



Review

Rational design and functionalization of covalent organic frameworks for multivalent metal ion storage

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ABSTRACT

Multivalent-ion batteries (MVBs) have demonstrated considerable potential for scalable energy storage, owing to advantages including high energy density, enhanced safety, and environmental sustainability. However, the diffusion dynamics of MVBs in conventional electrode materials are sluggish due to MVBs' high charge density and the large radius of hydrated ions, which can easily lead to severe degradation of the electrode structure, posing significant challenges for practical applications. COFs and their derivatives show considerable promise for application in MVBs, owing to their programmable crystalline architectures, large specific surface areas, and precisely controllable active sites. Therefore, after a thorough discussion of the challenges facing MVBs, including the storage and diffusion difficulties of multivalent ions and the side reactions of the battery, this paper provides a systematic overview of the recent advances of COFs for MVBs. The structure–activity relationships of their structural design strategies and energy storage mechanisms are analyzed to illustrate their unique advantages. Finally, the properties and modification methods of COFs and their derived materials as electrode materials for MVBs (Zn, Ca, Mg, and Al ion batteries) are discussed in detail. The paths forward are expected to provide theoretical references and technical routes for the design of advanced multivalent metal-ion batteries.

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1. Introduction

The growing adoption of renewable energy and the burgeoning electric vehicle sector have intensified the demand for next-generation electrochemical energy-storage solutions characterized by high energy density, low cost, and enhanced safety [1–3]. Multivalent ion batteries (MVBs), including magnesium (MIBs), aluminum (AIBs), zinc (ZIBs), and calcium (CIBs), present a viable alternative to lithium-ion batteries (LIBs). Their ability to transfer multiple electrons per ion enables theoretical capacities potentially 2–3 times greater than those of LIBs (Fig. 1a). Furthermore, factors like the natural abundance of these elements and stable redox potentials position MVBs as strong contenders for future grid-scale energy storage systems [4–6]. Nevertheless, the large charge density inherent in multivalent ions and the slow ion insertion/extraction kinetics result in a significantly higher diffusion

barrier in conventional electrode materials, causing severe polarization effects and capacity attenuation [7]. The reversibility of metal anodes can be significantly compromised by dendritic formation, surface passivation/corrosion, and competitive hydrogen evolution reactions, posing safety risks due to potential short-circuit initiation [8]. Furthermore, cathode instability manifested through active material dissolution and parasitic by-product accumulation accelerates capacity fading while inducing structural degradation, as illustrated in Fig. 1b [9]. In addition, poor interfacial compatibility between multivalent ions and electrolytes, slow solid-state diffusion kinetics, and the lack of suitable and efficient host materials are common challenges. Therefore, breakthroughs for electrode material design are urgently needed. In response to these scientific challenges, significant research efforts, including those from our group, have been devoted to developing innovative electrode materials, electrolytes, and interface engineering strategies for MVBs. Our sustained research in this domain, encompassing advanced mechanisms in zinc-ion batteries, novel electrode designs for calcium-ion storage, and electrolyte optimization for magnesium-ion systems, provides a foundational perspective for

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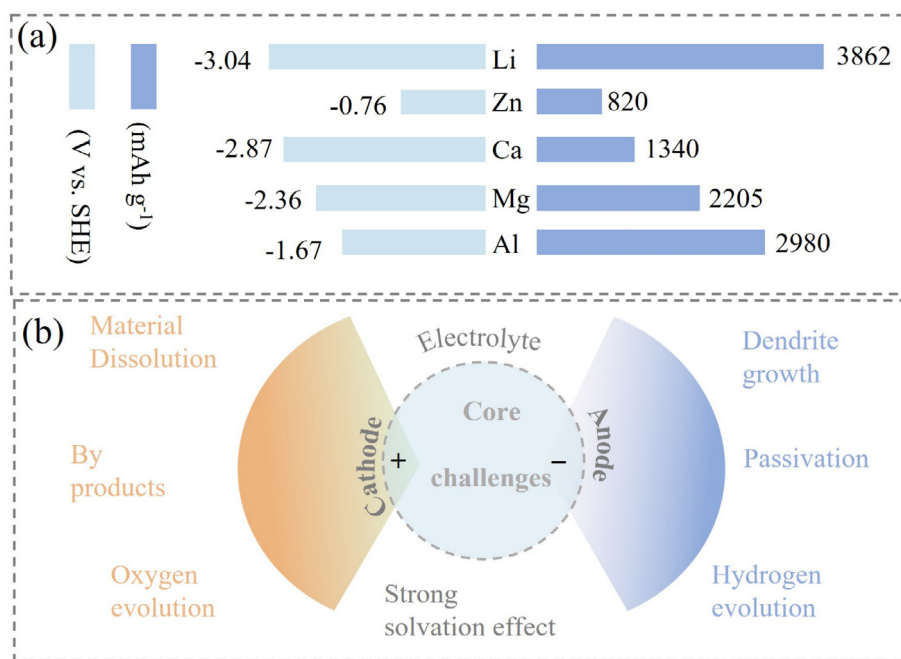


Fig. 1. (a) Reduction potential and specific capacity of several common metal carriers (left is the value of potential (V vs. SHE), right is the value of specific capacity (mA h g⁻¹)). (b) Common problems of MVIBs in the cathode and anode.

this review. Building upon this groundwork, the exploration of new materials with well-defined structure–property relationships remains paramount for the advancement of MVIBs.

As a novel porous crystalline material, COFs have rapidly emerged in energy storage research and garnered significant interest due to its highly designable topological structure, excellent chemical stability, flexible functionalization strategies and tunable pore size distribution (Fig. 2). COFs possess a high specific surface area, meaning they have a large internal space with numerous surface sites that provide ample storage space for ions [10]. Additionally, many COF materials contain redox-active groups such as carbonyl, imine and quinone structures. These groups can undergo redox reactions with ions, enabling them to be stored and released [11]. Compared with traditional inorganic porous materials, COFs can precisely construct periodic pore structures with dynamic covalent bonds, thereby effectively facilitating ion/electron transport and mitigating the volume expansion of electrode materials during charge–discharge cycles (Fig. 2a–c) [12]. This provides a new way to solve the bottlenecks of kinetic retardation and capacity attenuation in energy storage devices [13,14]. At present, COFs have demonstrated mature application potential as electrode materials in alkali metal ion battery (Fig. 2d). By regulating COFs' morphology and structure, the exposure and utilization of active sites can be significantly promoted, which effectively improves the storage capacity for lithium ions. Yang et al. constructed chemically stable fully *sp*² carbon-conjugated COFs (BTT-ICTO) as LIBs cathodes [15]. A series of BTT-ICTO@CNT-x composites were further precisely regulated from “butterfly-shaped” to “cable-like” through an in situ controllable growth strategy, which promoted the exposure of active sites and enhanced the conductivity of COF composites. When the unique “cable-like” BTT-ICTO@CNT is employed as lithium-ion batteries (LIBs) cathode, it exhibits exceptional capacity (396 mA h g⁻¹ at 0.1 A g⁻¹ with 97.9 % active sites utilization rate) and exceptional cycling stability (The attenuation rate is 0.00365 % after 8000 cycles at 2.0 A g⁻¹). Wu et al. constructed a bipolar COF featuring both C–N and C=N redox-active centers by introducing flexible building units containing *sp*³-hybridized nitrogen [16]. This molecular structure enables the

reversible storage of anions (PF₆⁻) and cations (Li⁺), while the flexibility of the units effectively weakens interlayer π - π stacking, allowing the direct formation of a 3D flower-like hierarchical architecture composed of 2D hexagonal nanosheets via a one-step solvothermal process. This open morphology significantly increases the specific surface area, facilitating electrolyte infiltration and ion/electron transport, thereby achieving a high specific capacity (207 mA h g⁻¹), excellent rate capability, and long-term cycling stability. This work highlights the crucial role of synergistic optimization of molecular structure and morphology in COFs for enhancing electrochemical performance. Sodium-ion batteries (SIBs) have problems such as kinetic sluggishness, large volume changes and limited specific capacity as a result of the large radius of Na⁺. The targeted incorporation of redox-active moieties into the COF skeleton can increase the Na⁺ storage capacity. Kang et al. designed and synthesized an azatriangulenetrione-containing COF (designated CityU-33) as an electrode material for SIBs [17]. Leveraging its inherent multiple redox active sites and rapid intercalation kinetics, CityU-33 exhibits a discharge capacity of up to 410.4 mA h g⁻¹ at 0.1 A g⁻¹, alongside exceptional long-term cycling stability—maintaining 97 % capacity retention after 2000 cycles and achieving 288 mA h g⁻¹ at 0.2 A g⁻¹. Similarly, in potassium-ion batteries, effective potassium storage can be achieved through structural design of COFs. Cheng et al. [18] demonstrated a bulk COF (TQBQ-COF) with triquinoxalynylene (TQ) and benzoquinone units (BQ) in the *sp*²-carbon-conjugated (π -conjugated) periodic skeletons could act as a reliable anode for high-capacity, fast, and stable K⁺ storage. It has been clearly demonstrated that C=O and C=N groups, along with cation- π interactions, provide highly accessible redox active sites for potassium ion storage. The double bonds within these C=O and C=N groups confer exceptional chemical stability and outstanding electronic conductivity upon this *sp*²-conjugated carbon framework, enabling it to store potassium ions.

COFs have emerged as promising electrode materials for MVIBs, owing to their unique structural advantages, including programmable porosity, tunable functional groups, and high stability. The precisely ordered nanopores in COFs enable selective ion

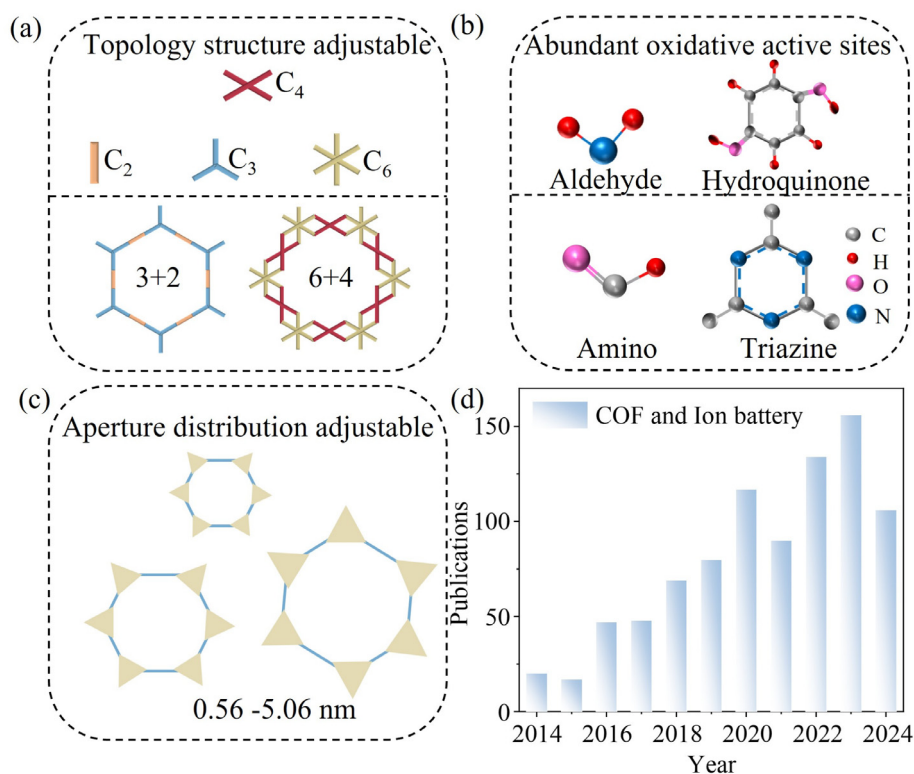


Fig. 2. (a) Symmetry in monomer assembly within COFs (C₂, C₃, C₄, C₆) and partial COF topologies (C₂ + C₃; C₄ + C₆). (b) The portion of the molecular structure capable of storing multivalent ions. (c) Schematic diagram of COFs with different pore sizes. (d) The number of publications on COFs in ion batteries over the last decade. (Published articles about COFs and ion battery are listed chronologically under the topics “Covalent Organic Frameworks” and “Ion battery”. Data obtained from the Web of Science.)

