrolyte | Ionic Conductivity | Thermal Stability | Other Properties |
|----------------------|-------------|--------------------|-------------------|-----------------|
| PVDF/SnO₂ | 1 M LiPF₆ in EC/DMC (1:1 w/w) | - / - | Excellent thermal stability and high ionic conductivity. | Use of SnO₂ nanoparticles in a PVDF electrospun separator; Good cycling performance. |
| PVDF/ZnO | 1 M LiPF₆ in EC/EMC (1:2) | - / - | Piezo-separator for integration on a self-charging power cell; Enhanced electrochemical performance. |
| PVDF/ZnO | 1 M LiPF₆ in EC/DEC (1:1) | - / - | Piezo-separator for self-charging power cells; Stable and efficient performance. |
| PVDF/ZrO₂/PEO | 1 M LiTFSI in DOL/DME (1:1) | - / - | GPE for lithium-sulfur batteries; High discharge capacity and rate performance. |
| PVDF-HFP/Al₂O₃ | 0.5 M NaTf/EMITf | - / - | Introduction of Al₂O₃ in a gel polymer electrolyte; Improved mechanical properties. |
| PVDF-HFP/Al₂O₃ | 1 M LiPF₆ in EC/DEC +2% VC | - / - | Colloidal Al₂O₃ composite separator; enhance the mechanical strength of the PVDF-HFP separator. |
| PVDF-HFP/Al₂O₃ | 1 M LiPF₆ in EC/DMC/EMC (v/v/v = 1:1:1) | - / - | Producing a low cost membrane, with a simple and easy scalable manufacturing process; High electrolyte uptake and good electrochemical stability and performance. |
| PVDF-HFP/Al(OH)₃ | 1.15 M LiPF₆ in EC/EMC (3:7, v:v) | 84 / 127 | Upgrading the battery safety operation by the addition of metal hydroxides in composite separators; Suitable electrolyte uptake. |
| PVDF-HFP/Al₂O₃/CMC | 1 M LiPF₆ in EC/DEC/PC/EMC (2:3:1:3) | 42.7 / - | Composite separator with Al₂O₃/CMC; Safer and more stable separators. |
| PVDF-HFP/BN | 1 M LiPF₆ in EC/DEC (1:1) | - / - | 3D separator; improved cycling stability |
Membranes 2018, 8, x FOR PEER REVIEW 17 of 41

PVDF-HFP  CA  1 M LiPF₆ in EC/DMC  85 / 310  1.89×10⁻³ / 136 (8C) with lower voltage polarization Porous and honeycomb-structured membrane; higher lithium-ion transference number and improved rate performance  

PVDF-HFP  Clay  1 M LiPF₆ in EC/DEC/EMC (1:1:1, v/v/v)  - / -  1.49×10⁻³ / - New technique to incorporate clay sheets in a PVDF-HFP matrix, as separator; Thermal stability and higher ionic conductivity.  

PVDF-HFP  EMImNiO-LiNiO  -  - / -  3.92×10⁻⁴ / (20°C) 57 (C) Introduction of anion based IL and lithium salt in a GPE; High thermal stability, good electrochemical properties.  

PVDF-HFP  GO  1 M LiPF₆ in EC/DEC/EMC (1:1:1)  - / 71  1.11×10⁻³ (25°C) / - Addiction of GO in separators to increase thermal properties; improved electrochemical and mechanical properties.  

PVDF-HFP  Graphene  1 M LiPF₆ in EC/DMC/EMC (1:1:1)  88 / 470  3.61×10⁻³ / 149 (C) PVDF-HFP/graphene GPE by NIPS; Increased porosity, uptake and ionic conductivity.  

PVDF-HFP  HMSS  1 M LiPF₆ in EC/DEC (1:1)  -70 / 285  2.57×10⁻³ (25°C) / - Development of PVDF-HFP with HMSS separators; Increased wettability and porosity.  

PVDF-HFP  Li₃Al₃Ti₇(PO₄)₆  1 M LiTFSI + 0.25 M LiNO₃ in DME/DOL (1:1)  34 / 143.9  8.8×10⁻⁴ (25 °C) / 1614 Ceramic/polymer membrane for lithium-sulfur cells; High ionic conductivity and discharge capacity.  

