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Battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium ion battery applications

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Poly(vinylidene fluoride), PVDF, and its copolymers exhibit interesting properties for use as separator membranes in lithium-ion battery applications. This review presents the developments and summarizes the main characteristics of these materials for battery separator membranes. The review is divided into three categories regarding the composition of the polymer membranes: single polymers, polymer composites and polymer blends. For each category, the main characteristics for battery separator membranes and the ion transport behaviour is presented. Finally, guidelines for further investigations are outlined.

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1 Introduction

After Pike Research Consulting, the market of portable batteries will reach \$30.5 billion dollars in 2015 with an annual growth rate of 8.5%.¹ The most used type of portable batteries are lithium-ion batteries as they are light, cheap, show high energy density, low charge lost, no memory effect, prolonged service-life and high number of charge/discharge

cycles. The market for lithium-ion (Li-ion) cells is mainly focused in portable electronic devices such as notebook computers and mobile phones. The first Li-ion batteries were commercialized 1991.^{2,3} This commercialization was preceded by several scientific achievements, including the pioneering work of Yazami⁴ regarding the use of lithium-graphite as a negative electrode. A Li-ion battery is an electrochemical cell that converts chemical energy into electrical energy.^{5,6} The basic constituents of an electrochemical cell are the anode, cathode and the separator, as illustrated in Fig. 1.

The separator membrane separates the anode and the cathode and it is essential in all electrochemical devices.^{7,8} The role of the separators is to serve as the medium for the transfer of the lithium ions between both electrodes and to

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Maria Manuela Silva obtained a Research Assistant position in the Department of Chemistry of the University of Minho (Braga, Portugal) in 1991. She received her PhD in Chemistry from the University of Minho in 1999 and was promoted to Assistant Professor at the same University. Her research activities focus on the synthesis and characterisation of solid polymer electrolytes (SPE) and their application in the domains of solid state electrochemistry (solid state batteries and electrochromic devices). She is also interested in the chemistry (synthesis via sol-gel) of silica-based organic-inorganic hybrid materials.

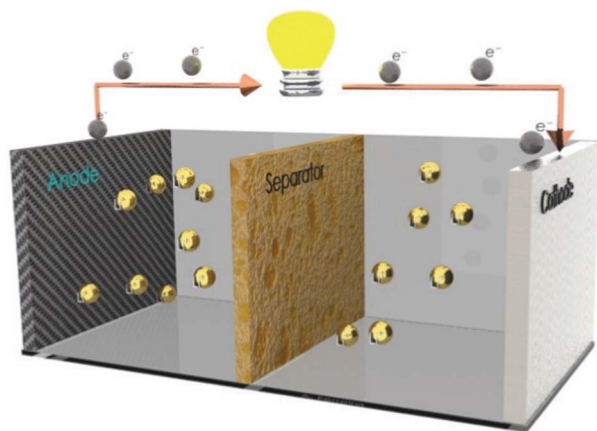


Fig. 1 Schematic representation of the main components of a lithium-ion battery.

control the number of lithium ions and their mobility.⁹ The separator is constituted by a polymer matrix soaked by the electrolyte solution, *i.e.*, a liquid electrolyte where salts are dissolved in a solvent, water or organic molecules. Most commonly, the liquid electrolyte solution is composed by a lithium salt in a mixture of one or more solvents. The solvents present in the electrolyte solution must meet a combination of requirements for battery applications, which are, in some cases, not easy to achieve, as for example, high fluidity *vs.* high dielectric constant.¹⁰ The characteristics of an ideal solvent are high dielectric constant, for dissolving high salt concentrations; low viscosity, for improving ion transportation; to be inert to all cell components and to be in the liquid state in a wide temperature range. The nonaqueous solvents most used in electrolyte solutions belong to organic esters and ethers

classes.¹¹ In both classes, the most used solvents are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC). Other possibility for the fabrication of polymer electrolyte separators is by incorporating the lithium salts directly into the polymer matrix.¹²

A large diversity of requirements determine the performance of separator membranes for battery applications, such as low ionic strength, mechanical and dimensional stability, physical strength to allow easy handling, resistance to thermal and chemical degradation by electrolyte impurities and chemical reagents, to be easily wetted by liquid electrolytes and to show uniform thickness.^{9,12,13} Table 1 summarizes the typical values and the relevance of the main requirements of lithium-ion battery separators, adapted from.^{12,13}

The materials used as separators for batteries are mainly polymers or polymer composites with dispersed fillers of various types. The most used polymers are poly(ethylene) (PE),^{14,15} poly(propylene) (PP),¹⁶ poly(ethylene oxide) (PEO),^{17–19} poly(acrylonitrile) (PAN)^{20–22} and poly(vinylidene fluoride) (PVDF) and its copolymers.^{23–27} The most used fillers incorporated into the polymer hosts are inert oxide ceramics (Al₂O₃, SiO₂, TiO₂), molecular sieves (zeolites), ferroelectric materials (BaTiO₃) and carbonaceous fillers, among others, with the main function of increasing the mechanical stability and/or ionic conductivity of the separator.²⁸

Fig. 2 illustrates the increasing number of published scientific articles related to lithium ions battery separators and polymer electrolytes.

The strong growth of work in this field in the past decade results from the development of new materials and processing techniques, which allows rapid and efficient technology transfer of the novel developed materials.

PVDF is semi-crystalline polymer in which the amorphous chains are embedded between the lamellar crystalline structures with a degree of crystallinity ranging from 40% to 60%. It exhibits four polymorphs called α , β , γ , δ .^{29,30} The most common and important polymorphs of PVDF are the α - and β -phases. The α -phase is non-polar, it is the phase thermodynamically more stable when the material is obtained from the melt and when the solvent is evaporated at temperatures above 80 °C.³¹ The β -phase is the most interesting phase for technological applications due to its electroactive properties: piezoelectric, pyroelectric and ferroelectric.³² The β -phase is obtained with a porous microstructure directly by solution at crystallization temperatures below 70 °C³³ or by mechanical stretching of the α -phase at temperatures between 70 °C and 100 °C.³⁴ The dielectric constant of the β -phase ranges between 10 at 13 and the conformational repeating unit (planar zigzag, all-*trans*) has a dipolar moment of 7×10^{-30} Cm.³⁵

The semi-crystalline copolymer poly(vinylidene fluoride-co-trifluoroethylene), P(VDF-TrFE), shows, for specific molar ratios of VDF and TrFE, a polar ferroelectric transplanar chain conformation similar to the one of the β -phase of PVDF.³⁶ P(VDF-TrFE) exhibits the ferroelectric (FE)-paraelectric (PE)



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Table 1 Ideal value and relevance of the typical parameters for lithium-ion battery separators

Parameter	Ideal Value	Relevance
Thickness (μm)	<25	Determines the mechanical strength of the membrane and the risk of inner battery electrical shorting.
Electrical resistance (MacMullin no.)	<8	Describes the relative contribution of a separator to cell resistance.
Gurley (s)	$\sim 25/\text{mil}$	Expresses the time necessary for a specific amount of air to pass through a specific area of the separator with a specific pressure.
Porosity (%) / Pore Size (μm)	40/<1	Determines the permeability required for battery separators.
Shrinkage (%)	<5% in both MD and TD	Dimensional stability. The separator should not shrink when exposed to the electrolyte solution.
Tensile strength (%)	<2% offset at 1000 psi	The separator should stand mechanical stress between the electrodes.
Shutdown T ($^{\circ}\text{C}$)	130	The temperature safety range of the battery that is provided by the separator.
High-temperature melt integrity	>150	Separators with good mechanical properties at high temperatures may provide a larger safety margin for batteries
Skew (mm m^{-1})	<0.2	When a separator is laid out, the separator should be straight and not bowed or skewed.

phase transition at a Curie temperature, T_c , below the melting temperature, T_m . Both temperatures depend on the crystallization conditions and molar ratio of VDF and TrFE.^{37–39} The copolymer poly(vinylidene fluoride-*co*-hexafluoropropylene), P(VDF-HFP), is also a semi-crystalline polymer with a degree of crystallinity significantly reduced due to the addition of hexafluoropropylene (HFP).⁴⁰ Therefore, it shows high flexibility as compared to PVDF⁴¹ and a dielectric constant of 8.4.