sieving through size exclusion effects, significantly reducing ionic diffusion resistance while achieving targeted multivalent-ion adsorption [19,20]. Notably, the high density of polar functional groups (e.g., C=O, C–N) within the organic framework can stabilize multivalent ions via coordination interactions, thereby synergistically enhancing both cycling stability and energy density [21]. These inherent merits have been extensively validated through theoretical simulations and experimental studies, positioning COFs as a versatile platform for advanced battery design. Recent progress demonstrates COFs’ exceptional capability in addressing critical challenges of current battery systems. In aqueous zinc-ion batteries (ZIBs), where dendrite growth, hydrogen evolution, and corrosion reactions severely limit performance, ultrathin COF films (20–100 nm) deposited on zinc anodes have shown remarkable effectiveness in inhibiting dendrite formation and mitigating interfacial side reactions [22,23]. Theoretical investigations further reveal the structure–property correlations underlying these improvements. For instance, through density functional theory calculations, Adnan Ali Khan et al. demonstrated that the QHHTP-DPB framework with dual-functional quinone rings (C=O) and hierarchical porosity exhibits strong Mg²⁺ binding affinity, achieving a theoretical capacity of 720.48 mA h g^{−1} at 0.39 V open-circuit voltage when fully loaded [24]. Similar breakthroughs have been achieved in aluminum-ion systems. Luo et al. developed DAQ-TpO/CNT composite which combines COFs’ abundant C=O/C–N active centers with carbon nanotubes’ conductivity, enabling efficient AlCl₃ storage through coupled redox and pseudocapacitive mechanisms. This design achieves 290 mA h g^{−1} specific capacity with unprecedented cyclability (32,000 cycles) and rate performance [25]. Beyond the structural advantages of COFs, innovative reaction mechanisms can also be leveraged to overcome kinetic limitations. For instance, Mai group proposed a fast-charging mechanism based on Zn²⁺-catalyzed water splitting and *OH stor-

age effectively resolves issues of slow diffusion of multivalent ions within electrode materials and interfacial transport, thereby achieving ultra-high-rate performance in ZIBs [26]. While these achievements highlight COFs’ potential, the field still faces fundamental challenges. Current research has begun mapping structure–property relationships through framework engineering and interface customization strategies [27], with particular focus on topological design principles for MVIBs applications [28]. However, critical knowledge gaps persist regarding the correlation between structural parameters (e.g., pore size distribution, functional group density) and electrochemical performance, as well as the detailed energy storage mechanisms governing MVIBs.

Therefore, we systematically review the latest research progress of COFs in MVIBs, focusing on the relationship between, their structural design and energy storage mechanisms. First, starting from the core challenges of MVIBs, the unique advantages of COFs in regulating topological structures, modifying active sites and optimizing interfaces are described. And the design principles and foundations of COF materials in MVIBs are clarified. Second, the performance and modification methods of COFs in calcium, magnesium, aluminum and zinc ion batteries are discussed. Finally, the research direction of COFs electrodes is proposed, including machine learning assisted molecular screening, heterogeneous structure construction and soft package battery integration process, in order to provide theoretical reference and technical path to design MVIBs with desirable performance.

2. Storage mechanism and core challenges of MVIBs

Within electrochemical energy storage systems, secondary batteries serve as crucial apparatus for energy conversion. During charging, external electrical energy drives chemical transforma-

tions within the battery, accumulating energy as electrochemical potential. Subsequently, upon discharge, this stored chemical energy is reconverted into electrical output [29,30]. The fundamental architecture of these batteries consists of the anode, cathode, electrolyte, and separator. Charge transfer within the system is enabled by ionic movement across the electrolyte between the electrodes [31]. The electrolyte-filled diaphragm enables ion transfer during charging/discharging process and prevents direct contact between the electrodes. The charging efficiency of a battery depends on the interplay between electrode material and active ions, which is governed by a variety of mechanisms. The charge storage capacity of a battery bears relation to the potential difference between the electrochemical reactions occurring at the electrodes and the number of electrons involved in each reaction [32]. MVIBs achieve the energy storage by reversible embedding/detaching of high charge density multivalent ions in electrode materials, and their theoretical capacity can be up to 2–3 times of that of Li-ion batteries [33]. The performance characteristics of MVIBs (including cycling stability, power density and energy density) are significantly affected by the electrode materials. Therefore, the systematic study of the direct correlation between the intrinsic properties of multivalent ions and the properties of electrode materials is an important means to promote MVIBs.

The core challenges facing MVIBs include the following three main components: a) slow kinetic diffusion of multivalent ions, b) lack of high-performance electrode materials, and c) poor matching ability between electrode materials and electrolyte (Fig. 3). Owing to the large charge density of multivalent metal ions and the highly ionic nature of the main body lattice, Coulombic correlation between the guest ions and the adjacent lattice enhances, which generates a high ionic diffusion energy barrier, impeding ion migration and resulting in reduced charging and discharging rate of the cell [34,35]. The sluggish kinetics also induce localized stress within the host lattice, triggering transition metal dissolution from the cathode and eventual structural degradation. The diffusion mechanism of ions in the crystal lattice hinges on long-range diffusion in crystalline structures. This process fundamentally involves ions moving between stable or metastable interstitial positions by traversing regions of higher energy.

Conceptually, each displacement can be described as a “jump” along a diffusion pathway, where the highest energy point along this path defines the migration barrier—also known as the activation energy [36]. The stable or sub-stable sites are primarily determined by the ion's coordination environment and the arrangement of anions and tend to be tetrahedral or octahedral. Rapid migration can be realized when the coordination of stable sites is incompatible with the ionic coordination tendency and the sub-stable sites can provide a more favorable coordination. Therefore, in the same lattice framework, even for ions Mg^{2+} and Zn^{2+} of analogous size and charge, their different coordination tendencies can lead to very different diffusion energy barriers [37]. Li^+ and Zn^{2+} are most commonly found in 4-coordination, Mg^{2+} and Al^{3+} in 6-coordination, and Ca^{2+} in 8-coordination. Therefore, Zn^{2+} must overcome the high migration barrier in spinel, while Mg^{2+} exhibits a lower migration barrier. Ca^{2+} has a higher coordination number, leading to instability in low-coordination environments, while the high migration barrier of Al^{3+} is partly attributed to stronger electrostatic repulsion [38]. Generally, multivalent species possess compact ionic radii and high electronegativity, suggesting their suitability for intercalation into electrode host materials. However, in practice, this potential remains unrealized due to complex diffusion kinetics stemming from their multivalent nature rather than geometric factors alone [39]. Consequently, addressing the inherent limitations of MVIBs to enable reversible ion intercalation in stable cathodes constitutes a crucial and foundational scientific challenge.

The multivalent metal ions with the large charge density properties make them typically more reactive and capable of rapidly accepting or delivering more electronic charge, enabling them to strongly interact with water molecules or other solvent molecules in solution to form hydrated ions [40]. This strong solvation effect may affect the free movement of ions, and then affect their adsorption and reaction on the electrode surface [41], resulting in poor matching ability between electrode materials and electrolytes. On the one hand, its strong polarization effect causes the structure of the solvated layer to be abnormally compact, such as the solvation energy of multivalent ions being significantly larger than that of Li^+ [42]. Furthermore, the generation of stable hydrated ions

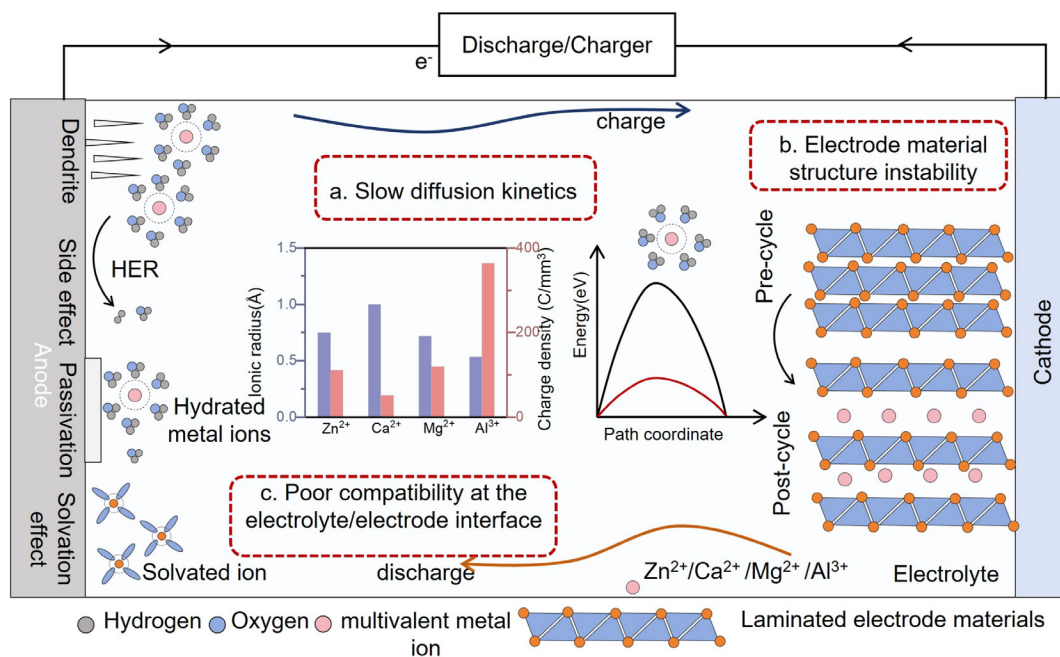


Fig. 3. Storage mechanism and core challenges of MVIBs (including key scientific issues pertaining to the cathode, anode and electrolyte).

(e.g., $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$) between the polyvalent ions and solvent molecules (especially water molecules) can significantly restrict the free migration of ions [43]. This strong solvation effect not only increases the dissociation barrier, but also hinders the effective ion adsorption on the surface of electrode and charge transfer through 'solvent cage' effect, resulting in kinetic retardation [44]. Moreover, the large charge density exacerbates side reactions at the interfaces between electrolyte and electrode. At the cathode, the dissolution of the electrode material and the formation of by-products can shorten the battery life and lead to electrode degradation. On the metal anode side, the generation of a passivation layer on the metal severely impairs the reversibility of the electrodeposition/stripping process [45]. This phenomenon is common in ZIBs and MIBs. Therefore, the core of these issues lies in designing low-coordinating solvents to weaken the solvation effect, developing a stable electrode/electrolyte interface to inhibit side reactions, and stabilizing ion transport by optimizing the solid electrolyte interface layer.

3. Types of topology structure and synthesis methods of COFs

COFs are crystalline porous polymers constructed from organic building blocks via strong covalent bonds. They are characterized by predictable structures, high porosity, and adjustable functionality [46]. Due to the diversity of organic monomers and various kinds of bonds between the reacting monomers, different types of COFs are formed after the condensation reaction [47]. The following COFs have been successfully developed: triazine, boric acid, imine, and β -ketoenamine. To date, most of the reported COFs are two-dimensional, while merely a small number of three-dimensional instances. Unraveling the topological structures of 2D and 3D COFs, along with their composites and derivatives, necessitates explicit knowledge of covalent bond orientation [48]. Achieving precise bond alignment typically requires monomers possessing a structurally rigid core capable of spatially arranging functional groups in predetermined geometries. COF design is fundamentally guided by reticular chemistry principles. Through the strategic selection of diverse building blocks, key characteristics like pore size and shape can be tailored [49].

Prevalent topological architectures of 2D COFs, COF-based composites, and the derivatives include $[\text{C}_2 + \text{C}_4]$, $[\text{C}_2 + \text{C}_3]$, $[\text{C}_3 + \text{C}_3]$ and $[\text{C}_3 + \text{C}_2]$. Contingent upon the specific geometry of the constituent topological units, these 2D-COF frameworks are categorized into hexagonal, square, rhombic, and triangular configurations, dictated

by the functionality and spatial arrangement of the monomeric building blocks [50]. In 2D COFs, the layers are connected by π - π interactions and intralayer covalent bonds, while 3D COFs require the orthorhombic symmetry of the T_d or node unit to enable the polymer network to grow in three dimensions. The symmetry-driven design forms the core principle behind the structural diversity of COFs. In Fig. 4a, some common topology diagrams of 2D and 3D COFs are given. The high selectivity of COFs' organic monomers dictates the choice of synthetic methods for frameworks with distinct linking bonds.

