

Review Article

Lithium-ion battery separators: Recent developments and state of art

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Abstract

Lithium-ion battery separators are receiving increased consideration from the scientific community. Single-layer and multilayer separators are well-established technologies, and the materials used span from polyolefins to blends and composites of fluorinated polymers. The addition of ceramic nanoparticles and separator coatings improves thermal and mechanical properties, as well as electrolyte uptake and ionic conductivity. The state-of-art separators are actively involved in the cell chemistry through specific functional groups on their surface. Among the numerous properties, safety features and long cycle life are high-priority requirements for next-generation lithium-ion batteries.

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Keywords

Lithium, Li-ion, Batteries, Separators, Layer, Multilayer, Ceramic, Multifunctional, PVDF, Polyolefin, Trap, Dispense, Ions.

Introduction

Owing to the demand for “green” products, lithium (Li)-ion batteries have received considerable attention as an energy storage system [1,2]. Although the separator, which is placed between the anode and the cathode, is not directly involved in electrochemical reactions, its structure and its properties play an important role in cell performance. The primary purpose of the separator is to prevent the physical contact of electrodes while serving as the electrolyte reservoir to enable ion transport. Nowadays, separators have new important requirements; for example, separators for

electric vehicles or energy storage stations need high thermal and mechanical stability, together with a high electrolyte wettability [3]. Li-ion batteries experience critical issues when operated at extreme temperatures. The spatial and temporal fluctuations of temperature inside batteries originating from internal ‘hot spots’ (regions of high current density) may result in internal short circuits and lead to thermal runaway [4]. Low temperatures (below 0 °C) are detrimental for Li-ion battery performances with a loss in power and energy capabilities or even damage in the structure of cells [5].

While separators may be divided into categories according to their structure (such as microporous membranes, nonwoven mats, gel polymer electrolytes, and composite membranes [6]), new trends suggest a classification based on the number of layers, ceramics addition, and surface modification [5,7–9]. This change is due to a shift of focus from obtaining a specific membrane morphology to implementing new desired properties, especially in terms of safety. The state-of-art separators have a thickness less than 10 μm [1], and the risk of electrolyte degradation or dendrite formation is increased in batteries with high-energy density [2]. In general, modern Li-ion batteries are affected by three major degradation modes: (1) dissolution of transition metals from positive electrodes; (2) chemical loss of Li⁺ ions; and (3) decomposition of solution components [9]. Large overpotentials prevent the theoretical voltage and specific capacity of the cell from being obtained and contribute to heat generation and lithium plating [10].

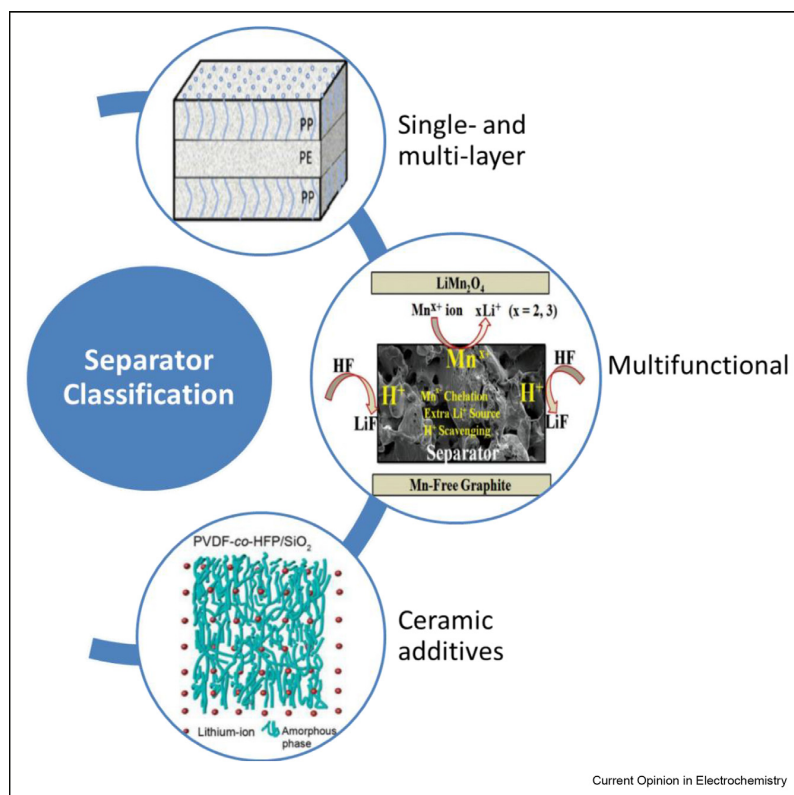
In this review, we discuss current trends for Li-ion battery separators. We introduce and analyze the characteristics, performance, and modifications of single-layer and multilayer, ceramic-based, and multifunctional separators (Figure 1). Table 1 summarizes pertinent information about the separators discussed in this review.