In the copolymer poly(vinylidene fluoride-*co*-chlorotrifluoroethylene), P(VDF-CTFE), the amount of chlorotrifluoroethylene, CTFE is essential for determining properties and applications.⁴² For 25–70% mol of VDF, the P(VDF-CTFE) is amorphous⁴³ being for the remaining concentrations a semicrystalline copolymer with a hexagonal structure.⁴⁴ The dielectric constant of P(VDF-CTFE) is 13⁴⁵ and shows high electromechanical response for 9 and 12 mol% CTFE content.⁴⁶

PVDF and its copolymers poly(vinylidene fluoride-*co*-tri-fluoroethylene), PVDF-TrFE, poly(vinylidene fluoride-*co*-hexafluoropropylene), PVDF-HFP, and poly(vinylidene fluoride-*co*-chlorotrifluoroethylene), PVDF-CTFE show strong advantages

for their use as separator membranes in comparison to polyolefins⁴⁷ and other used materials due to their strong polarity (high dipolar moment) and high dielectric constant for a polymer material, which can assist ionization of lithium salts. It is also possible to control the porosity of the materials through binary and ternary polymer/solvent systems. Further, they are wetted by organic solvents, chemically inert, show good contact between electrode and electrolyte and are stable in cathodic environment.^{48–56} Different processing techniques, such as solvent casting, electrospinning and hot-press have been used for the development for battery separators from these materials.^{57–62}

This review focused on battery separators and polymer electrolytes based on PVDF and its copolymers, PVDF-HFP, PVDF-TrFE and PVDF-CTFE, for lithium-ion battery application due to the recent advances and their large potential for energy storage applications. A summary of the obtained results will allow establishing the maturity of these materials for the intended purpose as well as to reflect on the future steps to be taken both in research and technology transfer.

This review is structured in three sections devoted to the state of the art in single polymers, composites and polymer blends, respectively. For each section, the materials and electrolyte solutions will be presented as well as the main characteristics of the materials, such as porosity, ionic conductivity and related properties. Some remarks on the electrodes of batteries based on the aforementioned separators will be provided and, finally, the main problems and future directions will be presented.

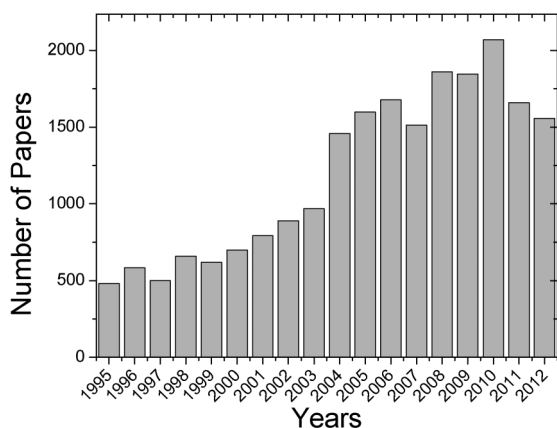


Fig. 2 Research articles published on battery separators and polymer electrolytes for lithium ion battery applications. Search performed in Scopus database with the keywords “battery separators” and “polymer electrolytes”.

2 Polymer electrolytes based on poly(vinylidene fluoride) and its copolymers

2.1 Single polymer and copolymers

Fluorinated polymers such as PVDF and its copolymer show advantages when compared to commercial polyolefine separators (PE) due to their high polarity and dielectric permittivity, which provides larger affinity with polar liquid electrolytes. The characteristics of the developed PVDF and copolymer

Table 2 Developed polymer electrolytes based on PVDF and co-polymers, presented in chronological order, and their main properties

