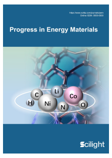
Progress in Energy Materials
https://www.sciltp.com/journals/pem



Review

Polyimide Separators Navigating Challenges and Opportunities in Next-Generation Lithium Batteries

Shijie Zhong [1,†], Haodong Xie [1,†], Quan Li [2], Yunfa Dong [1], Shengyu Zhou [1], Zhihao Zhu [1], Jiecai Han [1], Jipeng Liu [3], Yuhui He [1,*], Yupei Han [4,*]

[1] National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, and Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, China
[2] Chongqing Academy of Science and Technology, Chongqing 401100, China
[3] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150080, China
[4] Department of Chemistry, University College London, London WC1H0AJ, UK
* Correspondence: yuhui.he@stu.hit.edu.cn (Y.He); yupei.han.21@ucl.ac.uk (Y.Han)
† These authors contributed equally to this work.

How To Cite: Zhong, S.; Xie, H.; Li, Q.; et al. Polyimide Separators Navigating Challenges and Opportunities in Next-Generation Lithium Batteries. *Progress in Energy Materials* **2026**, *1*(1), 2.

Received: 29 November 2025
Revised: 29 December 2025
Accepted: 8 January 2026
Published: 28 January 2026

Abstract: The development of lithium-ion batteries towards higher energy density and enhanced safety is hindered by the performance limitations of their core component: the separator. The inherent drawbacks of traditional polyolefin separators, namely poor thermal stability (pronounced melting and shrinkage at elevated temperatures) and insufficient electrolyte affinity (leading to high interfacial impedance), represent critical obstacles that must be overcome. Polyimide (PI), renowned for its exceptional thermal resistance, mechanical strength, and chemical stability, emerges as an ideal alternative material. However, transforming dense PI polymers into high-performance porous separators faces three major challenges: (i) achieving precise construction of high porosity and interconnected pore channels while maintaining excellent thermal stability; (ii) balancing high porosity with high mechanical strength and further optimizing the electrochemical interface; and (iii) overcoming the bottlenecks of high cost and scalable manufacturing to meet industrial demands. This review systematically summarizes strategies and progress in addressing these challenges. First, we analyze preparation strategies for porous structures, discussing breakthroughs achieved by nonsolvent-induced phase separation (NIPS), thermally induced phase separation (TIPS), and electrospinning methods and electrospinning methods in constructing fine structures such as nanofiber networks and vertical channels. Subsequently, we focus on performance optimization and functionalization: enhancing mechanical and thermal stability through inorganic compositing and surface armoring; optimizing ion transport and interfacial compatibility via polar modification and wettable coatings; and imparting advanced functionalities like smart responsiveness and catalytic conversion to adapt to emerging battery systems such as lithium-sulfur and lithium-metal batteries. The discussion consistently centers on the transition from laboratory research to industrial application, evaluating the practical potential of various strategies. Finally, we outline future directions, emphasizing the need to bridge the gap from material innovation to commercial application through rational design and engineering innovation, aiming to provide a clear roadmap for developing next-generation, safe, high-performance lithium battery separator solutions.

Keywords: polyimide separators; lithium batteries; high safety; interfacial engineering; functionalized separators

Copyright: © 2026 by the authors. This is an open access article under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).
Publisher's Note: Scilight stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

1. Introduction

Lithium-ion batteries, as a cornerstone of modern electrochemical energy storage technology, have their energy density, power density, and safety largely determined by the performance of their internal components [1–3]. Among these, the separator, a critical component that prevents electrical short circuits by isolating the cathode and anode while facilitating efficient ion transport, directly impacts the overall battery performance and safety margins. However, traditional polyolefin separators (e.g., PE, PP), which have long dominated the market, suffer from inherent limitations due to their material properties. These include inadequate thermal stability (prone to melting and shrinkage at high temperatures, potentially leading to thermal runaway), poor electrolyte affinity (hydrophobicity causing high interfacial impedance), and limited mechanical strength (restricted ability to resist lithium dendrite penetration) [4–8]. These shortcomings increasingly become bottlenecks constraining the development of next-generation lithium batteries with high energy density and enhanced safety.

To overcome these limitations and align with the growing imperative for sustainable energy storage, polyimide (PI), a high-performance engineering plastic, stands out as a highly promising alternative separator material. Its appeal lies not only in its exceptional molecular structure and physicochemical properties [9–14] but also in its potential to contribute to longer-lasting, safer batteries—key factors for sustainability and circular economy goals where material longevity and reduced failure rates minimize environmental impact. The core advantages of PI are: First, outstanding thermal stability and intrinsic safety. PI possesses extremely high glass transition and thermal decomposition temperatures (typically >500 °C), enabling it to maintain dimensional integrity even at 200 °C or higher [12,15]. This fundamentally avoids internal short circuits caused by separator meltdown, establishing a robust thermal safety barrier for batteries. Second, excellent mechanical properties and potential for dendrite suppression. The high modulus and strength of PI provide superior puncture resistance, more effectively physically blocking the growth of lithium dendrites and extending battery cycle life [16–18]. Third, good electrolyte affinity and chemical stability. The polar imide rings in the PI molecular chain confer good wettability towards carbonate-based electrolytes, favoring the formation of low-impedance interfaces with high ionic conductivity [19]. Furthermore, its stable aromatic heterocyclic structure imparts excellent chemical and electrochemical inertness, ensuring long-term stability in harsh battery operating environments. Driven by the demand for higher safety and performance in applications such as electric vehicles and energy storage, PI separators are transitioning from laboratory research to initial industrial implementation. While large-scale adoption in mainstream consumer electric vehicles is still evolving due to cost considerations, commercialization has progressed in specialized and high-reliability markets. For instance, companies like DuPont have long developed PI-based nanofiber separators for enhanced battery power and lifespan. Furthermore, several Chinese enterprises (e.g., Yucheng Technology, Jiangxi Xiancai, Senior, Changchun Gaoqi) have recently announced pilot-scale production, small-batch supply, or the establishment of production capacity for PI-based or PI-coated separators, targeting applications in high-end power tools, aerospace, and other scenarios where their superior thermal stability and rate performance justify the cost. The examples cited in this review, primarily from laboratory-scale research, provide the fundamental scientific and technical insights that underpin these ongoing industrialization efforts.

However, to translate these promising starts into widespread commercial success, several core scientific and technological challenges must be systematically addressed. Despite the remarkable intrinsic advantages of PI, the path from an ideal material to a practical device is not straightforward. To successfully apply PI in battery separators, researchers must confront and overcome three core challenges:

I. The challenge of constructing porous structures: Dense PI itself is unsuitable for separators; it must be fabricated into porous membranes with high porosity, uniform, and interconnected pore channels [20,21]. How to precisely create pores in PI via controllable and scalable processes is the primary prerequisite for its functionalization.
II. The challenge of performance balancing and optimization: High porosity often conflicts with high mechanical strength. Maintaining sufficient mechanical strength to withstand processing tension and dendrite penetration while ensuring excellent ion transport capability is difficult [22–24]. Additionally, how to further optimize its interfacial properties or endow it with new functionalities beyond traditional separators, such as smart response or catalytic conversion, is key to enhancing its overall competitiveness.
III. The bottleneck of cost and scalable manufacturing: High-performance PI monomers and complex, energy-intensive manufacturing processes (e.g., high-temperature imidization) result in high costs [25,26]. Simultaneously, many excellent laboratory preparation strategies (e.g., precise phase separation, electrospinning) face significant challenges when transitioning to continuous, high-speed industrial production [27,28].

This review will systematically summarize research progress on polyimide separators. First, we will delve into preparation strategies for their porous structures, exploring how techniques like phase separation and electrospinning enable precise structural control. Next, we will summarize various paths for performance optimization and functionalization, demonstrating how compositing, doping, and surface engineering can impart superior comprehensive properties and special functions to PI separators. Finally, we will conclude with a summary of the field's status and future outlook, aiming to provide valuable insights for promoting separator innovation in high-safety, high-performance lithium batteries.

2. Preparation Strategies and Structural Control of PI Porous Separators

The functionality of a separator is essentially determined by its microstructure. Therefore, constructing the intrinsically dense polyimide material into a porous structure with suitable pore size, high porosity, and three-dimensional interconnected pores is a prerequisite for its application as a battery separator [29,30]. The preparation strategy not only dictates the basic morphological characteristics of the separator but also directly influences its mechanical strength, ion transport pathways, and interfacial interactions with the electrolyte, thereby affecting the overall battery performance and safety [31,32]. Beyond the intrinsic structure of the separator itself, the strategic placement of a functional interlayer between the separator and the electrode has emerged as a powerful complementary approach to mitigate system-specific failure modes. This is particularly impactful for lithium-sulfur batteries, where the shuttling of soluble polysulfides is a major challenge [33]. Performance optimization often requires a holistic view of the cell's internal architecture, integrating advanced separators with tailored interfacial components. Currently, various distinctive technical routes have been developed for preparing PI porous separators. This chapter will systematically review the most representative ones, namely phase separation, electrospinning, and other innovative preparation strategies, focusing on how different methods achieve precise structural construction through sophisticated process control, laying the foundation for subsequent performance optimization.

2.1. Phase Separation Methods

Phase separation methods induce phase separation in a homogeneous polymer solution, followed by the removal of one phase to create a porous structure [34,35]. They are key techniques for preparing PI separators with complex 3D interconnected pore channels. Based on the driving force for phase separation, they are mainly divided into TIPS and NIPS, which exhibit significant differences in pore formation mechanisms and final structures [36–38].

TIPS induces phase separation between the polymer and solvent by controlling the temperature change of the solution system, with the pore formation process relying on precise thermodynamic control [39–42]. The advantage of this method lies in its ability to form unique interpenetrating nanofiber networks or sponge-like structures, and it readily allows for uniform pore size control, potentially even imparting special functional response characteristics to the separator.

As shown in Figure 1a,b, the innovative work of Bai et al. [43] demonstrated the potential of TIPS for smart functionalities. They employed a strategy of salt formation between polyamic acid and triethylamine. During subsequent thermal imidization, the removal of TEA created an *in-situ* porous structure within the film. More importantly, this PI porous membrane exhibited unique thermal pore-closing properties: when the temperature increased to 300 °C, the pore structure closed, rendering the film dense and effectively blocking mass and heat transport. This intelligent response characteristic provides extremely reliable thermal safety protection for batteries, representing a cutting-edge direction in separator design. Deng et al. [44] successfully prepared a cross-linked polyimide aerogel separator via molecular structure design combined with a sol-gel process, a method rooted in TIPS. This material possessed a highly porous 3D network structure, conferring not only high flexibility and a porosity of up to 68.5% but also exceptional long-term cycling stability—a capacity retention of 93.6% after 1000 cycles at 1 C. Notably, the thermal runaway trigger temperature for graphite/NCM523 pouch cells using this separator significantly increased to 204.9 °C from 140.4 °C for commercial PE separators, fully demonstrating its substantial advantage in thermal safety.

Unlike the temperature-driven TIPS, NIPS induces phase separation by immersing the polymer solution into a nonsolvent bath, tending to form finger-like or sponge-like pore structures. This method shows unique advantages in preparing ultra-thin separators and constructing nanoscale fine pores, particularly suitable for advanced battery systems with stringent space constraints and demands for high ion transport efficiency.

The work of Gu's team [45] showcased precise control over the phase separation process (Figure 1c,d). Utilizing NIPS, they finely tuned the NMP/water ratio in the coagulation bath, successfully transitioning the separator pore morphology from finger-like pores to sponge-like pores, obtaining a PI separator with a sponge-like interpenetrating porous structure and a maximum porosity of 75.2%. This optimized pore structure effectively stabilized lithium deposition/stripping behavior, enabling the battery to deliver a high capacity of 121.80 mAh g^{-1} even at a high rate of 5 C, significantly outperforming cells using Celgard-2400 separator (54.3 mAh g^{-1}). The PI/polymer ionic liquid composite separator prepared by Lin and Ye et al. [46] using NIPS is a typical example (Figure 2a). It exhibited a thickness of only 7 µm, with uniformly distributed nanoscale pores (pore size < 10 nm) and a high porosity of 60.1%. This ultra-thin structure with nanoscale pores is particularly beneficial for rapid lithium-ion transport in lithium-sulfur batteries and effectively suppresses polysulfide shuttling. For real-world application, the target thickness for PI separators typically aligns with industry trends towards 10–15 µm to maximize energy density while ensuring mechanical robustness. The demonstrated feasibility of sub-10 µm PI membranes in research provides a valuable benchmark, but the optimal thickness must balance ionic resistance, mechanical handling strength, and cost-effectiveness for mass production. The microfluidics-confined microfluidic phase separation strategy developed by Wang's team [47] represents an important process innovation. This strategy utilized the capillary action of A4 paper to constrain nonsolvent diffusion, allowing more effective control over phase separation kinetics compared to traditional immersion NIPS, ultimately forming submicron-sized, sponge-like, and interconnected open pore channels. This well-designed structure endowed the separator with excellent rate capability and structural reversibility—after cycling at different rates, the capacity fully recovered to the initial 161.9 mAh g^{-1} when the rate returned to 0.1 C, significantly higher than the recovery capacity of the reference PP separator. In the pursuit of ultimate ion transport efficiency, the ion track-etching technique employed by Zhang's team [48] is exemplary. As illustrated in Figure 2b–f, this technique, involving heavy ion irradiation and chemical etching steps, produced a PI track-etched membrane with vertically aligned, low-tortuosity nanochannels. This near-ideal pore structure enabled Li/$LiFePO_4$ cells equipped with this separator to achieve an initial specific capacity of 143 mAh g^{-1} at 1 C rate, and maintain a capacity retention of 85.92% after 200 cycles even at an elevated temperature of 80 °C. The superspreading strategy combined with NIPS by Huang's team [49] resulted in a PI separator with highly uniform pore size (86–121 nm), enabling a discharge capacity of 120 mAh g^{-1} at a high rate of 5 C, superior to the traditional Celgard 2500 separator. Li et al. [50] further applied NIPS to prepare a polyimide covalent organic framework composite separator, leveraging the hierarchical porous structure and polar functional groups of PI-COF to synergistically enhance the separator's ionic conductivity and interfacial compatibility, demonstrating excellent cycling stability in lithium metal batteries.