Discussion

Single-layer and multilayer separators

Because thick separators (>50 μm) decrease the areal power density, most commercial batteries have used thin (<25 μm) polyolefin monolayer microporous separators, whose characteristics are good mechanical strength, excellent chemical stability, low cost, and

Figure 1



Separator classification. Single-layer and multilayer cartoon reprinted from the study by Shi et al [53], copyright 2015, with permission from Elsevier; ceramic additive schematic reprinted from the study by Boateng et al [33], copyright 2018, with permission from WILEY; multifunctional schematic reprinted from the study by Banerjee [46], copyright 2016, with permission from WILEY.

advantageous thermal shutdown properties [11]. Mechanically and electrochemically stable polymers, such as fluorinated or aromatic polymers, have also been considered, as explained in the following paragraphs [7]. Among other polymers, poly(vinylidene fluoride) (PVDF) and its copolymers possess high polarity, low degree of crystallinity, high dielectric constant, good chemical stability, and good electrolyte wettability owing to the presence of the C–F group [5,7]. Han et al. [12] directly deposited a layer of PVDF-hexafluoropropylene (HFP) separator on a graphite anode through electrophoretic deposition in a surfactant-free colloidal system, resulting in a separator with high thermal stability (3% shrinkage at 160 °C for 5 h) and high mechanical strength (33 MPa). Although poly(vinylidene fluoride-co-trifluoroethylene) has been rarely used in Li-ion batteries, its semicrystalline and nonreactive nature, flexibility, thermal stability, and piezoelectric properties make it a promising candidate [13]. An electrospun core-shell fiber structure combining PVDF-HFP (for electrolyte stability) and

poly(acrylonitrile) (for thermal and mechanical stability) resulted in a highly porous structure and excellent electrochemical properties but with only 19 MPa for tensile strength [14], whereas an electrospun fluorinated polyimide separator has shown robust mechanical properties (~32 MPa stress at break) after cross-linking with thermal annealing at 300 °C [15].

PVDF-HFP separators can be improved with an interparticle chain structure [16]. First, the polymer is partially dissolved in acetone, cast on a substrate, and dried. Then, through an electrolyte soaking and drying procedure, both undissolved polymer particles and polymer chains rearrange toward a higher density structure, and the particles are no longer visible. The prepared separator has a highly porous and polar structure, with 188 wt% electrolyte uptake. The interactions between solvents and nonsolvents influence the formation of pores and phase transformation process [17,18], leading to different morphologies, such as sponge-like or finger-like pores with an asymmetric

distribution [5]. With a similar concept, a separator can be prepared with two different solvents, such as N-methyl pyrrolidone and acetone. The variation in solvent evaporation rate creates a hierarchical structure with high porosity, leading to enhanced ionic conductivity (Figure 2). The authors attribute a near-zero capacity fading at 10C after 1000 cycles to the increased Li^+ transport channels due to the interisland structure [17,19].

Dual-layer poly(ethylene)/poly(propylene) (PE/PP) and trilayer (PP/PE/PP) separators are advantageous to address safety issues that may arise from single-layer separators. A multilayer PE/PP separator made via a combination of multilayer coextrusion and thermally induced phase separation shows high thermal stability with shutdown capability at wide temperature window [20]. Its highly porous structure provides enhanced electrolyte uptake and ionic conductivity. Similar to multilayer coextrusion, a template method by use of CaCO_3 can create a PE–PP multilayer separator with an adjustable thermal shutdown capability, with high thermal stability at 160 °C [21]. A trilayer structure of PP/PE/PP microporous membranes provides unique puncture strength (at least 300 g mil⁻¹), and the low-melting PE layer acts as a thermal fuse, while the high-melting PP layers provide physical integrity above PE melting point [11,20]. To obtain a more homogeneous distribution of current and fast migration of Li ions between electrodes, other materials may be used in the layers, such as cellulose nanofibers and glass microfibers, which combine a nanoporous and a microporous structure [22]. The high and uniform porosity enhances electrolyte uptake and improves the electrochemical performance, while a thermal annealing at 200 °C for 30 min increases the thermal stability.