Material	Electrolyte solution/lithium ions	Porosity (%) /Fiber Diameter* (electrospun) (nm)	Uptake (%)	$\sigma_i / (S\text{ cm}^{-1})$ at 25 °C	Ref.
PVDF-HFP	1 M LiPF ₆ in EC/PC	—	60	0.8×10^{-3}	68
PVDF	1 M LiPF ₆ + PC/EC/3DMC	70	65	3.7×10^{-3}	63
PVDF	1 M LiTFSI in EC/DEC (2/3 in volume ratio)	—	—	6.7×10^{-3}	27
PVDF	10% LiBF ₄ in EC/PC (1 : 1)	—	—	3.4×10^{-4}	69
PVDF	10% LiPF ₆ in EC/PC (1 : 1)	—	—	4.7×10^{-4}	69
PVDF	10% LiAsF ₆ in EC/PC (1 : 1)	—	—	6.6×10^{-4}	69
PVDF	1 M LiTFSI in EC/DEC	0	20	5.6×10^{-8}	72
PVDF	1 M LiTFSI in EC/DEC	23	32	2.7×10^{-6}	72
PVDF	1 M LiTFSI in EC/DEC	30	41	1.0×10^{-6}	72
PVDF	1 M LiTFSI in EC/DEC	70	60	9.8×10^{-5}	72
PVDF	1 M LiTFSI in EC/DEC	75	65	1.3×10^{-4}	72
PVDF-HFP	1 M LiPF ₆ in 1/1 w/w (EC/DEC)	—	—	$1.5\text{--}2.0 \times 10^{-3}$	73
PVDF	1 M LiPF ₆ in 1/1 w/w (EC/DEC)	23	33	2.2×10^{-5}	74,75
PVDF	1 M LiPF ₆ in 1/1 w/w (EC/DEC)	30	39	2.4×10^{-5}	74,75
PVDF	1 M LiPF ₆ in 1/1 w/w (EC/DEC)	38	45	1.5×10^{-4}	74,75
PVDF	1 M LiPF ₆ in 1/1 w/w (EC/DEC)	71	77	1.0×10^{-3}	74,75
PVDF-HFP	1 M LiClO ₄ -EC/PC (1 : 1)	83	220	1.5×10^{-3}	76
PVDF	1 M LiPF ₆ -EC/PC	—	—	2.0×10^{-3}	77
PVDF	1 M LiPF ₆ -EC/DMC/DEC (2/2/1)	70	142	5.0×10^{-2}	78
PVDF-HFP	1 M LiPF ₆ -EC/DMC (1/1)	23	76.4	0.3×10^{-3}	79
PVDF	1 M LiTFSI in distilled water	100–800*	50–73	$1.6\text{--}2.0 \times 10^{-3}$	64
PVDF-HFP	1 M LiBF ₄ in 1/3 w/w (EC/GBL)	—	120	3.4×10^{-3}	80
PVDF	1 M LiPF ₆ -EC/DMC/DEC (2/2/1)	—	—	3.5×10^{-3}	81
PVDF	20 wt% LiClO ₄	—	—	8.7×10^{-4}	82
PVDF	1 M LiPF ₆ -EC/DMC/DEC (2/2/1)	70	—	3.1×10^{-3}	83
PVDF-HFP	1 M LiPF ₆ -EC/DEC (1/1)	70–90	—	1.2×10^{-3}	84
PVDF	LiBF ₄ -PC:EC	—	—	1.0×10^{-3}	85
PVDF	EC/PC/LiPF ₆ = 43/43/7 (in wt%)	—	—	1.0×10^{-3}	86
PVDF	15 wt% of LiFePO ₄	—	—	6.7×10^{-6}	87
PVDF	1 M LiPF ₆ -EC/DMC/DEC (1/1/1).	750–1630*	300–400	6.7×10^{-2}	88
PVDF-HFP	0.5 M LiTFSI in BMITFSI	<1000*	750	2.3×10^{-3}	65
PVDF-HFP	0.5 M LiBF ₄ in BMIBF ₄	<1000*	600	2.3×10^{-3}	65
PVDF-HFP	1 M LiPF ₆ in EC/DMC	59	165	9.1×10^{-2}	89
PVDF-HFP	1 M LiCF ₃ SO ₃ in TEGDME	59	210	1.8×10^{-2}	89
PVDF	1 M LiPF ₆ -EC/DMC/EMC (1/1/1)	70	230	1.4×10^{-3}	50
PVDF	1 M LiCF ₃ SO ₃ in TEGDME/DIOX (1/1)	—	250	0.6×10^{-3}	90
PVDF-HFP	1 M LiPF ₆ -EC/DMC/EMC (1/1/1)	—	—	1.8×10^{-3}	91
PVDF-HFP	1 M LiPF ₆ -EC/DMC (1/1)	78	321	3.36×10^{-4}	92
PVDF-HFP	1 M LiPF ₆ -EC/DMC/DEC (1/1/1)	70	—	1.4×10^{-3}	66
PVDF	1 M LiPF ₆ -EC/DMC/EMC (1/1/1)	—	230	4.8×10^{-3}	67
PVDF-HFP	0.3 M Mg(CF ₃ SO ₃) ₂ in EMITf	—	—	4.8×10^{-3}	93
PVDF	1 M LiPF ₆ -EC/DMC (1/1)	77	—	1.9×10^{-3}	56
PVDF-CTFE	1 M LiPF ₆ -EC/DMC (1/1)	230*	800	2.0×10^{-3}	94
PVDF	50 wt% LiTFS	—	—	1.7×10^{-2}	95
PVDF-HFP	40 wt% LiTf	—	—	7.8×10^{-5}	96
PVDF-HFP	0.8 M LiTFSI in 1 g 13TFSI	—	670	3.2×10^{-4}	97
PVDF-HFP	LiTFSI-PC (0.15/0.3 wt%)	—	—	1.0×10^{-5}	98
PVDF	1 M TEABF ₄ in AN	80	117	1.8×10^{-3}	53
PVDF	1 M LiPF ₆ -EC/DEC (4/6)	48	142	—	99
PVDF-TrFE	1 M LiClO ₄ -PC	72	255	2.7×10^{-7}	23,100
PVDF-TrFE	LiClO ₄ ·3H ₂ O (<i>n</i> = 1.5)	67	—	3.5×10^{-11}	101

membranes are summarized in Table 2 as achieved in chronological order.

The porous battery separators of fluorinated polymers are most commonly obtained by phase inversion processes such as thermal induced phase separation (TIPS), using solvent and non-solvent system and electrospinning.^{27,63–65}

The achieved porosity of the battery separators ranges between 0 to 90% and the pore size from 0.5 μm to 16 μm .^{23,63} Porous membranes with controlled porosity and pore sizes of 2 μm ⁶⁶ and 1 μm ⁶⁷ were also obtained by adding urea and

salicylic acid, respectively, as foaming agents for PVDF or PVDF-HFP.

In 1996, Tarascon *et al.* produced the first Li-ion battery with a fluorinated polymer (PVDF-HFP) as battery separator.⁶⁸ The performance of such a battery compares favourably in terms of gravimetric or volumetric energy density, life cycle, power rate and self-discharge with its liquid counterparts, while having enhanced safety characteristics, larger shape flexibility and scale ability. One of the main advantages of fluorinated polymers is their ability to be tailored in different geometries, including very thin cells.

Kataoka *et al.*²⁷ showed that the ionic conductivity depends on the immersion time of the polymer membrane in the electrolyte solution and on the aging time after removal from the solution. PVDF for polymer electrolytes is optimized with 1 : 1 EC : PC plasticizer in salts such as LiAsF₆ (lithium hexafluoroarsenate), LiPF₆ (Lithium hexafluorophosphate) and LiBF₄ (Lithium tetrafluoroborate). Nevertheless, LiAsF₆ gives better results for ionic conductivity than LiBF₄ and LiPF₆, irrespective of the nature of the polymer and the amount of plasticizer.⁶⁹ Salts with a polarizing cation and a large anion with a well delocalized charge, and therefore with low lattice energy, are the most suitable for polymer electrolytes.⁷⁰

Modifications of the properties of PVDF have been achieved by radiation grafting for improving adhesion to electrodes, leading to good rate performance and stable cycle life.⁷¹

From Table 2 it is observed that PVDF and PVDF-HFP with LiPF₆ and LiCF₃SO₃ in different organic solvents lead to the best values of ionic conductivity ($1.8 - 5 \times 10^{-2} \text{ S cm}^{-1}$).

PVDF polymer as battery separator was found to be effective in enhancing the lithium transport number due to selective interactions with the anion. The ionic conductivity of PVDF is associated to the total solution uptake, which depends on the gelation process related to porosity and pore size. The solution introduced in the polymer is stored in the pores and then penetrates into the polymer, swelling the polymer network.⁷² Other possibility for obtaining polymer electrolytes taking advantage of the properties of PVDF is by coating a microporous polyolefin membrane with a fluorinated polymer.⁷³ The cells with these polymer electrolytes showed good electrochemical and rate performance during cycling. Ideal membranes for porous polymer electrolytes based on PVDF for battery applications should present high porosity and small pore diameters with a narrow distribution. Experimental results show that porosity should be >80% and pore diameter should be <1 μm .⁷⁶ This porous structure has been also achieved with electrospun nanofiber webs.⁶⁴

The effect of the liquid organic solvents in PVDF microporous membranes was studied by Saunier *et al.*⁸¹ It was observed that the affinity of PVDF for the liquid electrolyte may affect its mechanical strength and compromise battery safety. This indicates that the thermal and mechanical stability is affected when too much solvent is incorporated into the polymer. The reversible modifications can also affect the membrane properties, as the glass transition and melting temperature are lowered.⁸¹

