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Review

Constructing polyolefin-based lithium-ion battery separators membrane for energy storage and conversion

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Abstract: Owing to the escalating demand for environmentally friendly commodities, lithium-ion batteries (LIBs) are gaining extensive recognition as a viable means of energy storage and conversion. LIBs comprise cathode and anode electrodes, electrolytes, and separators. Notably, the separator, a crucial and indispensable element in LIBs that mainly comprises a porous membrane material, necessitates substantial research focus. Scholars have consequently strived to devise novel systems that augment separator efficiency, bolster safety measures, and surmount existing constraints. This review endeavors to equip researchers with comprehensive information on polyolefin-based separator membranes, encompassing performance prerequisites, functional attributes, scientific advancements, and so on. Specifically, it scrutinizes the latest innovations in porous membrane configuration, fabrication, and enhancement that utilize the most prevalent polyolefin materials today. Consequently, robust and enduring membranes fabricated have demonstrated superior effectiveness across diverse applications, facilitating a circular economy that curbs waste materials, reduces operational expenses, and mitigates environmental impact.

Keywords: lithium-ion battery; separator membrane; energy storage and conversion; polyethylene; polypropylene

1. Introduction

LIBs are recognized globally as being among the most viable and potent energy storage and conversion technologies currently accessible, featuring prominently across sectors including mobile devices, electric vehicles (EVs), and energy storage systems [1,2]. In light of the escalating global demand for renewable energy and sustainable progression, the societal and economic importance of LIBs is progressively gaining traction [3–6]. Owing to their exceptional energy density, extended life span, broad operating temperature range, and superior battery voltage, LIBs have ascended as the preeminent candidate in the domain of energy storage cells, offering significant benefits across various sectors like aerospace, artificial satellites, reliable power supply for military and civilian electronic equipment [7]. Consequently, the potential applications of LIBs indicate considerable promise, calling for an enhanced focus on LIB performance, specifically addressing measures related to electrochemical efficiency (such as energy density) and security [3,8].

LIBs primarily comprise positive (cathode) and negative (anode) electrodes [9,10], electrolytes and separators [11]. Within this assembly, the separator, principally comprising a porous membrane material, holds an essential and pivotal

role within LIBs. This permeable membrane accommodates electrolytes and is incorporated between the battery's cathode and anode electrodes, serving as a significant component within LIB separators [12,13]. During the operation of LIBs, lithium ions (Li^+) navigate between cathode and anode electrodes via the separator, facilitating electrical conductivity [14]. Taking the typical lithium iron phosphate ($LiFePO_4$) battery as an example, during charging, the positive electrode (cathode) material releases Li^+, which transport towards the negative electrode (anode) through the separator membrane. Meanwhile, electrons will flow from the positive electrode to the negative electrode via an external circuit, and the opposite will occur during discharging (**Figure 1**). Significantly, the fundamental performance attributes of the membrane encompass thickness, mechanical resilience, porosity, wettability, thermal contraction, electrochemical stability, among others [15–17]. Hence, judicious material choice and meticulous structural design of separators dictate these performance characteristics and play a pivotal role in guaranteeing the secure operation and enduring charge/discharge cycles of LIBs.

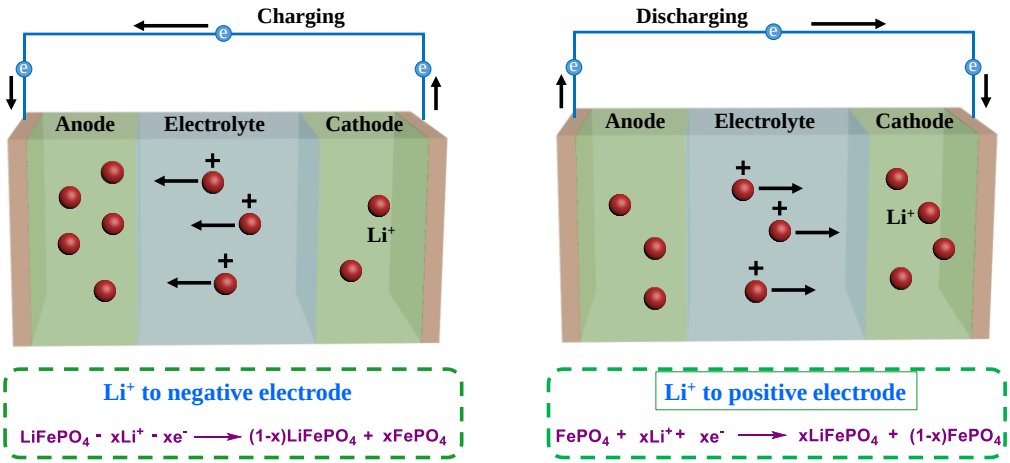

Figure 1. Schematic illustration of the fundamental operating mechanism of a typical LIB and equations of Li^+ transport for negative and positive electrodes of a typical $LiFePO_4$ battery.

Polyolefin microporous membranes, predominantly fabricated from polyethylene (PE), polypropylene (PP), and their blends, have become the predominant separator in the secondary rechargeable battery sector. Notably, ultra-high molecular weight polyethylene (UHMWPE) has gained substantial market share, polymerized with Ziegler–Natta catalysts at low pressure via a procedure described in research [18]. Such affordable membranes, suitable for mass commercialization, are, however, restricted by inherent poor thermal stability (low Tm) and flammability, along with potentially subpar electrolyte wetting properties [7,19]. Compared to other materials, polyolefin is often utilized for its exceptional features in commercial LIBs, albeit its inherent thermal shrinkage issue and inadequate electrolyte wettability, etc. Consequently, the exploration of enhanced polyolefin membranes remains a fervent area of research, with noteworthy advancements being achieved at an accelerated pace.

Significantly, the application of sustainable electrochemical energy storage and conversion apparatuses exhibits extensive advantages in fostering a circular and eco-friendly economic system [1,10,13,20,21]. Positioned as an economically viable

strategy for clean power, the primary goal of LIB separators is to devise and fabricate novel membranes for superior battery performance [22]. This review underscores the importance of polyolefin-based porous membranes for separators in LIBs, encompassing the essential prerequisites and performance metrics for optimal separators, incorporating the chemical, mechanical, electrical, and electrochemical attributes of porous separator membranes for batteries. Furthermore, this review scrutinizes contemporary breakthroughs in the fabrication, configuration, alteration, and enhancement of porous membranes, utilizing polyolefin materials. Collectively, the advancement of robust, proficient, and pioneering LIB separators serves a critical function in actualizing the principles of a circular economy, along with the overarching goals of resource optimization and environmental sustainability [23].