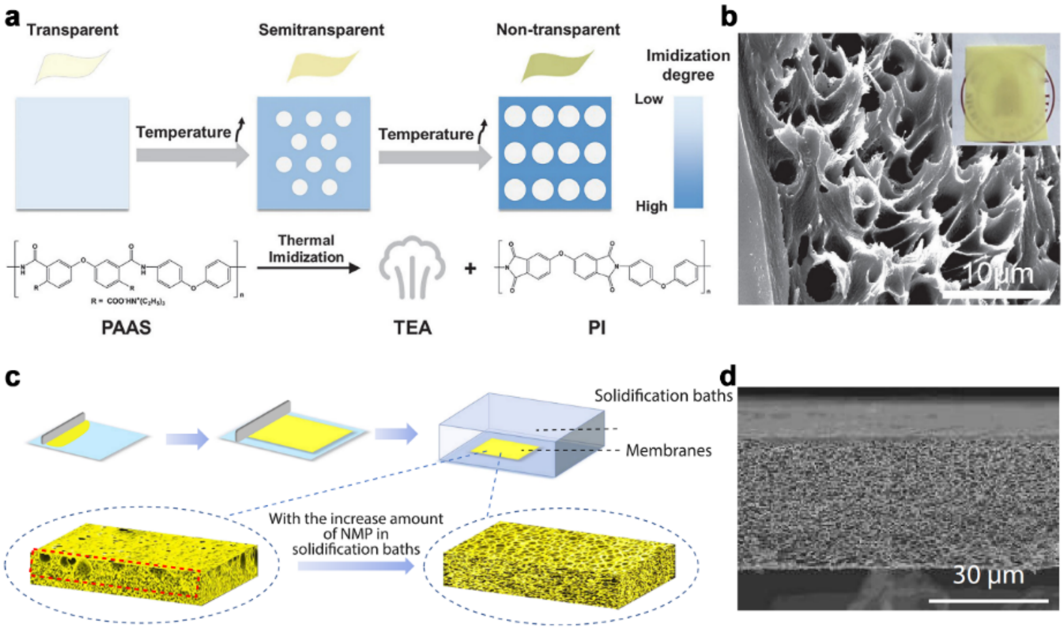


Figure 1. (**a**) Illustration depicting the morphological transition from a PAAS film to a PI film. (**b**) Cross-sectional SEM micrographs of the films processed at 220 °C, accompanied by their corresponding optical images (inset). Reproduced with permission [43]. Copyright 2024, Elsevier B.V. (**c**) Process flow diagram illustrating the fabrication steps of PI separators. (**d**) Cross-sectional view of the PI-85:15 separator. Reproduced with permission [45]. Copyright 2022, Chinese Chemical Society Institute of Chemistry.

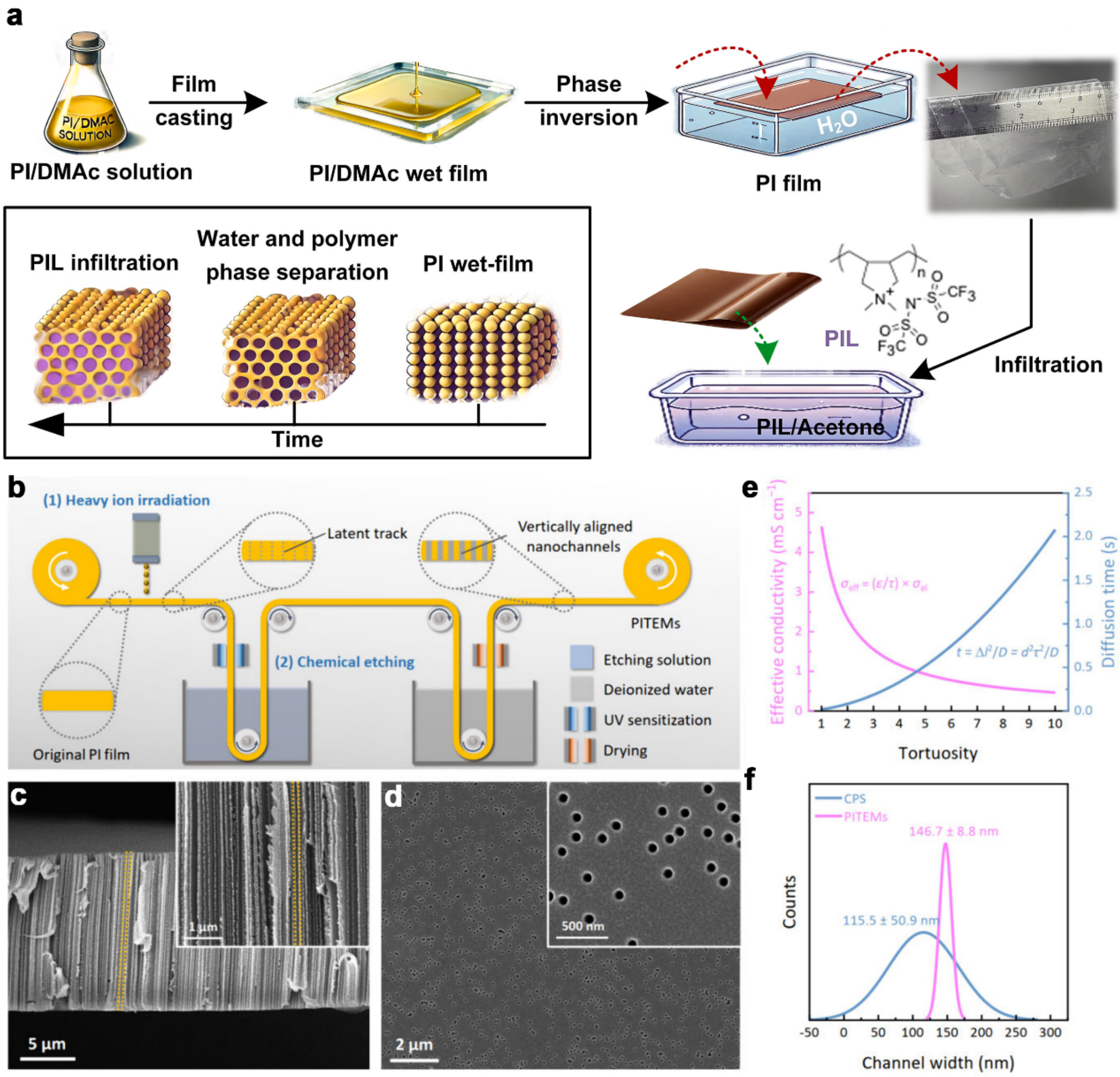


Figure 2. (**a**) Schematic of the PI/PIL separator fabrication process. Reproduced with permission [46]. Copyright 2025, Elsevier B.V. (**b**) Diagram showing the continuous production of PITEMs, involving two main stages: heavy ion irradiation and chemical etching. (**c**) Cross-sectional and (**d**) top-view SEM micrographs of PITEMs, where the insets present corresponding high-resolution details. (**e**) Relationship between the effective transport coefficient and Li^+ diffusion time as a function of separator tortuosity. The yellow dashed line indicates the channel within PITEMs. (**f**) Channel width distribution comparison for CPS and PITEMs. Reproduced with permission [48]. Copyright 2024, American Chemical Society.

2.2. Electrospinning Method

Electrospinning is currently the most mainstream and flexible method for preparing PI nanofiber separators [51–53]. It uses a high-voltage electrostatic field to draw a polymer solution (typically polyamic acid, PAA) into fibers, which are subsequently thermally imidized to form a 3D porous network composed of randomly stacked fibers. The prominent advantage of this method lies in its unparalleled structural designability, allowing easy customization of separator pore size, porosity, and functionality by adjusting spinning parameters, designing special fiber morphologies, and compositing with functional components to meet diverse application needs [54,55]. The technique excels at producing separators with high surface area-to-volume ratios and tunable pore architectures, ranging from submicron to several micrometers, which are critical for facilitating rapid ion transport and high electrolyte uptake. Moreover, the compatibility of electrospinning with a wide array of additives, such as ceramic nanoparticles (e.g., SiO_2, Al_2O_3), polymer blends, and organic-inorganic hybrids, enables the straightforward fabrication of composite separators with enhanced thermal stability, mechanical strength, and interfacial properties.

In terms of innovative fiber structure design, researchers have significantly improved the comprehensive performance of electrospun separators through clever process control. Yang et al. [56] used coaxial electrospinning to directly prepare core-shell fibers with PI as the core and PVDF-HFP as the shell, perfectly combining the superior thermal stability of PI (no significant thermal shrinkage at 200 °C) with the excellent electrolyte affinity of PVDF-HFP (contact angle as low as 8.7°). This biomimetic structural design provides a model for resolving material property conflicts. Beyond simply merging properties, such core-shell architectures can also be engineered to enable staged responses under thermal or mechanical stress, adding a new dimension to separator safety design. As shown in Figure 3, Liu's team [57] successfully created adherent structures between fibers by co-electrospinning PAA with polystyrene followed by thermal imidization, significantly reducing the average pore size from ~1.63 µm for traditional PI separators to 0.78 µm. This structural optimization effectively enhanced the separator's dendrite resistance, enabling batteries based on this c-PI separator to maintain a high capacity of 100.1 mAh g^{-1} after 1600 cycles even at an ultra-high rate of 10 C. The formation of these adherent junctions not only refines the pore structure but also markedly improves the mechanical integrity of the fibrous mat, preventing layer delamination during battery assembly and cycling. The work of Sun and Chen's team [58] pushed the structural control of electrospinning to new heights. They innovatively applied hot-stretching (optimal force 3N) to electrospun PAA nanofiber membranes during thermal imidization, combined with subsequent *in-situ* homogeneous PI reinforcement, preparing a PI-S-3-Re separator with a mechanical strength as high as 120.9 MPa. This study fully demonstrates that improving molecular chain regularity and orientation through physical stretching is an effective way to enhance the mechanical properties of electrospun fiber membranes.

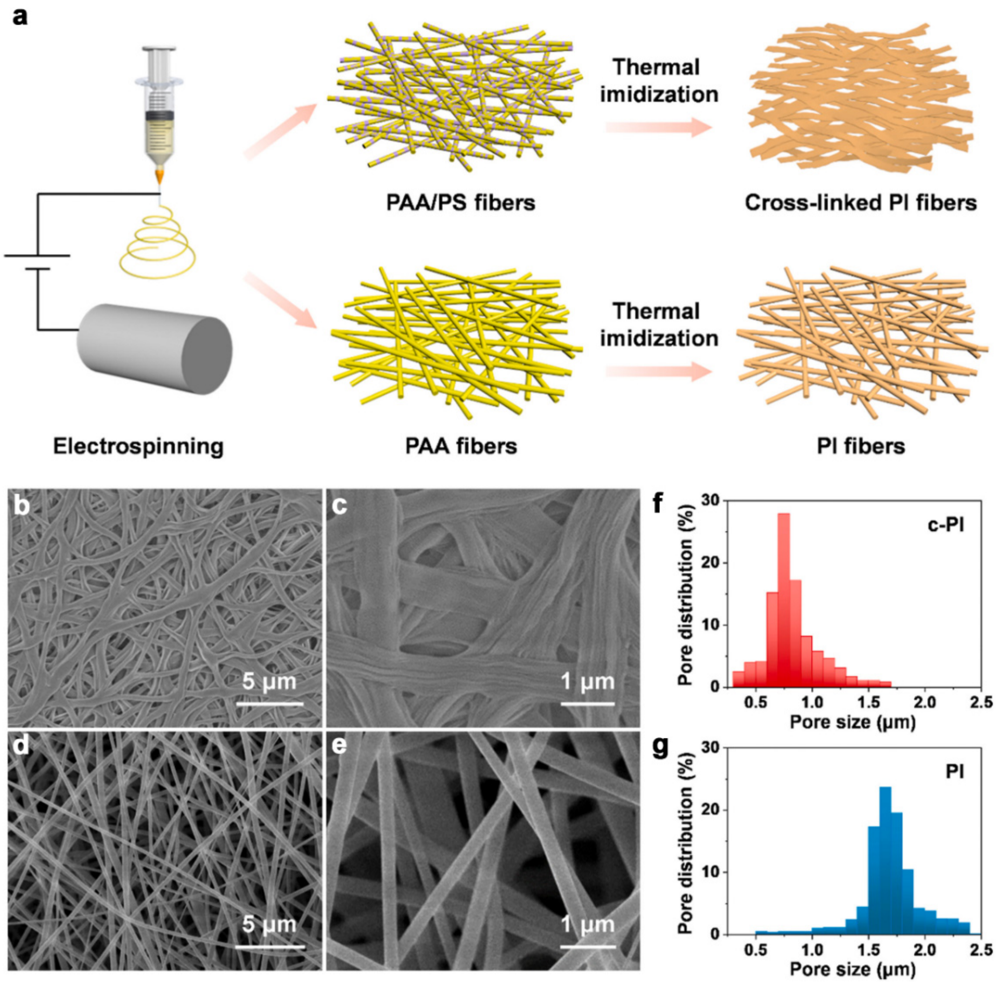


Figure 3. (**a**) Fabrication process of cross-linked PI and corresponding PI separators. SEM images of (**b**,**c**) c-PI and (**d**,**e**) PI samples. (**f**,**g**) Pore-size distributions of c-PI and PI, respectively. Reproduced with permission [56]. Copyright 2022, Elsevier B.V.

In the field of inorganic-organic composites, electrospinning serves as an ideal platform for constructing multifunctional composite separators. Wu et al. [59] employed electrospinning combined with a composite-hydrolysis strategy to *in-situ* armor a scandium hydroxide coating on PI fiber surfaces, simultaneously and effectively addressing the two core challenges of insufficient mechanical strength and poor electrolyte wettability of pure PI separators. The optimized separator exhibited a high capacity retention of 96.7% after 300 cycles at 1 C rate. Lu et al. [60] incorporated SiO_2@PZS composite microspheres into electrospun fibers, constructing a separator with an astonishing porosity of 356.21% and an ionic conductivity of 26.20 mS cm^{-1}, far superior to commercial Celgard separators. The assembled battery retained a capacity of 211.9 mAh g^{-1} after 100 cycles at 0.5 C rate, significantly higher than that with Celgard separator, highlighting the great potential of composite structures in enhancing electrochemical performance (Figure 4). Pan's team [61] used a one-step electrospinning and electrospraying method to uniformly compound WO_3 nanoparticles into PI fibers, increasing the separator's ionic conductivity to 3.09 mS cm^{-1} (PT4 sample) and achieving a high capacity retention of 92% after 200 cycles at 1 C rate. In the exploration of green and sustainable materials, Song's team [62] introduced both oxidized lignin and halloysite nanotubes into PI electrospun fibers. Leveraging the synergistic effect of biomass and natural nanotubes, the prepared PI-OL@10% HNTs separator not only exhibited excellent performance (lithium ion transference number up to 0.865) but also embodied a design philosophy combining environmental friendliness with high performance.