The ionic conductivity of the PVDF microporous membranes is also affected by solvent/polymer and solvent/salt interactions, ionic dissociation and tortuosity value.⁸³ It was proven also that interactions between PVDF and PC mainly occur in the surface area of the PVDF crystalline phase, whereas interactions between PC, PVDF, and lithium salt mainly occur in the amorphous area.⁴⁹

It was also observed that ionic conductivity decreases in the order EC/DEC > EC/EMC > EC/DMC among the electrospun PVDF fiber-based polymer electrolytes with the same weight fraction of EC.⁸⁸

For PVDF-HFP-based solid polymer electrolytes, lithium triflate salt effectively reduces the degree of crystallinity of the polymer and increases the ionic conductivity of the mem-

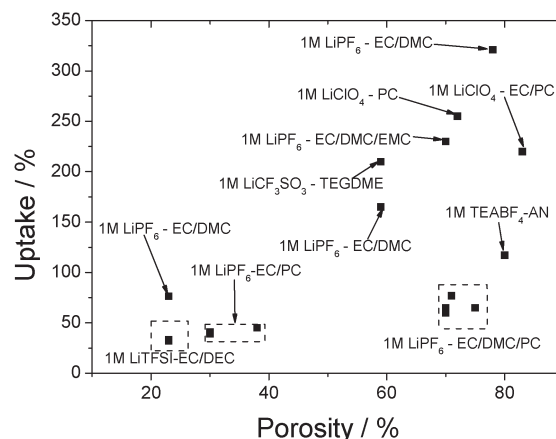


Fig. 3 Porosity vs. uptake for various electrolyte solutions incorporated into PVDF membranes.

brane.⁹⁶ Costa *et al.* demonstrated which parameters—porosity, treatment of lithium ion and processing technique—influence at most the electrical performance of PVDF-TrFE membranes for battery separators. The membrane that exhibits the highest ionic conductivity is a porous membrane prepared by the uptake technique. The performance of the membrane for battery applications are, therefore, strongly influenced both by porosity and processing technique due to its influence in the specific surface available for lithium ion adsorption and trapping.¹⁰²

The ionic conductivity depends not only on the characteristics of the electrolyte solution but also on the properties of the membrane—porosity and pore size—as shown in Fig. 3.

In Fig. 3, it is observed that for the same porosity are obtained different uptake ratios and ionic conductivities (Table 2) due to the interactions with the cations and anions produced from the Li salts by the solvation process. The viscosity of the solvent also influences the transport and the transference numbers of the ions.^{103,104}

Therefore, the main problem still to be optimized for battery separators persists: to obtain a combination of good ionic conductivity with high uptake ratio and excellent mechanical properties without deterioration of the ionic conductivity in the temperature range of the lithium-ion battery operation.

PVDF was proven to battery separator by Yamamoto *et al.* in a 4.4 V Li-ion polymer battery. The discharge capacity reached 520 Wh l⁻¹ and the capacity retention ratio was 91.4% at 3C.⁸⁶

2.2 Polymer and copolymer composites

To solve some of the problems existing in single polymer membranes, battery separators have been developed by the incorporation of suitable fillers into the host polymer for improving mechanical strength, thermal stability and ionic conductivity. Among these fillers are oxide ceramic, zeolites, ferroelectric ceramics, carbon, *etc.*^{28,105} These fillers can be divided into two groups: the fillers that participate in the ionic conduction process and the fillers that are not involved in the lithium transport process.²⁸

Table 3 Polymer electrolytes from PVDF based composite materials and their properties, presented in chronological order

Material	Fillers	Electrolyte solution/lithium ions	Porosity (%)	Uptake (%)	$\sigma_i/(S\text{ cm}^{-1})$ at 25 °C for maximum amount	Ref.
PVDF-HFP	SiO ₂	1 M LiPF ₆ in EC/DMC (1 : 1)	—	100–250	$0.87\text{--}3.1 \times 10^{-3}$	106
PVDF-HFP	MgO	1 M LiPF ₆ in EC/DMC (1 : 1)	—	40	4.0×10^{-4}	107
PVDF	SiO ₂	1 M LiPF ₆ in EC/PC (1/1)	—	—	—	112
PVDF	SiO ₂	1 M LiClO ₄ in EC-PC (1/1)	—	—	—	112
PVDF	SiO ₂	1 M LiPF ₆ in EC-PC (1/1)	—	—	3.5×10^{-2}	113
PVDF-HFP	MMT	LiCF ₃ SO ₃ in PC	—	—	1.0×10^{-3}	108
PVDF-HFP	SiO ₂	1 M LiTFSI in EC/DEC (1/1)	77	—	2.7×10^{-2}	114
PVDF-HFP	SBA-15	1 M LiPF ₆ in EC/DMC/EMC (1/1/1)	59	76	0.8×10^{-3}	111
PVDF-HFP	MCM-41	1 M LiPF ₆ in EC/DMC/EMC (1/1/1)	14	30	4.6×10^{-2}	111
PVDF-HFP	NaY	1 M LiPF ₆ in EC/DMC/EMC (1/1/1)	9	39	3.0×10^{-3}	111
PVDF-HFP	TiO ₂	DMBITFSI/LiPF ₆	—	—	1.3×10^{-3}	115
PVDF-HFP	AlO[OH] _n	5 wt% of LiN(CF ₃ SO ₂) ₂	—	—	1.1×10^{-2}	116
PVDF-HFP	TiO ₂	LiClO ₄ in EC/PC	26	110	4.1×10^{-2}	117
PVDF-HFP	MgO	LiClO ₄ in EC/PC	27	62	3.7×10^{-2}	117
PVDF-HFP	ZnO	LiClO ₄ in EC/PC	23	61	5.5×10^{-2}	117
PVDF-HFP	MCM-41	LiClO ₄ in EC/PC	42	93	6.1×10^{-2}	117
PVDF-HFP	SBA-41	LiClO ₄ in EC/PC	52	82	5.0×10^{-2}	117
PVDF-HFP	MMT	1 M LiPF ₆ in EC:DMC (1/1)	—	40	2.5×10^{-3}	118
PVDF-HFP	LiAlO ₂	1 M LiClO ₄ in EC:DEC (1/1)	87	121	8.1×10^{-3}	119
PVDF-HFP	ZrO ₂	1 M LiClO ₄ in EC:DEC (1/1)	86	91	11×10^{-3}	120
PVDF-HFP	TiO ₂	1 M LiPF ₆ in EC/DMC/DEC (1/1/1)	67	—	0.9×10^{-3}	121
PVDF-HFP	SiO ₂	1 M LiClO ₄ in EC/PC (1 : 1)	—	—	4.3×10^{-3}	122
PVDF-HFP	SiO ₂	LiClO ₄ + PC + DEC	—	—	1.0×10^{-2}	123
PVDF-HFP	TiO ₂	1 M LiPF ₆ in EC/DMC (1/1)	—	125	1.0×10^{-3}	124
PVDF-HFP	TiO ₂	1 M LiPF ₆ in EC/DMC (1/1)	60	359	1.7×10^{-3}	92
PVDF-HFP	MgO	1 M Mg(ClO ₄) ₂ in EC/PC (1/1)	—	—	8.0×10^{-3}	125
PVDF-HFP	DMOImPF6	0.5 M NH ₄ PF ₆	—	—	3.0×10^{-5}	126
PVDF	SiO ₂	—	136	—	—	127
PVDF-HFP	BaTiO ₃	LiBETI + EC + PC	—	—	0.8×10^{-3}	128
PVDF-HFP	Al ₂ O ₃	1 M LiPF ₆ in EC/DEC (1/1)	—	—	—	129
PVDF-HFP	Effervescent disintegrant	1 M LiPF ₆ in DMC/EC/EMC (1/1/1)	55	—	1.2×10^{-3}	130
PVDF-HFP	α -MnO ₂	1 M LiTFSI-PMMITFSI	—	—	1.3×10^{-3}	131
PVDF	MCM-41 + SO ₄ ²⁻ /ZrO ₂	1 M LiPF ₆ in EC/DMC/DEC (1/1/1)	62	161	1.0×10^{-3}	132
PVDF-HFP	SiO ₂	1 M LiPF ₆ in EC/DEC (1/1)	68	—	0.61	133
PVDF	Fe ₂ O ₃ , SnO ₂ and CoO	1 M LiPF ₆ in EC/DMC (2/1)	—	—	—	134
PVDF	Organic clays	—	75	—	—	135
PVDF	MMT	1 M LiClO ₄ in PC/DEC (1/1)	—	177	2.3×10^{-3}	109
PVDF	TiO ₂	1 M LiPF ₆ in EC/DMC (1/1)	65–79	—	—	136
PVDF-HFP	SiO ₂	1 M NaTf in EC/PC (1 : 1)	—	—	4.1×10^{-3}	137
PVDF	SiO ₂	1 M LiPF ₆ in EC/DMC (1/1)	75	—	1.4×10^{-3}	138
PVDF-HFP	SiO ₂	1 M LiPF ₆ in EC/DEC (1/1)	61	—	0.9×10^{-3}	139
PVDF-HFP	Cellulose	1 M LiTFSI in BMPyrTFSI	58	712	4.0×10^{-4}	140
PVDF-TrFE	MMT	1 M LiClO ₄ ·3H ₂ O-PC	90	335	8.0×10^{-7}	141
PVDF-TrFE	NaY	1 M LiClO ₄ ·3H ₂ O-PC	36	233	2.0×10^{-6}	142