PVDF-HFP  LiTFSI/SN  -  - / -  1.97×10⁻³ (20°C) / - Production of supercapacitors with GO electrodes and GPE; High ionic conductivity.  

PVDF-HFP  LLTO  1 M LiPF₆ in EC/DMC/EMC (1:1:1)  69.8 / 497  13.897×10⁻³ (25°C) / 155.56 Incorporation of LLTO in a PVDF-HFP separator; Improved ionic conductivity.  

PVDF-HFP  PI  1 M LiPF₆ in EC/DMC (1:1)  73 / 350  1.46×10⁻³ / - Evaluation of a bicomponent
| Membranes \(2018, \text{8} \), \text{x FOR PEER REVIEW} | 18 of 41 |
|---|---|---|---|
| PVDF-HFP | PET/SiO\(_2\) | 1 M LiPF\(_6\) in EC/DEC (1:1) | 60 / - | 9.3x10\(^{-4}\) / - | 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\(_2\)O\(_4\) | 1 M LiPF\(_6\) in EC:DEC (1:1, v/v) | - / - | 2.80x10\(^{-3}\) / 140 (0.1C) | Influence of different quantities of MgAl\(_2\)O\(_4\) filler in the membrane; Good ionic conductivity. MgAl\(_2\)O\(_4\) as filler of thin and flexible separator; Good thermal stability and stable cycling performance. | [104] |
| PVDF-HFP | MgAl\(_2\)O\(_4\) | 1 M LiPF\(_6\) in EC/DEC (1:1, w/w) | 60 / 81 | 10\(^{-3}\)(30 °C) / 140 (C/10) | Upgrading the battery safety operation by the addition of metal hydroxides in composite separators; High thermal stability and good capacity retention. | [105] |
| PVDF-HFP | Mg(OH)\(_2\) | 1.15 M LiPF\(_6\) in EC/EMC (3:7, v:v) | 64 / 115 | 8.08x10\(^{-4}\) / 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\(_6\) in EC/DEC (1:1, v/v) | 40 / 251 | 9.01x10\(^{-4}\) / 105 (0.1C) | Use of montmorillonite as filler; High thermal stability and stable cycling performance. | [107] |
| PVDF-HFP | NaA | 1 M LiPF\(_6\) in EC/DEC (1:1, v/v) | 65 / 194 | 2.1x10\(^{-3}\) / - | Separator with incorporation of NaA zeolite; Excellent thermal stability and wettability. | [108] |
| PVDF-HFP | NaAlO\(_2\) | 0.5 M NaTf/EMiTf | - / - | 5.5–6.5x10\(^{-3}\) (25°C) / - | Introduction of NaAlO\(_2\) in a gel polymer electrolyte; Improved ionic conductivity. | [14] |
| PVDF-HFP | m-SBA15 | 1 M LiPF\(_6\) in EC/DEC (1:1) | - / 82.83 | 3.23x10\(^{-3}\) / 156 (0.1C) | A PVDF-HFP composite membrane with m-SBA15 as filler; High coulomb efficiency. | [109] |
| PVDF-HFP | m-SBA15 | 1 M LiPF\(_6\) in EC/DEC (1:1) | - / 85.36 | 3.78x10\(^{-3}\) / 198.6 (0.1C) | Effect of the addition of a silica filler on a PVDF- | [110] |
| Membrane Type | Material | Electrolyte | Conductivity | Density | Properties |
|---------------|----------|-------------|--------------|---------|-------------|