The expanding repertoire of COF synthetic strategies encompasses established approaches including solvothermal, ionothermal, microwave-assisted, mechanochemical, and sonochemistry-mediated fabrication [51]. The solvent-thermal synthesis method utilizes organic compounds or non-aqueous solvents to react in a closed system. By controlling solvents, monomers, catalysts, and temperature, the morphology, composition, and crystallinity of COFs can be optimized [52]. Its advantage lies in the ability to produce highly crystalline materials. However, it faces challenges such as stringent reaction conditions, cumbersome steps, lengthy processes, and high solvent consumption, making large-scale application difficult. Microwave heating utilizes microwave electromagnetic waves to induce high-frequency molecular motion for internal heating, offering advantages such as fast reaction rates, low energy consumption, and uniform heating. However, it requires specialized equipment and has limited applications. Ionic thermal synthesis employs ionic liquids or low-melting-point mixtures as media, enabling rapid reactions at atmospheric pressure without soluble precursors, resulting in stable products. However, it imposes special requirements on reaction apparatus [53]. Mechanical grinding involves grinding monomers (such as 1,3,5-trihydroxy-trimethylbenzene and p-phenylenediamine derivatives) at room temperature without solvents, monitoring product formation through color changes in the reactants. The resulting COFs retain pore channels and crystal structures but have low specific surface areas [54]. Solvothermal synthesis is one of the most common methods, in which the monomers react in a solvent at high temperature and pressure to form a highly crystalline framework. In contrast, in ionic thermal synthesis, ionic liquids are used both as a solvent and as a catalyst in the preparation of MOFs. Microwave-assisted synthesis accelerates the formation of COFs by applying microwave radiation, which allows for rapid reactions in a shorter period of time [55]. Finally, mechanochemical methods involve solid-state reactions driven by mechanical forces without

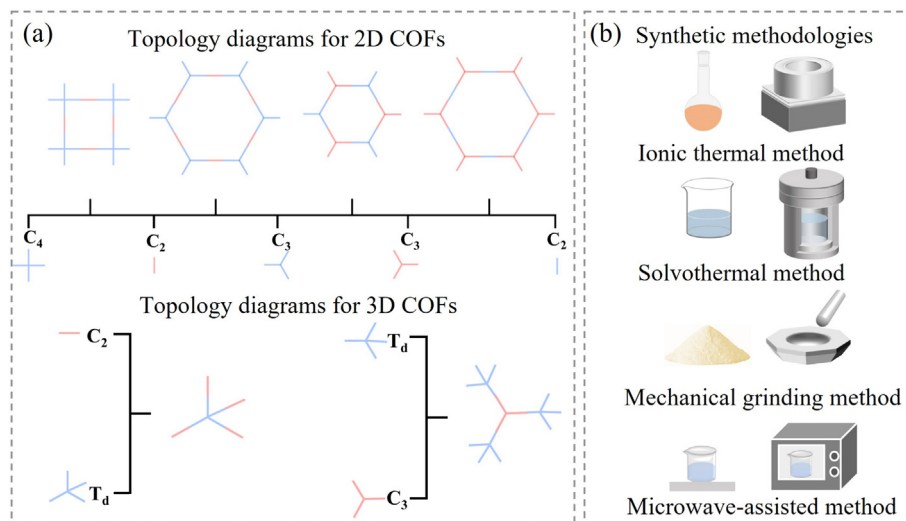


Fig. 4. Some common 2D and 3D COF topology diagrams (a) and synthesis methods (b).

the use of solvents. Fig. 4b summarizes the chemical synthesis reactions of different types of COFs.

4. COFs in MVIBs

Although MVIBs have garnered significant interest owing to their high energy density and low cost, the strong electrostatic interactions within them lead to slow ion diffusion kinetics, which remains a major obstacle. COFs have unique functional applications in MVIBs due to their ordered pores, tunable functional groups and high stability. During charge–discharge cycles, the organic molecules or functional groups within COFs can reversibly accept or release ions in a controlled manner, enabling efficient energy storage. Organic electrode materials are categorized as n-type and p-type based on the charge state they reach during redox reactions [56]. For the N-type organics, they are reduced to form negatively charged anions throughout the reduction reaction. Taking the LIB as an example, as the COFs is reduced, the negatively charged material will reach equilibrium with the help of the cationic moment (Li^+), completing the charge and discharge process. The P-type organics are oxidized to form positively charged cations during the reaction [57,58]. The electrode materials derived from COFs are conceptualized as redox-active sites encapsulated in a porous organic framework. Therefore, the integration of redox units within the framework offers a straightforward method for creating high-performance electrodes. Unlike traditional organic electrode materials, COFs has an elastic framework structure, characterized by a crystalline structure and high porosity, opening up new avenues for innovative material design. Recently, a growing number of academic papers have demonstrated the successful use of COFs materials as electrode materials for MVIBs, thus confirming their practicality (Fig. 5).

4.1. Design strategies and principles for COF-related materials in MVIBs

The rational design and optimization of COFs for advanced multivalent-ion batteries depend fundamentally on a deep under-

standing of their structure–property relationships. In polyvalent ion batteries, the electrochemical performance is largely dictated by the microstructure, molecular structure and electrode structure of the COFs electrode material. Theoretical capacity is determined by the quantity of redox active sites available per molecule, while the actual capacity is influenced by variables including particle size, conductivity and pore size. Adjusting these structures through molecular engineering can affect the transport of electrons and ions, and thus the rate performance. Simultaneous modification of the linker groups and structural units is an effective way to optimize the quantity of available active sites, which can increase the overall capacity of the electrode material [59]. In addition, the molecular structure also plays a crucial role. P-type redox links generally generate higher voltages than n-type redox links. The addition of electron-withdrawing or electron-donating groups can change the LUMO energy level, which can affect the voltage and capacity of the cell. COFs with optimal pore sizes and high conductivity are more likely to approach their theoretical capacities, but factors such as junction stability and redox activity may limit cycling performance [60]. Previous reviews have seldom explored the application of COFs in MVIBs. Thus, this review aims to fill this gap by providing a systematic and in-depth analysis of COFs. This chapter outlines the functionalization design strategy of COFs in MVIBs. It focuses on the design of COFs' ion transport channels, the types of COFs frame, and the composite strategies of COFs (Fig. 6). The aims are to clarify the structural advantages of COFs and their working mechanisms, and to promote the universal application of functionalized COFs-based materials in MVIBs. The specific content includes the following three aspects.

- 1) The design of pore structure: channel engineering and ion transport optimization (Fig. 6a). It is noteworthy that the core challenge with multivalent ions lies in their sluggish solid-phase diffusion kinetics. By regulating pore size to reduce the initial energy barrier for ions entering the material's interior (adsorption and desolvation), efficient transfer from liquid to solid phase can be achieved. This addresses the critical issue of embedding multivalent ions. Unlike

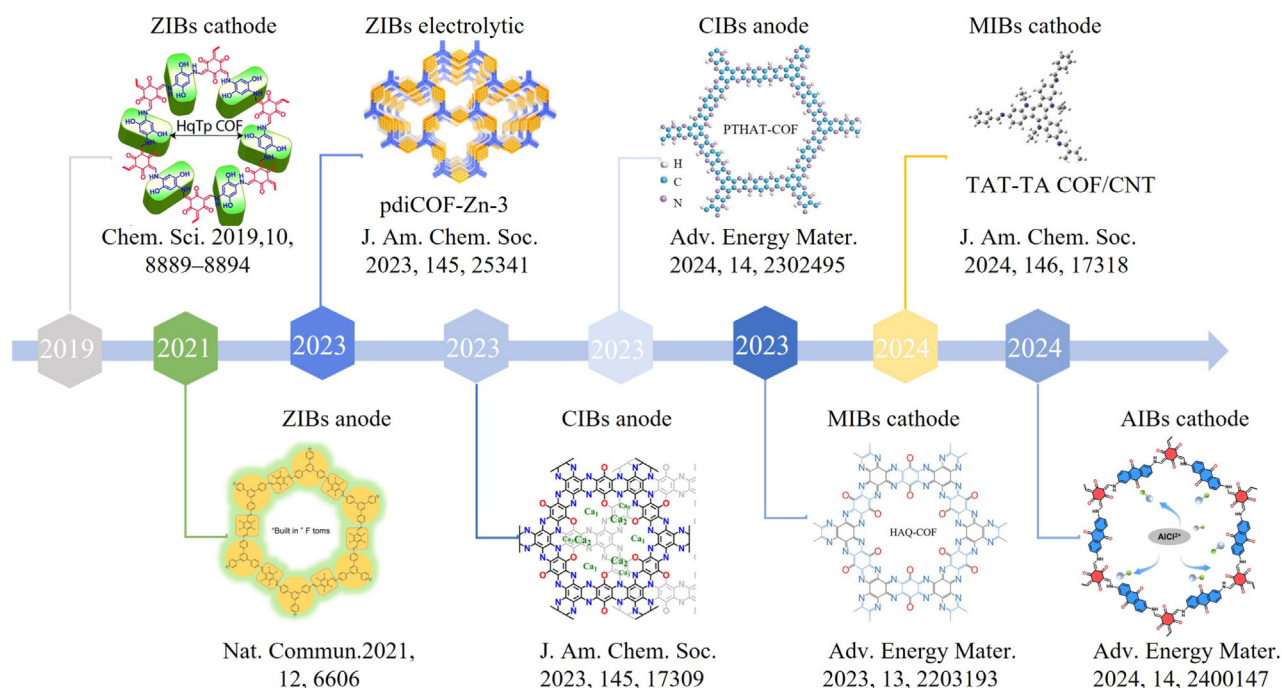


Fig. 5. Major publications on COFs materials in MVIBs over the past five years.

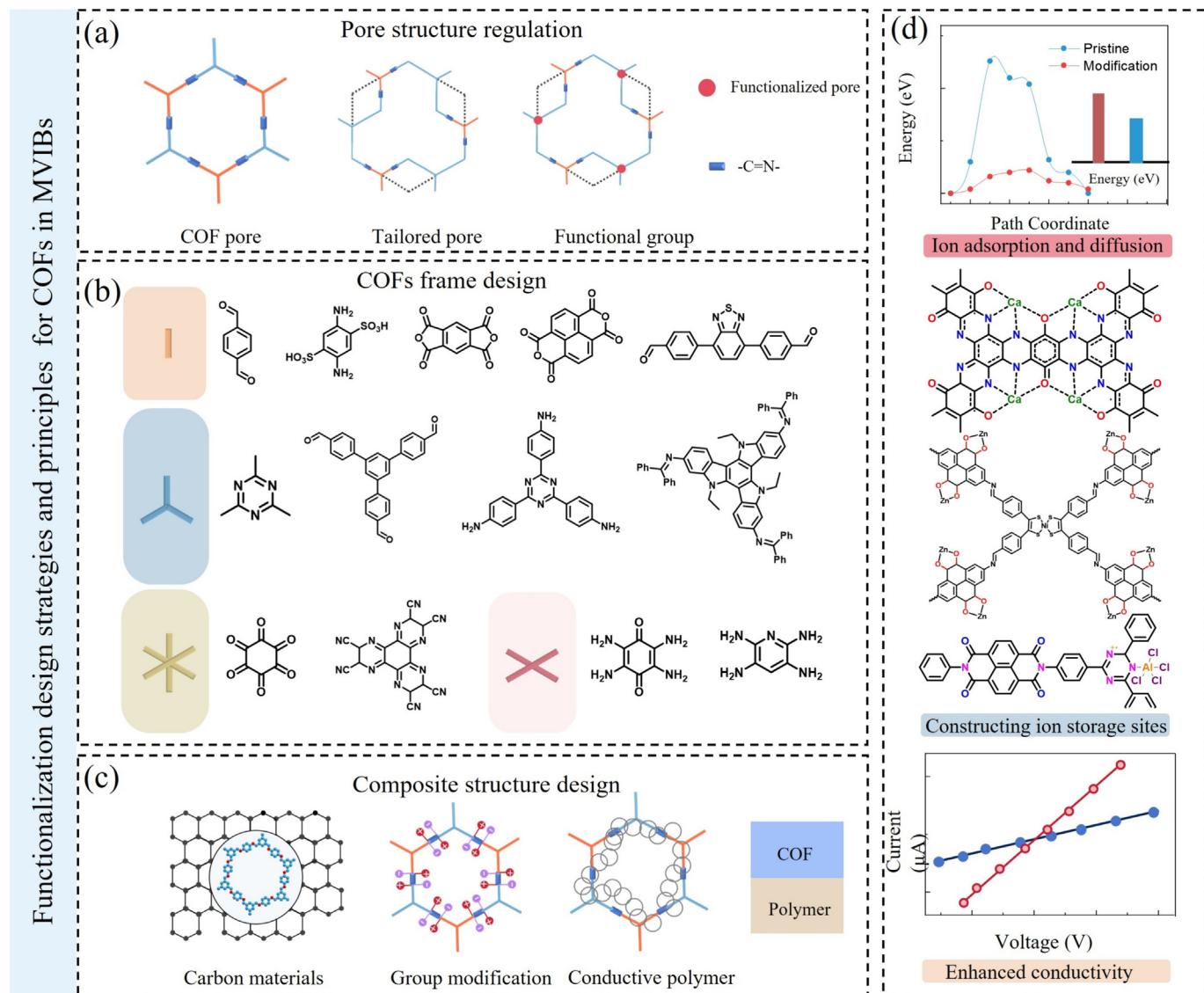


Fig. 6. Functionalized design strategies and principles of COFs in the field of MVIBs. (a) Pore structure design for COFs. (b) Representative COFs structures in MVIBs and their building blocks. (c) Typical composite structure strategies for improving COFs conductivity. (d) Design principles for COFs functionalization in MVIBs.