2. Performance parameters and characteristic of LIB separators membranes

Arranged between the cathode and the anode, the LIB separator is pivotal in thwarting potential shorts circuits due to direct interaction between the cathode and the anode active components, concurrently facilitating swift Li^+ transportation during charging and discharging procedures [24–28]. The separator serves as a pivotal component within LIBs, crucial in optimizing battery functionality and safety across diverse application environments. A multitude of technologies and methodologies are thus enlisted to evaluate membrane performance, encompassing parameters such as membrane thickness [29,30], tensile strength [31,32], puncture resistance [33], thermal stability, porosity [7], pore size [34], electrolyte wettability, chemical stability, electrolyte absorption and retention rate, dimensional stability [35], air permeability [36], electrochemical performance [37] and so on (**Figure 2**). Given their deployment in extensive equipment platforms like EVs or energy storage facilities, LIBs separator membranes necessitate superior mechanical strength, capacity, thermal stability, rate capability, excellent electrochemical performance and prolonged cycle performance [38]. Consequently, an ideal separator must satisfy specific critical physical and chemical attributes (**Figure 3**).

Given that the separator material is a non-conductive agent tasked with safeguarding electrodes indispensable for establishing ion transfer channels amid intricate electrochemical mechanisms, its intrinsic physical and chemical traits significantly influence battery functionality. Typically, the employment of a thinner and more permeable separator leads to diminished internal resistance, which subsequently increases discharge capacity [39,40]. Yet, elevated porosity and reduced thickness may compromise the separator's structural resilience, underscoring the necessity for materials that strike an equilibrium between electrochemical and mechanical properties for enhancing overall battery efficiency [36,41].

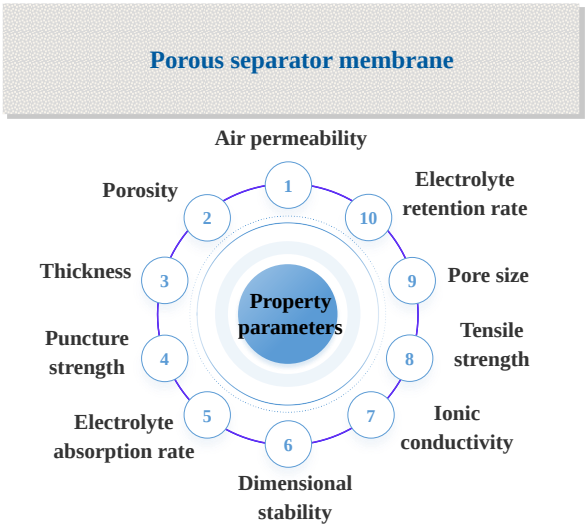

Figure 2. Illustration demonstrating the property parameters to be taken into account when devising suitable separator membranes for rechargeable LIBs.

Significantly, lithium dendrites can develop during extended charging/discharging cycles, representing the predominant and potentially catastrophic sources of internal shorts within LIBs [42]. A thicker separator offers enhanced mechanical resilience, diminishing the likelihood of short circuits during assembly. Typically, separators utilized for LIBs possess a thickness of less than 25 μm [43]. Herein, attaining a specific degree of mechanical robustness with adequate puncture and tensile strength is crucial, and this can be achieved through the utilization of a thinner separator with elevated porosity, thereby decreasing the internal impedance of the battery and enhancing high-speed discharge capabilities [32].

In addition, LIBs inevitably generate considerable heat during charging/discharging, particularly under short circuit or excessive charging. The role of the separator is paramount for maintaining exceptional dimensional stability and robust mechanical resilience across the temperature spectrum spanning from −20 °C to 90 °C [29]. Presently, there exist two predominant coating methodologies employed to enhance LIBs thermal endurance, namely inorganic coatings and organic coatings [44–46]. Specifically, the inorganic ceramic layers comprise inorganic particles and binders, encompassing but not confined to aluminum oxide (Al_2O_3), boehmite, zirconium dioxide (ZrO_2), etc. Conversely, organic coating, also referred to as organic composite modification, involves the application of an organic compound (such as polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), polydopamine (PDA), aramid, polyimide (PI) and their blends) onto the surface of the separator membrane, demonstrating outstanding liquid absorption and retention capacities, coupled with superior adhesion characteristics [7].

Besides, thermal shutdown constitutes an integral role in the separator's effectiveness, culminating in the sealing of the micropores when the battery encounters a short circuit and the temperature deviates outside its specified operational limits, thereby preventing uninterrupted ion passage and averting thermal runaway [30]. This shutdown mechanism ensues from a blend of two materials possessing varying melting temperatures (T_m). The safety window temperature denotes the difference in T_m

between these constituents [47]. Furthermore, the inclusion of a less thermally resilient material confers higher sensitivity to temperature fluctuations, wider safety windows, and enhanced overall security functionality on the membrane [29].

Moreover, membrane materials are required to optimize ion transport, establish unimpeded and spacious channels for Li^+ passage, and operate as an electron insulator to ensure insulation between the anode and cathode. The permeation property of the separator is an essential trait that can be numerically analyzed by the MacMullin number and Gurley value [48]. Furthermore, uniform permeation is vital for attaining extended cycle longevity, promoting efficient Li^+ transportation throughout charging and discharging processes, implying the necessity for sufficient porosity [49], with commercially prevalent separator pores typically measuring less than 1 μm. Concurrently, to augment safety during operation, it is often advisable that porosity remains below approximately 50%.