| PVDF-HFP OIL | 1 M LiPF₆ in EC/DEC (1:1) | 2 × 10⁻³ (25°C) / 141 (C) | - / 13 | High coulomb efficiency. | [111] |
| PVDF-HFP SiO₂ | 1 M LiPF₆ in EC/DMC (1:2) | 65.41 - / 124.5 (C) | 65.41 / 217 | Non-flammability, good cell performance. | [16] |
| PVDF-HFP SiO₂ | 1 M LiPF₆ in DMC/EMC/DC/VC (46.08:22.91:27.22:3.79) | 8.47 × 10⁻³ (25°C) / 154.4 | 26.7 / 202 | Synthesis of dual asymmetric structure separators with SiO₂ particles; High thermal stability and electrolyte uptake. | [112] |
| PVDF-HFP TiO₂ | 1 M LiPF₆ in EC/DMC/EMC (1:1:1, v:v:v) | 3.45 × 10⁻³ / 122 (10 C) | 58 / 330 | Evaluation of the performance of a nanocomposite polymer membrane with addition of TiO₂; Excellent electrochemical performance. | [85] |
| PVDF-HFP ZrO₂ | 1 M LiPF₆ in EC/DEC (1:1) | 1.48 × 10⁻³ Scm⁻¹ (25°C) / 126.8 mAhg⁻¹ (0.5 C) | 71 / 182 | Preparation of ZrO₂/PVDF-HFP by the dip-coating method; High wettability, ionic conductivity and thermal resistance. | [113] |
| PVDF-HFP ZrO₂ | 1 M LiPF₆ in EC/EMC (1:3) | 2.06 × 10⁻³ (25°C) / 149.7 | - / - | Improvement of the electrochemical properties of a electrospun membrane; High uptake and ionic conductivity. | [114] |
| PVDF-HFP ZrO₂ | 1 M LiPF₆ in EC/DEC/DMC (1:1:1) | 3.2 × 10⁻⁴ / 646 (0.2 C) | 87.53 / 351.2 | Inorganic fibers as substrates to separators; High thermal stability and good mechanical properties. | [115] |
| PVDF-HFP ZrO₂ | 1 M LiPF₆ in EC/DMC (1:1) | 10⁻³ (25°C) / 75 (C) | 60 / 160 | Development of thin and flexible ZrO₂ separators; High porosity and thermal stability. | [116] |
| PVDF-HFP ZrO₂ | 1 M LiPF₆ in EC/DMC (1:1) | 2.695 × 10⁻³ (25°C) / - | 95.7 / 481 | Incorporation of ZrO₂ in PVDF-HFP electrospun membranes; | [117] |
| Membrane Type | Components | Electrolyte | Efficiency | Applications |
|---------------|------------|-------------|------------|--------------|
| FEP/PI       | CV and PVDF | EC/DMC (1:1, v:v) | 77.9 / 212 | Improved thermal and mechanical properties. |
| PI/PVDF      | SiO<sub>2</sub> | EC/DEC (1:1, v:v) | 1.76×10<sup>3</sup> / 150 | PP/PVDF-HFP separator, with the inclusion of SiO<sub>2</sub> nanoparticles; Favorable chemical stability and discharge capacity. |
| PI/PVDF-HFP  | TiO<sub>2</sub> | EC/DEC (1:1, v:v) | 1.88×10<sup>3</sup> / 161 | Electrosprin PI/PVDF-HFP membrane, with addition of TiO<sub>2</sub> nanoparticles; Excellent electrochemical properties. |