other porous materials, the pores of COFs can be pre-designed using a topology diagram (Fig. 4). These diagrams guide the growth of polymers into ring-like structures with distinct polygonal shapes by combining monomers with varying degrees of symmetry [61]. In these cases, the pore size, shape and walls of COFs are entirely determined by the structure of the monomers [62]. The angles of the pores in COFs are determined by their topology, and different angles can create distinct corner spaces and channels. These angles are a key factor in triggering synergistic effects between pores [63]. The topological structure of COFs (such as two-dimensional layered and three-dimensional interpenetrating networks) directly influences ion transport pathways and the accessibility of storage sites. For example, two-dimensional COFs form nanoscale channels (with the pore size of 1–3 nm) via interlayer π - π stacking, providing a “ion highway” for rapid diffusion of multivalent ions. In contrast, three-dimensional COFs feature a multi-level pore structure (microporous-mesoporous synergy) that mitigates volume expansion caused by ion insertion [64,65]. These

structural advantages can be further modulated and enhanced through meticulous material design. Sheng et al. constructed an ultra-thin COFs film with sub-nanometer channels. Hydrogen bonding sites were neatly arranged along these channels, resulting in high permeability to monovalent cations and extremely low permeability to multivalent cations. This demonstrated excellent ion sieving performance [66].

The functionalization of COFs pore interfaces is directly related to the pore wall surfaces, which constitute the interface for molecular-ion interactions. Functional groups such as OH, F, and Br can be introduced into the COF framework during synthesis via direct polymerization methods. The incorporation of these groups endows COFs with diverse functionalities. Guo et al. developed a series of zinc-affinity COFs as model platforms to achieve controllable H_2 release and Zn^{2+} flux in ZABs [67]. Based on this, it can be concluded that the design of the pore structure and functional groups of COFs can promote the effective storage and transport of multivalent ions.

- 2) The regulation of COFs frame: chemical adsorption and electronic structure modification. The battery's capacity is directly determined by the number of available active sites. Multivalent ions carry multiple charges, enabling each site to store greater charge capacity. Consequently, the efficacy and quantity of sites are paramount. Integrating active sites as intrinsic components of the COF framework allows for atomic-level precision in site positioning and maximized distribution, circumventing the issues of uneven site distribution and low utilization rates inherent in conventional materials. The essence of a topological design diagram is to describe the direction of covalent bond formation and guide the growth of the polymer main chain. To ensure that the direction of each covalent bond is clear, the monomer needs to have a relatively rigid skeleton, in which the reaction sites are distributed in different geometric shapes [68]. Therefore, selecting suitable reaction sites is crucial for MVIBs. The functional groups in the COFs framework directly participate in the storage of multivalent ions through electrostatic interactions, coordination bonds, or redox active sites. For example, redox active units containing quinone groups can achieve high-capacity storage of Zn^{2+} through reversible quinone/hydroquinone transformations [69]. COFs modified with sulfonic acid groups ($-\text{SO}_3\text{H}$) enhance ion adsorption energy through strong acid-base interactions [70,71]. Additionally, nitrogen-rich functional groups (such as triazine and imine bonds) can provide lone pair electrons to form coordination bonds with multivalent ions while reducing charge transfer impedance. Therefore, it is an effective strategy to design and control the type, quantity and position of active sites in COFs skeleton to prompt multivalent ion storage. Typical COFs structural units applied in the field of multivalent ion battery energy storage in recent years are shown in Fig. 6b.
- 3) The construction of composite structure: synergistic enhancement of conductivity and stability. In multivalent ion batteries, the strong interactions between multivalent ions and host materials enhance the kinetic hysteresis effect. Consequently, through constructing highly conjugated frameworks or composite networks with conductive agents, electron compensation for charge fluctuations at sites during redox reactions accelerates. This facilitates swift and complete ionic storage reactions, thereby enhancing rate performance and active material utilization. COFs are typically formed from structural units, such as aromatic rings, which are connected by covalent bonds. There is close π - π stacking

between the layers. This close stacking makes it difficult for electrons to transfer between layers, limiting their conduction to the limited area within each layer and restricting overall conductivity [72]. To address the issue of poor intrinsic conductivity in COFs, a composite strategy can be used to construct an efficient dual ion/electron transport network (Fig. 6c). For instance, a vertical heterostructure of COFs and graphene utilizes the high conductivity of graphene to achieve rapid electron transport [73]. Additionally, combining COFs with conductive polymers can use flexible polymer buffers to mitigate volume strain, thereby enhancing cycling stability. Goung et al. constructed Pyrr-TPB-DMTP-COF by integrating pyrrole units (Pyrr) into the edge positions of TPB-DMTP-COF. Connecting these COF frameworks to conductive polymers through pore wall engineering and polymerization reactions is also an effective strategy for enhancing conductivity. PPyr-TPB-DMTP COF develops polypyrrole into a new chain conformation, in which all pyrrole rings are aligned in the same direction. Compared with the original framework, the electrical conductivity is improved by eight orders of magnitude, with a carrier mobility as high as $13.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [74].

Based on this, it is evident that optimizing ion transport pathways through pore structure design, selectively regulating framework active sites to enhance ion adsorption and storage capacity, and constructing composite structures to synergistically improve electronic conductivity and mechanical stability represent systematic functional design strategies for the application of COFs materials in multivalent metal ion batteries (Fig. 6d). The relevant content of typical functionalized COF materials reported to date is summarized in Table 1. These strategies complement each other and collectively aim to overcome the core bottlenecks in the field of MVIBs. The subsequent sections of this chapter will focus on these three core directions, delving into specific functional design cases, mechanism analyses, and performance enhancement effects. The overarching goal is to provide theoretical foundations and practical guidance for the rational design and development of advanced COFs electrode materials for high-performance MVIBs in the future.

4.2. Energy storage mechanisms in COFs in MVIBs

In COFs, energy storage is not achieved through a single mechanism, but is instead realized through the synergistic action of multiple mechanisms [89,90]. This structural foundation is pivotal

Table 1
Electrochemical performance of various COF-based materials in MVIBs.

COFs type	Storage location	Electrolyte	Potential window (V)	Capacity (mA h g^{-1} at Ag^{-1})	Capacity retention (%)	Number of cycles	Ref.
FCOF film	Anode	2 M ZnSO_4	1.0–1.8	130 @1	92	1000	[75]
COF-PTO	Cathode	1 M $\text{Zn} (\text{CF}_3\text{SO}_3)_2$	0.2–1.6	105@10	98	18,000	[76]
COF-TMT-BT	Cathode	1 M $\text{Zn} (\text{CF}_3\text{SO}_3)_2$	0.5–1.6	283.5@0.1	96.2	2000	[77]
TA-PTO-COF	Cathode	2 M ZnSO_4	0.6–1.4	255@0.1	–	1000	[78]
PI-DT-COF	Anode	1 M ZnSO_4	–	89.8@2	84.1	1600	[79]
PI-COF	Cathode	2 M ZnSO_4 + 0.5 M LiSO_4	0.1–1.8	464.4@1	85.3	100	[80]
COF-TMT-BT	Cathode	2 M $\text{Zn} (\text{CF}_3\text{SO}_3)_2$	0.5–1.6	283.5@0.1	–	2000	[77]
HqTp-COF	Cathode	1 M CaCl_2	0–1.7	119.5@1	73.7	1600	[81]
PTHAT-COF	Anode	6.67 M CaCl_2	–0.6––1.05	106.6@0.25	89.9	10,000	[82]
TB-COF	Anode	3.4 M CaCl_2	0–1.9	253@1	74	3000	[83]
HAQ-COF	Anode	1 M MgSO_4	0–1.5	105.8@1	85.6	10,000	[84]
Trizine based COF	Cathode	0.5 M $\text{Mg} (\text{TFSI})_2$	0.8–2.5	107@0.02	99.4	3000	[85]
TAT-TA-COF/CNT	Cathode	0.3 M $\text{Mg}[\text{B}(\text{hfp})_4]_2 \cdot 3\text{DME}$	2.0–3.6	40@5C	84	1000	[86]
2D-NT-COF30	Cathode	4 AlCl_3 -3EMImCl	0.5–2.2	132@0.1	99.9	4000	[87]
DAQ-TpO COF	Cathode	AlCl_3 -3EMImCl	0.3–2.2	290@0.2	92.5	32,000	[24]
TPA-COF	Cathode	AlCl_3 -3EMImCl	–	161.2@1	84.8	3000	[88]

in ensuring the high capacity and excellent rate performance of COF electrode materials. Firstly, it is evident that redox reactions constitute the most fundamental energy storage mechanism within COFs [91]. This objective is realized through the integration of electrochemically active functional groups as structural units within a rigid framework. During the processes of charging and discharging, these functional groups undergo reversible electron transfer (oxidation or reduction). In order to maintain charge equilibrium, ions in the electrolyte insert into/extract from the COF's channels [92]. For instance, consider the reversible carbonyl/enolization reaction of the anthraquinone unit. This mechanism facilitates high theoretical capacity, with voltage plateaus typically determined by the redox potentials of the active functional groups. Zhang et al. [83] discovered that nitrogen-rich covalent organic framework materials (TB-COF), featuring multiple carbonyl structures, serve as high-performance anode materials for aqueous CIBs while exhibiting high capacity. The carbonyl/enol conversion within TB-COF constitutes the primary source of this high capacity. Furthermore, this study identified new C=C active sites within the calcium ion storage mechanism of TB-COF. This C=C active site has a redox potential within the low-potential range of -0.5 to -1 V vs Ag/AgCl.

Secondly, coordination interactions are intrinsically linked to redox reactions. The polar functional groups (e.g., C=O, C=N) on the COF skeleton can act as Lewis's base sites, reversibly coordinating with multivalent metal ions, thereby stabilizing the ions and contributing capacity [84]. Beyond the electrode material itself, COFs can also exert a coordination effect at the electrolyte/electrode interface. For example, Huang et al. incorporated COF-1 nanoparticles into the magnesium electrolyte [93]. These nanoparticles preferentially captured TFSI⁻ anions via weak chemical adsorption, thereby inhibiting their decomposition on the magnesium anode surface. This process facilitated the formation of an ultrathin, MgO-rich solid electrolyte interphase (SEI) layer. This SEI layer simultaneously blocks electron tunnelling while facilitating rapid Mg²⁺ transport. The result is a Coulombic efficiency of 98.6 % for the magnesium metal anode, as well as significantly enhanced cycling stability. Thirdly, pseudocapacitive behavior plays a pivotal role in the energy storage of COFs. The rapid Faraday reaction kinetics are primarily attributable to their high specific surface area and ordered nanoscale pore networks, which facilitate swift adsorption and desorption of ions at or near the surface, circumventing slow solid-state diffusion [94].