The characteristics of PVDF and copolymer composites for separator membranes are summarized in Table 3 in chronological order.

From Table 3 it is observed that separator membranes with the different fillers increase the ionic conductivity with respect to the pristine polymer matrix (Table 2), the characteristics/properties of fillers playing an important role in the conduction mechanism of separator membranes.

Du Pasquier *et al.* showed that the combination of a phase-inversion process and the presence of finely divided silica in the separator results in the formation of a stable porous structure, in which the pores are mechanically reinforced by the silica particles at their inner surface and the ionic conductivity of the PVDF-HFP membrane increases.¹⁰⁶

The addition of MgO fillers increases the compatibility between separator and electrodes (anode and cathode) and

batteries with these membranes exhibit high power density (at 3C rate was $> 280\text{ W kg}^{-1}$).¹⁰⁷

Some authors verified that the presence of Montmorillonite (MMT) fillers have an effect on the nano-scale microenvironment for composite materials and a positive increment of the charge carriers and its mobility, the membranes exhibiting high electrochemical characteristics for Li-ion battery applications.¹⁰⁸ Further, this filler is adequate for battery separators as it enhances the uptake of liquid electrolyte due to the excellent affinity of clays towards electrolyte molecules.¹⁰⁹

The effect of powder particle size on battery separator was studied by Takemura *et al.* It was observed that composites with 0.01 μm ceramic powders (Al₂O₃) showed excellent cycling properties.¹¹⁰

The addition of molecular sieves has expanded the electrochemical stability window of polymer electrolytes, enhanced the interfacial stability of polymer electrolyte with lithium

electrodes, and inhibited the crystallization of the PVDF-HFP matrix.¹¹¹

Stephan *et al.* verified that the incorporation of inert fillers reduces the crystallinity of the polymer host, acts as 'solid plasticizer' capable of enhancing the transport properties and provides better interfacial properties towards lithium metal anodes.¹¹⁶

The uptake of electrolyte solution is not related directly to the surface area or dielectric constant of the oxides. It may be due to the affinity of the metal oxide toward the electrolyte solution.¹¹⁷ The incorporation of fillers such as SiO₂ and Al₂O₃ in the PVDF membrane promotes amorphicity, explaining the conductivity enhancement in PVDF-based electrolytes.¹⁴³

PVDF-HFP with SiO₂ nanoparticles has been prepared for Na/S batteries with a first discharge capacity of 165 mA h g⁻¹.¹³⁷

Galvanostatic cycling experiments of PVDF membranes with SiO₂ showed that these membranes have a behaviour similar to the corresponding liquid electrolyte, without significant differences in capacity.¹¹²

Miao *et al.* showed that TiO₂ added to the composite electrolyte membranes helps to improve mechanical strength, electrolyte uptake, ionic conductivity, and the electrode/electrolyte interfacial stability.⁹²

Composite polymer electrolytes containing ionic liquids have been found to be thermally stable up to 300 °C and show results adequate to be used as battery separators.¹²⁶

The nature of the filler and the filler content play therefore a very delicate role in the ionic conductivity of the composite materials.¹²⁸ The maximum amount of fillers found in the different works was 32 wt%. The ionic conductivity of the composite materials as battery separators depends on the nature of the fillers, the characteristics of the membrane (porosity) and the electrolyte solution type (lithium salts and solvent). For ionic conductivity improvement, the Lewis acid-base interactions between filler surface groups, polymer matrix and cations/anions play an essential role.

Different fillers also incorporate complementary characteristics to the separator membranes. The molecular sieves produce a specific conducting pathway on the membranes and improve mechanical strength.^{132,142} The MMT particles do not affect the morphology of the polymer matrix and increase of electrochemical behaviour of the battery separator.^{108,118,141} The inert oxide ceramics (Al₂O₃, TiO₂, ZrO₂) reduce the degree of crystallinity and promotes of Li⁺ transport at the boundaries of the filler particles.¹⁴⁴ Ferroelectric ceramic fillers (BaTiO₃) increase the polarity of the battery separator due of the high dielectric constant of the fillers and due to the charge separation.²⁸ The interfacial stability between electrodes and battery separators as well as the ionic conductivity are improved with fillers based of carbon (CNT, CNF).¹⁴⁵

Fig. 4 shows the best ionic conductivity of the composite materials obtained with the different fillers.

Fig. 4 shows that the best ionic conductivities are achieved for MgO, ZnO and MCM-41 fillers. The MgO and ZnO are inert oxide ceramics that change the dynamics of the polymer chains and MCM-41 are molecular sieves with strong Lewis acid centers in their frameworks and increase the Li⁺ transference number

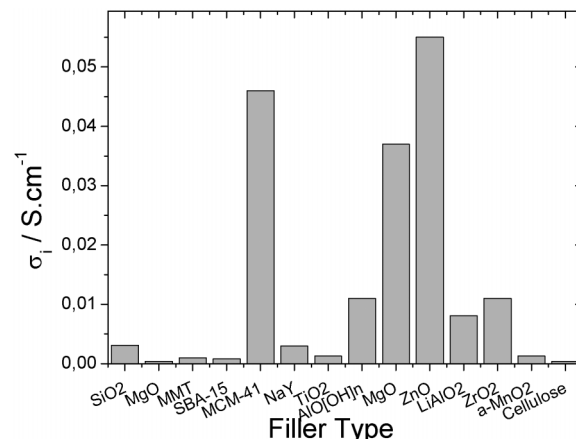


Fig. 4 Ionic conductivity for different filler types.