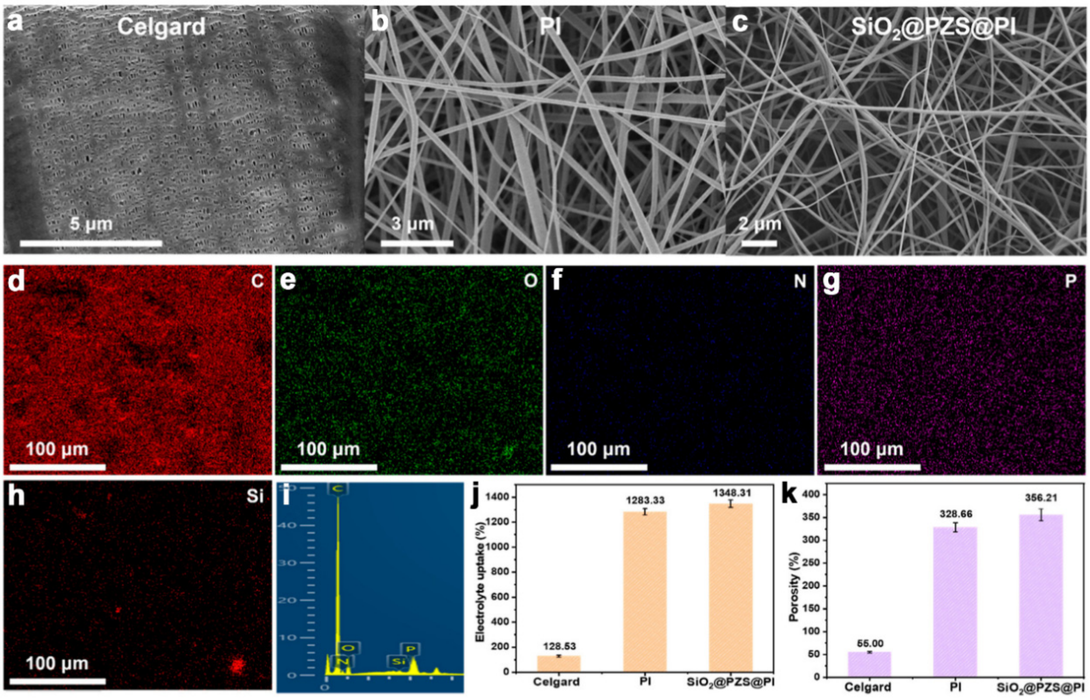


Figure 4. (**a**–**c**) The morphologies of Celgard, PI, and SiO_2@PZS@PI separators are shown in the SEM images. (**d**–**h**) The elemental distribution and (**i**) EDS result are provided for the SiO_2@PZS@PI sample. Furthermore, (**j**) the electrolyte uptake and (**k**) porosity of all separators are compared. Reproduced with permission [60]. Copyright 2025, American Chemical Society.

Regarding surface chemistry and functionalization, Qian et al. [63] electrospun a mixture of PVDF and fluorinated PAA, obtaining a PVDF/F-PI composite separator after imidization. The F-PI backbone provided a negatively charged environment, promoting uniform lithium ion transport, and the assembled lithium metal symmetric cell achieved stable cycling for 2400 h. These studies collectively demonstrate that electrospinning, due to its exceptional structural designability and ease of compositing, has become one of the most powerful tools for developing high-performance, multifunctional PI-based separators.

2.3. Other Preparation Methods and Strategies

Beyond the mainstream phase separation and electrospinning methods, researchers have developed various unique preparation strategies. These methods often impart special structures or functions to PI separators that are difficult to achieve through traditional means, showcasing the diversity of technical routes and providing new ideas for addressing specific challenges in the industrialization of PI separators.

Template methods and biomimetic strategies open new avenues for preparing PI separators with highly ordered pore structures. Yuma Shimbori et al. [64] successfully prepared a PI separator with a 3D ordered macroporous (3DOM) structure using a colloidal crystal template method. Its regular pore channels provide ideal paths for rapid ion transport. To overcome the insufficient mechanical strength of the pure PI 3DOM structure, they further introduced polybenzimidazole for reinforcement. The prepared PI+PBI composite separator achieved a maximum tensile strength of 20.6 MPa, significantly better than the pure PI membrane. This work demonstrates the effectiveness of composite strategies in compensating for inherent material defects.

Surface engineering and coating technologies are efficient means for functionally modifying commercial base membranes or endowing separators with new characteristics. As shown in Figure 5a, Wu's team [18] used electrostatic spraying to prepare PI microspheres, which were then loaded onto a commercial Celgard polypropylene separator via a blade-coating process. This simple secondary processing method effectively improved the thermal stability (almost no shrinkage at 150 °C) and electrochemical performance of the PP separator, providing a feasible path for upgrading existing separator products. Wang et al. [65] prepared core-shell structured ZrO_2@PI microspheres via a composite-hydrolysis method and applied them as a coating on a commercial PE separator (Figure 5b). This design cleverly utilized the high-temperature stability of the ZrO_2 shell and the lightweight nature and mechanical support of the PI core. The coating area density was only 2.52 g m^{-2}, much lower than traditional Al_2O_3/PE separators, achieving lightweight coating while enhancing thermal safety, which is positive for reducing the overall battery weight.

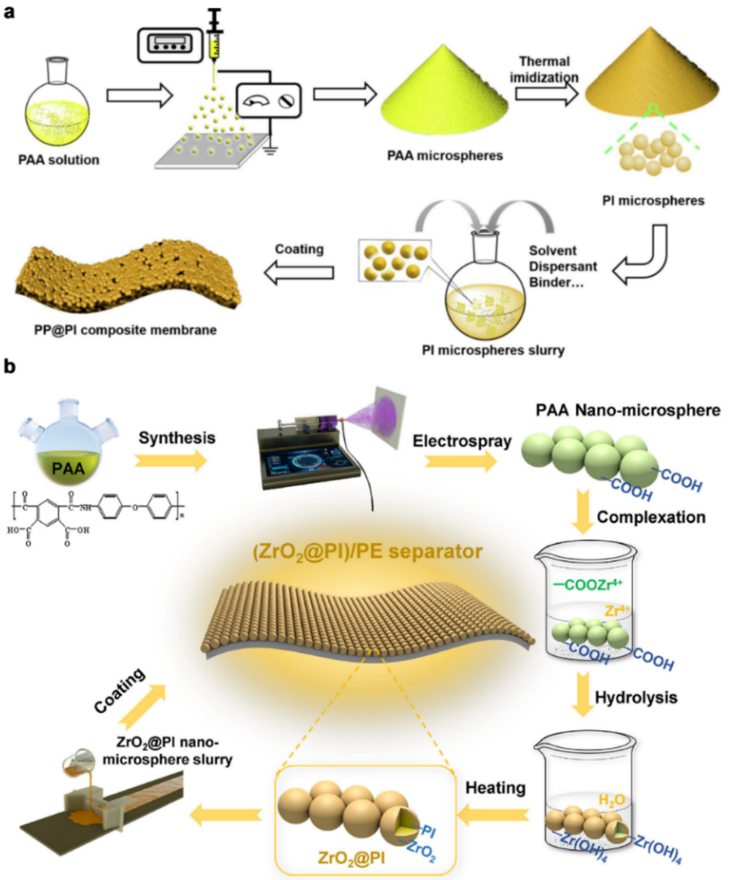


Figure 5. (**a**) Structural schematic of the PP@PI microsphere composite membrane. Reproduced with permission [18]. Copyright 2022, Elsevier B.V. (**b**) Preparation process of the ZrO_2@PI core-shell nano-microsphere and the corresponding (ZrO_2@PI)/PE separator via blade coating. Reproduced with permission [65]. Copyright 2022, Elsevier Ltd.

Frontier process exploration aimed at industrialization focuses on solving the cost and scalability challenges of PI separator preparation. The self-limiting electrospray deposition technology employed by Jonathan's team [66] is quite innovative. This technique can directly deposit a uniform, conformal porous PI separator onto planar $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ electrodes, achieving integrated separator-electrode preparation. The resulting SLED PI separator had a high porosity of about 70%, and the porous structure remained stable up to about 350 °C. Although the high-rate performance in full-cell configuration requires further optimization, as a proof of concept, this technology provides a novel idea for separator preparation in batteries with complex geometries. The work of Seok Hun Kang's team [67] targeted next-generation all-solid-state batteries. They used laser drilling to prepare a high-porosity (69%) PI scaffold, then coated it with Li_6PS_5Cl solid electrolyte via roll-to-roll tape casting, successfully constructing a composite solid electrolyte membrane with a thickness of only 27 μm, combining high ionic conductance (146 mS cm^{-2}) and mechanical strength (7.15 MPa @6% strain). This work demonstrates the great potential of PI materials beyond traditional liquid battery systems and provides a successful example for the integrated design of separators/electrolytes in all-solid-state batteries.

The diverse preparation strategies discussed above endow PI separators with distinct structural characteristics and performance trade-offs. Table 1 provides a comparative summary of these key methods, highlighting their principles, structural outcomes, and scalability, which can serve as a guide for selecting appropriate techniques for specific application needs.

Table 1. Comparison of primary preparation methods for polyimide porous separators.

Method	Principle	Typical Pore Structure	Advantages	Disadvantages/Challenges	Industrialization Prospect
Thermally Induced Phase Separation (TIPS)	Temperature-driven phase separation and solvent removal	Sponge-like, interpenetrating nanofiber network	High porosity, good pore size uniformity, potential for smart responsiveness	High energy consumption, solvent recovery, limited to specific PI-solvent systems	Moderate. Challenges include high energy consumption for thermal control and solvent recovery, but compatible with some roll-to-roll processes.
Nonsolvent-Induced Phase Separation (NIPS)	Immersion in non-solvent bath to induce phase separation	Finger-like, sponge-like pores	Suitable for ultra-thin membranes, nanoscale pores, relatively fast	Potential macrovoid defects, extensive solvent/ non-solvent use	Good. Highly compatible with scalable roll-to-roll wet processing; however, control over solvent exchange kinetics is critical for uniform quality.
Electrospinning	Electrostatic drawing of polymer jets to form fibers	3D network of randomly stacked nanofibers	High design flexibility, tunable porosity/fiber diameter, ease of compositing	Low production efficiency, weak mechanical strength of as-spun mats, high voltage	Challenging. Throughput and the mechanical strength of as-spun mats are key bottlenecks; advances in multi-needle or needleless systems are improving scalability.
Track-Etching	Heavy ion irradiation creating latent tracks, followed by chemical etching	Vertical, low-tortuosity nanochannels	Ideal straight pore channels, superior ion transport	High cost of irradiation, limited porosity, complex process	Low. The reliance on high-energy heavy ion irradiation facilities results in prohibitively high capital and operational costs. The two-step process (irradiation and etching) is complex and difficult to scale for high-volume, low-cost separator production.
Template Method	Using a sacrificial template to define pores	Highly ordered macroporous (3DOM) structure	Perfectly ordered pore arrangement, excellent for fundamental study	Template removal complexity, insufficient mechanical strength, high cost	Low. The necessity of synthesizing and subsequently removing the sacrificial template adds multiple complex steps, increasing cost and limiting production throughput. The obtained ordered porous structures often suffer from intrinsic mechanical fragility.

3. Performance Optimization and Functionalization Strategies for PI Separators

Successfully constructing a porous structure is the foundation for applying PI separators. However, to meet the stringent requirements for safety and cycling stability in high-energy-density lithium batteries, their performance must be systematically optimized and new functionalities imparted. This pursuit moves beyond mere material substitution into the realm of rational design and architectural engineering. The optimization strategies discussed in this chapter can be understood through three interdependent architectural paradigms: (i) Multi-scale structural hybridization, which tackles intrinsic property trade-offs by constructing hierarchical composites; (ii) Active interface engineering, which redefines the separator's role from a passive barrier to a dynamic component that regulates ion transport and interfacial chemistry; and (iii) System-tailored functional integration, which customizes the separator's architecture to address the dominant failure mechanisms of specific next-generation battery systems. The following sections detail these strategies, consistently highlighting how specific material and process choices translate into targeted architectural outcomes.

3.1. Enhancing Mechanical and Thermal Stability

Although PI materials possess excellent intrinsic properties, their electrospun fiber membranes or porous membranes still need to address mechanical challenges such as electrode burrs and lithium dendrite growth in practical applications. Constructing multi-level reinforced structures can significantly improve the mechanical integrity and thermal safety margin of separators.

Compositing with inorganic nanoparticles and surface armoring are effective ways to enhance mechanical properties. The innovation of Chen et al. [68] lay in *in-situ* constructing an aluminum compound armor layer on PI nanofiber surfaces through a complexation-hydrolysis process. This strong interfacial bonding endowed the separator with a tensile strength of 107.6 MPa, approaching commercial polyolefin levels, while maintaining the intrinsic thermal stability of PI. Notably, this strategy simultaneously addressed the two major challenges of insufficient mechanical strength and poor electrolyte wettability of electrospun PI separators, demonstrating a synergistic design approach. The development by Sun’s team [69] was more systematic. As illustrated in Figure 6, By optimizing precursor viscosity to increase molecular chain length and combining *in-situ* bonding and reinforcement technology, they prepared a core-sheath structured PIE separator with a mechanical strength exceeding 90 MPa, one of the highest values reported to date. This design also cleverly introduced a thermal shutdown function, where the PEI layer melted at about 290 °C to block pores, achieving passive safety protection. These studies exemplify the multi-scale structural hybridization paradigm. The challenge of balancing the mechanical weakness of a highly porous electrospun mat with the need for thermal stability is not solved by a single material, but by designing a composite architecture. In Chen’s work, the ‘armor’ is not merely a coating; it creates a reinforcing nano-scale shell on each fiber, transforming the failure mode from fiber slippage to collective load-bearing. Sun’s approach takes this further by integrating a functional polymer layer (PEI) that introduces a macroscopic, system-level response (thermal shutdown) into the architecture. This represents a shift from seeking a ‘stronger material’ to designing a ‘smarter structure’ where different materials and morphologies are assigned specific roles at different scales to achieve an overall performance unattainable by any single component.

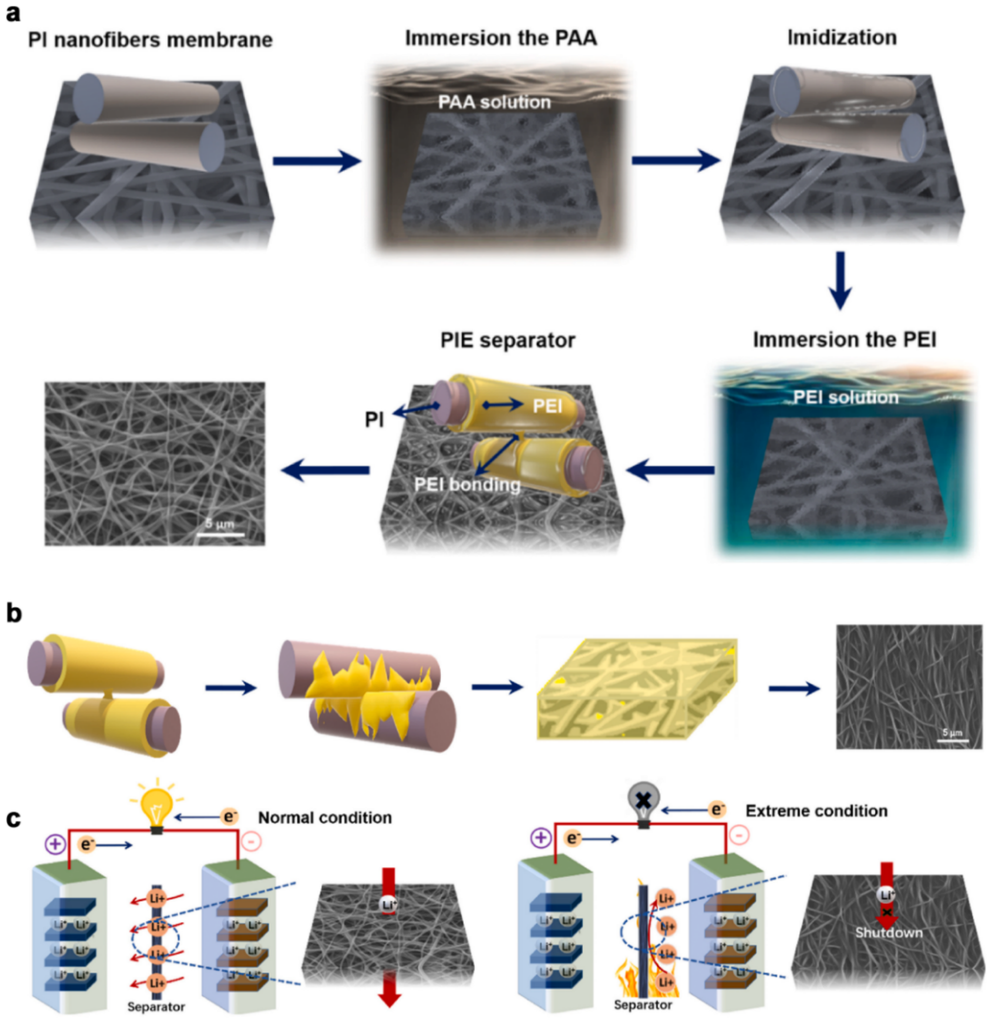


Figure 6. (**a**) Schematic of the PIE separator fabrication process via *in-situ* bonding and strengthening. (**b**) Schematic of the separator’s shutdown function. (**c**) Schematics of battery operation under normal and extreme conditions. Reproduced with permission [69]. Copyright 2021, Elsevier B.V.