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 were used into PVDF and its copolymers composites in order to improve thermal and mechanical stability as well as the ionic conductivity value.

Mechanical improvement of separators has been achieved by developing sandwich type composite separators, by a successive electrospinning method and based on PMIA [79]. The addition of DNA-CTMA in a PVDF matrix allows the development of flexible membranes, with interesting mechanical properties, highlighting its favorable stretch property, allowing foldable separators with elevated elasticity [71].

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

The use of SnO<sub>2</sub> nanoparticles in a PVDF electrospun separator can raise the mechanical strength of the membrane, thus leading to a more tough and durable battery [106]. Improved security operation for lithium ion batteries, due to suitable flammability resistance, has been addressed by developing PVDF/LiPVAOB composites membranes [33].

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

PVP/PVDF membranes incorporated with carbon black nanoparticles were produced for supercapacitor applications. The separators showed improvements in mechanical properties and dielectric constant values [19].
GPEs based on boron-containing cross-linker proved to have high thermal resistance, maintaining their dimensional stability up to 150°C, due to their stable PVDF matrix. Also, the ionic conductivity and electrochemical stability were improved when compared to commercial separators [68].

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

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

The dipping of PVDF nanofiber membranes into Al2O3 proved to improve the thermal stability of the produced separator and its ionic conductivity. It also shows a low discharge capacity decay, even at high discharge rates [111].

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

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

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

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

![Image](https://via.placeholder.com/150)

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

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

The incorporation of Meldrum’s acid groups in the PVDF structure proved to increase the ionic conductivity of the membrane, as well as the cycling performance, in particular at high C-rates [74].
PVDF/PFSA electrospun nanofibers allow the development of membrane with high mechanical stability and ionic conductivity with high discharge capacity and cycling stability [81].

A GPE membrane was developed by blending PVDF with PEO and ZrO2. This membrane showed high electrolyte uptake, excellent rate performance and discharge capacity for application in lithium-sulfur batteries [88].

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

A nonaflate anion-based IL and lithium salt was introduced on a GPE, allowing the development of membrane with high thermal stability and electrochemical properties. When used alongside with a LiCoO2 cathode, this separator also showed good discharge capacity and capacity of retention [96].

The addition of MgAl2O4 as filler in electrospun fibrous PVDF-HFP separator, contributes to improve the electrochemical performance, with high discharge capacity and excellent cycle life results [104].

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

The enhancement of the electrochemical performance has been extensively addressed by composites membranes with TiO2 nanoparticles [119], and clay nanosheets [95], the later improving interfacial areal connection between the polymer structure and clay, facilitating the ion transport.

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

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

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

The addiction of ZrO2 filler increases the porosity, ionic conductivity and thermal resistance of the PVDF membranes. The presence of polar constituents and high connected interstitial voids facilitate electrolyte absorption, increasing the ionic conductivity and the performance of the membranes [113]. When a layer of ZrO2 was added between two layers of PVDF-HFP, the obtained separator presents even better electrochemical properties [114].

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

HMSS/PVDF-HFP composite separators with improved porosity were developed, the presence of SiO2 spheres created a well-developed microporous structure, leading to higher wettability and ionic conductivity [98].

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

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

A comparative study of Al2O3 and NaAlO2 particles in a gel polymer electrolyte proved that NaAlO2 membranes presents higher ionic conductivity than Al2O3, as well as improved mechanical properties [14].
ZrO2 membranes with PVDF-HFP as binder were produced by solvent casting methods. These separators present high porosity and thermal stability, but show lower mechanical strength than commercial available membranes [116].

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

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

Regardless of the fillers type used, Table 5 shows that most of the work is devoted to increase ionic conductivity and electrochemical performance compared to pure matrix. In particular, inert oxide ceramics (Al2O3, TiO2, SiO2, ZrO2) reduce the degree of crystallinity, enhance mechanical properties and ionic conductivity value. Carbon materials (CNF, Graphene, rGO) improve safety and interfacial stability between electrodes and separator membranes and lithium fillers as Li1.3Al0.3Ti1.7(PO4)3, LiTFSI and LLTO increase ionic conductivity value of the separators.

