

Porous Polymers Regulating Mass Transport in Zinc-Ion Batteries

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Abstract. Zinc-ion batteries, with their advantages of abundant resources, safety, environmental friendliness and low cost, are gradually becoming a research hotspot in the next-generation green energy storage systems. However, the disordered growth of zinc dendrites and the low ion transport efficiency have become the main obstacles to improving their performance and commercialization. This paper systematically reviews the microstructure characteristics of typical porous materials such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), hyper crosslinked polymers (HCPs), and conjugated microporous polymers (CMPs), and discusses their application strategies in core fields such as anode interface regulation, electrolyte optimization, and composite electrode construction. This study further analyzed the key role of solid-state and hydrogel polymer electrolytes in the construction of flexible and highly safe energy storage devices. Although porous polymers perform well in the laboratory, large-scale preparation, cost, stability, and lifespan remain engineering challenges. Future research needs to develop low-cost and high-throughput synthesis methods, combine multi-scale simulation and in-situ characterization, optimize material design, and promote its practical application in zinc/metal ion batteries.

Keywords: Porous polymers, zinc-ion batteries, mass transport, zinc dendrites, electrolyte, cycling stability.

1. Introduction

Driven by the global energy transition and carbon neutrality goals, safe, sustainable, and economically efficient electrochemical energy storage systems have become a cutting-edge research topic of mutual interest to both academia and industry. Especially in the context of the increasing penetration of renewable energy and the rapidly growing demand for grid flexibility, the development of new energy storage batteries that combine safety and performance advantages has become an important pathway for achieving deep decarbonization of energy systems. Zinc-ion batteries (ZIBs) are a secondary battery system based on a zinc metal anode and an aqueous electrolyte. With its abundant resources, low manufacturing costs, and high safety, it is increasingly emerging as a promising candidate for energy storage technology following lithium-ion batteries. Zinc, as an anode material, not only has a high electrochemical equivalent but also can be used to prepare electrodes with conventional equipment. Its extraction cost is significantly lower than that of rare metals such as lithium and cobalt, making zinc-ion batteries economically competitive in large-scale energy storage applications. The high structural flexibility of zinc-ion batteries provides them with a differentiated competitive advantage. From separators, electrolytes to electrode materials, all can achieve fine performance control through polymer materials, laying a technical foundation for system integration and flexible applications. The broad prospects of zinc-ion batteries in flexible energy storage devices.

However, zinc-ion batteries still face many bottleneck problems that need to be solved urgently in actual operation, among which the growth of zinc dendrites is the most challenging problem. During repeated charge and discharge cycles, the uneven deposition of zinc on the surface of the negative electrode can cause dendrites to penetrate the separator, thereby triggering short circuits and posing serious safety risks.

Although safety is the core advantage of zinc-ion batteries, if dendrite growth and the resulting unevenness and interfacial side reactions cannot be effectively suppressed, their practical application

potential will still be limited. In the key components of zinc-ion batteries, porous polymer materials have emerged as a core material platform for achieving high-performance batteries due to their excellent pore structure regulation capabilities, good ion transport properties, and outstanding mechanical and thermal stability. Different types of porous polymers exhibit unique advantages in terms of conductivity, structural stability, and interface adaptability, enabling functional synergy across multiple layers such as electrodes, electrolytes, and separators. This optimizes zinc ion diffusion pathways, suppresses dendrite formation, and enhances cycle life. Therefore, systematically categorizing and characterizing porous polymers is of significant theoretical and practical importance for developing efficient and safe zinc-ion battery systems.

This paper focuses on the microstructure characteristics and functional design of porous polymers (such as MOFs, COFs, HCPs, CMPs), aiming to systematically explore the application potential of porous polymer materials in solving key scientific problems of zinc-ion batteries (such as zinc dendrite growth, low ion transport efficiency, etc.). To provide innovative material solutions for the development of a new generation of zinc-based energy storage systems with high safety and long service life.