In terms of multifunctional composite systems, the work of Jia’s team [70] demonstrated a systematic optimization approach. They incorporated boehmite nanoparticles into a PVDF-CTFE and F-PI matrix, followed by electron beam irradiation modification, achieving synergistic optimization of thermal stability (27.4% thermal shrinkage at 180 °C), mechanical strength (~34 MPa), and electrolyte affinity. This strategy of multi-parameter synergistic enhancement is significant for practical applications. Chen et al. [71] constructed a more complex hierarchical structure, using BTO-PI nanofibers as the skeleton filled with LLTO-PEO-FEC-LiTFSI (LPFL) hybrid electrolyte. The resulting BP@LPFL composite electrolyte maintained a capacity of 124 mAh g^{-1} after 200 cycles at 0.1 C rate and room temperature, demonstrating good mechanical support and electrochemical stability.

Surface densification and crosslinking strategies enhance interfacial stability while maintaining the porous structure. Cheon et al. [72] addressed the issue of excessively large pores in PI separators by using a multi-step dip-coating method with Al_2O_3 particles as pore-blocking precursors, successfully controlling the coating loading at 4.4 mg cm^{-2}. The shrinkage rate was only 16.2% at a high temperature of 550 °C, a thermal stability indicator significantly superior to most polymer-based separators. The study by Palanisamy et al. [73] further confirmed the superiority of Al_2O_3 compositing. The PI-Al_2O_3 separator had a thermal decomposition temperature as high as 525 °C, and released only 25 J g^{-1} of heat during thermal runaway testing, far lower than the 211 J g^{-1} for the PP separator, proving its safety advantage from a thermal management perspective.

In recent years, core-shell structure design has shown unique advantages. As illustrated in Figure 7a–d, Wu's team [74] coated PI fibers with a SiO_2 shell via an *in-situ* nano-encapsulation hydrolysis method, dramatically increasing the tensile strength from 9 MPa to 73.69 MPa while reducing the electrolyte contact angle to 6.8°. This core-shell structure not only enhanced mechanical properties but also improved interfacial properties through surface chemical modification. Li's team [75] used a self-adsorption crosslinking technique to coat meta-aramid on PI nanofiber surfaces. The resulting PI-MA core-shell separator achieved a tensile strength of 67 MPa, showed no significant deformation at 300 °C, and the lithium symmetric cell operated stably for 1000 h at 2 mA cm^{-2}, proving its excellent dendrite suppression capability. The q-PBI@PI separator from Sun's team [76] further increased the mechanical strength to 82.8 MPa while achieving a lithium ion transferenhce number of 0.63, showcasing a design concept of multifunctional integration (Figure 7e,f).

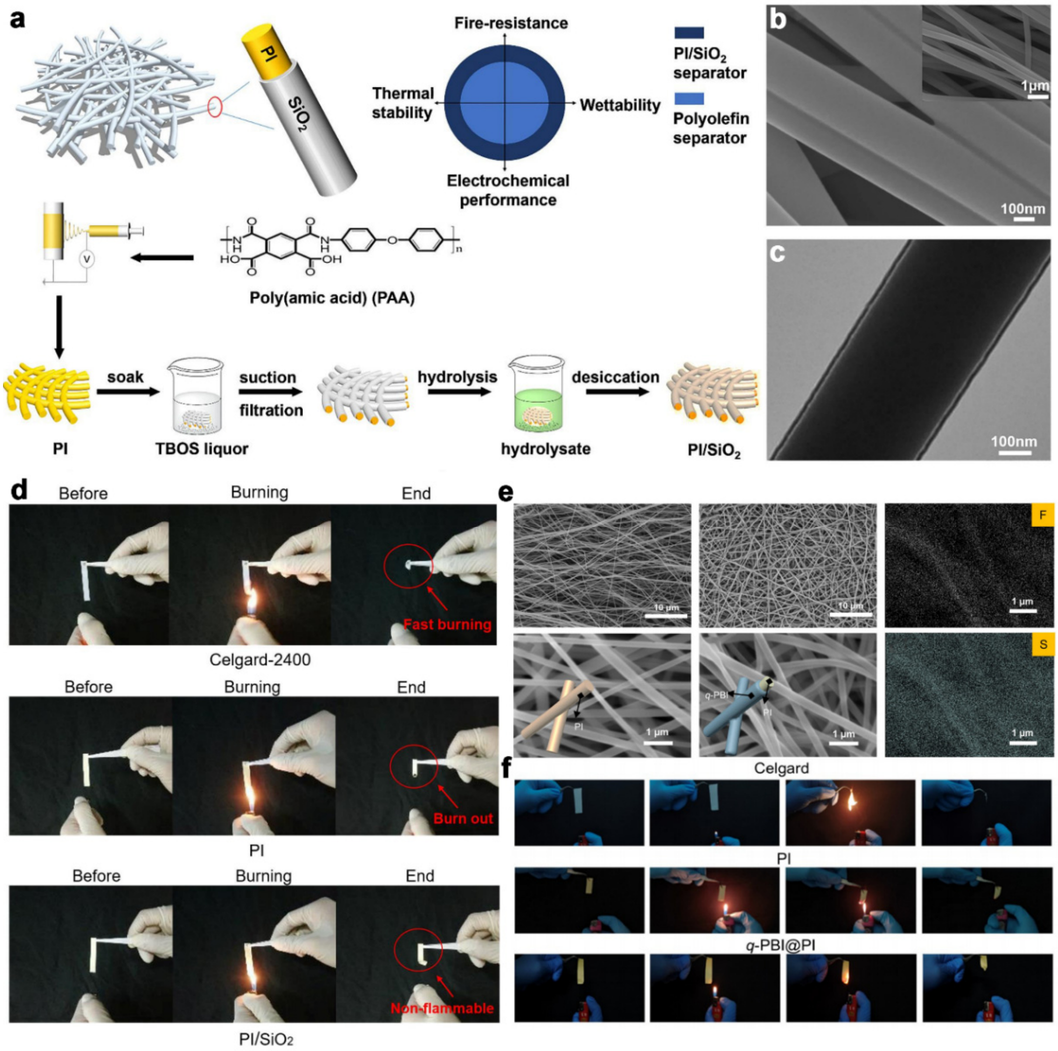


Figure 7. (**a**) Schematic of the *in-situ* SiO_2 nano-encapsulation process on the PI nanofiber separator. (**b**,**c**) Microstructure of the PI/SiO_2 composite revealed by SEM and TEM, respectively. (**d**) Digital photographs demonstrating the flame retardancy of various separators. Reproduced with permission [74]. Copyright 2021, Elsevier B.V. (**e**) SEM morphology and corresponding EDS maps (F, S) of the q-PBI@PI membrane, compared with initial PI. (**f**) Results of combustion tests. Reproduced with permission [76]. Copyright 2024, Science China Press.

The aforementioned studies underscore that enhancing the mechanical and thermal stability of PI separators primarily relies on constructing multi-level reinforced structures. The reinforcement mechanisms can be categorized as follows: (i) Particle reinforcement: Inorganic nanoparticles (e.g., Al_2O_3, SiO_2) act as physical barriers, deflecting micro-cracks and bearing external stress, thereby improving tensile strength and modulus. (ii) Surface armoring: A continuous, robust coating layer on fiber surfaces not only provides superior puncture resistance but also effectively seals large pores, mitigating dendrite penetration. The interfacial bonding strength between the armor and the PI matrix is crucial for long-term stability. (iii) Cross-linking and densification: Cross-linkers or densified layers at fiber junctions enhance the integrity of the porous network, transforming the failure mode from individual fiber slippage to collective energy dissipation. Understanding these underlying mechanisms is vital for the rational design of next-generation high-strength separators.

3.2. Optimizing Electrochemical Performance and Interfacial Compatibility

Excellent interfacial properties are crucial for ensuring high-rate capability and long cycle life of batteries. Surface physicochemical modifications of PI separators can significantly improve their electrolyte affinity, ion transport efficiency, and interfacial stability.

Wettable polymer coatings are a direct method to improve interfacial properties. The PI/PVDF-HFP core-shell fiber separator prepared by Yang et al. [56] using coaxial electrospinning is an exemplary design. The PVDF-HFP shell provided excellent electrolyte affinity (contact angle 8.7°), while the PI core ensured thermal stability. This division of labor enabled the separator to achieve both high electrolyte uptake (366.6%) and low interfacial impedance (166 Ω). The PVDF-HFP@PI composite separator by Han et al. [77] further demonstrated the thermal safety advantage of this design, maintaining 85.7% capacity retention after exposure to 140 °C, offering a solution for high-temperature application scenarios.

Surface chemical modification controls interfacial behavior at the molecular level. As shown in Figure 8a, Huang et al. [20] chemically grafted zwitterionic groups ($-SO_3$) onto PI fiber surfaces. This modification increased the separator's ionic conductivity to 1.99 mS cm^{-1} and the lithium ion transference number to 0.632. Notably, the capacity retention rate reached 91.87% after 100 cycles at 2 C rate, proving its excellent interfacial stability. As illustrated in Figure 8b–j, Liao et al. [78] employed magnetron sputtering to deposit a 100-nm-thick silicon nitride coating on both sides of a commercial PI separator. This precise interface engineering reduced the contact angle to 0° and enabled stable cycling for over 200 cycles at 0.5 C rate in a 110 °C high-temperature environment, demonstrating the potential of industrial-grade surface treatment technologies.

The design of functional interfacial layers further expands the role of separators. The PI/PVDF composite separator developed by Zhong et al. [79] utilized the imide rings in PI to effectively scavenge HF from the electrolyte through the formation of -CO...H-F hydrogen bonds (Figure 9). This unique mechanism inhibited transition metal dissolution and cathode structure degradation, resulting in a high capacity retention of 91.4% after 200 cycles at 60 °C. These advancements are driven by the principle of active interface engineering. The traditional separator-electrolyte interface is a site of high impedance and uncontrolled reactions. The architectural innovation lies in intentionally designing this interface to become a functional zone. The PI/PVDF design represents a more complex chemical architecture where the PI backbone is not just a support but an active participant, its imide rings strategically positioned to chemically trap harmful HF. This transforms the separator from a bystander into a chemical regulator within the cell's ecosystem. The architectural goal is no longer just low resistance, but interfacial stability and homeostasis, proactively managing the electrochemical environment to extend cycle life. Song et al. [26] introduced lignin rich in polar groups into the PI matrix. This green modification strategy not only improved sustainability but also increased the separator's lithium ion transference number to 0.787, demonstrating the application potential of biomass materials in high-performance batteries.

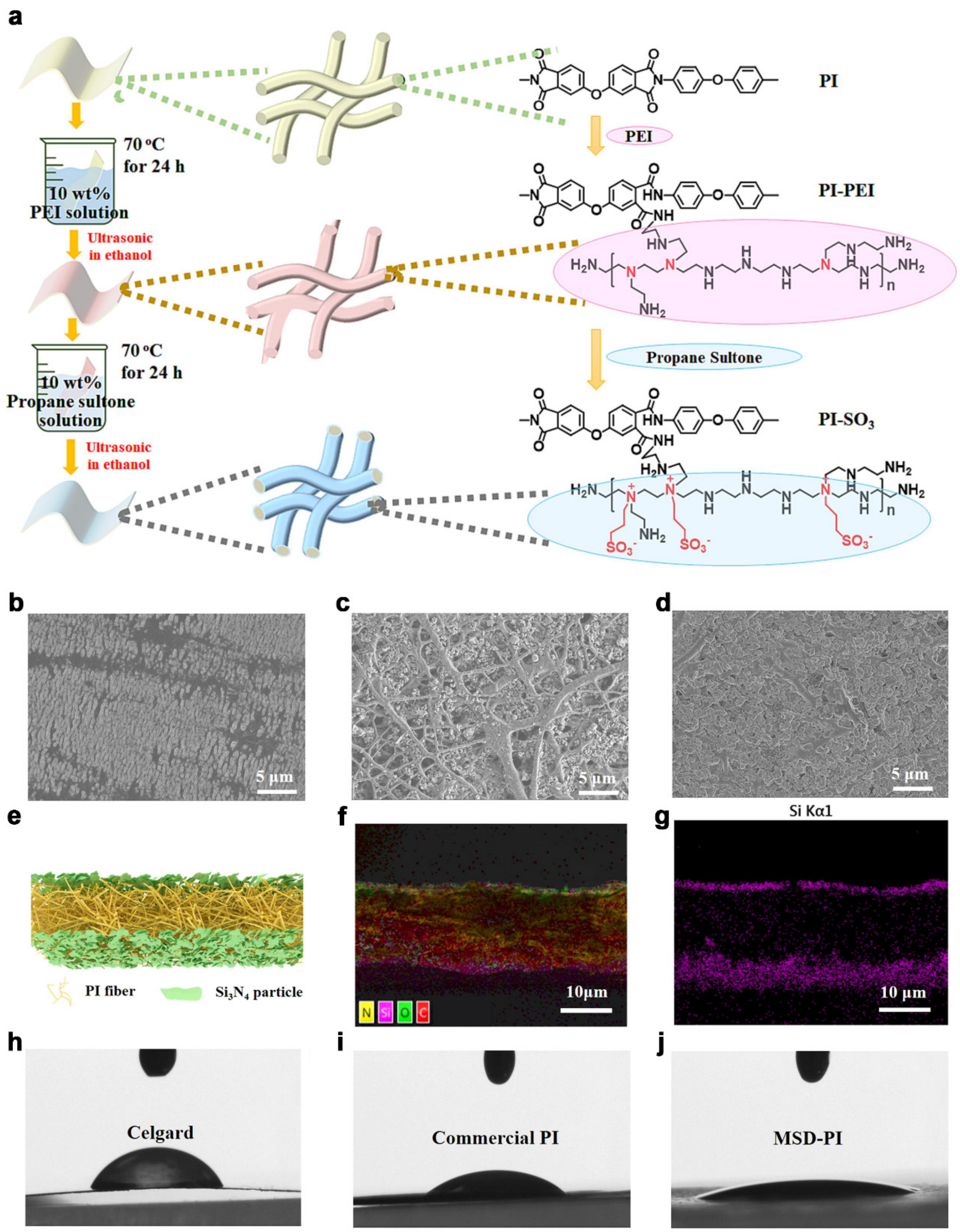


Figure 8. (**a**) Preparation flowchart of PI-SO_3. Reproduced with permission [20]. Copyright 2024, Elsevier B.V. SEM images of surface morphologies of various separators. Surface SEM images of different separators: (**b**) Celgard 2325, (**c**) commercial PI, and (**d**) MSD-PI. (**e**) Schematic diagram of the MSD-PI separator structure. Cross-sectional elemental mapping of the MSD-PI separator: (**f**) distribution of N, Si, O, and C; (**g**) Si element. Initial contact angles of the liquid electrolyte (1 M $LiPF_6$ in EC/DMC, 1/1 *v*/*v*) on various separators: (**h**) Celgard 2325, (**i**) commercial PI, and (**j**) MSD-PI. Reproduced with permission [78]. Copyright 2020, Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by ELSEVIER B.V. and Science Press.