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

### 3.4. Polymer blend separator membranes

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

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

| Materials | Blends | Electrolyte solution | Porosity and uptake (%) | Conductivity (S·cm⁻¹) and capacity (mAh·g⁻¹) | Main goal/achievement | Ref |
|-----------|--------|----------------------|-------------------------|---------------------------------------------|-----------------------|-----|
| PVDF      | HDPE   | 1 M LiPF₆ in EC/DEC/DMC (1:1:1) | 58 / 260 | 2.54×10⁻³ Scm⁻¹² / 156.1 mAhg⁻¹ (25°C) | Production of a sponge like PVDF/HDPE film; High ionic conductivity and cycling performance. | [121] |
| PVDF      | HTPB-g-MPEG | 1 M LiPF₆ in EC/DMC/EMC (1:1:1) | 56 / 350 | 3.1×10⁻³ / 116 C | Enhance the stability of entrapped liquid electrolyte and corresponding ion conductivity. | [122] |
| PVDF      | MC     | 1 M LiPF₆ in EC/DEM/EMC (1/1/1, w/w/w) | - / 138.6 | 1.5×10⁻³ / 110 C | PVDF composite separator with cellulose material; | [123] |
| Membrane | Cross-Linking Agent | Electrolyte | Current Density | Cutoff Voltage | Note |
|----------|---------------------|-------------|----------------|---------------|------|
| PVDF MEP | 1 M TEABF₄ in AN/PC and 1 M LiPF₆ in EC/DEC | 77 / - | 1.3×10⁻² / - | 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 LiPF₆ 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 LiPF₆ in EC/DMC/DEC (1:1:1) | 77.7 / 414.5 | 2.9×10⁻³ (25°C) / - | Improved thermal and mechanical properties; High cycling stability. [126] |
| PVDF PAN | 1 M LiPF₆ in EC/DMC/EMC (1:1:1) | - / 320 | 1.45×10⁻³ / 145.71 (0.2C) | Production of an electrospun blend membrane; High thermal and mechanical stability. [127] |
| PVDF PBA | 1 M LiPF₆ in EC/DEC/DMC (1:1:1) | - / 120 | 8.1×10⁻⁴ (25°C) / 95 (0.1C) | Preparation of a cross-linked PBA/PVDF GPE; Good cycling stability. [128] |
| PVDF PDMS-g-(PPO-PEO) | 1 M LiPF₆ in EC/DMC/EMC (1/1/1, w/w/w) | 80.1 / 512 | 4.5×10⁻³ / 120 (1C) | Porous separator; Good electrochemical stability. [129] |
| PVDF PEGDA | 1 M LiPF₆ in EC/DMC (1:1) | - / - | 3.3×10⁻³ / 117 (0.1C) | Separator produced by thermal polymerization; High capacity retention. Production of blend membranes by electrospinning; improved conductivity and uptake. [130] |
| PVDF PEO | 1 M LiPF₆ in EC/DMC (1:1) | / 530 | - / - | Production of blend membranes by electrospinning; improved conductivity and uptake. [131] |
| Membrane Type | Polymer | PVDF, PEO | LiPF$_6$ 1 M | EC/DMC (1:1) | - / 527 | - / - | High electrolyte uptake, low shutdown temperature. | [132] |
| Membrane Type | Polymer | PVDF, PET | - | 80 / 270 | - / - | Synthesis of a hybrid separator; High wettability and electrolyte uptake. | [133] |
| Membrane Type | Polymer | PVDF, PI | LiPF$_6$ 1 M | EC/PC/DEC/VC (35.4:17.2:45.1:2.3) | - / - | 1.3×10$^{-3}$ / 141 | Preparation of the separator by electrospinning; Improved thermal stability and mechanical properties. | [134] |