2. Types and Properties of Porous Polymers

2.1. Porous Framework Materials

Metal-Organic Frameworks (MOFs), with their highly tunable pore structure and large specific surface area, demonstrate multi-dimensional regulation of ion transport, interfacial stabilization and flexible device construction in zinc ion batteries. In the regulation of zinc ion transport, the regular nanopore channels of MOFs can be used as ion sieves to selectively guide the directional deposition of Zn^{2+} and effectively inhibit the growth of dendritic crystals; at the same time, the open pore structure of MOFs significantly enhances the diffusion rate of Zn^{2+} in the electrode materials, thus improving the multiplicity performance and capacity retention of the battery [1]. In terms of the stability of the electrode interface, the structural water molecules in the MOFs skeleton form a “water-locking effect” through the hydrogen bonding network, which inhibits the occurrence of water decomposition side reactions in the electrolyte [2], whereas the composite electrode materials of the MOFs further enhance the long-term stability of the electrode/electrolyte interface through the provision of abundant active sites and a stable framework structure. of the electrode/electrolyte interface for long-term stability. In addition, in the construction of flexible devices, the composite of MOFs with hydrogel electrolytes not only retains the mechanical adaptability and interfacial compatibility of the flexible system, but also enhances the ionic conductivity and structural integrity of the electrolyte through the pore structure of MOFs [3], providing an innovative solution for the development of flexible zinc-ion batteries. The MOFs have been used in the optimization of key performances of zinc-ion batteries through their unique structural designability and multifunctional properties. ion batteries through their unique structural designability and multifunctional properties.

Covalent organic frameworks (COFs), as regular porous crystalline materials connected by covalent bonds, exhibit unique modulation capabilities in zinc ion batteries by virtue of their tunable pore size, high stability, and excellent structural rigidity. In terms of zinc ion transport optimization, the pore size of COFs can be precisely regulated by the monomer structure and synthesis conditions to match the hydrated ion size of Zn^{2+} , constructing a low-impedance, high-throughput ion migration pathway, and significantly enhancing the cycling stability and capacity retention [4]. In addition, COFs exhibit excellent chemical resistance in complex electrolyte environments, effectively resisting the erosion of aqueous electrolytes and maintaining the stability of the electrode structure. In terms of interfacial regulation, the 3D interpenetrating porous network of COFs can form continuous and uniform zinc ion migration channels, significantly reducing the risk of dendrite formation and enhancing the safety of the system. COFs, with their precisely adjustable pore size, excellent chemical stability, and unique pore structure, have demonstrated significant advantages in the regulation of zinc ion transport, interfacial stabilization, and the enhancement of battery safety, and have become

a highly promising functional material in the field of zinc-ion batteries. COFs have shown significant advantages in the regulation of zinc ion transport, interfacial stabilization and improvement of battery safety.

2.2. Functional Porous Polymers

Hyper-crosslinked polymers (HCPs) are ideal materials for battery diaphragm design due to their unique structural and performance advantages. First, HCPs are synthesized under mild conditions and from a wide range of monomer sources, which significantly reduces the production cost and has the potential for large-scale application. Secondly, their highly cross-linked 3D network structure gives the materials excellent mechanical strength and stability, which can effectively inhibit the penetration of zinc dendrites and extend the cycle life of the battery. In addition, the pore size distribution of HCPs can be precisely regulated, which not only optimizes the Zn^{2+} transport path and reduces the ion migration resistance but also promotes the isotropic diffusion of zinc ions through nanoscale uniform ion channels and suppresses side reactions such as hydrogen precipitation. This combination of low cost, excellent mechanical properties, and structural designability has enabled HCPs to show significant application value in the field of high-performance battery diaphragms.

Conjugated Microporous Polymers (CMPs) With their unique π -conjugated structure and nanoporous properties, CMPs show significant advantages in high-performance electrode composites. On the one hand, the continuous conjugated chain structure of CMPs can form a stable electron transport channel at the electrode/electrolyte interface, which significantly reduces the interfacial impedance and improves the electrochemical reaction kinetics. On the other hand, the porous network structure of CMPs not only promotes the rapid migration of zinc ions to maintain uniform zinc deposition and interfacial stability, but also optimizes the zinc deposition kinetics by building a synergistic ion-electron transport system through the dual acceleration strategy of the surface/inner surface. In addition, CMPs have excellent bonding properties, which enhance the mechanical stability and structural integrity of the electrodes, thereby significantly extending the cycle life of the battery. This combination of high electrical conductivity, fast ion transport and excellent mechanical properties makes CMPs ideal for zinc-based battery electrode composites.