Cation- π interactions refer to the electrostatic attraction arising between cations and aromatic rings or conjugated systems possessing delocalized π electrons [95]. Within COFs, the π electron clouds of aromatic rings or conjugated structures exhibit a specific distribution of electron density. Cations such as Li⁺ or Na⁺, owing to their positive charge, exert an electrostatic attraction upon these π electron clouds, thereby forming cation- π interactions [96]. By introducing groups or structures with specific cation-binding capabilities, COFs can be functionalized through cation- π interactions [97]. For instance, Cheng et al. [90] incorporated porous covalent organic framework materials featuring alternating electron donor- π acceptor structures into glass fiber separators to achieve precise and uniform regulation of zinc ion transport and deposition behaviors. The connection between the electron donor and acceptor via π -conjugated benzene rings and imine bonds not only promotes electron delocalization but also enhances the structural stability of the material. The zinc symmetric battery utilizing this modified membrane achieved stable cycling performance exceeding 1200 h.

In summary, the storage mechanisms within COF electrode often intertwine and act synergistically. Through meticulous molecular engineering design, the relative dominance and contribution ratios of these mechanisms can be finely tuned, thereby

providing a broad platform for the development of high-performance multivalent ion batteries.

4.3. Application of COFs-Related materials in MVIBs

Rechargeable MVIBs are similar to LIBs in that their energy conversion process relies on the synergistic interaction of three core components. Firstly, a cathode material capable of storing and releasing multivalent ions, which can reversibly intercalate and deintercalated multivalent cations such as Zn²⁺, Mg²⁺, Al³⁺, and Ca²⁺. Secondly, an efficient electrolyte system ensures the stable transport of multivalent ions between the cathode and anode. Finally, the anode employs a base-metal-free anode structure, which not only possesses abundant resource reserves and excellent processing performance, but also exhibits ultra-high volumetric energy density characteristics. Although considerable progress has been made in MVIB research, the technology's path to industrial maturation continues to be hindered by unresolved fundamental issues in electrode and electrolyte materials. COFs are recognized as prospective electrode materials owing to their distinctive attributes, encompassing inherent insolubility in electrolytes, ample porosity, precise open channels facilitating ion migration, and π -conjugated extended framework enhancing charge transfer.

Common issues in MVIBs anode materials include low coulombic efficiency and irreversibility, as well as dendrite growth, electrochemical corrosion, and side reactions [98]. These issues are particularly pronounced in ZIBs and CIBs. The 2D COFs as a surface coating [99] and 3D construction can effectively improve the comprehensive performance of anodes [100]. The development of MVIBs cathode materials primarily faces scientific challenges related to kinetic limitations [101]. Although multivalent ions have small volumes, most mature lithium-ion battery cathode materials cannot be applied to MVIBs due to their low multivalent ion mobility. The high charge density of multivalent ions leads to greater Coulomb interactions with the surrounding lattice, forming high energy barriers that hinder solid-state diffusion processes [102]. This can also trigger irreversible phase transitions, structural collapse, or transition metal dissolution, leading to poor cycle stability and reduced rate performance. To address these issues, selecting COFs and their derivatives with larger pore sizes and higher specific surface areas as electrode materials can effectively enhance the transport of multivalent ions. The tunable functional group structure of COFs can also chemically adsorb metal ions and grow in situ within the carbon material, thereby enhancing conductivity and increasing ion storage capacity [103]. Combining carbon-based materials with strong conductivity and excellent catalytic performance with COFs to achieve multifunctionality has a unique effect on enhancing the performance of MVIBs [104].

In addition, the desolvation energy of multivalent ions increases with the increase in their charge density, thereby hindering their diffusion at the electrode interface. This phenomenon has been observed in many MIBs and AIBs. The continuous consumption of the electrolyte caused by side reactions, especially in aqueous systems, also poses significant challenges to their development [105]. To address these challenges, strategies such as adjusting electrolyte composition and adding additives for electrolyte optimization have been employed. COFs with ordered one-dimensional channels and structural stability make them ideal candidate materials for solid electrolytes [106]. Compared to inorganic ionic conductors, COFs exhibit permanent porosity, structural tunability, and enhanced chemical stability. Additionally, based on their charge characteristics, COFs can be classified into neutral and ionic types [107]. In particular, ionic COFs exhibit permanently open channels and tunable pores composed of charged building blocks, enabling a wide range of ion-ion and ion-dipole interactions. Ionic

COFs can be used as solid-state electrolytes, separators, or additives in electrode materials or as modifying layers for electrodes.

4.3.1. Application of COF-correlated materials for ZIBs

Water-based ZIBs have become a promising candidate in energy storage because they offer an appealing combination of high capacity, low expense, and environmental benefits [108]. COFs offer innovative solutions paving the way for high-performance ZIBs through precise structural tuning, multi-scale pore design, and functional group modification [109]. This chapter will systematically review the key application progress of functionalized COFs in ZIBs [110]. The anode electrode of zinc ion batteries is usually composed of metallic zinc, which is susceptible to issues like HER, dendrite formation, and corrosion. Compressed COFs powders and COFs films formed by interfacial polymerization (subsequently transferred to the electrode) have been demonstrated to stabilize reactive Zn metal surfaces, provide zinc-friendly porous channels, ensure uniform zinc ion transport, and enable branch-free crystal cell operation. Bartosz A. Grzybowski et al. reported a polyimide-based carbon–oxygen bonded framework material (PI-DT-COF) for application as a Zn anode coating with specifically designed sawtooth-shaped jump sites and zinc-affinity groups. The PI-DT-COF coating has specific zigzag sites along the 1D channel that can accelerate the diffusion kinetics of Zn^{2+} , reduce the surface energy, and homogenize the ion distribution as well as electric fields [79]. Excellent cycle life has been shown in symmetric-cell (2000 cycles at 60 mA cm^{-2}) and full-cell (1600 cycles at 2 A g^{-1}) assembled by PI-DT-COF.

Additionally, ultra-thin, porous, and fluorinated COF (FCOF) films can also be used as protective layers on zinc anode surfaces to inhibit dendrite growth (Fig. 7a) [75]. One-dimensional ordered fluorinated nanochannels facilitate accelerated ion conduction, restrict water penetration, and mitigate electrolyte corrosion of the zinc anode (Fig. 7b). The symmetrical FCOF@Zn configuration demonstrates exceptional electrochemical durability, sustaining stable performance for 750 h under extreme current density conditions of 40 mA cm^{-2} . This work demonstrates that by modifying and functionalizing the COF pore channels, ion transport and interfacial stability can be effectively regulated, thereby resolving dendrite formation and corrosion issues in zinc anodes. In ZIBs, organic cathode materials often suffer from limited capacity and inadequate structural stability. COFs offer a promising alternative, as their rigid crystalline architectures not only ensure structural robustness but also provide a high density of accessible redox-active sites for ion storage [111,112]. The capacity of COF-based cathodes can be further enhanced through rational design that incorporates multiple and tunable redox centers within the framework. A notable example is a polyimide-based COF (PI-COF), which features ordered crystalline domains, hierarchical porosity, and dual redox-active groups ($\text{C}=\text{O}$ and $\text{C}=\text{N}$) [80]. This material demonstrates a high reversible capacity of $464.2 \text{ mA h g}^{-1}$ at 1.0 A g^{-1} in a hybrid $\text{Zn}^{2+}/\text{Li}^{+}$ electrolyte ($2.0 \text{ M ZnSO}_4 + 0.5 \text{ M Li}_2\text{SO}_4$), leveraging multiple accessible reaction sites for efficient zinc-ion storage. This design highlights a strategy for optimizing the COF framework by constructing a multi-level pore structure and integrating multiple active sites, thereby simultaneously enhancing ion accessibility and storage capacity. In addition to carbonyl and imine motifs, other functional units can also be engineered into COF structures to serve as effective redox centers. For instance, the benzothiazole unit in COF (COF-TMT-BT) has been explored as a new zinc storage electrochemical active group [77]. The benzothiazole group contains S and N atoms, which can reversibly coordinate Zn^{2+} through controlled ionic complexation and release (Fig. 7c, d). When integrated as a cathode material in aqueous ZIBs, COF-TMT-BT delivers a high capacity of $283.5 \text{ mA h g}^{-1}$ at a current density of 0.1 A g^{-1} , with maximum energy and power densities of

219.6 Wh kg^{-1} and 23.2 kW kg^{-1} , respectively. These studies demonstrate the multi-functionality of COFs in ZIBs. Through rational structure–function design, ideal high-performance electrode materials can be constructed.

Furthermore, incorporating COFs into gel electrolyte systems allows for the full exploitation of their structural advantages. The ordered porous framework of COFs provides structured pathways for ion transport, while their surface functional groups enable targeted regulation of ionic interactions. The stable covalent framework significantly enhances the mechanical and chemical stability of the electrolyte. Qiu et al. constructed a COF-based hydrogel electrolyte (TCOF-S-Gel) [113] and they utilize the solvation effect of polyacrylamide chains to weaken the electrostatic interactions between Zn^{2+} ions and the sulfonic acid groups ($-\text{SO}_3^-$) lining the COF pores. This facilitates Zn^{2+} deintercalation and forms an ion-transport step (Fig. 7e), thereby significantly enhancing ionic conductivity and the migration number of Zn^{2+} ions. Benefiting from the precise regulation of the ionic microenvironment by the ordered channels of the COF, TCOF-S-Gel exhibits significantly higher ionic conductivity than pure PAM gel across different temperatures (Fig. 7f). The $\text{Zn}||\text{MnO}_2$ full cell based on this electrolyte demonstrates both high specific capacity (248 mA h g^{-1}) and extended cycle life (no significant capacity decay after 1400 cycles).

Besides directly using COFs as electrode material, compounding it with high conductivity carbon material represents a viable alternative for enhancing the performance of ZIBs. As a stable conductive connecting component, graphene can further activate most of the active sites in COFs, effectively improving the cycle stability of ZIBs. Research indicates that COFs, possessing extended porous structures and abundant active sites, exhibit synergistic enhancement of H^{+} storage capacity when combined with graphene. This occurs following molecular-level C–O modification that induces electron delocalization. Consequently, they enable the cooperative storage of Zn^{2+} and H^{+} within aqueous electrolytes [114]. These symmetric all-organic batteries achieve ultra-long cyclability exceeding 15,000 cycles while retaining 80 mA h g^{-1} capacity under high-rate operation (5 A g^{-1}) in pouch cells.

4.3.2. Application of COF-correlated materials for CIBs

CIBs have emerged as a promising next-generation high-energy–density storage technology, owing to their high theoretical capacity (1337 mA h g^{-1}), low reduction potential (-2.87 V vs. SHE), and abundance in the Earth's crust (calcium content of 4.1 wt%). However, the development of CIBs currently faces multiple challenges. The high charge density and relatively large ionic radius (0.099 nm) of divalent Ca^{2+} ions result in stronger interactions with the host crystal lattice compared to monovalent cations, leading to slow diffusion of Ca^{2+} ions in inorganic crystals and a tendency to induce strong polarization effects [115]. Furthermore, existing small-molecule and polymer-based calcium storage materials suffer from poor stability in aqueous solvents, limited capacity, and relatively high redox potentials [116]. Current research focuses on developing integrated methodologies to enhance electrochemical cycling durability, boost high-rate performance, and elucidate fundamental ion transport mechanisms in the system. In polymers, COFs possess rich porous structures. COFs are essentially insoluble in water, and their porous structures allow for rapid ion diffusion [117,118]. Therefore, researchers have applied COFs to the storage of multivalent metal ions. Li et al. investigated the properties of HqTp-COF as an anode material for aqueous CIBs. HqTp-COF exhibited a short-range ordered structure and a pore size of 1.8 nm . Mechanistic studies have revealed reversible calcium ion intercalation/desorption behavior with the $-\text{C}=\text{O}$ as the active site in HqTp-COF (Fig. 8a). The outstanding rate performance is mainly attributed to the energy storage mechanism of pseudoca-