| Membrane Type | Polymer | PVDF, PMMA/CA | LiPF$_6$ 1 M | EC/DMC (1:1, w/w) | 99.1 / 323 | - / - | Elevated porosity and electrolyte uptake. | [135] |
| Membrane Type | Polymer | PVDF, P(MMA-co-PEGMA) | LiPF$_6$ 1 M | EC/EMC/DMC (1/1/1, w/w/w) | - / 372 | 3.01×10$^{-3}$/ - | Porous separator; Improved capacity retention. | [136] |
| Membrane Type | Polymer | PVDF, PMMA/SiO$_2$ | - | 80.1 / 293.2 | 1.97×10$^{-3}$ / - | Evaluation of the effect of PMMA and SiO$_2$ blend on a PVDF electrospun membrane, as separator; High electrolyte uptake and improved ionic conductivity. Separators for supercapacitors; High uptake and power density. | [137] |
| Membrane Type | Polymer | PVDF, PVP | Li$_{4}$N-BF$_4$/ PC | - / 360 | 1.8×10$^{-2}$(25°C) / - | Separators for supercapacitors; High uptake and power density. | [138] |
| Membrane Type | Polymer | PVDF, TAIC | Li$_{4}$ABF$_4$ in AN/PC and LiPF$_6$ in EC/DEC | 75 / - | 1.4×10$^{-2}$/ - | Manufacturing of separator by phase inversion, with TAIC as cross-linking agent. High ionic conductivity. | [34] |
| Membrane Type | Polymer | PVDF-TrFE, PEO | LiTFSI 1 M | PC | 44.5 / 107 | 5.4×10$^{-4}$ / 124 (C/5) | Research about the physical and chemical properties of a PVDF-TrFE/PEO blend | [139] |
| Membrane Type | Component(s) | Electrolyte | Electrochemical Performance | Thermal Stability | Notes |
|---------------|--------------|-------------|----------------------------|------------------|-------|
| PVDF-HFP CA   | 1 M LiPF₆ in EC/DMC/EMC (1:1:1, v/v/v) | 66.36 / 355 | 6.16×10⁻³ / 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. |
| PVDF-HFP HDPE | -            | 71 / 300    | 2.97×10⁻³ / 140.5 (25°C) / 140.5 (C) | Preparation of the separator by non-solvent induced phase separation; High ionic conductivity. | |
| PVDF-HFP PANI | 1 M LiPF₆ in EC/DMC (1:1) | 83 / 270 | 1.96×10⁻³ / - | High thermal stability, electrolyte uptake and ionic conductivity | |
| PVDF-HFP PEG/PEGDMA | 1 M LiClO₄ in EC/DEC (1:1, v/v) | 71 / 212 | 1.70×10⁻³ / - | Investigation about a strengthened electrospun nanofiber membrane separator; High porosity and electrolyte uptake. | |
| PVDF-HFP PLTB | 1 M LiPF₆ in EC/DMC (1/1, v/v) | 70 / 260 | 1.78×10⁻³ / 138 (0.5C) | Excellent electrochemical performance. | |
| PVDF-HFP PSx-PEO3 | 1 M LiTFSI in EC/DMC (1:1, w:w) | - / 520 | 4.2×10⁻³ / 125 (20 °C) / 123 (C) | Production of a safe PVDF-HFP blended membrane, which can be sprayed; Elevated electrolyte uptake. | |
| PVDF-HFP PVSK | 1 M LiTFSI + 0.25 M LiNO₃ in DME/DOL (1:1) | 27 / - | - / 1220 | Improved cycling performance. | |
| PVDF-HFP PVC | 1 M LiPF₆ in EC/DMC (1:2) | 62 / 230 | 1.58×10⁻³ / 125 (0.1 C) | Tri-layer polymer membrane; Good mechanical and thermal stability. | |
| PEI/PVDF x-PEGDA | 1 M LiPF₆ in EC/DMC/EMC (1:1:1) | 64.6 / 235.6 | 1.38×10⁻³ / 160.3 (0.2C) | Production of x-PEGDA coated PEI/PVDF membranes; high |
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].