Notably, the chemical durability of a separator denotes its capacity to withstand chemical reactions with electrolytes and electrodes [50]. In order to meet the requirements of various LIBs exposed to organic solvents, polyolefin-based separators with increased strength are frequently used [51,52]. Incorporating inorganic nanomaterials such as Al_2O_3, SiO_2, TiO_2, ZrO_2, among others, into these separators can further enrich their stability and robustness [30]. The Li||$LiFePO_4$ cell using UHMWPE separator membrane complexed with SiO_2 displayed significant discharge capacities of 165 mAh g^{-1} at 0.1 C-rate and 123 mAh g^{-1} at 5 C-rate, coupled with excellent cycling performance exceeding 100 cycles [51]. Meanwhile, a TiO_2-grafted PE separator not only demonstrated significantly enhanced stability even at 150 ℃, but also superior electrochemical performance compared to bare PE separators [52]. Similarly, a ZrO_2-modified PE separator showed outstanding cyclic performance, retaining 96.2% of initial capacity after 50 cycles, and enhanced stability even under 200 ℃ conditions [53]. Notably, modified LIB separators mainly include inorganic coating, organic coating, and mixed/composite coating, depending on the coating material. In the contemporary industry, modified LIB separators with inorganic coatings are the prevailing coating separator materials, such as boehmite and Al_2O_3, which are the predominant inorganic coating materials. Inorganic coating materials can enhance the thermal stability of membranes, diminish thermal shrinkage, bolster puncture resistance, and enhance self-discharge. Nevertheless, it is pertinent to note that the application of inorganic coating modified LIBs separators may induce pore blockage, thereby impacting the ion conductivity and the lifespan of the battery.

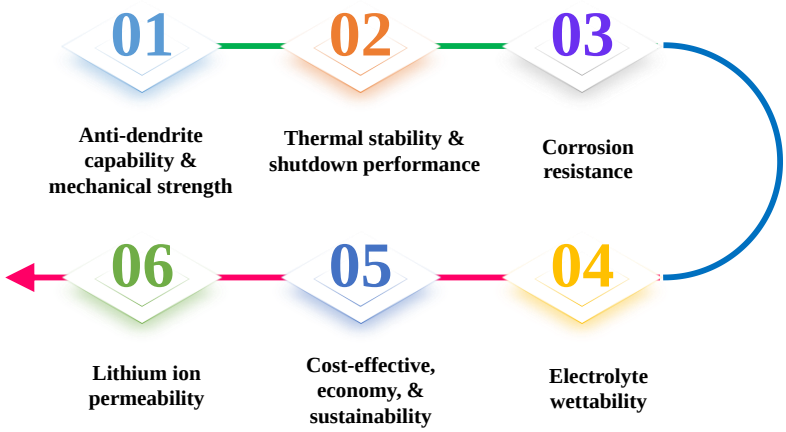

Figure 3. Detailed representation of separator performance prerequisites to contemplate when design the suitable separator for rechargeable LIBs.

Additionally, if the electrolyte can rapidly and comprehensively permeate the separator, the intrinsic impedance of LIBs can be significantly reduced, thereby enhancing ionic conductivity and charge and discharge capability [54]. Inadequate wettability increases separator resistance, affecting cycling performance and charging/discharging proficiency [55,56]. Therefore, it becomes imperative to alter the surface of the membranes to render them more hydrophilic. It should be underscored that hydrophilic functionalities can be grafted onto membrane surfaces through thermal spraying by judicious selection of suitable gases, culminating in enhanced durability, encompassing carbonyl, hydroxyl, carboxyl, sulfonyl and amino groups [57].

3. Recent advances in polyolefin-based porous separator membranes

Presently, LIB separators available on the market are predominantly microporous polyolefin membranes represented by PE, PP, and others. Research progress related to LIB separators has been extensively reported, yet primarily concentrated on the modification of polyolefin separators. This article aims to provide a comprehensive overview of recent breakthroughs in polyolefin-based porous separator membranes in the LIB field (**Table 1**).

Table 1. Summary of polyolefin-based separator membranes discussed in this review.

Substrate Material	Additives	Preparation methods	Thickness (μm)	Porosity (%)	Thermal Shrinkage (%)	Electrolyte Uptake (%)	Ionic Conductivity (mS cm^{-1})	Battery Performance	Ref.
PP	ZIF-67–CH_3OH	wet method	30	52.53	3.33% at 120 ℃ for 0.5 h	142	0.78	86.9%·after 100 cycles at 1 C under 25 ℃; 61.5%·after 100 cycles at 1 C under 55 ℃	[58]

Table 1. (*Continued*).

Substrate Material	Additives	Preparation methods	Thickness (μm)	Porosity (%)	Thermal Shrinkage (%)	Electrolyte Uptake (%)	Ionic Conductivity (mS cm^{-1})	Battery Performance	Ref.
PP	SiO_2–TEOS	wet method	25.6		4.6% at 150 ℃ for 0.5 h		0.16	140 mAh g^{-1} at 0.2 C; 96.14%·after 65 cycles at 0.2 C	[59]
PP	SiO_2	wet method	18	42		113.7	0.80 (PP-5); 0.82 (PP-12)	67.2 mAh g^{-1} at 7 C; 87% after 200 cycles at 0.5C	[60]
PP	PAAB–Li	wet method	24	61.8		195.8	0.96	119.4 mAh g^{-1} at 1 C; 78.0% after 250·cycles at 1 C	[61]
PP	PI	wet method	24	54.78	0% at 150 ℃ for 0.5 h	207.62	0.35	144.3 mAh g^{-1} at 5 C; 80.1%·after 200 cycles at 1 C	[62]
PP	BTCEAD	wet method		38.2 ± 1.30 (8% GD); 32.7 ± 2.24 (18% GD); 24.3 ± 1.49 (31% GD)		144 ± 5.9 (8% GD); 212 ± 4.5 (18% GD); 292 ± 9.4 (31% GD)	0.56 (8% GD); 0.51 (18% GD) 0.37 (31% GD)	84.59%·after 175 cycles at 0.5 C (8% GD); 97.97%·after 175 cycles at 0.5 C (18% GD)	[63]
PP	sepiolite/PVDF	wet method	32	62%	0% at 140 ℃ for 0.5 h	653	0.98 mS·cm^{-1}	115.3 mAh·g^{-1} at 10C rate; 97.06% after 200 cycles at 1C rate	[64]
PP/PAN/cotton		wet method		63	<4% at 160 ℃ for 1 h	269	1.99	166.7 mAh g^{-1} at 1 C; 93.8%·after 100 cycles at 1 C	[65]
PP/PE		dry method	25	54.6	0% at 160 ℃ for 0.5 h	157	1.46	98% (coulombic efficiency) after 30 cycles at 0.2 C	[66]
PE	γ-AlOOH	wet method	26	55.63	0% at 170 ℃ for 0.5 h	187	1.00	75.1% (95.1 mAh g^{-1}) after 200 cycles at 1 C	[67]
PE	SiO_2–PZS	wet method	20.4 ± 1.2			155.2 ± 14.3	1.04	115 mAh g^{-1} at 8 C;	[68]
PE	alumina or boehmite	wet method	12			308 (W-PE-A); 335 (W-PE-B)	1.04 (W-PE-A); 1.81 (W-PE-B)	higher than 80 mAh/g after 200 cycles at 4C	[69]
PE	poly-aromatic solid electrolyte	wet method	12–13	47.2	4.09% at 115 ℃ for 1 h; 42.54% at 145 ℃ for 1 h	126.4	0.36	84.01% (151.25 mAh g^{-1}) after 200 cycles at 2 C	[70]

Table 1. (*Continued*).