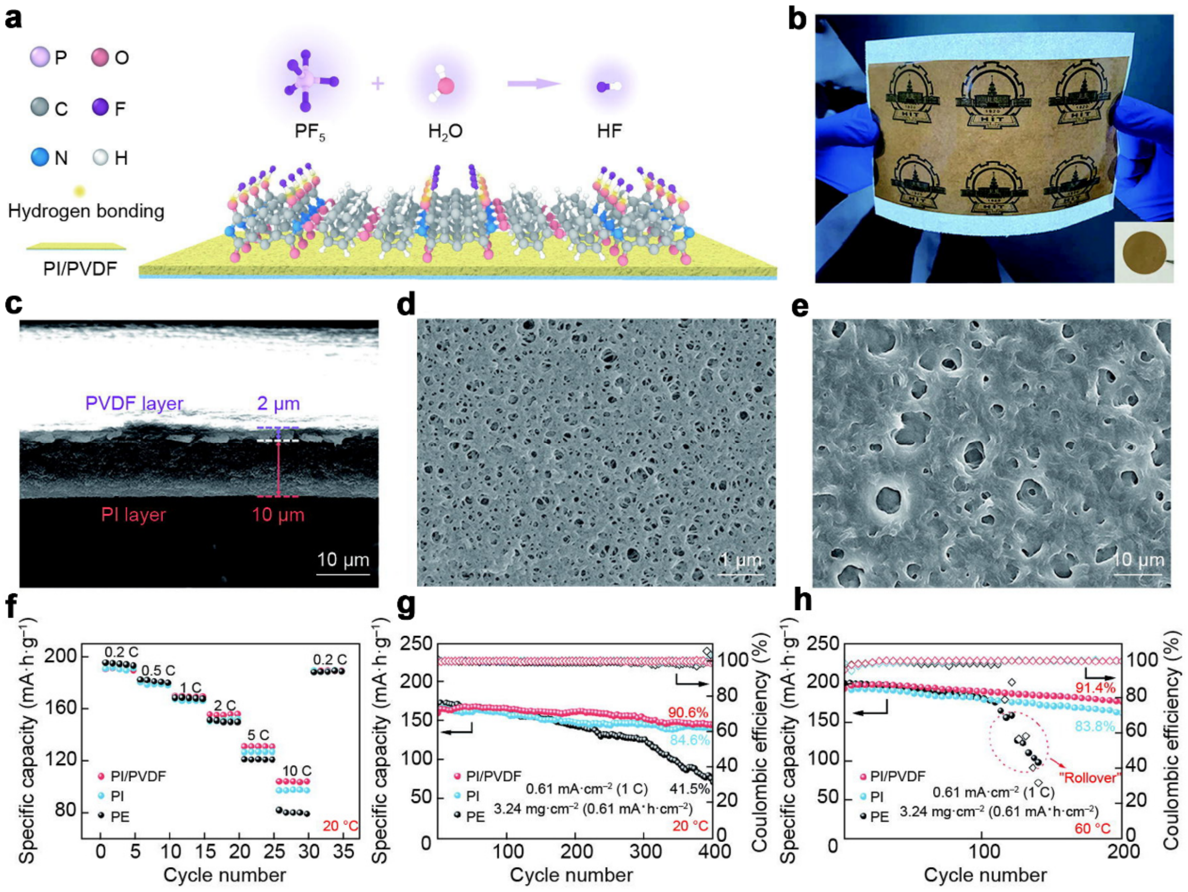


Figure 9. (**a**) Mechanism schematic illustrating the suppression of Li||NCM811 battery capacity decay by the PI/PVDF separator [79]. (**b**) Photograph of a large-area ultraporous PI/PVDF separator (45 mm × 35 mm), featuring the Harbin Institute of Technology (HIT, China) logo, with an inset showing a 16-mm diameter sample. (**c**) Cross-sectional morphology and surface SEM images of the (**d**) PI layer and (**e**) PVDF layer in the composite separator. (**f**) Rate capabilities at room temperature and cycling performance at (**g**) 20 °C and (**h**) 60 °C of cells employing PE, PI, and PI/PVDF separators (test condition: 1 C current density, 3.24 mg cm^{-2} loading; 1 C = 188 mAh g^{-1}).

Advanced surface engineering technologies provide more possibilities for interface optimization. These techniques allow for precise nanoscale alterations of the separator's surface chemistry and morphology without compromising its bulk porous structure, directly addressing interfacial impedance and compatibility issues. Beyond simple coatings, methods such as chemical grafting, plasma treatment, and atomic layer deposition (ALD) enable the creation of robust, molecularly tailored interfaces that can selectively interact with ions or electrolytes. Feng et al. [24] introduced APTMDS via hydrolysis crosslinking to enhance mechanical properties, then improved electrolyte affinity through surface self-polymerization of PDA. The APTMDS forms a robust siloxane network that reinforces fiber junctions, while the subsequently polymerized polydopamine (PDA) layer provides a universally adherent and hydrophilic platform that dramatically improves wetting and homogenizes lithium-ion flux. This multi-step modification strategy enabled the separator to achieve a discharge specific capacity of 128.17 mAh g^{-1} at a high rate of 5 C. As shown in Figure 10a–c, the *in-situ* anchored γ-Al_2O_3 strategy by Chen et al. [80] increased the ionic conductivity from 0.81 mS cm^{-1} for pure PI to 1.74 mS cm^{-1}, with a high capacity retention of 98% after 100 cycles at 0.5 C rate, proving the effectiveness of inorganic-organic interface optimization. The *in-situ* growth of γ-Al_2O_3 ensures strong bonding with the PI matrix, preventing particle detachment. This ceramic layer not only provides thermal stability but also introduces abundant Lewis acid sites that can interact with electrolyte anions, thereby enhancing lithium-ion transference number and promoting more uniform deposition.

The alkali etching strategy by Jiang's team [81] and the PEI grafting method by Yan's team [82], by opening imide rings to expose polar groups and introducing amino functional groups respectively, significantly improved the interfacial lithium ion transport kinetics. These studies collectively indicate that precise surface chemical control is key to optimizing electrochemical performance. As illustrated in Figure 10d, the PTSL-PI composite separator by Yim's team [83] extended modification into the safety realm, achieving a capacity retention of 82.4% after 170 cycles, much higher than the 45.7% for PE separator, demonstrating the necessity of comprehensive performance optimization.

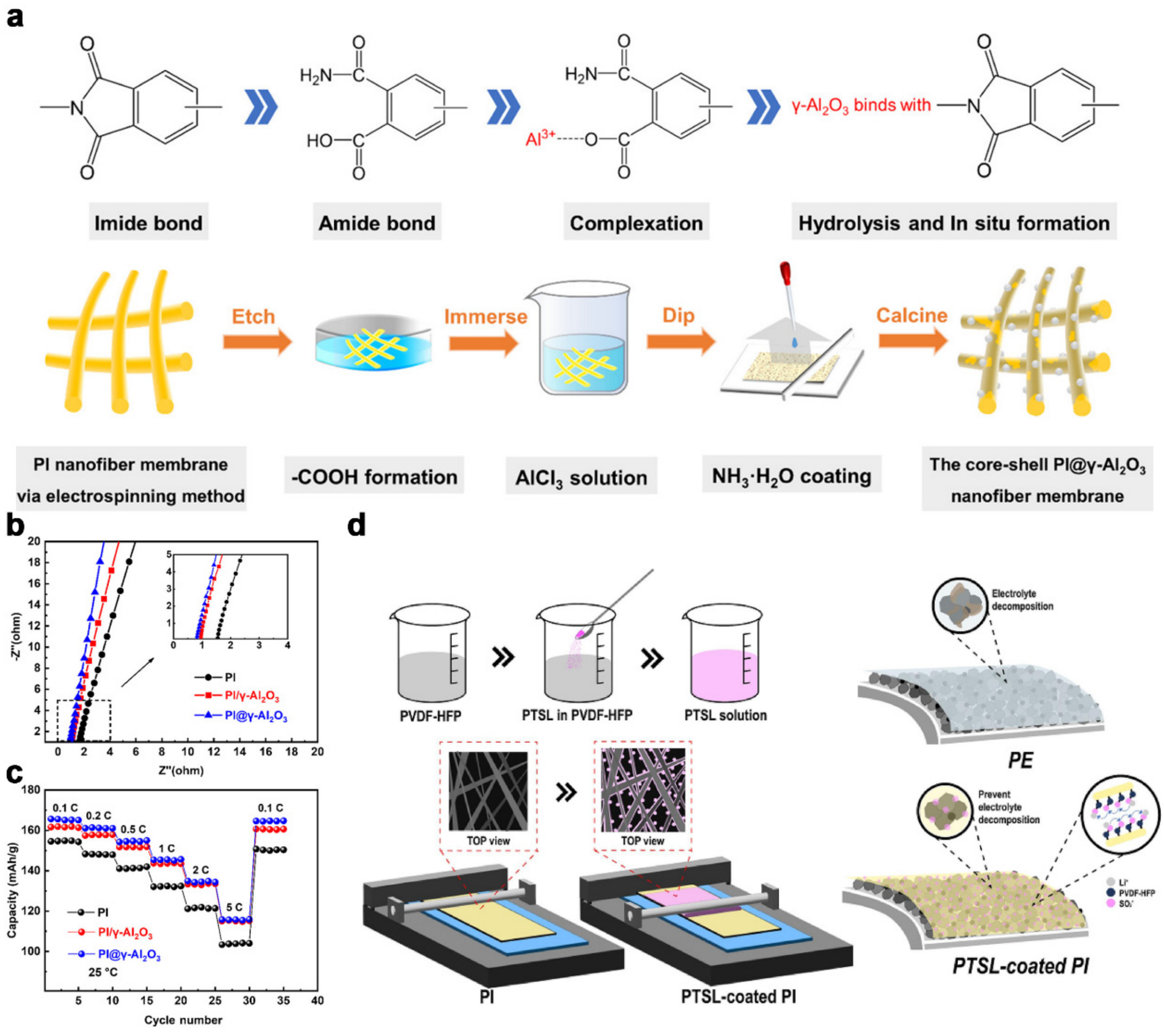


Figure 10. (**a**) Schematic illustrating the synthesis of the core-shell PI@γ-Al_2O_3 nanofiber membrane. Electrochemical performance of cells with different separators: (**b**) impedance profiles and (**c**) discharge capacities at various C-rates. Reproduced with permission [80]. Copyright 2023, American Chemical Society. (**d**) Coating process for preparing PTSL-modified PI. Reproduced with permission [83]. Copyright 2024, The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V.

3.3. Introducing Special Functions and Application Expansion

Moving beyond the passive role of traditional separators, endowing PI separators with specialized functions for specific battery systems is a current research frontier. These studies transform the separator from a simple physical barrier into a functional platform for solving specific electrochemical problems.

Multifunctional separator design for lithium-sulfur (Li-S) batteries is the most representative. As shown in Figure 11a–d, the PICMOC multifunctional composite separator constructed by Wang et al. [84] on a commercial PP substrate innovatively combined the thermal stability and flame retardancy of PI with the catalytic and adsorptive functions of CMOC, where $Co_2Mo_3O_8$@C served as a catalyst and adsorbent, effectively anchoring and accelerating the conversion of polysulfides, delivering a discharge capacity of 460.5 mAh g^{-1} even at a high rate of 2 C. This performance significantly surpasses that of cells using a conventional PP separator (<350 mAh g^{-1} under comparable conditions), which rivals the capacity of some other reported advanced high-performance polymer-based separators [85]. The TiN/PI composite separator by Chen's team [86], synergizing with a phosphorus-doped porous carbon cathode, achieved effective chemical anchoring and catalytic conversion of soluble polysulfides, maintaining a discharge specific capacity of 630 mAh g^{-1} after 140 cycles at 1 C rate, a performance far exceeding traditional polypropylene separators (Figure 11f–l).

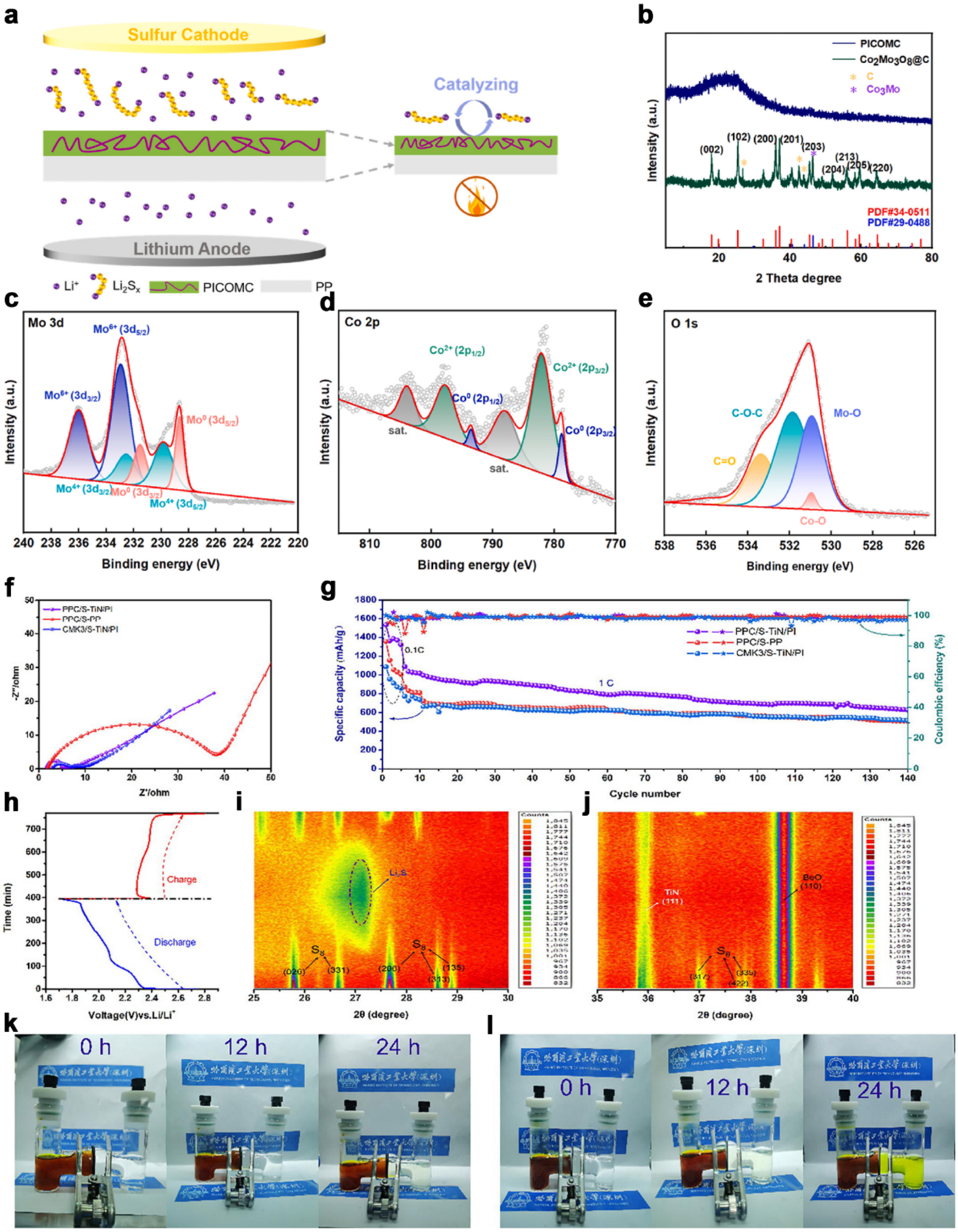


Figure 11. (**a**) The working schematic of PICOMC separator, (**b**) XRD patterns of CMOC materials and PICMOC separators, XPS spectra of COMC (**c**) Mo 3d, (**d**) Co 2p and (**e**) O 1s. Reproduced with permission [84]. Copyright 2025, Elsevier B.V. (**f**) AC impedance of different cells; (**g**) cycling performance of different cells at 1C; (**h**–**j**) *In-situ* XRD pattern of the PPC/S-TiN/PI cell during the first cycle; H-type cells using TiN/PI (**k**) and PP (**l**) separators. Reproduced with permission [86]. Copyright 2022, Elsevier B.V.