2.3. Electrolyte Systems

2.3.1. Polymer Electrolytes: Solid/Gel Electrolytes Enhancing Interface Stability

Polymer electrolytes, as the core materials of solid/gel electrolyte systems, exhibit significant value in the interfacial stability and structural reliability enhancement of zinc ion batteries (ZIBs) due to their unique high flexibility and excellent ionic conductivity. It has been shown that molecular structure design can significantly optimize the Zn^{2+} migration kinetics while promoting the formation of a stable solid electrolyte interface (SEI), thus synergistically enhancing the multiplicity performance and cycle life of the batteries [5]. More importantly, the pore structure and functional group properties of polymer electrolytes are closely related to their interfacial behaviors, and a reasonable structural design can effectively inhibit the growth of zinc dendrites and enhance the electrode/electrolyte interface compatibility. In addition, the coordination effect in polymer electrolytes can significantly inhibit side reactions such as hydrogen precipitation, which further improves the safety and energy efficiency of the battery. These properties make polymer electrolytes a key material system for realizing high-performance, long-life flexible zinc ion batteries.

2.3.2. Hydrogel Electrolytes: High Flexibility, Suitable for Flexible Batteries

Hydrogel electrolytes have shown significant advantages in the field of flexible zinc ion batteries (ZIBs) due to their unique three-dimensional network structure and high water content. These electrolyte materials not only have good ionic conductivity but also excellent mechanical flexibility, which can meet the special requirements of electrolyte materials for flexible electronic devices. It has been shown that the mechanical strength and ionic conductivity of hydrogel electrolytes can be synergistically enhanced by nanostructure modulation (e.g., introducing defect-engineered modified

Bi₂Se₃ nanoparticles into porous carbon nanofibers) [6]. Of particular note, some specially designed polymer hydrogels (e.g., porous structures based on pyrrotetrazole) even exhibit electronic-ionic dual-conductivity properties, which provide new possibilities for the development of high-energy-density flexible batteries. Optimization of the performance of hydrogel electrolytes requires precise regulation of the equilibrium relationship between their thickness and ionic conductivity, while the dual functions of dendrite inhibition and electrode protection can be achieved simultaneously by constructing ordered hierarchical membrane structures with zinc affinity and hydrophobicity properties [7]. Hydrogel electrolyte becomes a key material system to promote the development of next-generation flexible energy storage devices.

3. Structural Optimization and Performance Regulation Mechanisms of Porous Polymers in Zinc-Ion Batteries

3.1. Control of Electrode Structure by Porous Polymers

Among the key components of zinc-ion batteries, the design of the electrode structure directly determines ion migration behavior, charge storage efficiency, and cycling stability. Porous polymers, with their tunable pore structures, surface chemical designability, and high compatibility with various active materials, offer new avenues for optimizing electrode material structures and enhancing performance. Particularly in suppressing anode dendrites and enhancing cathode conductivity, porous polymers play an irreplaceable role in zinc-ion battery electrode systems due to their multifunctional roles as structural frameworks, interface regulators, and charge transport media.

3.1.1. Anode Dendrite Suppression Mechanism

The problem of dendrite growth in zinc anodes mainly stems from uneven electrochemical deposition and interfacial side reactions. Porous polymers can effectively inhibit the formation of dendrites through several mechanisms. First, their three-dimensional porous structure provides spatial confinement to guide the uniform deposition of zinc ions at specific sites to avoid localized aggregation. For example, carbon-based materials with hierarchical pore channels can limit the lateral growth of dendrites through physical constraints. Second, through surface functionalization modifications (e.g., doping of elements such as nitrogen and phosphorus), porous polymers can regulate the adsorption and diffusion behaviors of zinc ions and optimize the deposition kinetics. In addition, the flexible polymer skeleton adapts to volume changes during charging and discharging to maintain the structural integrity of the electrode. These synergistic effects significantly enhance the uniformity and cycling stability of zinc deposition. In summary, porous polymers, through the construction of spatial confinement, electric field regulation, interface functionalization, and pore size gradients, have become one of the key materials for addressing zinc anode dendrite issues, laying a solid material foundation for the development of next-generation high-safety zinc-ion batteries.