Ceramics and other composite separators

Ceramic coatings on the separator or the positive electrode has had some advantages in preventing internal short circuits due to metal particle penetration [23]. Electronic insulating metal oxides, such as SiO_2 , Al_2O_3 , SnO_2 [24], or silicone [25], can be included within the separator through sol–gel method [26], in situ deposition, film casting [27], or physical vapor deposition [28] on one or both sides of a polyolefin separator. The thin (as low as 2 μm) coating provides reduced shrinkage of the separator at shutdown temperatures, better cycling (in terms of C-rate capacities and cycle capabilities [6,26,27]), and improved electrolyte wetting because of the inorganic oxide ceramic phase [26,27,29]. The addition of hydrophobic silica aerogel to a PP separator, for example, creates a highly porous structure, high affinity to liquid electrolytes, and provides a thermal insulation capability [30]. Additional thin ceramic layers

on anodes can lower the risk of local particle penetration and of thermal runaway [31].

Complex coatings are becoming common. For example, it is reported [23] that the Sumitomo separator used by Panasonic and Tesla Motors involves a coating with ceramic particles and an aromatic polyamide to increase the penetration strength. Improved coatings should not impede ion flux but improve penetration strength or combine chemically with lithium dendrites [32]. The PVDF-HFP/ SiO_2 separator prepared in acetone, in a unique way without using a surfactant, exhibits high thermal stability (4.5% shrinkage 160 °C for 1 h), good mechanical strength (14 MPa), enhanced ionic conductivity (1.2 mS cm⁻¹), and long cycle performance [33]. The authors claim that the improvement in Li^+ transport efficiency indicates that the electrolyte is also absorbed by the SiO_2 nanoparticles, which decrease the polymer crystalline phase (Figure 3). The combination of ceramic nanoparticles with nanofibers creates a unique environment with excellent properties. Poly(vinyl alcohol)/ SiO_2 membranes fabricated through sol–gel electrospinning are simple but effective separators [29], whereas a more complex electrospun PVDF/poly(methyl methacrylate) (PMMA)/ SiO_2 separator [34] has excellent mechanical (tensile strength ~ 33 MPa) and cycling properties (capacity retention 91% at 0.2C after varying-rate capability measurements). Electrospinning can create ultrathin and strong porous PVDF/PE/PVDF trilayer separators [35], and the addition of silica nanoparticles results in an electrolyte uptake of 380 wt% and an ionic conductivity of 2.5 mS cm⁻¹. The sandwich-like structure delivers superior discharge capacity even at high current densities. Nanoparticles may also be deposited through atomic layer deposition [36]. The resulting separator shows a 0% shrinkage at 200 °C and robust fire retardant capability, without compromising the cell performance. Paper-based separators are an interesting alternative to polyolefin membranes for more economically viable separators [37].

Ionic liquid (IL) electrolytes are a safer alternative to existing organic electrolytes. A good compatibility between IL electrolytes and separator materials would increase the separator wettability, which is the current major drawback with these electrolytes [38]. A poly(methyl methacrylate-acrylonitrile-ethyl acrylate)-coated Celgard 2400 was investigated in lithium bis(trifluoromethanesulfonyl)imide/N-ethyl-N-methylimidazolium bis(trifluoromethanesulfonyl)imide IL electrolyte [39]. When equal parts of SiO_2 and Al_2O_3 are added to the separator, the improved bond strength of Si–O/Al–O cross-section points and the polymer network results in excellent thermal and mechanical stabilities. The authors report that chemical interactions between metal oxide nanoparticles and the

Table 1

Relevant literature on Li-ion battery separators.