Substrate Material	Additives	Preparation methods	Thickness (μm)	Porosity (%)	Thermal Shrinkage (%)	Electrolyte Uptake (%)	Ionic Conductivity (mS cm^{-1})	Battery Performance	Ref.
PE	PAI	wet method	14.5–15.0	35–55	1.7% (MD) and 1.1% (TD) at 130 ℃ for 0.5 h			98.8–99.5% after 10 cycles at 0 ℃	[71]
PE	hydroxyapatite	wet method	23.4	30–50	2456.4 ± 280.5% at 180 ℃		0.03	100% (150 mAh g^{-1}) after 200 cycles at 1 C	[72]
PE	BPO	wet method				85	0.89	98.1% after 70 cycles	[73]
PE	MA	wet method	16				0.306	>135 cycles at 1.5 mA cm^{-2} (1 C)	[74]
PE	PVDF	wet method	20	64	0% at 500 ℃		1.77	73% after 250 cycles	[75]
PE	HDPE wax/γ-AlOOH	wet method	10	44.0					[76]
PE	Al_2O_3, LDPE	wet method	18		1% at 185 ℃	407.23	0.39	98.9% (144.5 mAh g^{-1}) after 900 cycles	[77]
PE	CA–PEO–LPSQ	wet method	26 ± 1.5		9% at 120 ℃ for 1 h	185	5.79	82% after 300 cycles at 0.5 C	[78]
UHMWPE	PMP	wet method		65.4 ± 1.1	0.7% (MD) and 1.6% (TD) at 120 ℃ for 1 h	259.7%	1.17	172.8 mAh g^{-1} at 0.1 C; 99.89% after 100·cycles at 1 C	[79]
UHMWPE		wet method	2	78.3.					[80]
UHMWPE	liquid paraffin	wet and dry method	5; 12	30; 94					[81]
UHMWPE	nano-Al_2O_3	wet method	15.3	44.2	14.3% at 120 ℃ and 34.5% at 130 ℃ for 0.5 h	129.8	0.94	139.4 mAh g^{-1} at 0.2 C; 89.4% after 200·cycles at 1 C	[82]

3.1. PP Separator membranes

PP is often used as a LIB separator due to its robust chemical stability, thickness, and strength. Nevertheless, excessive thermal shrinkage at elevated temperatures could potentially trigger internal short circuits, escalating safety risks like fire or explosion [35]. Given the potential hazards of short circuits leading to combustion/detonation, researchers concentrated on mitigating the detrimental effects of thermal shrinkage on commercial PP separators through membrane surface alteration. Notably, inorganic coating is crucial for improving the overall performance of LIB separators, and is currently an important method in the battery separator manufacturing industry. Chen et al. [58] innovatively designed an organic-inorganic separator by directly adhering zeolitic imidazolate framework (ZIF)-67 particles onto PP separator surfaces. Two distinct ZIF-67 variants were synthesized: ZIF-67–hydrogen oxide (H_2O) and ZIF-67–methanol (CH3OH) using H_2O and CH_3OH as solvents, respectively. Notably, ZIF-67–CH_3OH demonstrated superior cell capacity

retention (61.5%) post 100 cycles at elevated 55 ℃, outperforming the uncoated PP separator (0.0%). Similarly, Zhao et al. [59] enhanced Celgard-2300 separators via surface chemical treatment with SiO_2-tetraethylorthosilicate (TEOS). Remarkably, the untreated separator displayed 38.6% shrinkage in the MD direction at 150 ℃ for 30 min compared to merely 4.6% contraction after modifications. Ding et al. [60] engineered a fumed SiO_2/*β*-iPP blend with PP, silica, and *β*-nucleating agent (*β*-iPP) coupled with complex bi-directional stretching methods to shape the pores' structure, achieving in-situ SiO_2 coating. This membrane revealed a precise microporous pattern with a 5% SiO_2 content, delivering enhanced discharge capacity at elevated current densities (67.2 mAh g−1 at 7 C). Remarkably, it ensured 87% capacity preservation beyond 200 cycles, outperforming non-SiO_2 PP membranes (i.e., 70.2% retention post 200 cycles). Additionally, Yan et al. [61] utilized PP as the structural framework to produce a novel multifunctional copolymer, i.e., poly (acrylonitrile-co-lithium acrylate-co-butyl acrylate) (PAAB–Li), via soap-free emulsion polymerization. Subsequently, the copolymer was employed to fabricate uniformly coated separators (PAAB–Li-aided PP separators) on PP substrates via a simple dip-annealing process. Cells incorporating these modified separators exhibited stable cycling performance for over 800 h, indicating the functional layer capability to suppress lithium dendrite growth. Notably, Romano et al. [83] pioneered in developing novel ultra-high molecular weight isotactic polypropylene (UHMWiPP) with reduced chain entanglement (disentangled-UHMWiPP), demonstrated its potential as a LIB separator due to its exceptional mechanical strength and thermal stability compared to isotactic PP. This innovative material can be processed via solid-state methods without solvents, resulting in a uni-axial orientation below its Tm. Recently, Hasanpoor et al. [84] refined methods for applying finely ground high purity alumina (HPA) to PP battery mesh. Suspending alumina particles in acetone solvent, along with poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), provided sufficient binding strength (**Figure 4**). The influence of alumina particle size, distribution, and calendaring on coating attributes and cell performance was studied using three HPA sources. The doctor blade method yielded an even monolayer with superior mechanical stability and heat stability.