3.1.2. Anode Conductivity Enhancement and Reaction Site Construction

In anode materials, porous polymers mainly solve the problems of insufficient electrical conductivity and loss of active substances. On the one hand, their high specific surface area and interconnected pores can construct a continuous electron conduction network and enhance the overall conductivity of the electrode. For example, oxygen-doped porous carbon frameworks not only provide efficient charge transfer pathways but also stabilize active substances through chemical bonding. On the other hand, the surface functional groups (e.g., oxygen-containing or nitrogen-containing groups) of the porous polymers can serve as additional redox active sites to promote multi-electron reactions. Meanwhile, the three-dimensional hollow structure can effectively buffer the volume expansion of the active substance and inhibit the structural degradation of the electrode material during the cycling process. These properties make porous polymers an ideal choice for improving the multiplicity performance and cycle life of cathode materials.

Therefore, by rationally designing the pore structure, chemical composition and spatial morphology of porous polymers, the performance of porous polymers can be further optimized in zinc ion batteries, which can provide important guidance for the development of electrode materials with high energy density and long cycle stability.

3.2. Performance Contributions of Porous Polymers in Electrolyte Systems

In recent years, porous polymers have demonstrated significant advantages in optimizing the electrolyte system for aqueous zinc ion batteries, and their unique structural properties have effectively solved the key problems of ionic conduction and interfacial stability. Studies have shown that the electrolyte performance can be significantly enhanced by constructing a three-dimensional porous polymer matrix: the silver vanadate nanowire-polymer composite system developed by Xie et al. successfully established a continuous ion transport channel, which reduces the Zn^{2+} diffusion resistance by about 40% and improves the battery multiplicity performance by more than two times [8]; the reduced graphene oxide coated with $\alpha\text{-MnO}_2$, which was innovated by Pradhan's team, has shown significant advantages in optimizing the aqueous zinc ion battery electrolyte system in recent years. The coated $\alpha\text{-MnO}_2$ structure not only realizes the efficient embedding/de-embedding of Zn^{2+} , but also improves the electrode cycling stability by 300% [9]. The porous polymers are able to simultaneously optimize the ion migration kinetics and electrode/electrolyte interfacial stability through their tunable pore structure and surface chemistry, providing an important theoretical basis and technical path for the design of new-generation high-performance zinc ion batteries.

4. Enhancing Battery Performance

Zinc-ion batteries (ZIBs) have gained significant attention as a promising candidate for next-generation energy storage systems due to their unique advantages in safety, material availability, and environmental friendliness. Porous polymers and their composites have demonstrated great potential in regulating ion migration, stabilizing interface reactions, and enhancing structural stability. Through systematic material structure design and interface control strategies, ZIBs have achieved significant progress in key performance metrics such as capacity, rate performance, cycle stability, and safety.

4.1. Electrochemical Performance

In the enhancement of electrochemical performance, capacity and rate response are the two core indicators directly reflecting a material's energy storage capacity and kinetic characteristics. Capacity and multiplicity performance can be significantly optimized by the rational design of porous composites. Du et al. constructed a Si/TiO₂ carbon fibre core–multi-level MXene@Co-MoS₂ shell composite material, demonstrating excellent interfacial electronic coupling ability and multi-level ion diffusion pathways, effectively enhancing the capacity and rate performance of lithium batteries. This structural strategy also holds significant potential for zinc-ion electrode materials [10]. Introducing porous composite materials to enhance the active reaction area at the interface is one of the key approaches to improving ZIB reaction efficiency.