Material	Ion conductivity (mS cm ⁻¹)	Thickness (μm)	Thermal shrinkage	Electrolyte uptake (wt %)	Tensile strength (MPa)	Preparation procedure	Ref.
PP/PE	1.35	25	~0% @ 150 °C ^a	148	13	Multilayer coextrusion and CaCO ₃ template method	[21]
PP/PE	1.46	25	3% @ 150 °C	157	16	Multilayer coextrusion and thermal induced phase separation	[20]
PP/silica aerogel	0.63	31	25% @ 160 °C	346	N/R ^b	PP separator coated with PVDF and silica aerogel slurry	[30]
PP/silicone	0.25	N/R	1% @ 160 °C	96	N/R	K ₂ Cr ₂ O ₇ -activated PP in trichloromethylsilane atmosphere	[25]
PE/SnO ₂	0.72	N/R	~0% @ 130 °C	119	160	Binder-assisted coating of SnO ₂ onto PE	[24]
SiO ₂ -grafted PE	0.84	15	4% @ 120 °C	N/R	N/R	3-Methacryloxypropyltrimethoxysilane and 1,8-bis(triethoxysilyl)octane react with UVO-treated PE separators	[49]
PE/SiO _x C _y H _z	0.36	12	10% @ 130 °C	105	N/R	PE separator is treated with hexamethyldisiloxane/O ₂ /Ar plasma	[50]
PP/PPTA	0.90	30	~0% @ 200 °C	N/R	35	Poly-p-phenylene terephthamide is polymerized and cast on Celgard PP	[43]
PP/PDA/SiO ₂	0.55	N/R	22% @ 160 °C	130	N/R	Celgard PP soaked in dopamine, then silane (GPTMS) solutions	[26]
PP/PVDF/metal oxide	1.69	35	18% @ 160 °C	218	N/R	Celgard PP coated (doctor blade) with PVDF/metal oxide soln.	[27]
PE/PVDF/SiO ₂	2.50	20	3% @ 170 °C	380	11	Layered electrospun PVDF/PE/PVDF solution with SiO ₂	[35]
PVDF/PMMA/SiO ₂	4.00	30	~0% @ 150 °C	406	33	Electrospun PVDF/PMMA/SiO ₂ solutions are hot pressed	[34]
PVDF-TrFE/Al ₂ O ₃	5.80	N/R	N/R	320	3	Polymer and Al ₂ O ₃ electrospun together in methyl ethyl ketone	[13]
PVDF-HFP	0.81	N/R	3% @ 160 °C	75	33	Electrophoretic deposition to bond separator and graphite anode	[12]
PVDF-HFP	1.08	N/R	5% @ 150 °C	188	16	Electrolyte-soaked polymer creates interparticle chain structure	[16]
PVDF-HFP/PE	1.01	24	~0% @ 150 °C	216	16	Hierarchical solvent liberation method	[17]
PVDF-HFP/PAN	1.73	70	~0% @ 150 °C	420	19	Core-shell structure via coaxial electrospinning	[14]
PVDF-HFP/cellulose	1.89	115	~0% @ 200 °C	310	1	PVDF-HFP, cellulose acetate in NMP cast on glass, treated with LiOH	[40]
PVDF-HFP/PE- <i>alt</i> -MALi ₂	1.90	50	N/R	110	N/R	PE- <i>alt</i> -MALi ₂ embedded in PVDF-HFP with phase inversion	[46]
PVDF-HFP/SiO ₂	1.26	30	5% @ 160 °C	420	14	Colloidal PVDF-HFP/SiO ₂ suspension cast on a metal plate	[33]
PVDF-HFP/Al ₂ O ₃	1.24	42	~0% @ 200 °C	240	N/R	Al ₂ O ₃ deposited with ALD on electrospun PVDF-HFP	[36]
PVDF-HFP/Al ₂ O ₃	3.27	N/R	~0% @ 150 °C	115	23	Instantly reformed gel with direct postsolidation	[19]
PVDF-HFP/Al ₂ O ₃	0.05	40	4% @ 150 °C	372	18	Phase inversion PVDF solution mixed with Al ₂ O ₃ solution	[4]
PVDF-HFP/LLZO	0.74	25	~0% @ 160 °C	251	18	Postsolidation of LLZO incorporated in PVDF-HFP gel	[44]
PE/P(MMA-AN-EA)/SiO ₂ /Al ₂ O ₃ /EMITFSI	3.20	N/R	N/R	N/R	160	Emulsion polymerization of MMA:AN:EA(4:2:1). Polymer and metal oxides in DMF are cast (doctor blade) on PE Celgard for phase inversion	[39]
P(MMA-POSS)	3.41	220	N/R	275	N/R	Phase conversion: polymer + vinyl-trimethoxysilane/nonwoven	[18]
PEEK/PMMA	1.03	41	~0% @ 150 °C	173	70	Chloromethylated PEEK and PMMA trilayer electrospun and pressed	[51]
Tissue paper/Al ₂ O ₃	1.64	48	~0% @ 130 °C	N/R	5	Al ₂ O ₃ spray coated on a tissue paper	[37]
PVA/SiO ₂	1.81	25	~0% @ 170 °C	405	11	Electrospinning of PVA and tetraethyl orthosilicate solution	[29]
PU/graphene oxide	3.73	100	~0% @ 170 °C	733	3	Polyurethane and graphene oxide in THF/DMF are electrospun	[41]
Cellulose/glass fiber	1.14	20	~0% @ 200 °C	N/R	N/R	3-step filtration: layered fibrous cellulose/glass/cellulose	[22]