Kwon's team [87] introduced graphene oxide into the PI matrix, utilizing its 2D structure and surface polar functional groups to physically block and electrostatically adsorb polysulfides. The prepared PI-GO separator exhibited a high initial discharge capacity of 1306.5 mAh g^{-1} at 0.2 C rate, and still retained a capacity of 730 mAh g^{-1} after 100 cycles. Zhu et al. [88] designed a more systematic three-layer structured separator with a PI nanosheet/Super P conductive network, possessing both chemical adsorption and electrocatalytic conversion functions. It achieved an area capacity of 11.5 mAh cm^{-2} under high sulfur loading (15.43 mg cm^{-2}), an indicator approaching practical requirements (Figure 12).

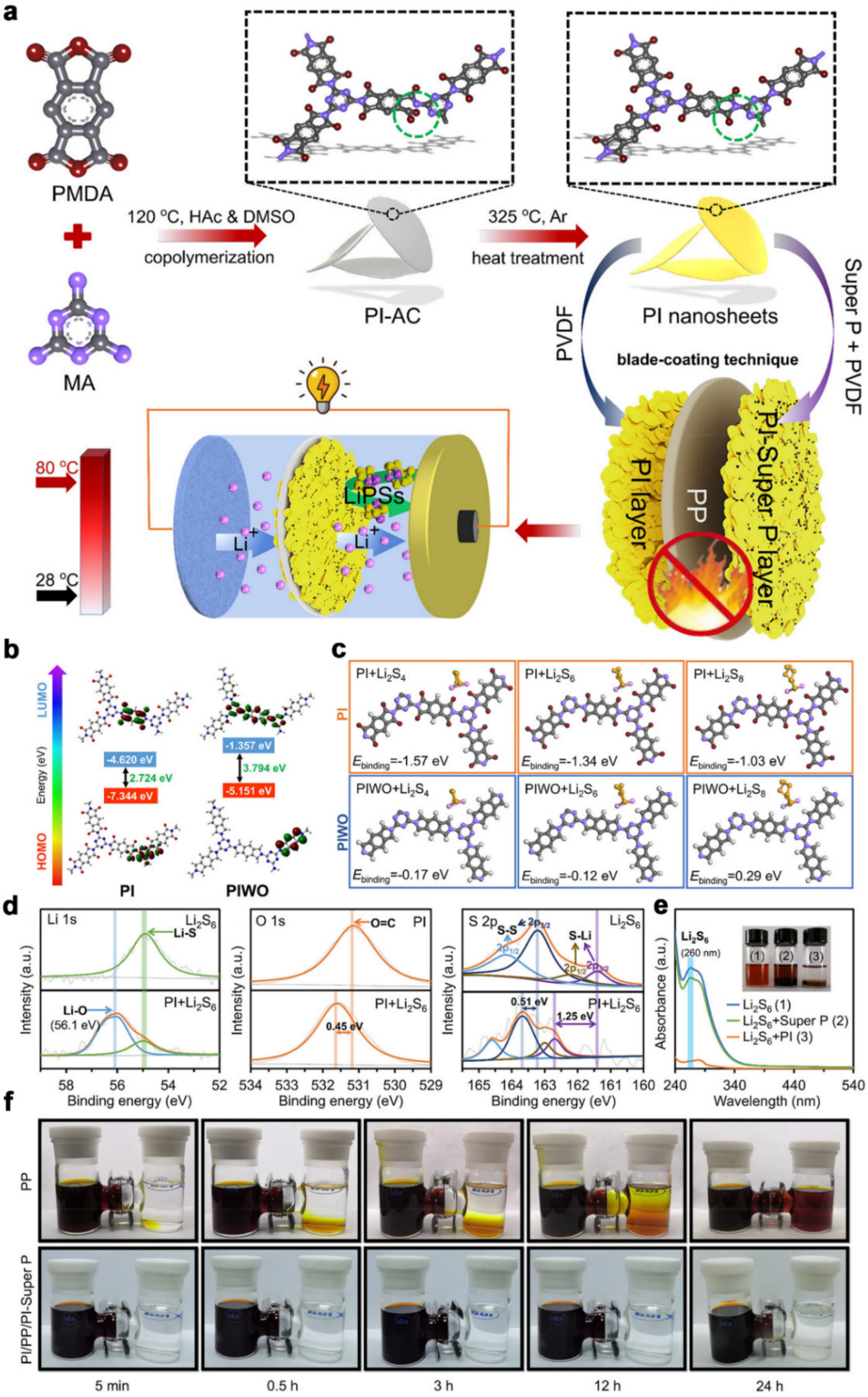


Figure 12. (**a**) Synthesis route of PI nanosheets and the corresponding configuration of lithium-sulfur batteries (LSBs) using a PI/PP/PI-Super P separator. (**b**) Calculated LUMO and HOMO energy levels for PI and PIWO monolayers. (**c**) DFT simulation results depicting the adsorption states of lithium polysulfides (LiPSs) on PI and PIWO surfaces. (**d**) High-resolution XPS spectra of Li 1s, O 1s, and S 2p for Li_2S_6, pristine PI, and the PI+Li_2S_6 mixture. (**e**) UV-vis absorption spectra of Li_2S_6 solutions after 5 h contact with Super P and PI nanosheets. (**f**) Visual comparison of Li_2S_6 diffusion tests across PP and PI/PP/PI-Super P separators. Reproduced with permission [89]. Copyright 2023, American Chemical Society.

Dendrite suppression and interface stabilization strategies for lithium metal batteries demonstrate unique value. The sandwich-structured polyimide-Celgard-polyimide/PEO-LiTFSI (PI-PP-PI/PEO-LiTFSI) composite solid electrolyte designed by He et al. [89] is a model of multifunctional integration: the commercial PP separator provided mechanical strength, while the electrospun PI nanofiber membrane contributed thermal stability and high polarity. This modular design approach achieved a high tensile strength of 21.1 MPa and shape integrity at 180 °C. The PI-PEO-TMP composite electrolyte by Li's team [90] broke temperature limits, enabling stable battery operation over an ultra-wide temperature range from −40 °C to 140 °C, with a high capacity retention of 90.5% after 300 cycles at 0.5 C rate and 120 °C, providing a solution for battery systems in extreme environments. This wide-temperature performance surpasses that of most gel polymer electrolytes and many organic/inorganic composite separators, which typically struggle with operation below −20 °C or above 100 °C, underscoring the unique stability window enabled by the PI matrix.

Intelligent safety protection is another important development direction for PI separators. The PBS/PI bilayer separator designed by Hu's team [91] realized an intelligent thermal shutdown function at abuse temperatures. When the ambient temperature rose to 115 °C, the PBS layer melted and sealed the pores within 5–10 min, reducing the battery capacity to near zero within 20 min. This rapid response mechanism offers a new technical path for battery thermal runaway protection.

Advanced interface engineering has made significant progress in suppressing lithium dendrites. The bead-chain-like PI coating modified by Yin et al. [92] on a commercial PE separator, utilizing its closely packed, uniform 3D submicron pore structure, induced the formation of a lithium-ion-enriched layer on the lithium anode surface, transforming lithium deposition behavior from dendritic growth to flat, dense block-like deposition, extending the cycle life of Cu||Li half-cells by 7 times. As illustrated in Figure 13a–d, the surface carboxyl-rich PI-COOH microsphere coating prepared by Wang's team [25] via etching-acidification not only improved the separator's thermal safety but also maintained high capacity after 280 cycles at 1 C rate, reflecting the synergistic enhancement of interfacial stability and safety.

As shown in Figure 13e–j, the PI@MoS_2 composite separator by Sun's team [93] utilized the MoS_2 coating to *in-situ* form a Li_2S protective layer during cycling, promoting uniform lithium deposition. The assembled pouch cell retained a capacity higher than 150.8 mAh g^{-1} after 150 cycles (1.5 C rate), a performance reaching practical levels. The coaxial electrospun PI@F-PMIA core-shell fiber separator by Zhao's team [23] achieved performance optimization through core-shell division of labor: the PI core provided mechanical strength and thermal stability, while the F-PMIA shell conferred excellent electrolyte affinity and gelation behavior, resulting in a high capacity retention of 83.1% after 200 cycles at 0.5 C rate, showcasing the advantage of precise structural design.

The development of functional separators for next-generation systems like Li-S and Li-metal batteries embodies the paradigm of system-tailored functional integration. In this approach, the separator's architecture is intrinsically co-engineered with the specific cell chemistry to address its dominant failure mechanisms. This shifts the separator's role from a generic, passive component to a customized, application-specific functional module. For Li-S batteries, the architectural focus lies on constructing integrated polysulfide management units. For Li-metal batteries, the design prioritizes architectures for dendrite mitigation and interface stabilization. Additionally, smart safety features can be embedded as precisely tuned responsive safety circuits. This approach represents an advanced level of architectural thinking in separator design, where material innovation is strategically directed towards integrated, system-level solutions.

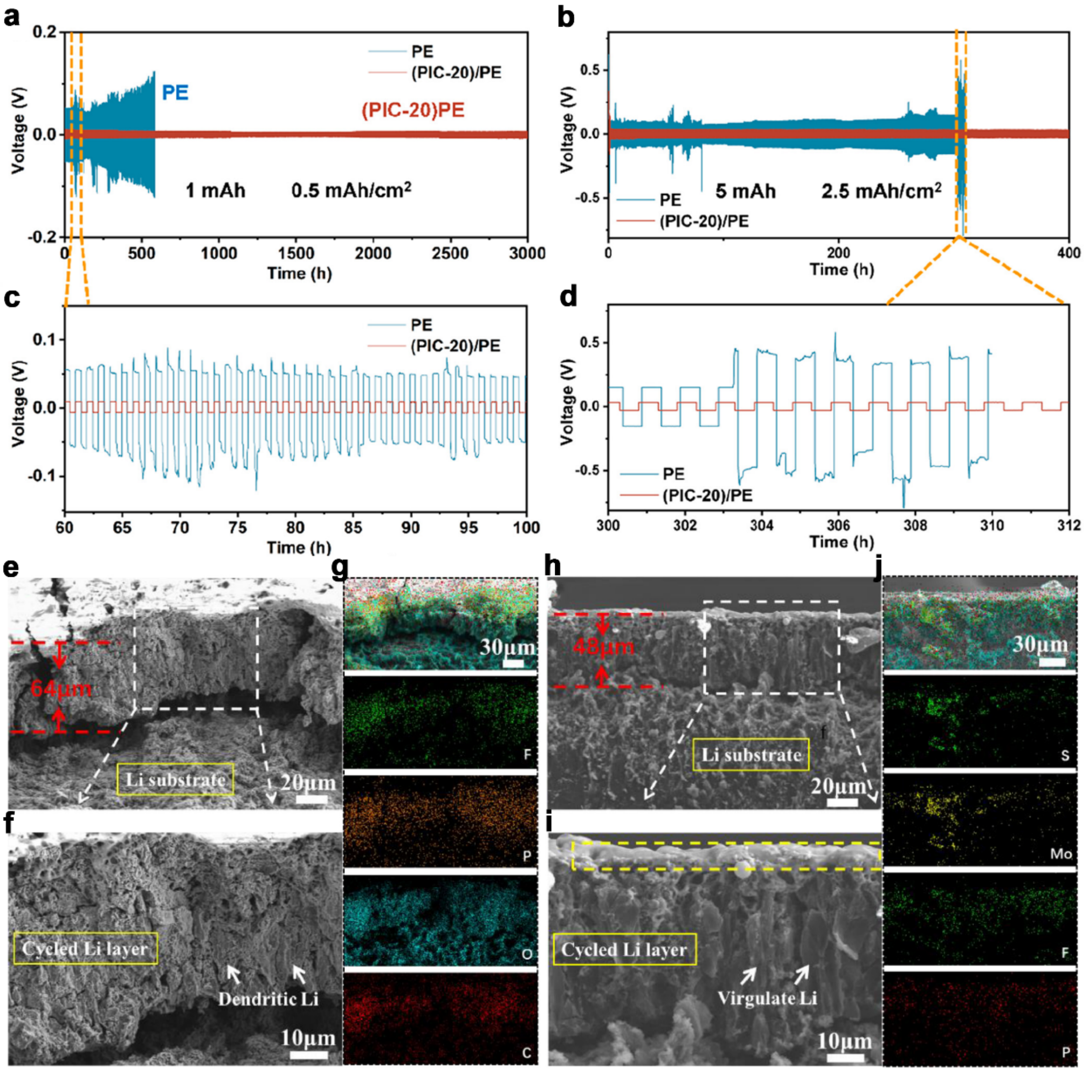


Figure 13. Electrochemical performance of symmetric Li//Li cells employing (PIC-20)/PE separators. Voltage-time profiles for cells with area capacities of (**a**,**c**) 0.5 mAh cm^{-2} and (**b**,**d**) 2.5 mAh cm^{-2}, comparing PE and (PIC-20)/PE separators. Reproduced with permission [25]. Copyright 2023, American Chemical Society. SEM characterization of Li anodes after 100 cycles (1 mA cm^{-2}, 1 mAh cm^{-2}). (**e**,**f**) Cross-sectional views at low and high magnification, and (**g**) corresponding EDS analysis of the pure Li electrode. (**h**,**i**) Cross-sectional views at low and high magnification, and (**j**) associated EDS analysis of the Li electrode paired with the composite separator. Reproduced with permission [93]. Copyright 2022, Elsevier Ltd. on behalf of The editorial office of Journal of Materials Science & Technology.