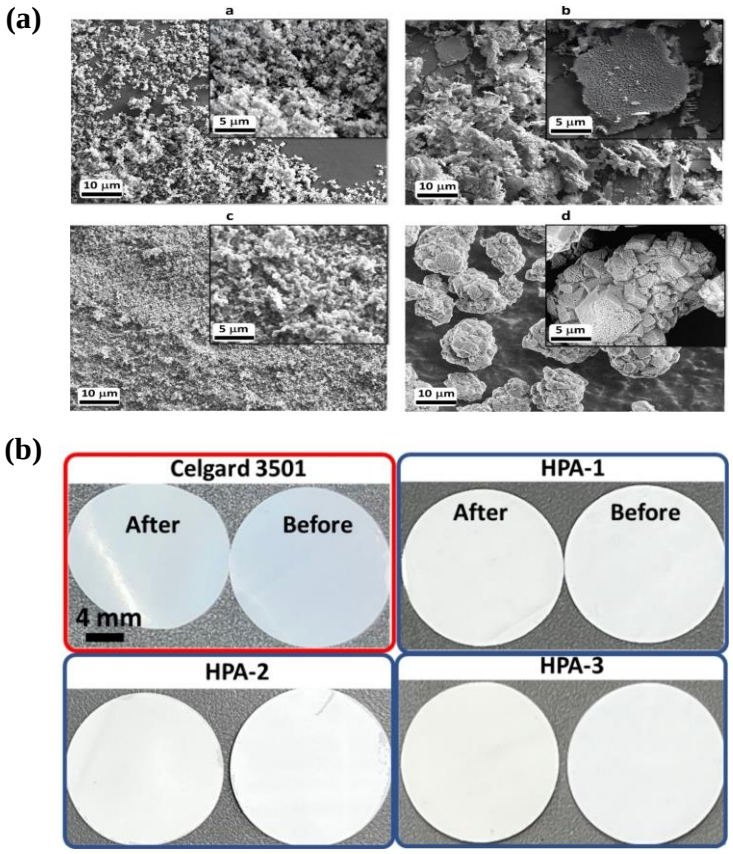

Figure 4. Characterization of HPA and HPA coated Celgard 3501 separator membrane. **(a)** SEM images illustrating the particle size and morphology of a) HPA-1, b) HPA-2, c) HPA-2 milled and d) HPA-3 samples; **(b)** procedure used as a comparative reference for aged Celgard 3501 with no coating, subjected to a temperature of 120 ℃ for an extended duration of 18 h, and in addition, the HPA coated Celgard 3501 adopting multiple particle sizes and morphologies.
Source: Reproduced with permission from [84], copyright John Wiley and Sons, 2024.

Similarly, organic coating or composite is crucial for improving the overall performance of LIB separators, which is currently another popular method for manufacturing battery separators. For instance, Yu et al. [62] showcased an efficacious PP@PI hybrid separator created using a highly porous, thermally stable PI microsphere barrier. The separator demonstrated superior performances like excellent thermal stability (minimal 150 ℃ shrinkage), fire resistance, water absorption, and electrolyte wetting behavior (contact angles of 7° and 5°, respectively). Notably, its ionic conductivity was boosted from 0.26 mS cm^{-1} to 0.35 mS cm^{-1}. Considering the substantial polarity gap between the PP-derived separator and the electrolyte hinder optimization of electrolyte wettability [56], to address this, Chen et al. [63] produced PP(s)-g-poly (ethylene glycol methacrylate) (PPEGMA) membrane, with varied grafting density (GD). Augmentations in PP(s)-g-PPEGMA ionic conductivity observed at 8% and 18% GD reached 0.56 mS cm^{-1} and 0.51 mS cm^{-1}, respectively. Notably, the 18% GD variant exhibited stable cycling for over 180 cycles. Besides, addressing LIBs thermal runaway necessitates novel safety enhancements. Here, Jiang et al. [85] proposed utilizing a thermo-responsive membrane fabricated by grafting poly (N-isopropylacrylamide) (PNIPAM) onto a PDA-modified PP membrane via the

Michael addition reaction. The smart membrane operates based on PNIPAM's upper critical solution temperature (UCST), which serves as the gating temperature, varying determinedly with the ratio of [EMIM][BF_4]. Below this, the gate molecule, grafted on the PP membrane, remains shrunken, facilitating the seamless transport of ions. If, however, due to mishandling, overheating occurs, the gate molecule becomes elongated beyond the gating temperature, effectively sealing off ion passage.

Besides, to promote the mass-production of separators in the LIBs industry, Lee et al. [86] developed a pore-connected PP-cellulose acetate (CA) membrane by coating CA onto a PP membrane. A new method was proposed to attach a CA/glycerin coating layer to a porous PP support without a separate binder. The pores of CA and PP were interconnected using a vacuum filtration device. By adding glycerin to the CA chains, the membrane region became more flexible due to glycerin plasticization. Water passes through the membrane under different pressures, resulting in the formation of interconnected pores between cellulose acetate and PP. The pore size and quantity could be adjusted by varying the molar ratio of glycerin. This simple and cost-effective manufacturing process holds potential for mass-produced separators in the LIBs industry. Sun et al. [64] developed a dual-functionalization of a PP separator utilizing electrospinning coated with a PVDF/sepiolite layer. Post functionalization, the synthesized xMS-PVDF@PP composite separator demonstrated superior porosity, electrolyte absorption, thermo-stability and Li^+ transport kinetics compared to the original PP. Notably, a Li||$LiFePO_4$ cell employing 20MS-PVDF@PP exhibited optimal rate and cycle performance, delivering a specific discharge capacity of 115.3 mAh g^{-1} at 10C and a capacity retention of 97.06% post 200 cycles at 1C. The immobilized sepiolite in the electrospun layer aids in uniform Li^+ distribution, suppresses lithium dendrite formation, and absorbs hydrogen fluoride (HF) to mitigate Fe^{2+} dissolution from the $LiFePO_4$ cathode, thus enhancing the overall electrochemical performance.