Cross-linked PEGDMA	3.00	100	N/R	N/R	N/R	N/R	PEGDMA, vinylsulfonic acid sodium salt, diethyl allylphosphate in UV	[52]
Fluorinated PI	1.50	35	N/R	620	32	FPI made with polycondensation, electrospraying, cross-linking		[15]

HFP, hexafluoropropylene; PEGDMA, poly(ethylene glycol) dimethacrylate; PEEK, poly(ether ketone); PE, poly(ethylene); PP, poly(propylene); ALD, atomic layer deposition; PPTA, poly(p-phenylene terephthalamide); PDA, polydopamine; PVDF, poly(vinylidene fluoride); PMMA, poly(methyl methacrylate); TrFE, trifluoroethylene; PAN, polyacrylonitrile; MaLi2, maleic acid; P(MMA-ANEA), poly(methyl methacrylate-acrylonitrile-ethyl acrylate); EMITFSI, Lithium bis(trifluoromethanesulfonyl)imide/N-ethyl-N-methylimidazolium bis(trifluoromethanesulfonyl)imide; POSS, silsesquioxane; PVA, poly(vinyl acetate); PU, Polyurethane; PI, polyimide.

^a ~0 = 'no visible shrinkage'.

^b N/R = 'not reported'.

electrolyte provide a high ionic conductivity (3.2 mS cm^{-1}) and high oxidation potential (5.7 V).

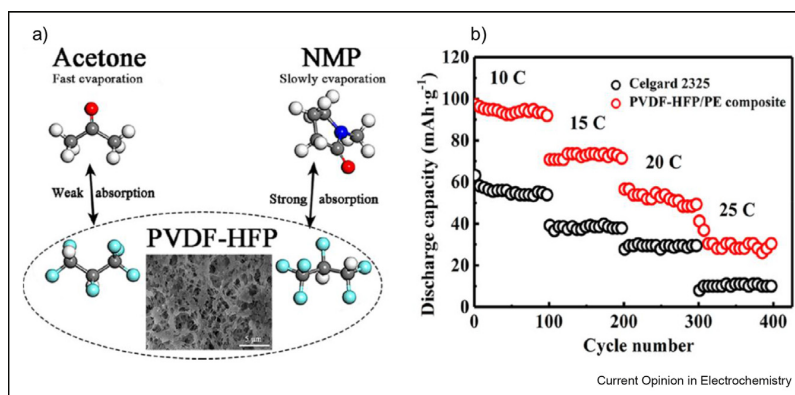
Organic materials, such as cellulose, are also used as fillers in polymers for the fabrication of composite separators due to increased ionic conductivity, electrolyte uptake, electrochemical performances, and abundance of raw material in nature [40]. Sometimes the use of inorganic materials as additives with polymers results in a nonuniform dispersion. Various particle surface modification techniques have been reported to solve this problem but the solutions are costly and time consuming. Graphene oxide has high dispersion in polymer matrices because of its polar groups, and graphene oxide-modified polyurethane separators show high electrolyte uptake (733 wt%), high ionic conductivity (3.7 mS cm^{-1}), and superior thermal stability (up to 300°C) as compared with metal oxides fillers [41]. Urethanes and fluorinated polymers, when modified with charged functional groups, may potentially be used as matrices for solid electrolytes. Scientists have recently focused on decoupling ionic conductivity from polymer segment relaxation to explore new ion transport mechanisms for solid electrolytes [1,40]. The fibrillar units of poly(p-phenylene terephthalamide or LLZTO ($\text{Li}_3\text{La}_2\text{Zr}_2\text{O}_{12}$) have been used to generate various migration routes for Li ions between electrodes [42,43]. LLZTO, in particular, suppresses lithium dendrite growth by forming a highly ductile quasi-solid composite separator [44].