In terms of electrolyte interface regulation, He et al. achieved significant optimization of the electrochemical stability of the zinc anode interface by constructing an organic solid-state electrolyte layer, reducing side reactions and enhancing rate response capability, thereby providing an effective interface protection strategy for high-power ZIBs [11]. Additionally, Giri et al. proposed a V₁₀O₂₄·12H₂O@rGO composite cathode material, which, due to its high structural openness and electronic conductivity continuity, demonstrated excellent specific capacity and high-rate discharge capability in aqueous ZIBs, indicating that porous frameworks play a core role in promoting rapid Zn^{2+} insertion/extraction and enhancing energy storage density [12].

Synergistic optimization of porous structure design, interface engineering, and material regeneration strategies can systematically enhance the energy density, power density and cycle stability of ZIBs.

4.2. Cycling Stability

Extending the cycle life of ZIBs hinges on addressing the issues of disordered zinc dendrite growth and interfacial corrosion. Jian et al. employed interface regulation technology to surface-engineer LGPS solid-state electrolytes, establishing a uniform ionic flux field between the electrolyte and anode, thereby effectively suppressing dendrite nucleation and achieving stable cycling for hundreds of cycles [13]. This approach provides an interface control paradigm for the long-term stable operation of solid-state ZIBs.

Tong et al. developed a polymer-metal composite interface layer based on Aquivion, which improved flexibility and wettability, alleviating mechanical stress concentration in the electrode during cycling, and significantly reducing interfacial delamination and corrosion rates, offering an effective technical approach to enhancing ZIB stability [14]. Similarly, Sadatian Abkenar et al. introduced vertically aligned carbon nanotube arrays to modify alloy anodes, which not only strengthened the electronic conduction network but also effectively suppressed dendrite longitudinal growth through spatial structure regulation [15].

Kumar et al. evaluated graphene aerogel-based electrode materials and noted that these materials possess continuous three-dimensional pore channels and high specific surface areas, enabling uniform current distribution at the microscopic scale, reducing the risk of dendrite formation caused by localized high Zn^{2+} concentrations, while enhancing interfacial wetting and electron/ion synergistic pathways, thereby delaying corrosion-induced performance degradation [16].

4.3. Safety

Leakage and volatilization of liquid electrolytes have always been the key safety issues restricting the practical application of aqueous batteries. The introduction of polymer-based solid-state electrolytes not only effectively solves the solvent leakage problem through intermolecular interactions but also significantly reduces the interfacial impedance of the zinc-metal anode and prolongs the battery cycle life. In particular, the highly ordered solid-state electrolyte constructed from MOF-derived materials can simultaneously inhibit water evaporation and uneven migration of zinc ions through the dual mechanisms of spatial site resistance and pore sieving, thus enhancing thermal stability and operating voltage window. At the same time, hydrogel electrolytes show unique advantages in the field of flexible energy storage by virtue of their three-dimensional cross-linking structure and high water content: the introduction of an elastic polymer network can alleviate the stress concentration caused by changes in the electrode volume, and by regulating the cross-linking density and the introduction of zinc affinity groups, the ion mobility can be maintained at high levels and the mechanical strength can be enhanced. Notably, such gel electrolytes can also stabilize the interfacial SEI layer and modulate the Zn^{2+} deposition morphology, thus reducing the risk of dendrite short-circuiting [18]. Dunn et al. further emphasized that solid-state electrolyte technology, as a core means of thermal runaway protection for energy storage systems, offers systematic safety advantages in terms of inhibiting electrolyte leakage and delaying the thermal reaction. In contrast, hydrogel systems with composite covalent organic frameworks achieve dual optimization of electrochemical performance and operational stability through the synergistic effect of ordered ionic conduction and structural enhancement [19]. Through the synergistic design of solid-gel state electrolytes, the intrinsic safety deficiencies of conventional aqueous batteries and the demand for flexible applications can be addressed simultaneously.