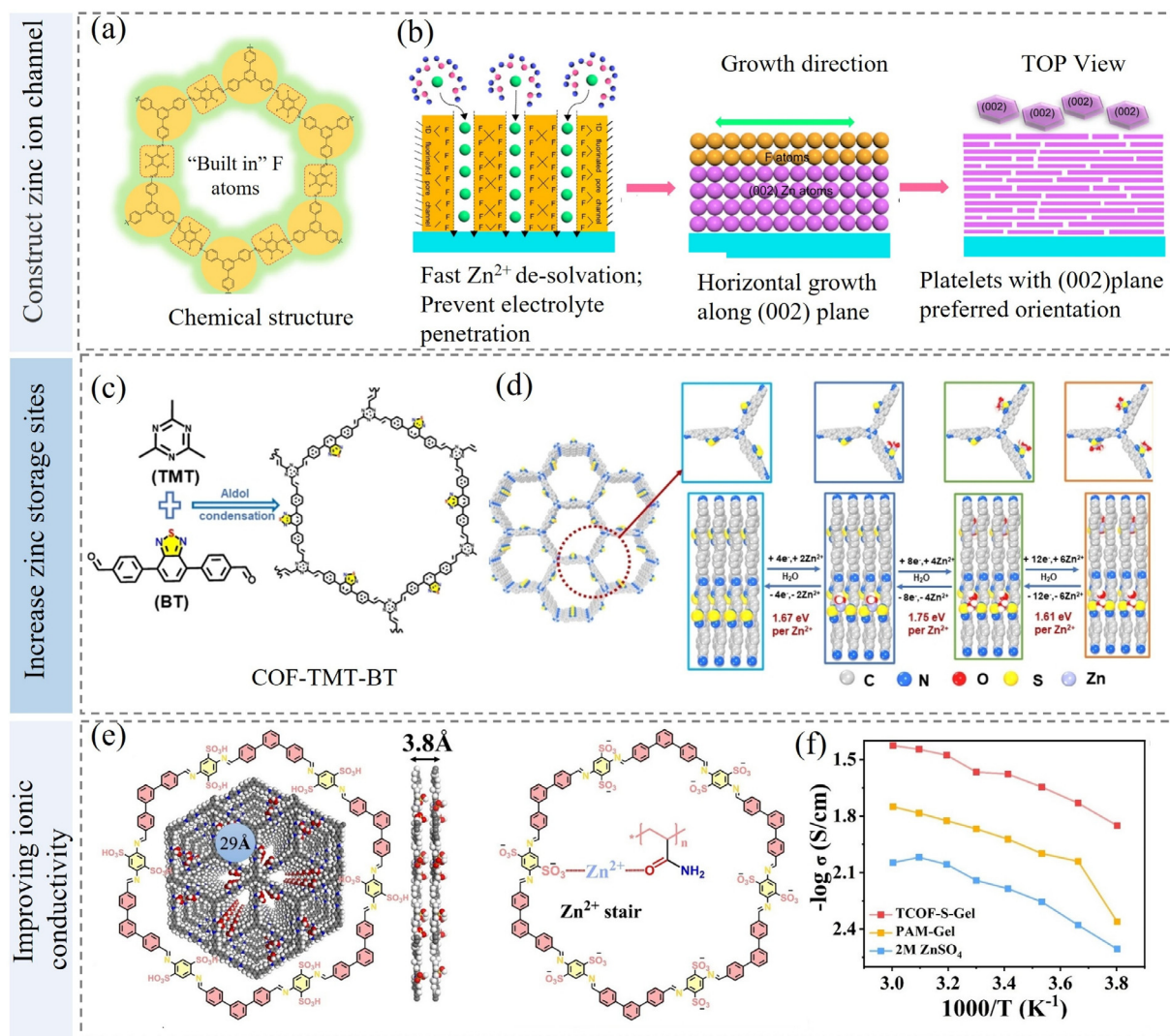


Fig. 7. (a) The physicochemical structure of the FCOF film. (b) Mechanism comparison of Zinc deposition mechanism of FCOF@Zn surfaces. Copied with permission [75]. Copyright 2021, Springer Nature. (c) The structure of the COF-TMT-BT. (d) Adsorption energy of COF-TMT-BT at different zincation stage. Copied with permission [77]. Copyright 2023, Wiley-VCH. (e) TCOF-S perspective view/side view and molecular formula diagram of theoretical simulation. (f) Ion conductivity of TCOF-S-Gel, PAM-Gel and 2 M ZnSO_4 at different temperatures. Reproduced with permission [113]. Copyright 2023, Wiley-VCH.

passive behavior [81]. Demonstrating both high energy storage capacity ($119.5 \text{ mA h g}^{-1}$ at 1 A g^{-1}) and superior rate retention, the HqTp-COF material sustained 78.7 mA h g^{-1} at exceptionally high current loads up to 50 A g^{-1} (Fig. 8b). Additionally, PTHAT-COF with repeated pyridine and pyridineamine units also demonstrated excellent structural stability as an anode material for aqueous CIBs (Fig. 8c). Analysis of the electronic properties of PTHAT-COF reveals that there is a significant difference in the molecular electrostatic potential (MESP) between the pyrazine unit and the pyridineamine unit. The more negative MESP values are closer to the pyrazine nitrogen atoms, and electrophilic cations (such as Ca^{2+}) tend to bind to these sites (Fig. 8d, e). During the charge-discharge cycle, C=N active sites can reversibly capture Ca^{2+} through chemical adsorption [82]. Therefore, the PTHAT-COF anode achieved a capacity retention rate of 89.9 % after 10,000 cycles, demonstrating its excellent long-term cycle stability.

It is worth noting that the organic electroactive sites on the COFs framework (e.g., C=O and C=C groups) produce free radical intermediates during charge-discharge cycles. The high reactivity and rapid reaction kinetics of these free radical intermediates can significantly enhance the capacity and rate capability of CIBs.

Based on this mechanism, researchers further optimized the electrochemical performance of the COFs by precisely designing their composition and structure. Shi et al. designed a nitrogen-rich covalent organic framework with multiple carbonyls (TB-COF) as an aqueous anode (Fig. 8f) [83]. The high nitrogen atom density and π -conjugated structure confer excellent electrical conductivity ($5.9 \times 10^{-9} \text{ S cm}^{-1}$) to TB-COF. Consequently, TB-COF shows a high-rate capacity of 104 mA h g^{-1} at a current density of 70 A g^{-1} . Further, it was confirmed that the carbonyl (C=O), pyridine (C=N), and benzene ring (C=C) structures formed by the redistribution of quinone ring electrons in the COF are active centers. The redox mechanism of C=C was verified for the first time by investigating the evolution process mediated by free radicals (Fig. 8g). Each repeating unit of the TB-COF can store up to nine Ca^{2+} ions through a three-step staggered intercalation mechanism, which engages three distinct types of calcium ion storage sites. This work not only demonstrates the structural advantages of COFs in multi-ion storage, but also provides crucial insights into radical-mediated electrochemical processes. Complementary to the design of organic electrodes, interface and electrolyte engineering also play a critical role. Wang et al. demonstrated that pre-embedding

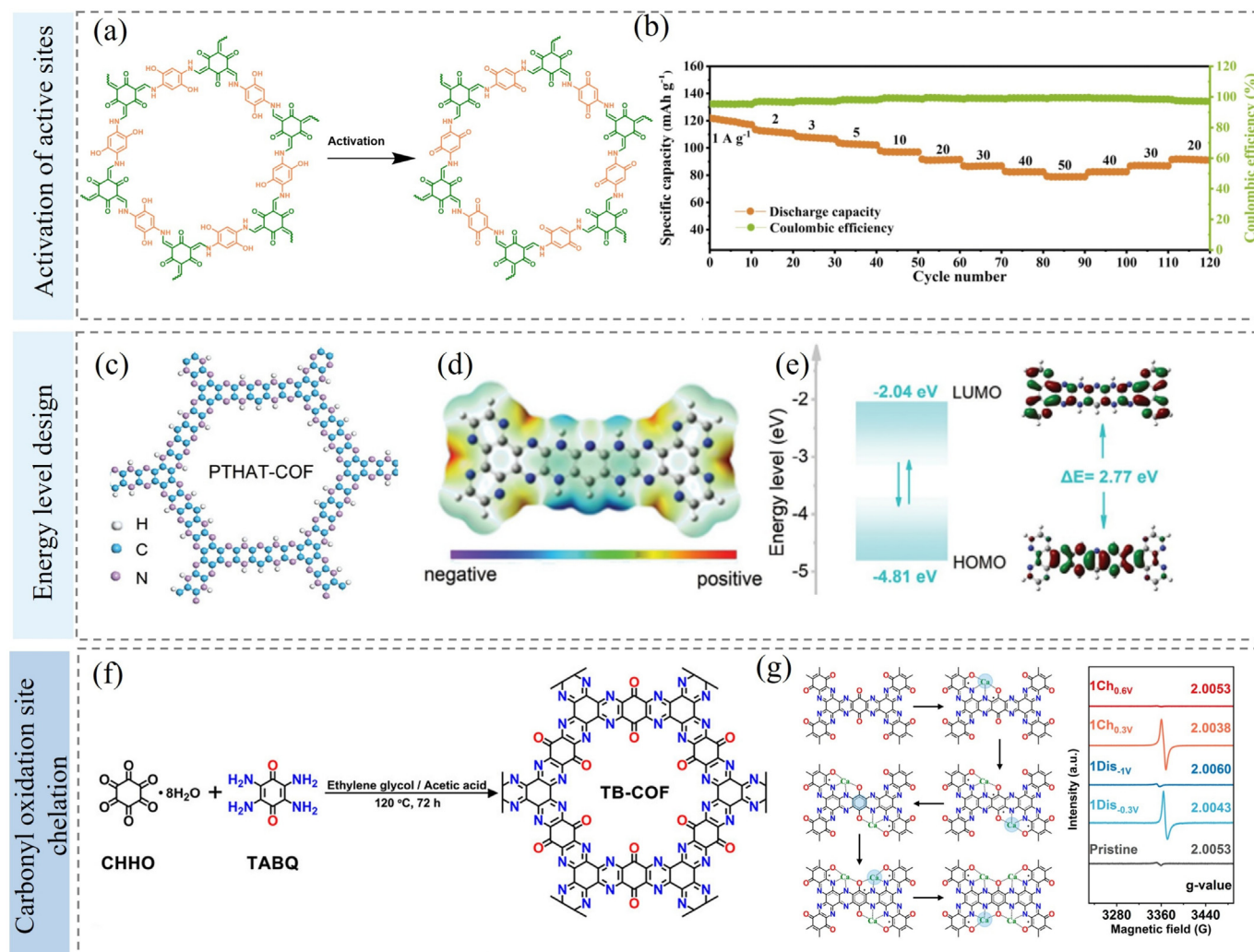


Fig. 8. (a) Schematic illustration of the conversion of C–OH groups to C=O groups in HqTp-COF in electrochemical activation. (b) Rate performance of HqTp-COF. Reproducing with permission [81]. Copyright 2022, The Royal Society of Chemistry. (c–e) Structural model and electronic properties of PTHAT-COF. Copied with permission [82]. Copyright 2024, Wiley-VCH. (f) Schematic diagram of TB-COF synthesis. (g) Changes in free radicals during redox reactions in PTHAT-COF electrodes and electron paramagnetic resonance (EPR) spectra during charging and discharging. Copied with permission [83]. Copyright 2023, American Chemical Society.

chemistry and coupled with simultaneous electrode and electrolyte engineering could significantly extend the room-temperature calcium storage lifespan of layered vanadium oxides from 1000 to 10,000 cycles, offering new insights for enhancing Ca²⁺ storage performance in organic electrolytes [119].

4.3.3. Application of COF-correlated materials for MIBs

Magnesium's high volumetric capacity (3833 mA h cm⁻³ vs. 2046 mA h cm⁻³ for lithium), abundant crustal reserves (104 times the atomic fraction of lithium), and metal deposition that is less prone to dendrites give MIBs the potential to transform the next-generation of energy storage. Nevertheless, several critical issues persist: (i) the sluggish Mg²⁺ diffusion kinetics caused by its high charge density, (ii) poor compatibility between conventional electrolytes and cathode materials, and (iii) the absence of high-performance host matrices that support reversible Mg intercalation [120]. While numerous materials including transition metal oxides/sulfides (TMOs/TMSs), layered and spinel oxides, Prussian blue analogues, vanadates, silicates, polyanionic phosphates, and organic compounds have been explored as cathodes for multivalent ion batteries (MIBs), very few have exhibited satisfactory elec-

trochemical performance. As a next-generation electrode material, COFs provide an innovator solution to break the bottleneck of magnesium-ion batteries with its unique structural designability. Its periodic nanopore channels can establish directional Mg²⁺ transport channels, while the built-in redox active sites can increase magnesium ion storage sites.