Multifunctional separators

Traditionally, battery separators are chemically and electrochemically inert. However, a new conceptual framework for Li-ion battery design proposes that separators should actively participate in the cell chemistry to enhance performance and enable additional features. Multifunctional chemically active separators may, for example, trap transition metal cations, such as Mn, attract acid species, or dispense Li ions, with significant battery performance benefits [9,45,46]. Keeping the surface of the graphite-negative electrode free from Mn impurities during the cell formation cycles is essential for the creation of a solid-electrolyte interface (SEI) with superior properties (maximally ionically conducting, while electronically insulating) that enables an improved capacity retention and prolonged cell life [46].

Banerjee et al. [47] reported a separator made with the PVDF-HFP matrix and a modified cross-linked styrene-divinylbenzene copolymer functionalized with disodium iminodiacetate groups. $\text{LiMn}_2\text{O}_4/\text{graphite}$ cells with the aforementioned separator showed no capacity loss at 55°C cycling even after saturation of the separator with Mn ions. The thin uniform SEI provides a uniform

Figure 2



PVDF-HFP/PE separator enabled by dual-solvent hierarchical gas liberation: (a) Illustration and scanning electron microscope image, (b) rate capability measurements. Reprinted with permission from the study by Luo et al [17], copyright 2018, ACS. PVDF, poly(vinylidene fluoride); HFP, hexafluoropropylene; PE, poly(ethylene).

current distribution and reduced losses of Li⁺ ions, and the resulting smaller interfacial resistances increase the capacity utilization and improve the power performance of Li-ion batteries [48]. The same group [46] embedded a poly(ethylene-*alternate*-maleic acid) into a PVDF-HFP matrix with a phase inversion procedure. The separator not only (1) traps dissolved Mn ions (proved by elemental analysis on separator after use) but also (2) scavenges hydrogen fluoride (Fourier-transform infrared spectroscopy showed a protonation of the Li carboxylate groups of the functional polymer due to hydrogen fluoride), and (3) it is a source of sacrificial Li⁺ ions. Multifunctional separators offer new possibilities to the

incorporation of ceramics into Li-ion battery separators. SiO₂ chemically grafted on a PE separator improves the adhesion strength, thermal stability (<5% shrinkage at 120 °C for 30 min), and electrolyte wettability as compared with the physical SiO₂ coating on a PE separator [49]. A surface-grafting method overcomes the issues of coating and improves the performances of conventionally polyolefin separators, but this technique is expensive and requires special equipment. Qin et al. [50] proposed a binder-free technique with reactive atmospheric pressure plasma containing Ar/O₂/hexamethyldisiloxane to functionalize a PE separator with a thin layer of SiO_xC_yH_z. The resulting polar functional groups