Notably, multilayer separator membranes are predominantly utilized in LIBs for their exceptional mechanical robustness and electrochemical sturdiness. For instance, Liu et al. [65] employed a wet-lay technique to incorporate cotton fibers and PAN into PP, yielding a PP/PAN/cotton fiber composite membrane. Given the abundance of polar hydroxyl (−OH) groups on cotton fibers and hydrophilic cyano groups (−CN) on PAN, this enhancement of hydrophilicity was significant. Empirical evidence suggests optimal performance at a cotton fiber content of 50 wt.% with reinforcement of ideal tensile strength (i.e., 1.644 kN m^{-1}), reasonable porosity (i.e., 63%), suitable wettability (aspiration height of 39 mm) and enhanced liquid absorbency (269%). Li et al. [66] successfully integrated multilayer coextrusion (MC) and TIPS methodologies to fabricate PP/PE multilayer separators (termed MC–TIPS PP/PE). Notably, the shrinkage of MC–TIPS PP/PE remained insignificant even at elevated temperatures up to 160 °C. Moreover, these separators exhibited superior porosity (54.6%) and electrolyte wettability (i.e., electrolyte uptake; 157%, electrolyte retention: 141%), leading to increased ionic conductivity (1.46 mS cm^{-1}) and thus superior battery operation. This cost-effective, eco-friendly and efficient methodology offers tremendous potential for the industry alike.

3.2. PE separator membranes

The microporous PE membrane commonly employed as LIB separator, notably exhibits thermal shrinkage and Li dendrite penetration, resulting in critical safety issues like short circuits, thermal runaway, and potential explosions. The researchers' efforts predominantly focus on enhancing PE membrane characteristics via surface modification, i.e., introducing both inorganic and organic layers, to enhance properties including wettability, strength, and thermal and dimensional stability [38]. Noteworthy, incorporating inorganic reinforcements like ZrO_2, Al_2O_3, TiO_2, SiO_2, etc., into the PE matrix mitigates membrane distortion at high temperatures, thereby bolstering LIB safety [33]. For instance, Wang et al. [67] integrated Al_2O_3 and boehmite (γ-AlOOH) as ceramic coating particles with water assistance to produce PE–Al_2O_3 and PE–AlOOH separators. The PE–AlOOH separator's –OH group enhanced its interaction with the coating layer, resulting in improved electrolyte absorption (187%), wettability (5.7° contact angle), and ionic conductivity (1.0 mS cm^{-1}). Additionally, for further optimizing, applying the core–shell design could also enhance PE-based separators' performance, Fu et al. [68] integrated SiO_2 nanoparticles into poly (cyclotriphosphazene-co-4,4'-sulfonyldiphenol) (PZS) to form SiO_2–PZS core–shell particles, subsequently coating these onto both sides of the PE microporous membrane yielding the PE–SiO_2@PZS separator. Hydroxyl and −NO functionalities on PZS nanoparticles synergize with Li^+, enhancing the dissociation of lithium salt ($LiPF_6$), thereby boosting LIBs ionic conductivity and discharge capacity. Qian et al. [69] compared commercial PE separators and alumina/boehmite-fortified versions. When compared against 50 cycles compaction at room temperature, compression at 60 ℃ caused severe damage to PE pore structure, impairing oxidation potential to 3.6 V, with nearly 50% capacity decline in 200 charge-discharge cycles. Vacated by coating, the decorated separator retained its original microstructure, maintaining an oxidation potential exceeding 4.2 V. Yet, despite its insulation, the deposited particles introduced decreased porosity, affecting discharge capacity, particularly at 4C rate. Comparatively, boehmite-covered separators' interface resistance was scarcely impacted, demonstrating superior capability during 60 ℃ cyclic texting, showcasing enhanced practicality.

Incorporation of organic compounds significantly enhances LIB separator performance and functionality. Currently, the utilization of organic layers or composites is an innovative approach to separator fabrication. For example, Ding et al. [70] prepared superior PE separators by applying a polyaromatic solid electrolyte (SPAEK, 60% sulfonated) coating. This layer of SPAEK presents significant enhancements to thermal stability and solvent wettability due to its retarding effect on phase separation. The subsequent polyelectrolyte coating enhanced the composite's electrolyte affinity and electrolyte absorption. Furthermore, this modified separator exhibited enhanced overall properties such as thermal stability and ionic conductivity. Consequently, the battery containing a $LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$ cathode and PE separator modified by SPAEK exhibited a remarkable capacity retention rate of 84.01%, with a specific capacity of 151.25 mAh g^{-1}, even after 200 cycles at 2 C. Thus, this modified separator holds promise for enhanced LIB performance and safety. For uniform coating, Wang et al. utilized gravure printing to apply pore-regulated

polyamide–imide (PAI) to PE substrates [71]. Heat treatment caused the PE layer to contract, sealing micropores, increasing electrical resistance, and creating an effective electrode barrier. Findings suggested that for pores between 0.17 and 0.85 μm, the electrochemical performance of PAI–PE-2 and PAI–PE-3 remained comparable to that of pure PE membranes.