5. Challenges and Future Directions

5.1. Current Bottlenecks

Currently, the application of porous polymers in zinc ion batteries still faces many challenges. In terms of scalable preparation, high raw material costs, complex multi-step synthesis processes (e.g., construction of selective ion transport layers), and difficulties in precise regulation of micro- and nano-pore structures on an industrial scale have severely constrained their large-scale production. In addition, the polymer matrix is prone to chain breakage, cross-linking density reduction and pore collapse during cycling, leading to impeded ion transport, uneven electrode deposition and increased interfacial impedance, affecting the long-term stability of the battery. Industrialized production also needs to overcome the mass transfer bottleneck caused by microstructural defects, and there is an urgent need to develop low-cost, environmentally friendly low-temperature synthesis processes, improve the batch consistency of the pore structure, and design polymer systems and post-processing technologies that are suitable for continuous production, to realize the sustainable manufacturing of high-performance porous polymer materials.

Porous polymers face severe stability challenges in the long-term cycling of zinc ion batteries. The polymer backbone undergoes chain breakage, crosslinking network relaxation, and pore collapse under mechanical fatigue and electrochemical erosion, leading to the blockage of Zn^{2+} transport paths and the decrease of mass-transfer efficiency; pore shrinkage, pore wall collapse, and the buildup of by-products (e.g., zinc hydroxide) during cycling further deteriorate the interfacial reaction homogeneity and lead to the fluctuation of localized current densities and zinc dendritic crystal growth. These multi-scale degradation mechanisms are subject to the coupling of electric-chemical force fields, and there is an urgent need to enhance the stability of the materials through molecular structure optimization (e.g., modulation of chain rigidity/flexibility, construction of self-supporting frameworks) and interfacial engineering (e.g., design of dynamic cross-linking, introduction of self-repairing groups), and to reveal the degradation mechanisms by combining in-situ characterization and simulation, so that the practical application of high lifetime zinc-ion batteries can be realized eventually.

5.2. Research Directions

In studying porous polymers for high-performance zinc-ion batteries, green, low-cost, and controllable synthesis methods are the key breakthroughs for achieving large-scale industrial applications. Currently, mainstream synthesis routes, such as solvent-thermal methods, hydrothermal methods, mechanical ball milling, and microwave-assisted methods, have demonstrated excellent structural control capabilities and cost-control potential at the experimental level. However, in engineering-scale applications, these methods still need to address the balance between raw material compatibility, production efficiency, and environmental friendliness.

In the future, the optimized design of porous polymers should focus on the construction of an “integrated structure” to achieve synergistic performance enhancement through the integration of ion transport channels, electronic conductive networks and mechanical support functions. Specifically, a gradient pore size design can be used to promote the directional diffusion of zinc ions, embedding π -conjugated groups or carbon nanosheets and other conductive units to build a continuous electron transport pathway, and at the same time, introducing a high-strength cross-linking structure to maintain the stability of the framework. This multi-scale and multi-functional synergistic design strategy can not only synchronously optimize ionic conductivity, electronic conductivity, and mechanical strength, but also significantly extend the material cycle life, providing a key solution for the development of high-performance zinc-ion batteries.

6. Conclusion

Porous polymers have demonstrated significant application potential in multiple key links of zinc-ion batteries due to their highly adjustable pore size structure, rich functional group modification ability and excellent chemical and mechanical stability. From regulating the migration rate of Zn^{2+} and enhancing the interfacial stability to inhibiting the growth of zinc dendrites and improving the cycle life, porous polymers have achieved multiple breakthroughs in material functionality and structural design compared with traditional systems. Through the systematic review of this study, it can be seen that different types of porous polymers, such as MOFs, COFs, HCPs, and CMPs play multiple roles in zinc-ion batteries, including electrolyte regulation, interface modification, ion channel construction, and conductive path extension. A multi-level structure-performance mapping network has been formed.

However, it must be pointed out that the wide application of porous polymers still faces several key challenges. Future research needs to achieve systematic breakthroughs in aspects such as material synthesis strategies, structure-function integration and mechanism interpretation. Overall, porous polymers, as a new type of material system with highly engineered structures and highly integrated functions, are driving a profound transformation of zinc-ion batteries from a paradigm of "safety substitution" to "performance leadership". With the joint efforts of interdisciplinary integration and theoretical experiment fusion, its potential as the core unit of the next-generation green energy storage materials will continue to be unleashed, and it is expected to become a key breakthrough for the performance leap and ecological transformation of aqueous batteries in the future.

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