4. Conclusions and Perspectives

The research and development of polyimide separators signify a major paradigm shift in lithium battery key materials, transitioning from passive isolation towards active functional design. Laboratory-scale research has demonstrated that advanced PI-based separators can achieve exceptional performance metrics, substantiating their potential: porosities exceeding 70%, ionic conductivities up to 26 mS cm^{-1}, tensile strengths surpassing 120 MPa, near-zero thermal shrinkage at 200 °C, and capacity retention above 90% after hundreds of cycles even at high rates. These key performance indicators (KPIs) represent substantial gains over traditional polyolefin separators, directly contributing to potential sustainability impacts through longer battery lifespan and enhanced safety. This review has systematically outlined the core scientific and technical issues involved in PI separators, from their intrinsic material advantages to practical applications. First, we clarified that PI materials, due to their exceptional thermal stability, mechanical strength, and chemical stability, represent an ideal choice to overcome the performance bottlenecks of traditional polyolefin separators. Then, we delved into the cornerstone of their functionalization—the construction of porous structures—systematically summarizing the progress and features of phase separation, electrospinning, and other innovative preparation strategies in building fine structures such as nanofiber networks, sponge-like pores, and vertical nanochannels. Building on this, we further reviewed studies on performance enhancement and functional empowerment of PI separators through strategies like compositing, doping, and surface engineering, demonstrating their great success in enhancing mechanical and thermal stability, optimizing electrochemical interfaces, and introducing special functions such as catalysis, adsorption, and smart responsiveness for emerging battery systems like lithium-sulfur and lithium-metal. These studies collectively indicate that PI-based separators have evolved from an alternative material into a key platform material driving the development of safe, high-performance, high-energy-density storage devices.

Despite the fruitful laboratory achievements, several core challenges must be overcome for the large-scale commercial application of PI separators. The high cost of high-performance PI monomers and the prolonged, energy-intensive imidization process pose significant economic and environmental hurdles. Addressing the cost challenge necessitates a holistic strategy targeting the entire value chain. On the materials front, research into low-cost monomer systems, including the use of non-traditional, potentially bio-derived diamines or dianhydrides, or the exploration of recycled monomer streams, is a recognized industrial pathway to reduce raw material expenses. Process innovation is equally critical. Techniques such as chemical imidization, which facilitates cyclization at lower temperatures, and the adoption of more economical precursor formulations or solvent systems, can dramatically reduce energy consumption and processing time, thereby lowering operational costs. Finally, the choice and engineering of the fabrication process itself are decisive for manufacturing economics. Scalable techniques like NIPS are inherently more amenable to high-speed, roll-to-roll production. For methods like electrospinning, which offers unparalleled design flexibility, the development of high-throughput variants (e.g., multi-needle or needleless systems) is a focused industrial research area aimed at overcoming throughput limitations. Designing the separator and its manufacturing process with scalability in mind from the earliest stage is essential to achieve the economies of scale required for cost-competitive production. Another major bottleneck lies in scalable manufacturing and quality control, where excellent laboratory techniques like precision electrospinning and controlled phase separation face difficulties in transitioning to continuous, high-speed, stable roll-to-roll industrial production, with the inherent conflict between the production efficiency of electrospinning and the strength of fiber membranes still requiring breakthrough engineering innovations. Furthermore, achieving synergistic optimization of multiple performance indicators remains a core scientific challenge. The separator must balance parameters such as porosity, ionic conductivity, mechanical strength, thickness, thermal stability, and cost. The high-performance benchmarks set by research (e.g., >70% porosity with >120 MPa strength) illustrate the ambitious targets but also highlight the delicate balance required. Excessively pursuing high porosity and ionic conductivity may compromise mechanical strength and electrolyte retention. Conversely, introducing too many functional components might enhance one property at the expense of others or increase interfacial complexity.

Looking forward, the research and development of PI separators will unfold across three interconnected dimensions. Deepening fundamental research and innovating design paradigms will require a greater emphasis on understanding the underlying mechanisms linking microstructure, macroscopic performance, and battery behavior. Leveraging artificial intelligence and machine learning, combined with high-throughput computation and experimentation, can accelerate the design and screening of novel PI molecular structures, porous architectures, and composite formulations, thereby realizing a paradigm shift from empirical trial-and-error to rational design. *In-situ* and real-time characterization of interfacial ion transport, dendrite growth inhibition, and polysulfide conversion will provide more direct scientific guidance for the design of functional separators. Breaking through core technologies and advancing engineering heavily relies on deep integration of industry, academia, and research to propel PI separators from the laboratory to the production line. The R&D focus must include bridging the gap between demonstrated lab-scale KPIs (e.g., consistent >90% capacity retention at high rates) and the requirements for stable, high-volume manufacturing. This involves developing scalable advanced preparation technologies alongside developing online monitoring and quality control technologies for real-time feedback on key separator parameters (ensuring porosity, thickness, and strength meet stringent specifications) and promoting standardization processes to establish performance evaluation standards and safety testing specifications. Expanding application fields and adapting to new systems is another exciting direction, as the potential applications of PI separators extend far beyond traditional liquid lithium-ion batteries due to their exceptional heat resistance, tunable interfacial properties, and flexible functionalization capabilities, making them potentially indispensable in all-solid-state batteries as a tough porous support scaffold or composite component to address interface contact and dendrite penetration issues, in lithium metal batteries as a high-modulus physical barrier and interface regulation layer crucial for realizing safe, long-life lithium metal anodes, and in sodium/potassium-ion batteries and lithium-sulfur batteries through targeted functional design to address unique challenges such as sodium dendrites and polysulfide shuttling. Moreover, the integration of artificial intelligence and machine learning with high-throughput computation and experimentation is poised to revolutionize the development cycle of PI separators, enabling the virtual screening of thousands of monomer combinations and fabrication conditions and shifting the field towards a data-driven, inverse-design paradigm.

Polyimide separators, leveraging their unique intrinsic material advantages and through ingenious structural design and multifunctional modification, have demonstrated immense potential to disrupt traditional separator technologies. Although challenges in cost, scalability, and performance balance remain, with continuous deepening of fundamental science, ongoing technological innovation, and close collaboration between industry, academia, and research, PI separators are expected to become a vital engine driving the commercialization of next-generation, safe, high-energy-density energy storage systems in the near future, providing critical material support for global sustainable energy development.

Author Contributions

S.Z.: Conceptualization, Methodology, Investigation, Data curation, Visualization, Writing—original draft, Writing—review & editing. H.X.: Writing—review & editing. Q.L.: Writing—review & editing. Y.D.: Writing—review & editing. S.Z.: Writing—review & editing. Z.Z.: Writing—review & editing. J.H.: Writing—review & editing. J.L.: Writing—review & editing. Y.H.: Writing—review & editing. Y.H.: Conceptualization, Writing—review & editing.

Funding

This work was supported by Chongqing Technology Innovation and Application Development Special Key Project, CSTB2023TIAD-KPX0010 and Chongqing Technology Innovation and Application Development Special Major Project, CSTB2023TIAD-STX0033, and Natural Science Foundation of Chongqing, China (CSTB2022NSCQ-MSX0246, CSTB2022NSCQ-MSX1572), and the Science Foundation of National Key Laboratory of Science and Technology on Advanced Composites in Special Environments.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

References

1. Du, L.Y.; Zhang, Y.M.; Xiao, Y.Y.; et al. A defect-rich carbon induced built-in interfacial electric field accelerating ion-conduction towards superior-stable solid-state batteries. *Energy Environ. Sci.* **2025**, *18*, 2949–2961.
2. Du, L.L.; Zhang, B.; Deng, W.; et al. Hierarchically self-assembled MOF network enables continuous ion transport and high mechanical strength. *Adv. Energy Mater.* **2022**, *12*, 202200501.
3. Shen, J.; Zhang, B.; Huang, W.; et al. Achieving thermodynamic stability of single-crystal Co-free Ni-rich cathode material for high voltage lithium-ion batteries. *Adv. Funct. Mater.* **2023**, *33*, 2300081.
4. Lagadec, M.F.; Zahn, R.; Wood, V. Characterization and performance evaluation of lithium-ion battery separators. *Nat. Energy* **2019**, *4*, 16–25.
5. Dai, J.H.; Shi, C.; Li, C.; et al. A rational design of separator with substantially enhanced thermal features for lithium-ion batteries by the polydopamine-ceramic composite modification of polyolefin membranes. *Energy Environ. Sci.* **2016**, *9*, 3252–3261.
6. Li, H.; Wu, D.B.; Wu, J.; et al. Flexible, high-wettability and fire-resistant separators based on hydroxyapatite nanowires for advanced lithium-ion batteries. *Adv. Mater.* **2017**, *29*, 201703548.
7. Huang, X.S.; Hitt, J. Lithium ion battery separators: Development and performance characterization of a composite membrane. *J. Membr. Sci.* **2013**, *425*, 163–168.
8. Xiang, Y.Y.; Li, J.S.; Lei, J.H.; et al. Advanced separators for lithium-ion and lithium-sulfur batteries: A review of recent progress. *ChemSusChem* **2016**, *9*, 3023–3039.
9. Chen, H.D.; Liu, X.H.; Zhang, S.Q.; et al. Full recovery of polyimide wastes into high-value products through break and reconstruction of imide ring. *Adv. Sci.* **2025**, *12*, 2414416.

10. Chen, L.; Yang, D.D.; Xin, J.H.; et al. High dielectric sulfonyl-containing polyimide binders optimize the long-term stability and safety of NCM811 lithium-ion batteries at high voltages. *Chem. Eng. J.* **2025**, *503*, 158670.
11. Deng, Y.R.; Pan, Y.L.; Zhang, Z.X.; et al. Novel thermotolerant and flexible polyimide aerogel separator achieving advanced lithium-ion batteries. *Adv. Funct. Mater.* **2022**, *32*, 2106176.
12. Zhang, Y.L.; Ruan, K.P.; Zhou, K.; et al. Controlled distributed $Ti_3C_2T_x$ hollow microspheres on thermally conductive polyimide composite films for excellent electromagnetic interference shielding. *Adv. Mater.* **2023**, *35*, 202211642.
13. Liu, X.J.; Zheng, M.S.; Chen, G.; et al. High-temperature polyimide dielectric materials for energy storage: Theory, design, preparation and properties. *Energy Environ. Sci.* **2022**, *15*, 56–81.
14. Han, B.; Ding, X.; Yu, B.Q.; et al. Two-dimensional covalent organic frameworks with Cobalt(II)-phthalocyanine sites for efficient electrocatalytic carbon dioxide reduction. *J. Am. Chem. Soc.* **2021**, *143*, 7104–7113.
15. Liaw, D.J.; Wang, K.L.; Huang, Y.C.; et al. Advanced polyimide materials: Syntheses, physical properties and applications. *Prog. Polym. Sci.* **2012**, *37*, 907–974.
16. Luo, X.X.; Li, W.H.; Liang, H.J.; et al. Covalent organic framework with highly accessible carbonyls and π-cation effect for advanced potassium-ion batteries. *Angew. Chem. Int. Ed.* **2022**, *61*, 202117661.
17. Yao, L.Y.; Ma, C.; Sun, L.B.; et al. Highly crystalline polyimide covalent organic framework as dual-active-center cathode for high-performance lithium-ion batteries. *J. Am. Chem. Soc.* **2022**, *144*, 23534–23542.
18. Yu, J.F.; Dong, N.X.; Liu, B.X.; et al. A newly-developed heat-resistance polyimide microsphere coating to enhance the thermal stability of commercial polyolefin separators for advanced lithium-ion battery. *Chem. Eng. J.* **2022**, *442*, 136314.
19. Wan, J.Y.; Xie, J.; Kong, X.; et al. Ultrathin, flexible, solid polymer composite electrolyte enabled with aligned nanoporous host for lithium batteries. *Nat. Nanotechnol.* **2019**, *14*, 705–711.
20. Huang, H.T.; Chen, K.J.; Li, C.Y.; et al. Zwitterion grafted polyimide separator for improving lithium-ion transport and its application in $LiCoO_2$ batteries. *Chem. Eng. J.* **2024**, *481*, 148577.
21. Jeong, T.Y.; Lee, Y.D.; Ban, Y.; et al. Polyimide composite separator containing surface-modified hollow mesoporous silica nanospheres for lithium-ion battery application. *Polymer* **2021**, *212*, 123288.
22. Li, X.G.; Liu, K.F.; Yan, Y.; et al. Thermostable and nonflammable polyimide/zirconia compound separator for lithium-ion batteries with superior electrochemical and safe properties. *J. Colloid Interface Sci.* **2022**, *625*, 936–945.
23. Zhao, H.J.; Deng, N.P.; Wang, G.; et al. A core@sheath nanofiber separator with combined hardness and softness for lithium-metal batteries. *Chem. Eng. J.* **2021**, *404*, 126542.
24. Feng, X.J.; Wang, H.Y.; Yan, L.X.; et al. Composite separator based on a polyimide nanofiber membrane for advanced lithium-ion batteries. *Acs Appl. Polym. Mater.* **2024**, *6*, 11028–11038.
25. Wang, Z.Y.; Liu, F.Z.; Li, X.G.; et al. Dual-functional separators regulating ion transport enabled by 3D-reinforced polyimide microspheres protective layer for dendrite-free and high-temperature lithium metal batteries. *Acs Appl. Mater. Interfaces* **2024**, *16*, 23826–23837.
26. Song, C.Y.; Gao, C.; Peng, Q.G.; et al. A novel high-performance electrospun of polyimide/lignin nanofibers with unique electrochemical properties and its application as lithium-ion batteries separators. *Int. J. Biol. Macromol.* **2023**, *246*, 125668.
27. Duan, H.Y.; Li, K.; Xie, M.; et al. Scalable synthesis of ultrathin polyimide covalent organic framework nanosheets for high-performance lithium-sulfur batteries. *J. Am. Chem. Soc.* **2021**, *143*, 19446–19453.
28. Xu, Z.X.; Li, M.; Sun, W.Y.; et al. An ultrafast, durable, and high-loading polymer anode for aqueous Zinc-ion batteries and supercapacitors. *Adv. Mater.* **2022**, *34*, 2200077.
29. Zong, Y.; He, H.W.; Wang, Y.Z.; et al. Functionalized separator strategies toward advanced aqueous zinc-ion batteries. *Adv. Energy Mater.* **2023**, *13*, 202300403.
30. Li, C.; Liu, R.; Xiao, Y.; et al. Recent progress of separators in lithium-sulfur batteries. *Energy Storage Mater.* **2021**, *40*, 439–460.
31. Ren, D.S.; Feng, X.N.; Liu, L.S.; et al. Investigating the relationship between internal short circuit and thermal runaway of lithium-ion batteries under thermal abuse condition. *Energy Storage Mater.* **2021**, *34*, 563–573.
32. Zhang, L.P.; Li, X.L.; Yang, M.R.; et al. High-safety separators for lithium-ion batteries and sodium-ion batteries: Advances and perspective. *Energy Storage Mater.* **2021**, *41*, 522–545.
33. Versaci, D.; Canale, I.; Goswami, S.; et al. Molybdenum disulfide/polyaniline interlayer for lithium polysulphide trapping in lithium-sulphur batteries. *J. Power Sources* **2022**, *521*, 230945.
34. Wen, C.; Ding, H.B.; Yang, Y. Numerical simulation of nanodroplet generation of water vapour in high-pressure supersonic flows for the potential of clean natural gas dehydration. *Energy Convers. Manag.* **2021**, *231*, 113853.
35. Wang, Y.; Liu, X.; Sheng, J.; et al. Nanoporous regenerated cellulose separator for high-performance lithium ion batteries prepared by nonsolvent-induced phase separation. *Acs Sustain. Chem. Eng.* **2021**, *9*, 14756–14765.
36. Hussain, A.; Raza, W.; Mehmood, A.; et al. Ionic potency regulation of coagulation bath induced by saline solution to control over the pore structure of PBI membrane for high-performance lithium metal batteries. *J. Energy Chem.* **2024**, *94*, 288–298.