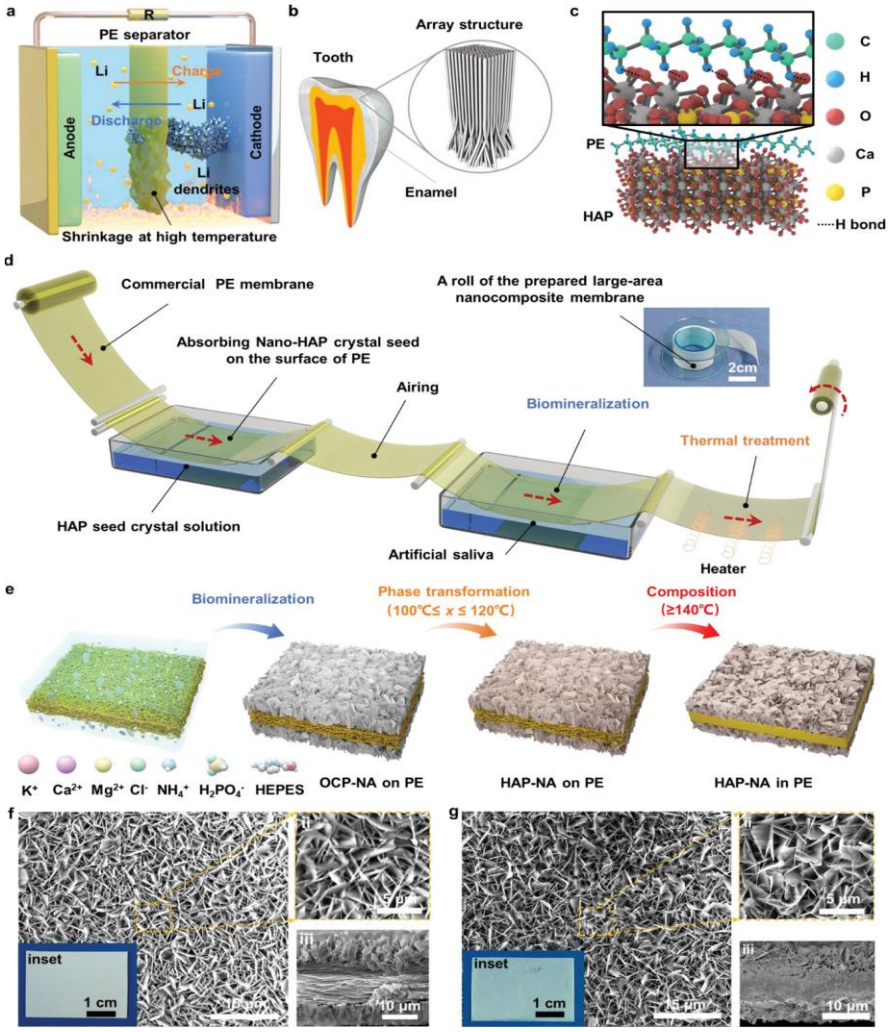

Figure 5. Schematic illustration of the design, fabrication, and microstructural SEM characterization of the enamel-inspired HAP-NA/PE nanocomposite separator membrane.

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Additionally, the introduction of organic polar groups through chemical modifications can boost the PE separator's hydrophilicity. Kim et al. [73] treated the PE separator of LIBs with benzoyl peroxide (BPO), introducing carbonyl functional groups to both surfaces. This resulted in a BPO–PE separator exhibiting exceptional rate capacity (86.7% at 3.0 C) and capacity retention over 70 cycles (98.1%), surpassing the pure PE separator's performance under the identical conditions (rate: 78.6%, retention: 91.7%). Moreover, light irradiation has also been harnessed to modify PE-based membranes, Sheng et al. [74] used low-dose γ radiation to activate the PE separator and UV light to graft MA onto it, yielding the PE-g-MA separator with a higher Li^+ transference number (0.49 vs. 0.29) and lower activation energy

(52.1 kJ mol^{-1} vs. 56.5 kJ mol^{-1}). Considering that lithium dendrites at the separator/electrode interface pose a deterrent to advances in LIBs. Here, Chen et. al. [75] enhanced PE separator's interfacial compatibility by coating it with PVDF gel via a facile phase transformation technique. They fabricate a composite separator integrating PE and PVDF. Enhanced interface compatibility emerged after gelation, with polarization onset as minimal as 0.14 V after 250 h of cycling. Interestingly, the addition of F groups in PVDF gel boosted the ionic conductivity of the composite separator (to 1.77 mS cm^{-1}), facilitating Li^+ transport due to F-Li^+ interactions. Post gelation, the battery's discharge capacity after 250 cycles stands at ~1.28 mAh, exhibiting only a 27% capacity loss. This study introduced a novel composite separator design strategy for LIBs.

Moreover, the technique of integrating organic/inorganic components in traditional battery separator coatings is becoming increasingly prevalent, enhancing the safety and exceptional charging/discharging capacity of LIB via a synergistic blend of organic and inorganic substances. For example, Xiao et al. [76] innovated a novel core–shell composite separator using synergistic incorporation of PE wax and boehmite, where the meltable high-density polyethylene (HDPE) wax fused and masked pores, obstructing Li^+ ion paths above 130 °C due to its suitable T_m (130 ℃). Consequently, this modification exhibited robust cycling durability with a capacity retention rate of 81% after 200 cycles, contrasting the unaltered PE separator's capacity retention rate of 71%. Recently, Jiang et al. [77] introduced a multilayer separator (ASPESA) separator structure via casting layers of low-density polyethylene (LDPE) and Al_2O_3 on each side of PE membrane, applying an eco-friendly approach. This separator manifested shutdown capability at 120 ℃, offering superior thermal stability up to 185 ℃ with minimal shrinkage (1%). Concurrently, the added LDPE and Al_2O_3 layers enhanced electrolyte wetting and intake (407.23%). In Li||$LiFePO_4$ cells, this multilayer ASPESA separator exhibited outstanding cycle performance, retaining 98.9% of initial discharge capacity (vs. 5th cycle) at 144.5 mAh g^{-1} after 900 cycles. Consequently, this multilayer separator holds a significant promise as a high-security separator in LIBs. Notably, the coating's microstructure significantly impacts ion migration, electrolyte storage, and the separator's resistance to deformation and thermal damage under diverse conditions [87]. Shin et al. synthesized a novel organic-inorganic complex (CA–PEO–LPSQ) utilizing PEO functionalized ladder-like polysilsesquioxanes (LPSQs) and 4-(chloroacetyl) catechol (CA) [78]. The protonated PE-M-9 separator demonstrated superior wettability to both aqueous fluids and battery electrolytes. Also, it displayed limited thermal shrinkage at 120 ℃ (9%), outperforming PE-M-8 (13%), PE-M-10 (11%), and uncoated PE (26%) separators. Capacity retention was excellent at 0.5 C, retaining 98% of initial capacity post-first cycle and 82% after 300 cycles. Recently, Yue et al. [72] proposed a novel approach involving in situ enamel mineralization engineering coupled with thermal treatment for crafting a large-area, three-dimensional hydroxyapatite (HAP) nanosheet array-enhanced PE nanocomposite separator, demonstrating enhanced mechanical strength and excellent resistances to shrinking (**Figure 5**). At 120 ℃, the nanocomposite exhibited outstanding breaking stress of 3.7 MPa, remarkable toughness of 434.4 .4 MJ m^{-3}, and boosted friction coefficient of 0.69, outperforming both commercial PE separators and previously reported ceramic/PE composites. The elongation retention

achieved by the product at 180 °C reaches an exceptional value of 2456.4%, indicating superior thermo-mechanical stability.