2.3 Poly(vinylidene fluoride) and copolymer based polymer blends

Another strategy for enhancing the ionic conductivity and other relevant properties of battery separator membranes such as mechanical and thermal properties is the fabrication of polymer blends. In the polymer blends for battery separators the strategy has been the following: one polymer should show a very good affinity with the liquid electrolyte and the other polymer must show excellent mechanical properties. The dimensional and electrochemical stability are also necessary requirements for polymer blends.

The developed PVDF and copolymers based polymer blend membranes are summarized in Table 4 in chronological order.

Table 4 shows that the polymer blends show high ionic conductivity and the polymers more used with PVDF and its copolymers are PMMA and PEO due to the increased adhesion of electrodes and battery separators as well as to the ability to solvate a wide variety of salts, respectively.

PVDF-HFP/PAN polymer blend membranes were prepared by Kim *et al.* and high ionic conductivity and good mechanical properties were observed for the gel polymer electrolytes.¹⁴⁶

PVDF-HFP/PE blend membranes show that PE particles dispersed in PVDF-HFP form a continuous film with 23 wt% of PE. The continuous PE film exhibits the ability to cut off the ion diffusion between cathode and anode and induces high ionic conductivity and good mechanical strength.¹⁴⁷

Rajendran *et al.* determined that the resulting ionic conductivity of the blend membranes is determined by the overall mobility of ion and polymer, which depends on the free volume around the polymer chain.¹⁴⁸ In the PMMA/PVDF (25–75) polymer blend with LiClO₄ an ionic conductivity of 3.14×10^{-5} S cm⁻¹ was obtained at room temperature.

PMAML/PVDF-HFP is a promising electrolyte candidate for rechargeable lithium ion polymer batteries as it shows high ionic conductivity (2.6 mS cm⁻¹ at room temperature and electrochemical window around 4.6 V) and good electrochemical stability.¹⁴⁹

Michael *et al.* demonstrated that PVdF-HFP/PVK with LiBF₄ offers the room temperature ionic conductivity of 0.72 mS cm⁻¹ with an ionic transference number of 0.49.¹⁵⁰

Table 4 Polymer electrolyte blends based on PVDF and copolymers and their properties, presented in chronological order

Material	Blends	Electrolyte solution/lithium ions	Porosity (%)	Uptake (%)	$\sigma_i/(S\text{ cm}^{-1})$ at 25 °C	Ref.
PVDF-HFP	PAN	1 M LiPF ₆ in EC/DMC (1/1)	76	82	1.9×10^{-3}	146
PVDF-HFP	PAN	1 M LiBF ₄ in EC/DMC (1/1)	76	80	1.2×10^{-3}	146
PVDF-HFP	PE	1 M LiClO ₄ /PC + EC	—	—	0.2×10^{-3}	147
PVDF	PMMA	10 mol% LiClO ₄	—	—	3.1×10^{-5}	148
PVDF-HFP	PVP	1 M LiBF ₄ in EC/DMC (1/1)	—	62	0.4×10^{-3}	152
PVDF	PAN	LiClO ₄ -PC-EC	—	—	—	153
PVDF-HFP	PEG	LiTFSI	—	—	1.0×10^{-5}	154
PVDF-HFP	PMAML	1 M LiBF ₄ in EC/DMC (1/1)	76	75	2.6×10^{-3}	149
PVDF	PMMA-PEGDA	1 M LiPF ₆ in EC/DMC/EMC (1/1/1)	—	600	4.5×10^{-3}	155
PVDF-HFP	PEG-PEGDMA	1 M LiPF ₆ in EC/DEC (1/1)	15	98	1.0×10^{-3}	156
PVDF-HFP	PVK	1.5 M LiBF ₄ in EC	—	—	0.7×10^{-3}	150
PVDF	PEGDA-PMMA	LiPF ₆ /LiCF ₃ SO ₃ in EC/DMC/EMC (1/1/1)	—	—	1.0×10^{-3}	157
PVDF	PE	1 M LiPF ₆ in EC/DEC/PC (35/60/5, w/w/w)	48	302	1.1×10^{-3}	151
PVDF	PE	1 M LiPF ₆ in EC/DEC/PC (35/60/5, w/w/w)	53	290	8.9×10^{-4}	158
PVDF-HFP	PEO	1 M LiTFSI in EC/PC	—	—	—	159
PVDF-HFP	PEO	1 M LiTFSI in EC/PC (1/1)	—	—	—	160
PVDF	PEO	1 M LiClO ₄ in PC	84	210	2.0×10^{-3}	161
PVDF-HFP	PAN	1 M LiClO ₄ in EC/DEC (1/1)	—	—	3.4×10^{-3}	162
PVDF-HFP	PVP-PEG	1 M LiPF ₆ in DMC/EMC/EC (1/1/1)	49	125	0.5×10^{-3}	163
PVDF-HFP	P(EO-EC)	LiCF ₃ SO ₃	65	61	3.7×10^{-5}	164
PVDF	PMMA	1 M LiPF ₆ in DMC/EMC/EC (1/1/1)	—	—	—	165
PVDF-HFP	PEG	1 M LiPF ₆ in DEC/EC (1/1)	90	100	1.0×10^{-4}	166
PVDF	PVC	NaClO ₄ + PC	—	—	1.5×10^{-4}	167
PVDF-HFP	PVA	1 M LiClO ₄ in EC/DEC (1/1)	86	90	7.9×10^{-3}	119
PVDF	PVC	LiClO ₄ + EC/PC	—	—	3.7×10^{-3}	168
PVDF	PAN	1 M LiClO ₄ in PC	85	300	7.8×10^{-3}	20
PVDF-HFP	PAN	1 M LiPF ₆ in EC:EMC (1 : 3)	83	—	6.7×10^{-3}	169
PVDF	PMMA	1 M LiPF ₆ in EC:DMC (1 : 1)	—	260	7.9×10^{-3}	55
PVDF	PDPA	1 M LiClO ₄ in PC	—	280	3.6×10^{-3}	24
PVDF-HFP	PEGDMA	1 M LiClO ₄ in EC/DEC	—	125	3.8×10^{-4}	170
PVDF	PEGDA-PEO-PPO-PEO	1 M LiClO ₄ in EC/PC (1/1)	32	63	1.9×10^{-3}	171
PVDF	PMMA	1 M LiClO ₄ in EC/PC (1/1)	—	292	1.9×10^{-3}	172
PVDF-HFP	SN	LiClO ₄	—	—	1.0×10^{-3}	173
PVDF-HFP	PE	1 M LiPF ₆ in EC/ DEC (1/1)	—	—	$0.8\text{--}1.2 \times 10^{-3}$	174
PVDF-HFP	PMMA	1 M LiPF ₆ in EC:DMC (1 : 1)	—	377	2.0×10^{-3}	175
PVDF-HFP	PET	1 M LiPF ₆ in EC:DMC (1 : 1)	—	—	0.8×10^{-3}	176
PVDF-HFP	PVA	8 wt% LiBF ₄ + 67 wt% EC	—	—	1.2×10^{-3}	177
PVDF	PDMS	1 M LiPF ₆ in EC:DMC:EMC (1 : 1 : 1)	55	250	1.2×10^{-3}	178
PVDF-HFP	PPG-PEG-PEG	1 M LiClO ₄ in EC/PC (1/1)	—	259	1.3×10^{-2}	179
PVDF-HFP	PMMA	1 M LiClO ₄ in EC/DEC (1/1)	50	403	1.7×10^{-3}	180
PVDF-TrFE	PEO	1 M LiClO ₄ ·3H ₂ O-PC	74	92	3.0×10^{-4}	181