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].

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].

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].

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].

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].

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].

Figure 7 - Preparation of PVDF-HFP/CA nanofiber separators for lithium ion batteries [140].
PVDF separators were manufactured by phase inversion technique, with two different cross-linking agents (TAIC and MEP) and with the application of gamma radiation. The produced membranes are characterized by good mechanical behavior and low electrical resistance [34].

Electrospun PVDF membranes blended with PMMA/SiO2 show good porosity and elevated electrolyte uptake [137]. Blended with PI further enhance their thermal and mechanical properties, ensuring a better battery performance than commercial PE separators [134].

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

In summary, PVDF-based battery separators allow to tailor all the properties/characteristics required for a new generation of separator membranes for lithium-ion batteries with high power and excellent cycling performance.
| Symbol | Abbreviation | Description |
|--------|--------------|-------------|
| (C₈H₇)₃CH₃NBF₄ | Triethylmethylammonium Tetafluoroborate | |
| [C2mim][NTf2] | 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) | |
| Al(OH)₃ | Aluminum Hydroxide | |
| Al₂O₃ | Aluminum Oxide | |
| AlO(OH) | Boehmite | |
| AN | Acetonitrile | |
| BC | Boron-containing cross-linker | |
| CA | Cellulose acetate | |
| CMC | Carboxymethyl cellulose | |
| CNF | Carbon nanofiber | |
| DEC | Diethyl Carbonate | |
| DEM | Diethoxymethane | |
| 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-methylimidazolium trifluoromethane sulfonate | |
| EMITFSI | 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonylimide) | |
| EP | Ethyl Propionate | |
| Et₄N-BF₄ | Tetraethylammonium tetrafluoroboratein | |
| GF | Glass fiber | |
| GO | Graphene oxides | |
| GPE | Gel polymer electrolyte | |
| H₂SO₄ | Sulfuric Acid | |
| HDPE | High density polyethylene | |
| HEC | Hydroxyethyl cellulose | |
| HMSS | Hollow mesoporous silica spheres | |
| HTPB-g-MPEG | Hydroxyl-terminated polybutadiene grafted methoxy polyethylene glycol | |
| KOH | Potassium hydroxide | |
| LiClO₄ | Lithium Perchlorate | |
| LiCoO₂ | Lithium cobalt oxide | |
| LiFAP | Lithium Tris(pentafluoroethane)-trifluorophosphate | |
| LiNO₃ | Lithium Nitrate | |
| LiPF₆ | Lithium Hexafluorophosphate | |
| LiPVAOB | Lithium Polyvinyl Alcohol Oxalate Borate | |
| Li-S | Lithium-sulfur | |
| LiTFSI | Lithium bis(trifluoromethanesulfonylimide) | |
LLTO
MA
MC
MEP
Mg(OH)₂
MgAl₂O₄
MMT
MOF-808
m-SBA 15
NaA
NaClO₄
NaTF
NCC
NIPS
NMP
OIL
P(MMA-co-PEGMA)
PAN
PANI
PBA
PC
PDA
PDMS-g-(PPO-PEO)
PE
PEG
PEGDA
PEGDMA
PEGMEA
PEI
PEO
PET
PFSA
PI
PLTB
PMIA
PMMA
POSS
PP
P-PAEK
PSx-PEO3
PSU
PTFE
PVA
PVC
PVDF
PVDF-co-CTFE
PVDF-co-HFP
PVDF-HFP

Li₀.₃₃La₀.₅₅₇TiO₃
Meldrum’s acid
Methyl Cellulose
Ethylene Oxide-propylene Oxide
Magnesium Hydroxide
Magnesium Aluminate
Montmorillonite
Zirconium (IV) metal-organic framework
Mesoporous Silica
NaA Zeolite
Sodium Perchlorate
Sodium trifluoromethane sulfonate
Nanocrystalline Cellulose
Non-solvent induced phase separation
N-methyl-2-pyrrolidone
Oligomeric Ionic Liquid (Bromide Bis(tri-fluoromethane)sulfonimide)
Poly(methyl methacrylate-co-poly(ethylene glycol) methacrylate)
Polyacrylonitrile
Polyaniline
Poly(butyl acrylate)
Propylene Carbonate
Polydopamine
Poly(dimethylsiloxane) graft poly(propylene oxide)-block-poly(ethylene oxide)
Polyethylene
Polyethylene glycol
Poly(ethylene glycol)diacrylate
Polyethylene glycol dimethacrylate
Poly(ethylene glycol) methyl ether acrylate
Polyetherimide
Polyethylenic Oxide
Polyethylene terephthalate
Perfluoro sulfonic acid
Polyimide
Polimeric Lithium Tartaric Acid Borate
Poly(m-phenylene isophthalalimide)
Polymethyl methacrylate
Polyhedral oligomeric silsesquioxane
Polypropylene
Phenolphthaleine-poly(aryl ether ketone)
Polysiloxane-comb-propyl(triethylene oxide)
Poly(sulfone)
Poly(tetrafluoroethylene)
Polyvinyl Alcohol
Poly(vinyl chloride)
Poly(vinylidene fluoride)
Poly(vinylidene fluoride-co-chlorotrifluoroethylene)
Poly(vinylidene fluoride-co-hexafluoropropylene)
Poly(vinylidene fluoride-co-hexafluoropropene)
Acknowledgments

Portuguese Foundation for Science and Technology (FCT): UID/FIS/04650/2013, PTDC/CTM-ENE/5387/2014, UID/CTM/50025/2013, project nº 28157/02/SAICT/2017 and grants SFRH/BPD/112547/2015 (C.M.C.), including FEDER funds through the COMPETE 2020 programme and National Funds through FCT. Financial support from the Basque Government Industry Department under the ELKARTEK and HAZITEK programs is also acknowledged.

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