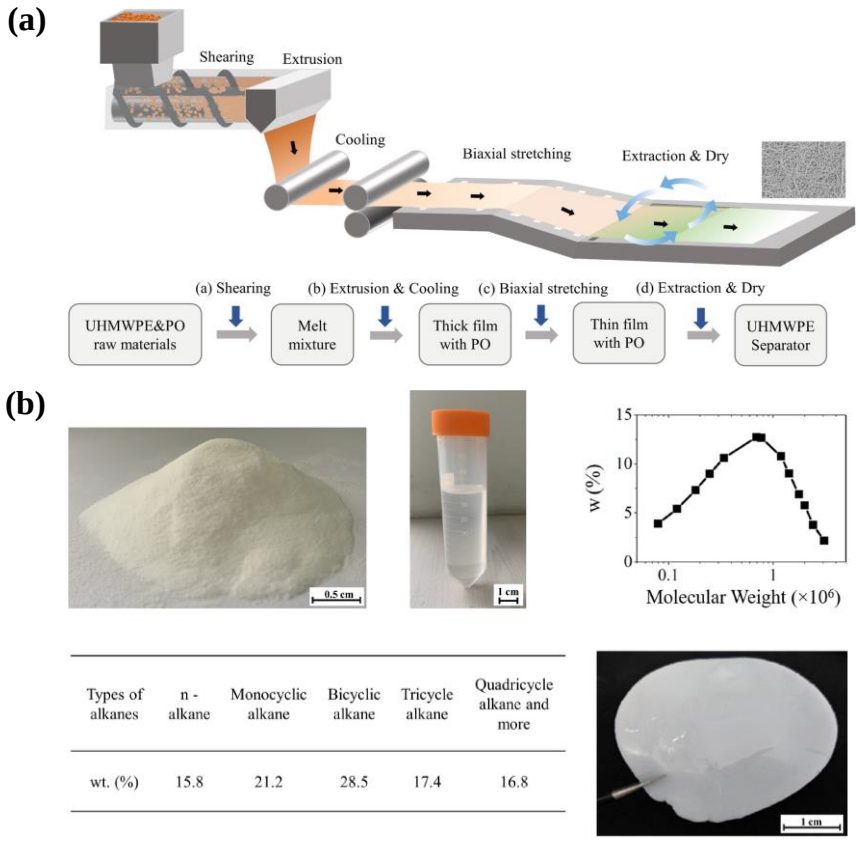

Figure 6. Schematics of the process and raw materials for separator membrane preparation in the study. **(a)** Illustration of the separator manufacture using wet biaxial-stretching processing; **(b)** characterization of UHMWPE and paraffin oil (PO).

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Significantly, UHMWPE holds a significant market share in commercial LIB separators due to its extreme puncture resistance, resilience against chemicals, exceptional microporosity, robust mechanical fortitude, high thermal stability, cost-efficient nature, etc. [89]. Babiker et al. [51] industrially synthesized UHMWPE/SiO_2 nanocomposites with minimal post-processing actions through biaxial stretching. Thermal shrinkage decreased notably, i.e., MD (1.7%) and TD (1%), as compared to pure UHMWPE (MD, 30.5%; TD, 27.6%). In addition, the composite demonstrated an extraordinary discharge capacity of 165 mAh g^{-1} at 0.1 C and 123 mAh g^{-1} at 5 C, along with excellent cycling performance (CE of 99.93% over 100 cycles; C-rate capability of 146.2 mAh g^{-1} at 1 C). Besides, organic additives like poly(4-methyl-1-pentene) (PMP) can further boost the performance of UHMWPE-based membranes. Habumugisha et al. [79] fabricated a UHMWPE/PMP blend membrane through sequential biaxial stretching, exhibiting low shrinkage after heat treatment (MD, 0.7%; TD, 1.6%). The rate capability test yielded a peak discharge capacity of 172.8 mAh g^{-1} at 0.1 C, exceeding the theoretical capacity of the $LiFePO_4$ cathode (170 mAh g^{-1}). Considering that any punctures produced on the membrane may potentially result in a

catastrophic failure of LIBs, Li et al. [80] designed a self-reinforced composite UHMWPE membrane with uniformly distributed nanopores (~200 nm) within interpenetrating nanofibrillar "shish-kebab" networks. This design resulted in a significant enhancement in tensile strength (550 MPa) and puncture resistance (1.5 N μm^{-1}) by preserving molecular orientation during pore closure. Furthermore, processing techniques can significantly influence the performance of UHMWPE-based membranes, Wu et al. [81] studied the impact of wet and dry methods on UHMWPE/liquid paraffin (LP) gel membranes. Results indicated that while dry method-derived separators showed improved electrochemical performance, they had inferior mechanical properties compared to those made via the wet method. Lastly, Ding et al. [82] successfully developed a separator with a uniform microporous structure and porous Al_2O_3 nanoparticles, prepared using a wet method and TIPS technique involving paraffin, nano-Al_2O_3, and UHMWPE The membrane exhibits superior electrochemical stability, ionic conductivity, and Li^+ transfer coefficients due to synergistic effects of uniform microporosity and Al_2O_3 nanospheres in the porous structure, facilitating efficient Li^+ transport and imparting exceptional performance. Recently, Wang et al. [88] developed commercial LIBs separators employing UHMWPE-PO blends. Using a dissipative particle dynamics model, they analyzed the influence of extrinsic (shear rate, cooling rate) and intrinsic (chain length) factors on blend microstructure (**Figure 6**). High shear induced minimal porosity (~28%) and small pores in UHMWPE with uniform chain length, while slow shear produced high porosity (~40%) and large pores. However, varying chain lengths did not alter porosity (~30%) but reduced pore size by ~35%. Post-shearing cooling rate proved crucial, rapidly increasing porosity by ~33% without altering pore size, while slowly cooling augmented porosity by ~74% and pore size by ~105%. This research provides a significant understanding of pore structure development during separator processing

4. Conclusions

LIBs are emerging as key solutions for energy storage and conversion, fulfilling the demand for environmentally friendly goods. With the global emphasis on sustainable energy, their considerable socio-economic and ecological importance is becoming evident. Intense studies in LIB separator membranes have spurred numerous advances in improving performance, boosting security measures, and overcoming intrinsic limitations. This review aims to provide an extensive database on LIBs separator membranes, covering performance requirements, functional elements, manufacturing techniques, applications, and effectiveness. It further explores recent developments in porous membranes made from polyolefins like PE, PP, UHMWPE, etc., including their synthesis, configuration, alteration, and sophistication. The advanced, robust membrane created through these initiatives has demonstrated superior efficacy across diverse applications, leading to a circular economy promoting waste minimization, cost reductions, and footprint confinement.

To conclude, the growing necessity for green products has elevated LIBs as primary energy storage and conversion options. The critical role of separator membranes requires extensive research targeting performance enhancement and resolution of related issues. In summary, this review's comprehensive content serves

as a valuable tool, facilitating a deep understanding of separator membranes and steering towards optimal performance, thereby advancing sustainable energy solutions

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