Figure 3

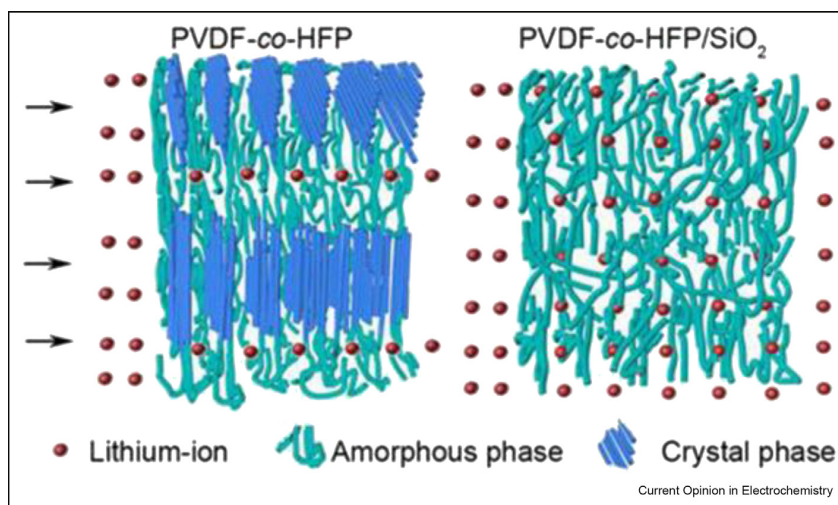
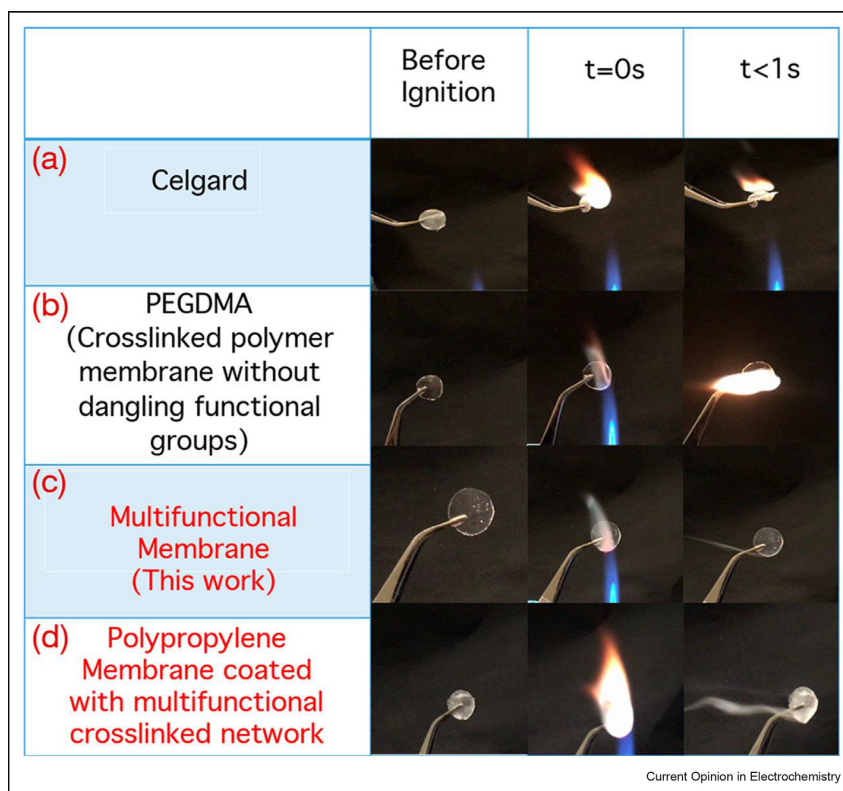


Illustration of the difference in the amorphous and crystal phases: (a) PVDF-co-HFP and (b) PVDF-co-HFP/SiO₂ separators. Reprinted from the study by Boateng et al [33], copyright 2018, with permission from WILEY. PVDF, poly(vinylidene fluoride); HFP, hexafluoropropylene.

Figure 4



Flame retardant properties of electrolyte-imbibed multifunctional membranes compared to commercial separator: (a) Celgard, (b) cross-linked poly-ethylene glycol dimethacrylate (PEGDMA), (c) multifunctional membrane, and (d) multifunctional membrane as a coating on the commercial separator. Reprinted with permission from the study by Stalin et al [52], copyright 2018, ACS.

on the PE substrate improve the wettability, electrolyte uptake, and ionic conductivity.

While an increase in performance is always desirable, multifunctional separators can also add new features, such as antishrinkage properties or flame retardancy [50,51]. Amino functionalized poly(ether ketone) (PEEK) with antishrinkage property and thermal stability was used in the outer layers of a trilayer separator, while PMMA was the intermediate layer [51]. The electrospun PEEK/PMMA/PEEK separator has high thermal stability (0% shrinkage at 150 °C) and high thermal shutdown window (100–270 °C). Cross-linked monofunctional sulfonate and phosphate species incorporated in a multifunctional oligomer separator introduce flame retardancy feature (Figure 4) and improve Li-ion transport properties [52].

Conclusions

The separator has an active role in the cell because of its influence on energy and power densities, safety, and

cycle life. In this review, we highlighted new trends and requirements of state-of-art Li-ion battery separators. In single-layer and multilayer polyolefin or PVDF-based separators, the combination of different polymer layers, the use of fluorinated polymers, the two miscible solvents, and the solvent/non-solvent techniques are all beneficial to increase the properties and performance of the separator. The addition of ceramic additives increases thermal and mechanical properties, but the traditional incorporation techniques do not provide additional functionality. Multifunctional separators, instead, offer a new range of possibilities when functional groups are incorporated in the separator, which is now chemically active and provides additional features in terms of safety and performance. Research needs to take into consideration both the market and safety needs. By nanoengineering the material network in a multifunctional separator, we would be able to create preferred pathways for ion transport in 3D structures that maximize both the Li ions motion and safety and reduce degradation.

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Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

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

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