A new type of separator was introduced by Lee *et al.*¹⁵¹ by coating poly(vinyl alcohol) (PVAc) on the surface of a PVDF/PE non-woven matrix. The coated separator exhibits smoother surface morphology and better adhesion properties toward electrodes.

Sannier *et al.*, produced a polymer blend of PVDF-HFP/PEO and also highlighted the role of the macroscopic blend interfaces toward dendrite in bi-layered separators.¹⁶⁰

For PVDF/PEO or PVDF-HFP/PEG blends, the addition of PEO or PEG in the PVDF matrix improves the pore configuration (connectivity) of the PVDF microporous membranes and increases ionic conductivity.^{161,166}

Electrospun membranes based on PVDF were prepared and modified *via* pre-irradiation grafting with PMMA. PMMA possesses good affinity for the liquid electrolyte and gelled PMMA could substitute nonconductive PVDF for being in contact with the electrodes.⁵⁵

Sohn *et al.* prepared a PVDF-HFP/PEGDMA coated PE separator for lithium ion battery applications by electron beam irradiation (EB). The EB treatment of the blend membranes containing PEGDMA was found to strongly

improve the thermal shrinkage of the separators by the formation of crosslinked networks, enhancing also electrolyte uptake and ionic conductivity.¹⁷⁰

The ionic conductivity of the polymer blends for battery separators depends on the affinity between polymers and the characteristics of the membrane (*e.g.* porosity, crystallinity, *etc.*), which also depends on the processing technique such as thermal induced phase separation (TIPS). Fig. 5 shows the best ionic conductivity for each developed polymer blend type.

The common element for the polymer blends with the best ionic conductivity is the presence of PVDF-HFP (Fig. 5) due to the lower degree of crystallinity, its dielectric constant, $\epsilon = 8.4$, and strong electron withdrawing functional groups (–C–F–).

3. Anode and cathode electrodes used with PVDF based separators

The two different types of electrodes, anode and cathode, immersed in the electrolyte solution create the electrical potential, *i.e.* the electrochemical cell.

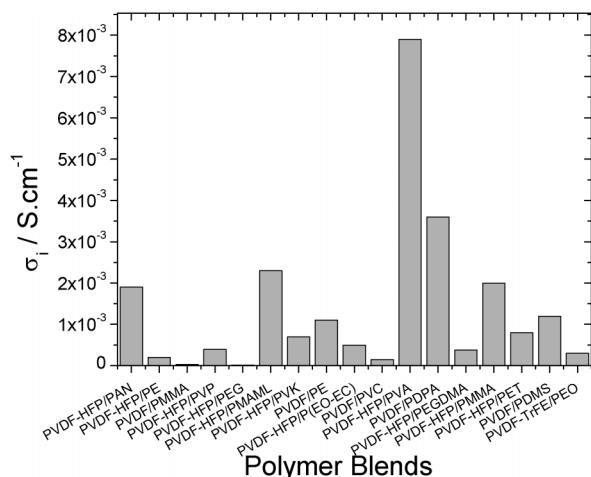


Fig. 5 Best ionic conductivity for the different polymer blends.

During charging process, electrons move from the cathode to the anode (Fig. 6, left) and during discharge the electrons move from the anode to the cathode (Fig. 6, right).¹⁸²

The anode is the negative active material. It is commonly based on carbonaceous materials and non carbon alloys where reversion reaction occurs.¹⁸³ Examples of carbonaceous materials used as anode materials are graphites, carbon nanotubes (CNT), carbon nanofibres (CNF) and lithium titanium oxides (Li₄Ti₅O₁₂). Carbonaceous materials show the largest potential for improving the lithium ion cells and versatile, strong and highly conductive electrodes have been obtained to be used as anodes in batteries systems.¹⁸⁴

The cathode is the positive active material. It is based on transition metal oxides and it is the main responsible for the cell capacity and cycle life.

Lithium cobalt oxide (LiCoO₂), lithium manganese dioxide (LiMnO₂), Lithium nickel oxide (LiNiO₂) and lithium iron phosphate (LiFePO₄) are some examples of materials used as cathodes.

For batteries with separator membranes based on PVDF and copolymers, the most used materials for the anode electrodes are Sn nanoparticles within a carbon matrix (Sn-C), graphite and lithium foil and for the cathode electrode are

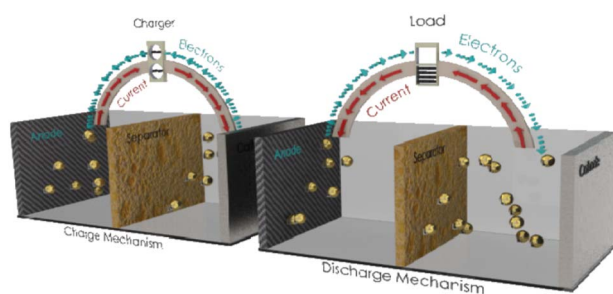


Fig. 6 Representation of the charge and discharge modes of the electrochemical cell.

LiFePO₄, LiCoO₂ and lithium nickel manganese oxide (LiNi_{0.5}Mn_{0.5}O₄).^{67,94,97}

The above-mentioned electrodes are of general use for different separator membranes and some work still remains to be developed in this area in order to optimize electrodes for PVDF based separators. Further, it is to notice that electrodes are typically formed by an active material, additives and a polymer binder. The polymer binder used both as anode and cathode for lithium-ion batteries can be also based on PVDF polymer due to its electrochemical, thermal and chemical stability as well as its easy processing.

4 Conclusions and further work

This review presents an overview on PVDF and its copolymers for separator membranes in lithium-ion batteries applications. The battery separator is a critical element for improving lithium-ion battery performance. The review reports the research and developments in this field in the last decade. The correlation between properties and the fabrication methods is fundamental in order to achieve adequate battery separators for applications. It is essential the knowledge and control of their structure, stability and ionic conductivity in order to increase performance of the materials as battery separators. The review is divided into three different categories due of its characteristics, *i.e.*, single polymers, composites and polymeric blends. Each category presents advantages and disadvantages:

For single polymers, PVDF and PVDF-HFP with LiPF₆ and LiCF₃SO₃ in different organic solvents provide the best values of the ionic conductivity ($1.8 - 5 \times 10^{-2}$ S cm⁻¹), and a large range of porosities and pore sizes can be obtained allowing tailoring membrane properties for the specific battery application. The ideal membrane for porous polymer electrolytes based on PVDF for battery applications should have high porosity and small pore diameters with narrow distribution. The experiments show that porosity should be >80% and pore diameter should be <1 μm. These characteristics are also obtained with up-scalable methods such as electrospinning.