Zou et al. synthesized quinone-functionalized 1,4,5,8,9,12-hexaazatriphenylene-based COF (HAQ-COF) (Fig. 9a), which was firstly applied to the host material of high-rate water magnesium ion battery to explore its magnesium storage mechanism. The authors demonstrated that the C=N and C=O sites in HAQ-COF are coordination sites for Mg²⁺, and it was found that up to 12 Mg²⁺ ions can be coordinated in the inner-hexagonal HAQ-COF structural units combined with calculations (Fig. 9b) [84]. Kinetic studies reveal that the diffusion dynamics of Mg²⁺ ions in HAQ-COF are controlled by the surface pseudocapacitance behavior. This alleviates the problem of slow solid-phase diffusion induced by the high surface charge density of divalent Mg²⁺ ions. Therefore, the MIBs cells assembled from COFs exhibit desirable rate performance as well as durable cycling stability. HAQ-COF exhibits a wide potential window in 1.0 M MgSO₄ solution, ranging from -0.75 to +0.75 V

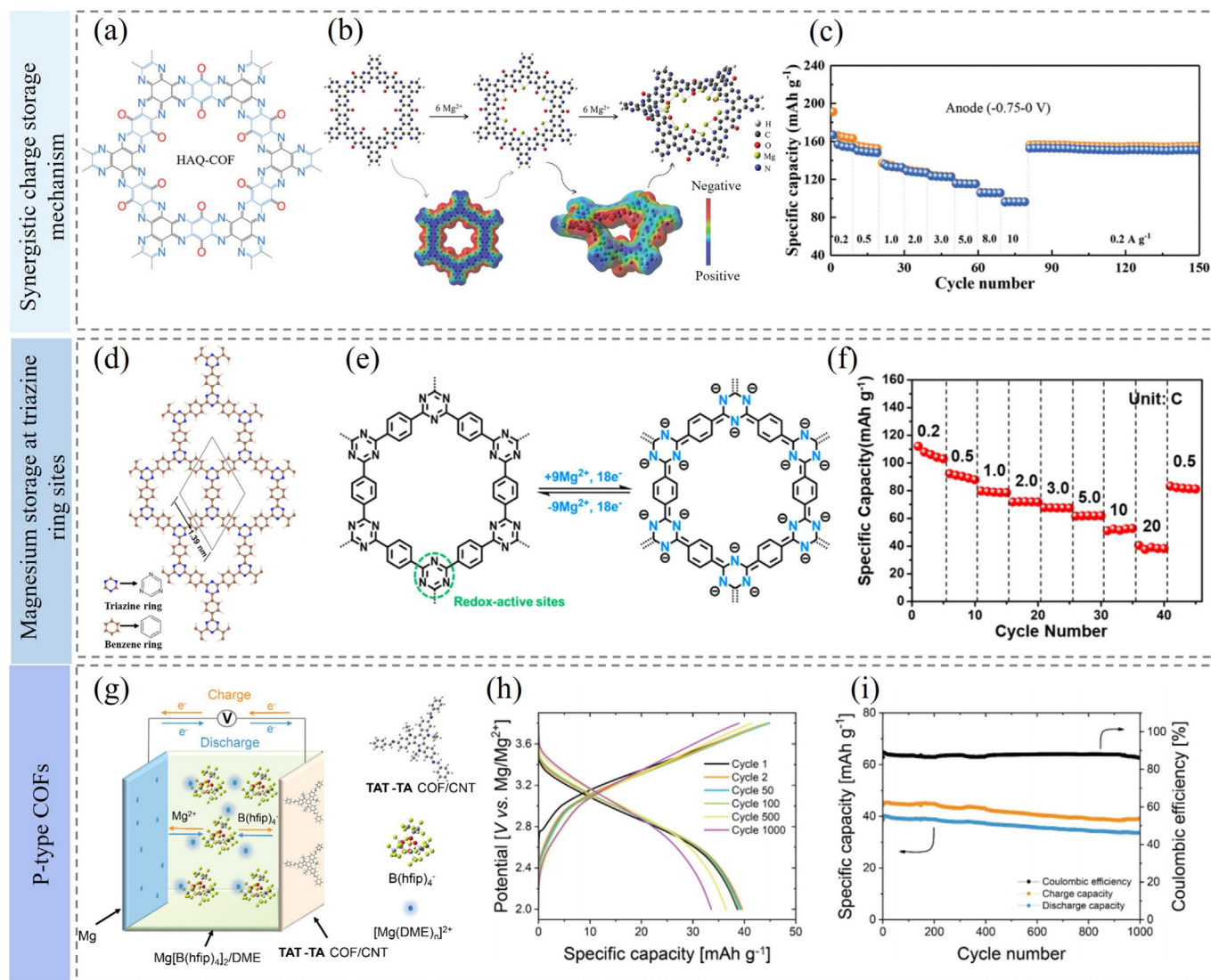


Fig. 9. (a) Molecular structure of HAQ-COF. (b) Theoretical model of the coordination process of Mg^{2+} ions. (c) The rate property of HAQ-COF. Copied with permission [84]. Copyright 2022, Wiley-VCH. (d, e) The molecular structure of triazine-based porous COFs and their possible electrochemical redox mechanisms. (f) Rate performance of the COF cathode in Mg storage. Copied with permission [85]. Copyright 2022, American Chemical Society. (g) Schematic diagram of TAT-TA COF/CNT electrodes in MIBs. (h, i) Charge-discharge curves and cycling stability of TAT-TA COF/CNT electrodes at 5C. Copied with permission [86]. Copyright 2022, American Chemical Society.

(vs. $Ag/AgCl$). Specifically, it provides a specific capacity of $177.4\ mA\ h\ g^{-1}$ within the negative potential range ($-0.75-0\ V$) and $118.5\ mA\ h\ g^{-1}$ in the positive potential range (-0.2 to $+0.75\ V$), respectively (Fig. 9c). Symmetric Mg^{2+} ion devices assembled on its basis offer a voltage of $1.5\ V$ and desirable energy density of $26.5\ Wh\ kg^{-1}$ as well as a power density of $3750\ W\ kg^{-1}$. Electrolytes also play a critical role in Mg storage [121]. The development of efficient and compatible electrolytes is a key research direction. Mai's group has previously systematized the latest advancements in electrolyte research for rechargeable magnesium batteries, focusing on strategies such as designing active cations, anion acceptors, and regulating solvation structures, which lay a solid foundation for understanding structure–function relationships in magnesium electrolytes [122].

In MIBs, the electrolytes are predominantly composed of a magnesium-based Lewis base paired with a Lewis acid such as $AlCl_3$ or $AlPh_3$. These systems are collectively termed magnesium-chloride complex electrolytes [123]. However, chloride-containing electrolytes exhibit corrosivity toward non-

inert metal current collectors, such as stainless steel and aluminium, and possess limited voltage windows, which impedes the utilization of high-voltage cathode materials [124]. Therefore, the development of novel cathode materials compatible with chlorine-free electrolytes and capable of efficiently storing magnesium has become crucial. For the first time, Sun et al. report a triazine-based porous COFs cathode with a dendrite-free Mg anode and chloride-free and Mg compatible electrolyte in Mg storage (Fig. 9d). The COFs were synthesized by rationally polymerizing 1,4-dicyanobenzene with $ZnCl_2$ in sealed quartz ampules at $400\ ^\circ C$. Electrochemical studies confirm that its triazine rings act as redox-active sites facilitating reversible magnesium ion uptake/release. This process exhibits ultrafast kinetics, largely driven by pseudocapacitive contributions (Fig. 9e). The material shows desirable electrochemical performance with a gravimetric power density of $2.8\ kW\ kg^{-1}$ coupled with an impressive energy density of $146\ Wh\ kg^{-1}$. When assessed as the cathode material, the COF-based electrode achieves a specific discharge capacity of $107\ mA\ h\ g^{-1}$ under $0.2C$ -rate conditions (Fig. 9f). Notably, it

indicates outstanding rate capability by maintaining 72 mA h g^{-1} at elevated 5C current density, while exhibiting outstanding cycling stability with merely 0.0196% capacity fade per cycle over 3000 charge–discharge cycles [85]. COFs incorporating well-defined redox-active groups have emerged as competitive materials for next-generation batteries. Despite the potential for high voltage and rapid performance, examples of p-type COFs for charge storage remain scarce. Recently, Sebastian M. Pallasch et al. synthesized a p-type and porous crystalline COF based on the azatruxene (TAT-TA COF) and demonstrated its utilization as a positive electrode in both lithium- and magnesium-ion battery systems (Fig. 9g) [86]. Notably, the $\text{Mg}||\text{TAT-TA COF}/\text{CNT}$ cell exhibits desirable rate capability, maintaining stable cycling even at 5C (655 mA g^{-1}), as displayed in Figs. 9h, i.

4.3.4. Application of COF-correlated materials for AIBs

AIBs offer a promising alternative for sustainable, high-capacity energy storage, leveraging abundant and eco-friendly aluminum as the active material. However, the kinetic behavior of the slow charge/discharge electrochemical reaction of the cathode material greatly limits the further development of AIBs [125,126]. Meanwhile, the structural instability of most cathodes in corrosive ionic

liquids often results in rapid capacity fading and poor cycling durability in aluminum-ion batteries [127]. Consequently, developing high-performance cathode materials has become a major research focus for advancing aluminum ion batteries. Currently, researchers have initiated the design study of electrode materials. The carbon materials (such as graphene, carbon nanotubes, and expanded graphite) and metal compounds (such as sulfide, selenide, and phosphide) have demonstrated excellent performance in AIBs [128]. However, the active carriers in rechargeable aluminum batteries are large-sized aluminum complex ions or high charge density Al^{3+} , leading to kinetic retardation and structural collapse of inorganic anodes during cycling.

In this context, organic cathode materials offer a compelling alternative due to their flexible molecular structures and unique coordination-based reaction mechanisms [129]. In particular, the molecular design of COFs enables precise integration of redox-active structural units into a rigid polymer framework with an ordered open channel structure, multiple active sites, and fast reaction kinetics [130]. These advantages can significantly improve the overall properties of the battery, especially its energy density, charge/discharge efficiency, and long-term cycle stability. Liu et al. report on the development of two polyimide 2D-COF materials for cathode applications [87]. Both 2D-COFs are materials with