37. Ho, C.C.; Su, J.F. Boosting permeation and separation characteristics of polyethersulfone ultrafiltration membranes by structure modification via dual-PVP pore formers. *Polymer* **2022**, *241*, 124560.
38. Tsai, C.Y.; Liu, Y.L. Crosslinked polyimide asymmetric membranes as thermally-stable separators with self-protective layers and inhibition of lithium dendrite growth for lithium metal battery. *J. Membr. Sci.* **2021**, *640*, 119816.
39. Li, Y.J.; Yang, H.C.; Ahmadi, A.; et al. A thermal resistant and flame retardant separator reinforced by attapulgite for lithium-ion batteries via multilayer coextrusion. *Polymer* **2022**, *253*, 125027.
40. Arundati, A.H.; Ratri, C.R.; Chalid, M.; et al. A combination of nonsolvent and thermally induced phase separation (N-TIPS) technique for the preparation of highly porous cellulose acetate membrane as lithium-ion battery separators. *Ionics* **2024**, *30*, 123–133.
41. Enchinton, A.; Martinez, A.C.; Gonzalez, K.R.; et al. 3D printing of highly porous polypropylene separators for lithium-ion batteries using fused deposition modeling and thermally induced phase separation. *Adv. Mater. Technol.* **2025**, *10*, 202500912.
42. Mohammadzad, M.K.; Pircheraghi, G.; Sharifi, H. Fabrication, characterization, and electrochemical performance of the HDPE/sepiolite nanocomposite as a novel separator for Li-ion batteries. *Express Polym. Lett.* **2021**, *15*, 1063–1080.
43. Bai, Y.T.; Yan, C.Q.; Li, Z.; et al. Preparation of high-strength polyimide porous films with thermally closed pore property by *in situ* pore formation method. *Acta Phys. Chim. Sin.* **2024**, *40*, 2306010.
44. Deng, Y.; Pan, Y.; Li, C.; et al. Advanced polyimide separator via co-precursor method for lithium-ion batteries with low thermal runaway risks. *J. Energy Storage* **2022**, *56*, 106100.
45. Gu, J.P.; Zhang, K.Y.; Li, X.T.; et al. Construction of safety and non-flammable polyimide separator containing carboxyl groups for advanced fast charing lithium-ion batteries. *Chin. J. Polym. Sci.* **2022**, *40*, 345–354.
46. Lin, Y.-H.; Huang, W.-M.; Li, J.-Y.; et al. Nonsolvent-induced phase separation polyimide/polymeric ionic liquid separators for high-performance and safe lithium metal-based batteries. *J. Membr. Sci.* **2025**, *728*, 124125.
47. Wen, G.; Cai, W.; Lv, S.; et al. A microfluid-on-microfluid phase separation strategy fabricates high-throughout porous polyimide separator for lithium-ion batteries. *Polymer* **2024**, *303*, 127102.
48. Zhang, Q.; Chen, L.; Li, X.; et al. Robust, high-temperature-resistant polyimide separators with vertically aligned uniform nanochannels for high-performance lithium-ion batteries. *ACS Nano* **2024**, *18*, 32162–32174.
49. Huang, X.; Cheng, S.; Huang, C.; et al. Superspreading-based fabrication of thermostable nanoporous polyimide membranes for high safety separators of lithium-ion batteries. *Small* **2024**, *20*, 2311219.
50. Jalees, S.; Hussain, A.; Iqbal, R.; et al. Functional PBI membrane based on polyimide covalent organic framework for durable lithium metal battery. *J. Energy Storage* **2024**, *101*, 113985.
51. Zhang, Y.S.; Zhang, X.L.; Silva, S.R.P.; et al. Lithium-sulfur batteries meet electrospinning: Recent advances and the key parameters for high gravimetric and volume energy density. *Adv. Sci.* **2022**, *9*, 202103879.
52. Liu, Z.Z.; Li, G.J.; Qin, Q.; et al. Electrospun PVDF/PAN membrane for pressure sensor and sodium-ion battery separator. *Adv. Compos. Hybrid Mater.* **2021**, *4*, 1215–1225.
53. Liu, Y.Y.; Lin, D.C.; Liang, Z.; et al. Lithium-coated polymeric matrix as a minimum volume-change and dendrite-free lithium metal anode. *Nat. Commun.* **2016**, *7*, 10992.
54. Deng, J.H.; Cao, D.Q.; Yang, X.Q.; et al. Cross-linked cellulose/carboxylated polyimide nanofiber separator for lithium-ion battery application. *Chem. Eng. J.* **2022**, *433*, 133934.
55. Yang, Q.; Deng, N.P.; Chen, J.Y.; et al. The recent research progress and prospect of gel polymer electrolytes in lithium-sulfur batteries. *Chem. Eng. J.* **2021**, *413*, 127427.
56. Yang, K.; Liu, Z.; Chai, J.; et al. High performance polyimide-based separator for 4.5V high voltage $LiCoO_2$ battery with superior safety. *Mater. Chem. Phys.* **2022**, *282*, 125975.
57. Wang, Y.; Guo, M.; Fu, H.; et al. Thermotolerant separator of cross-linked polyimide fibers with narrowed pore size for lithium-ion batteries. *J. Membr. Sci.* **2022**, *662*, 121004.
58. Sun, G.; Feng, X.; Zhang, X.; et al. *In-situ* reinforced polyimide nanofiber membranes for highly efficient and safe lithium-ion batteries. *J. Membr. Sci.* **2024**, *697*, 122549.
59. Liu, K.; Lin, D.; Dong, N.; et al. *In-situ* ScOOH coaxially armored polyimide nanofibrous separator with high electrolyte wettability and thermostability for high-safety and high-rate capability lithium-ion batteries. *J. Membr. Sci.* **2025**, *736*, 124722.
60. Wang, J.; He, C.; Jia, Y.; et al. Fire-proofing, mechanic-reinforcing, electrostatic-spinning strategies toward fabricating porous separator for superior and safer lithium-ion batteries. *ACS Appl. Polym. Mater.* **2025**, *7*, 4725–4738.
61. Pan, C.; Wei, X.; Feng, Y.T.; et al. WO_3-composited polyimide nanofibrous separator with superior mechanical properties and high capacity for lithium-ion batteries. *J. Mater. Sci.* **2023**, *58*, 10686–10698.
62. Song, C.; Luo, J.; Gao, C.; et al. Halloysite nanotubes enhanced polyimide/oxidized-lignin nanofiber separators for long-cycling lithium metal batteries. *Int. J. Biol. Macromol.* **2024**, *273*, 132640.
63. Qian, Y.S.; Chen, K.; Feng, Z.X.; et al. A Fluorinated-polyimide-based composite nanofibrous separator with homogenized pore size for wide-temperature lithium metal batteries. *Small Struct.* **2023**, *4*, 202200383.

64. Shimbori, Y.; Ooga, S.; Kajihara, K.; et al. Effect of polybenzimidazole addition to three-dimensionally ordered macroporous polyimide separators on mechanical properties and electrochemical performances. *Electrochemistry* **2024**, *92*, 23–00145.
65. Wang, Z.; Li, X.; Dong, N.; et al. Novel ZrO_2@Polyimde nano-microspheres-coated polyethylene separators for high energy density and high safety Li-ion battery. *Mater. Today Energy* **2022**, *30*, 101155.
66. Green-Warren, R.A.; Fassler, A.L.; Juhl, A.; et al. Self-limiting electrospray deposition (SLED) of porous polyimide coatings as effective lithium-ion battery separator membranes. *Rsc Appl. Polym.* **2024**, *2*, 1074–1081.
67. Kang, S.H.; Lee, H.; Hong, Y.J.; et al. High-performance, roll-to-roll fabricated scaffold-supported solid electrolyte separator for practical all-solid-state batteries. *Small* **2025**, *21*, 202502996.
68. Chen, Y.; Liu, H.; Luo, J.; et al. *In situ* aluminide armored polyimide nanofiber separators with ultrahigh strength and high wettability for advanced lithium-ion batteries. *Ceram. Int.* **2023**, *49*, 31953–31964.
69. Sun, G.; Jiang, S.; Feng, X.; et al. Ultra-robust polyimide nanofiber separators with shutdown function for advanced lithium-ion batteries. *J. Membr. Sci.* **2022**, *645*, 120208.
70. Jia, S.; Yang, S.; Pan, Y.; et al. Boehmite-PVDF-CTFE/F-PI composite separator irradiated by electron beam for high-rate lithium-ion batteries. *J. Membr. Sci.* **2024**, *704*, 122827.
71. Chen, H.H.; Yu, L.; Cao, X.; et al. The multicomponent synergistic effect of a hierarchical $Li_{0.485}La_{0.505}TiO_3$ solid-state electrolyte for dendrite-free lithium-metal batteries. *Nanoscale* **2022**, *14*, 7768–7777.
72. Cheon, J.; Park, S.H.; Kim, Y.; et al. Aluminum oxide and ethylene bis(diphenylphosphine)-incorporated poly(imide) separators for lithium-ion batteries. *Bull. Korean Chem. Soc.* **2022**, *43*, 1103–1110.
73. Palanisamy, M.; Lin, K.-W.; Lo, C.-T.; et al. *In situ* thermal safety aspect of the electrospun polyimide-Al_2O_3 separator reveals less exothermic heat energies than polypropylene at the thermal runaway event of lithium-ion batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 28310–28320.
74. Wu, D.; Dong, N.; Wang, R.; et al. *In situ* construction of High-safety and Non-flammable polyimide "Ceramic" Lithium-ion battery separator via SiO_2 Nano-Encapsulation. *Chem. Eng. J.* **2021**, *420*, 129992.
75. Li, X.; Liu, K.; Dong, N.; et al. A dendrite-blocking polyimide-meta-aramid separator with ultrahigh strength and thermostability for high-security lithium-ion battery. *Chem. Eng. J.* **2024**, *481*, 148525.
76. Sun, G.H.; Cui, J.Q.; Zhang, Q.S.; et al. Polybenzimidazolium-reinforced polyimide separators to inhibit dendrites for high-security lithium-ion batteries. *Sci. China-Chem.* **2025**, *68*, 3221–3229.
77. Li, M.; Wang, K.; Shen, F.; et al. An electrolyte-locked thermally stable composite separator for safe lithium ion batteries. *J. Alloys Compd.* **2023**, *938*, 168543.
78. Liao, C.; Wang, W.; Wang, J.; et al. Magnetron sputtering deposition of silicon nitride on polyimide separator for high-temperature lithium-ion batteries. *J. Energy Chem.* **2021**, *56*, 1–10.
79. Zhong, S.; Dong, L.; Yuan, B.; et al. Stabilizing high-nickel cathodes via interfacial hydrogen bonding effects using a hydrofluoric acid-scavenging separator. *Engineering* **2024**, *39*, 117–126.
80. Chen, Y.; Luo, J.; Xu, H.; et al. Core-Shell structured polyimide@γ-Al_2O_3 nanofiber separators for lithium-ion batteries. *ACS Appl. Energy Mater.* **2023**, *6*, 1692–1701.
81. Jiang, W.; Chen, Y.; Zhang, J.; et al. Alkali etching enhanced polyimide-based three-layer composite separator for lithium-ion batteries. *Ionics* **2024**, *30*, 3209–3221.
82. Yan, L.X.; Feng, X.J.; Wang, H.Y.; et al. Preparation of PEI-modified PI separators for advanced lithium ion batteries. *Ionics* **2025**, *31*, 453–465.
83. Seong Heo, J.; Yim, T. Lithium p-toluenesulfinate-coated poly(imide) separators for enhanced safety and electrochemical performances of lithium-ion batteries. *J. Ind. Eng. Chem.* **2025**, *144*, 746–753.
84. Wang, Y.; Yang, W.; Zhao, D.; et al. Design and fabrication of a multifunctional $Co_2Mo_3O_8$-modified separator for enhanced performance and safety in lithium–sulfur batteries. *Mater. Chem. Phys.* **2025**, *344*, 131170.
85. Lei, T.; Chen, W.; Hu, Y.; et al. A nonflammable and thermotolerant separator suppresses polysulfide dissolution for safe and long-cycle lithium-sulfur batteries. *Adv. Energy Mater.* **2018**, *8*, 1802441.
86. Chen, H.; Wei, Y.; Cao, X.; et al. Boosting polysulfide capture and redox conversion by functional separator combined with porous hosts for advanced Li-S batteries. *J. Electroanal. Chem.* **2022**, *918*, 116483.
87. Lee, Y.D.; Yuenyongsuwan, J.; Nanthananon, P.; et al. Polyimide hybrid membranes with graphene oxide for lithium–sulfur battery separator applications. *Polymer* **2022**, *255*, 125110.
88. Zhu, Y.; Zhang, Y.; Jin, S.; et al. Toward safe and high-performance lithium–sulfur batteries via polyimide nanosheets-modified separator. *ACS Sustain. Chem. Eng.* **2023**, *11*, 1434–1447.
89. He, Y.; Guo, J.; Bi, C.; et al. Sandwich-like polyimide nanofiber membrane of PEO-based solid-state electrolytes to promote mechanical properties and security for lithium metal batteries. *Int. J. Hydrogen Energy* **2025**, *109*, 1266–1273.
90. Li, M.; Wang, K.; Liu, J.; et al. Synergistically reinforced poly(ethylene oxide)-based composite electrolyte for high-temperature lithium metal batteries. *J. Colloid Interface Sci.* **2022**, *622*, 1029–1036.

91. Hu, W.; Zhu, G.; Chi, F.; et al. Searching for thermal shutdown separators in lithium-ion batteries: Paradigm and practice. *Int. J. Heat Mass Transf.* **2025**, *236*, 126248.
92. Yin, Y.; Wang, K.; Shen, F.; et al. Dendrite-suppressing separator with high thermal stability modified by beaded-chain-like polyimide coating for a Li metal anode. *Energy Fuels* **2021**, *35*, 8417–8422.
93. Sun, B.; Zhang, Z.; Xu, J.; et al. Composite separator based on PI film for advanced lithium metal batteries. *J. Mater. Sci. Technol.* **2022**, *102*, 264–271.