The thermal and mechanical stability of single polymer membranes can be improved both by including specific fillers and by the development of polymer blends.

Fillers have been used that contribute to the ionic conduction process and fillers that are not involved in the lithium transport process. Particularly interesting are the fillers, such as MgO, that increase the compatibility between the separator and the electrodes. Also interesting are the molecular sieves that have proven to extend the electrochemical stability window of polymer electrolytes, enhanced the interfacial stability of the polymer electrolyte with the lithium electrode and inhibited the crystallization of the polymer matrix.

With respect to the polymer blends, one of the components should show a very good affinity to the liquid electrolyte and the other polymer must show excellent mechanical properties.

The best blend membranes have been obtained with PVDF-HFP. Polymer blends also improve thermal shrinkage of the separators by the formation of cross linked networks and enhance electrolyte uptake and ionic conductivity.

With respect to the future trends, single polymers and copolymers have to be achieved with similar large degrees of porosity (~80%) but with hierarchical pore size structures down to pore sizes below 1 µm in an up-scalable way. This will allow to improve uptake without compromising mechanical properties and to obtain larger batch productions.

The incorporation of ionic liquids in the single polymer membranes is a promising field for more environmental friendly battery separators with high ionic conductivity at room temperature and wider electrochemical windows.

In composite materials, some work is needed, *e.g.* through surface functionalization, to improve compatibility between fillers and polymer matrix and therefore to improve the stability of the membrane.

Polymer blends are one of the most promising ways to improve PVDF based separator membranes. The progress in this category involves the fabrication of multilayers or hierarchical pore structures to enhance the thermal, electrical, mechanical and electrochemical properties of the battery separators and to improve compatibility with electrodes.

In conclusion, PVDF based polymer electrolytes offer broad engineering possibilities for membranes preparation with tailored microstructure and properties, showing therefore large potential for a new generation of more efficient battery separator membranes.

List of symbols and abbreviations

13TFSI	<i>N</i> -methyl- <i>N</i> -propylpiperidinium Bis(trifluoromethanesulfonyl) Amide
Al ₂ O ₃	Aluminum Oxide
AlO[OH] _{<i>n</i>}	Aluminum Oxyhydroxide
AN	Acetonitrile
BaTiO ₃	Barium Titanate
BMIBF ₄	1-Butyl-3-Methylimidazolium Tetrafluoroborate
BMITFSI	1-butyl-3-Methylimidazolium bis(trifluoromethanesulfonyl)imide
BMPyrTFSI	1-Butyl-3-Methylpyrrolidinium Bis (trifluoromethanesulfonyl)imide
CNF	Carbon Nanofibres
CNT	Carbon Nanotubes
CoO	Cobalt Oxide
CTFE	Chlorotrifluoroethylene
DEC	Diethyl Carbonate
DIOX	1,3-Dioxolane
DMBITFSI	1,2-dimethyl-3- <i>n</i> -butylimidazolium-bis-trifluoromethanesulfonylimide
DMC	Dimethyl Carbonate
DMOImPF ₆	2,3-Dimethyl-1-octylimidazolium Hexafluorophosphate

EC	Ethylene Carbonate
EMC	Ethyl Methyl Carbonate
EMITF	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
Fe ₂ O ₃	Iron Oxide
GBL	γ-butyrolactone
HFP	Hexafluoropropene
ILs	Ionic Liquid
LiAlO ₂	Lithium Aluminate
LiAsF ₆	Lithium Hexafluoroarsenate
LiBF ₄	Lithium Tetrafluoroborate)
LiBETI	Lithium Bis(perfluoroethanesulfonyl)imide
LiCF ₃ SO ₃	Lithium Trifluoromethanesulfonate
LiClO ₄	Lithium Perchlorate
LiClO ₄ ·3H ₂ O	Lithium Perchlorate Trihydrat
LiCoO ₂	Lithium Cobalt Oxide
LiFePO ₄	Lithium Iron Phosphate
LiPF ₆	Lithium Hexafluorophosphate
LiMnO ₂	Lithium Manganese Dioxide
LiNiO ₂	Lithium Nickel Oxide
LiNi _{0.5} Mn _{0.5} O ₄	Lithium Nickel Manganese Oxide
LiTFSI	Lithium Bis(Trifluoromethanesulfonyl)Imide
Li ₄ Ti ₅ O ₁₂	Lithium Titanium Oxides
MCM-41	Molecular Sieves
Mg(CF ₃ SO ₃) ₂	Magnesium Triflate
Mg(ClO ₄) ₂	Magnesium Perchlorate
MgO	Magnesium Oxide
NH ₄ PF ₆	Ammonium Hexafluorophosphate
MMT	Montmorillonite
MnO ₂	Manganese Dioxide
NaClO ₄	Sodium Salt
NaTf	Sodium Triflate
NaY	Molecular Sieves
PAN	Poly(acrylonitrile)
PC	Propylene Carbonate
PDPA	Polydiphenylamine
PDMS	Poly(dimethylsiloxane)
PE	Poly(ethylene)
PEG	Poly(ethylene glycol)
PEGDA	Poly(ethylene glycol diacrylate)
PEGDMA	Poly(ethylene glycol dimethacrylate)
PEO	Poly(ethylene oxide)
P(EO-EC)	Poly(ethylene oxide- <i>co</i> -ethylene carbonate)
PEO-PPO-PEO	Polyethylene oxide- <i>co</i> -polypropylene oxide- <i>co</i> -polyethylene oxide
PET	Poly(ethylene terephthalate)
PMAML	Poly(methyl methacrylate- <i>co</i> -acrylonitrile- <i>co</i> -lithium methacrylate)
PMMA	Poly(methyl methacrylate)
PMMITFSI	1,2-dimethyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide
PP	Poly(propylene)
PPG-PEG-PPG	Poly(propylene glycol)- <i>co</i> -poly(ethylene glycol)- <i>co</i> -poly(propylene glycol)
PVA	Poly(vinyl alcohol)

PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
P(VDF-CTFE)	Poly(vinylidene fluoride-co-chlorotrifluoroethylene)
P(VDF-HFP)	Poly(vinylidene fluoride-co-hexafluoropropene)
P(VDF-TrFE)	Poly(vinylidene fluoride-co-trifluoroethylene)
PVK	Poly(<i>N</i> -vinylcarbazole)
PVP	Poly(vinyl pyrrolidone)
SBA-15	Molecular Sieves
SiO ₂	Silicon Dioxide
SN	Succinonitrile
Sn-C	Sn nanoparticles within a carbon matrix
SnO ₂	Tin Dioxide
TEABF ₄	Tetraethylammonium Tetrafluoroborate
TEGDMA	Tetraethylene Glycol Dimethyl Ether
TEGDME	Tetra(ethylene glycol) Dimethyl Ether
TiO ₂	Titanium Dioxide
TrFE	Trifluoroethylene
VDF	Vinylidene Fluoride
ZnO	Zinc Oxide
ZrO ₂	Zirconium Dioxide

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