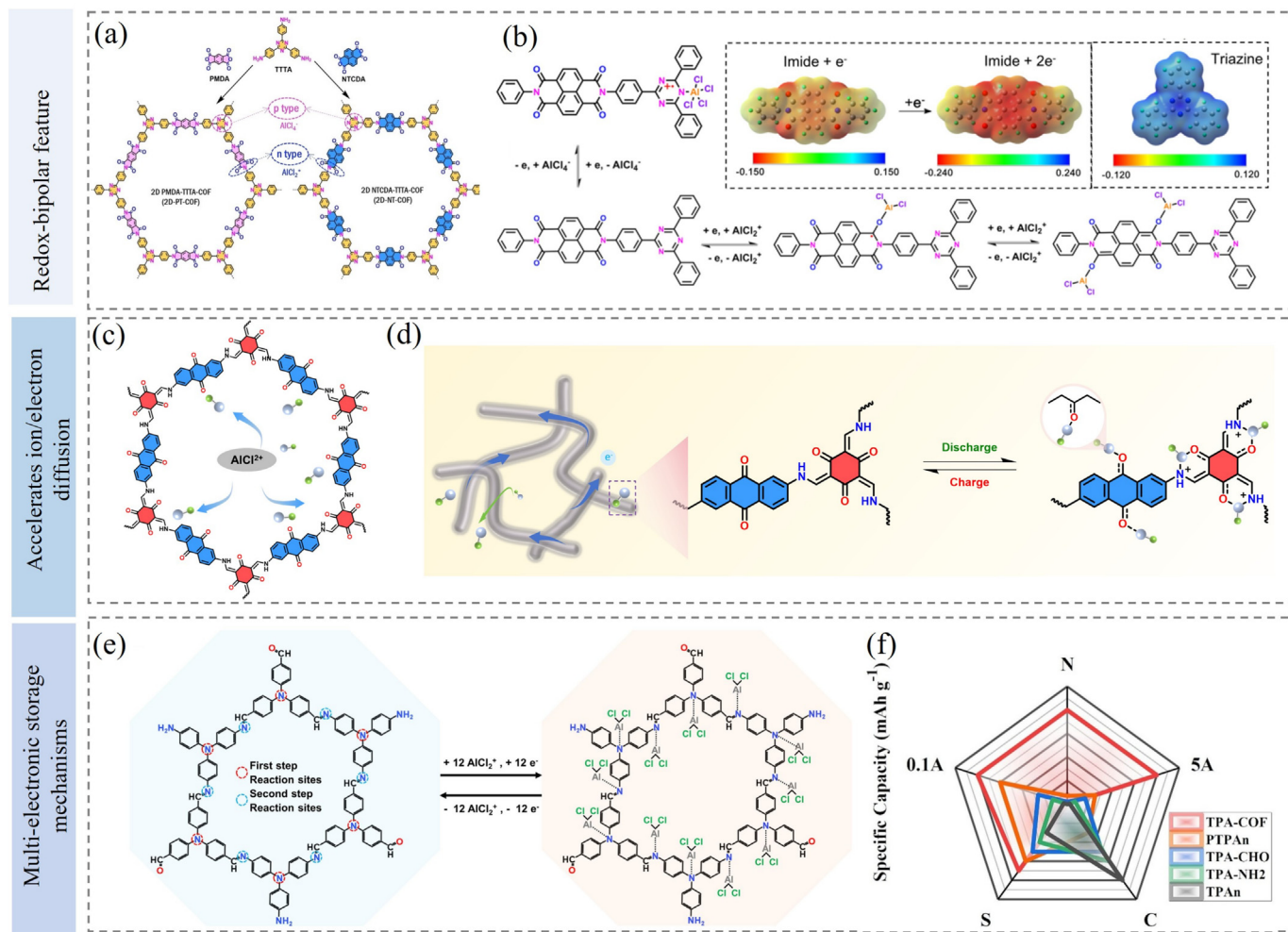


Fig. 10. (a) Design routes of redox-bipolar 2D COFs. (b) The charge-storage mechanism of the 2D-NT-COF electrode. Copied with permission [87]. Copyright 2023, Wiley-VCH. (c) Molecular structure of carbonyl-rich DAQ-TpO COF. (d) Schematic diagram of DAQ-TpO/CNT with multiple redox centers. Copied with permission [25]. Copyright 2024, Wiley-VCH. (e) Working principal schematic depicting ionic migration processes in TPA-COF cathode structures for aluminum-ion energy storage. (f) Performance comparison chart of different rechargeable aluminum-ion battery cathode materials. Copied with permission [88]. Copyright 2024, Elsevier.

redox amphiphilic features designed by incorporating n-type imine and p-type triazine molecules into a unified framework (Fig. 10a). The study further elucidates a unique redox-bipolar Faraday reaction mechanism, wherein the reversible reduction of imine units mediated by AlCl_2^+ occurs concurrently with the oxidation of triazine units catalysed by AlCl_4^- (Fig. 10b). This demonstrates the distinctive advantages of such materials in multi-ion storage and synergistic charge transfer.

Furthermore, Peng et al. demonstrated the pivotal roles of $\text{C}=\text{O}$ groups in the efficient storage of AlCl_2^+ (Fig. 10c). Carbonyl-rich framework was realized by building 2,6-diaminoanthraquinone (DAQ) and 1,3,5-triformylphloroglucinol (TpO) units on CNT. The in situ assembly resulted in a porous conducting structure called DAQ-TpO/CNT (Fig. 10d). The specific capacity of the aluminum cell using this DAQ-TpO/CNT as cathode was 290 mA h g^{-1} at 0.2 A g^{-1} current. The stable cycles of 32,000 at 10 A g^{-1} were achieved with good reversibility [25]. Stimulation studies have

shown that $\text{C}=\text{O}$ and $\text{C}-\text{N}$ groups are capable of multiple AlCl_2^+ storage. Meanwhile, the synergistic interaction between the COFs network and the conducting CNT channels greatly improves the stability of the structure and accelerates the ion/electron diffusion. Recently, new strategies have also emerged to solve the dissolution of conventional organic materials in the AIBs field and for the design of reversible storage sites for AlCl_2^+ in the COFs. A COFs (TPA-COF) with triphenylamine (TPA) as the main framework is reported by Wei et al. By introducing $-\text{CHO}$ and $-\text{NH}_2$ groups, the COF structure with multiple nitrogen active sites was successfully constructed, and its stabilized hexagonal macrocyclic architecture greatly improved the electrochemical performance [88]. The authors found that $\text{C}-\text{N}$ and $\text{C}=\text{N}$ are active sites for reversible storage of AlCl_2^+ ions. Ideally, there are 12 N sites in the TPA-COF macrocycle that can bind/separate AlCl_2^+ at different voltages. These N sites are located at the centers of six TPA-like structures and at the $-\text{NH}_2$ and $-\text{CHO}$ group binding bond positions between

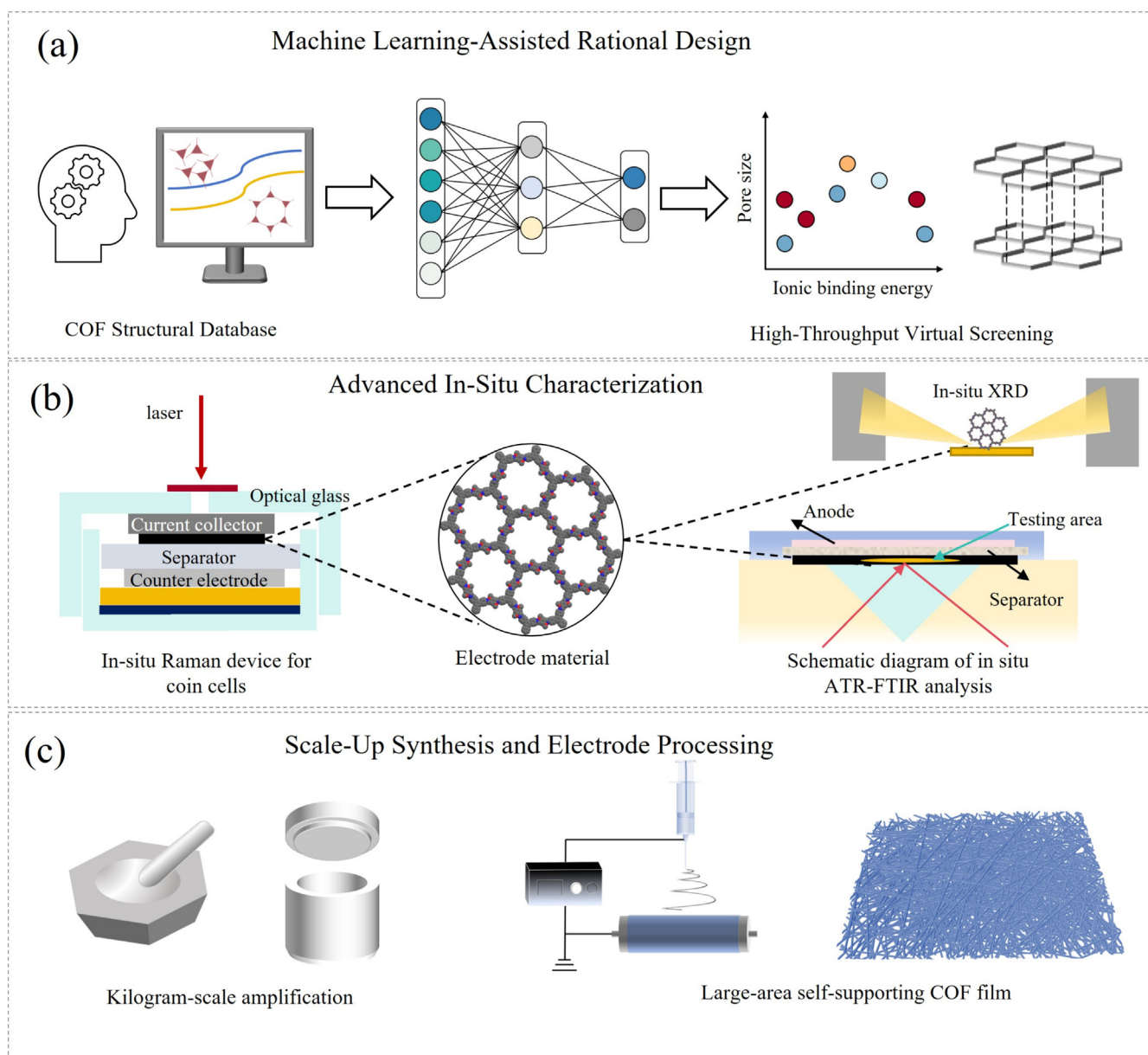


Fig. 11. Interdisciplinary strategies and technical pathways for advancing COF-based electrodes in MVIBs. (a) Virtual screening via machine learning. (b) Mechanism decryption via operando characterization. (c) Scale-up and electrode engineering.

two adjacent TPA-like structures (Fig. 10e). The unique advantages of the TPA-COF structure exhibit good overall electrochemical performance of AIBs, including current densities, long-term cycling and stability (Fig. 10f). Engineered with multisite nitrogen coordination, the TPA-COF cathode exhibits a specific capacity of 161.2 mA h g⁻¹ at 1 A g⁻¹ in AIBs, coupled with exceptional cyclability evidenced by a capacity retention of 84.8 % over 3000 charge–discharge cycles.

5. Conclusions and future perspectives

With their programmable porous structures, tunable functional groups, and robust covalent frameworks, COFs have demonstrated great potential in addressing the key challenges of MVIBs, such as sluggish ion diffusion, structural instability, and interfacial side reactions. This review systematically elaborates on three core design strategies for COF-based electrodes: 1) Pore engineering for optimized ion transport, 2) Framework functionalization for enhanced ion adsorption and redox activity and 3) Composite construction for improved electronic conductivity and mechanical stability. These strategies collectively contribute to the development of high-performance MVIBs, as evidenced by the promising electrochemical performances summarized in Table 1. The unique advantages of COFs in regulating topology, modifying active sites, and optimizing interfaces make them versatile platforms for next-generation energy storage systems.

Despite the significant progress, several challenges remain to be overcome for the practical deployment of COFs in MVIBs. The following perspectives are proposed to guide future research.

1. Machine learning-assisted rational design

The vast chemical space of COF building blocks makes empirical optimization of structures—such as pore size, redox potential, and stability—exceptionally challenging. Machine learning offers a powerful solution to accelerate this process (Fig. 11a). By training predictive models on existing databases of COF structures and their electrochemical properties, it becomes feasible to screen and identify optimal linker combinations. Key performance parameters, including pore dimensions tailored to specific multivalent ions, redox activity, and theoretical capacity, can be predicted prior to synthesis. Such in-silico screening not only prioritizes the most promising candidates for experimental validation but also helps conceptualize idealized COF architectures, thereby streamlining the discovery of high-performance materials and reducing development timelines.

2. Advanced in situ/operando characterization

A deeper mechanistic understanding of ion storage and migration within COF pores is essential for guiding material design. Advanced in situ or operando characterization techniques are critically needed to visualize dynamic processes under realistic battery operating conditions (Fig. 11b). For instance, in situ X-ray diffraction (XRD) and transmission electron microscopy (TEM) can directly monitor structural evolution, layer spacing changes, and phase transitions during ion intercalation. Techniques such as in situ Raman and infrared spectroscopy can track molecular-level vibrations, revealing the evolution of functional groups and host–guest interactions during cycling. Integrating these approaches will help establish unambiguous structure–property relationships and provide fundamental insights into the dynamics of ion (de)solvation and migration, ultimately informing the rational design of next-generation COF electrodes.

3. Scalable synthesis and electrode processing

Transitioning from laboratory-scale synthesis to gram- or kilogram-level production is crucial for the practical application of COFs in MVIBs (Fig. 11c). Future efforts could prioritize three key directions. 1) Developing scalable synthetic methods such as mechanochemical grinding and continuous-flow processes, which can reduce solvent use, shorten reaction times, and enable large-scale COF production with consistent quality. 2) Advancing electrode processing technologies to fabricate practical COF-based electrodes. For instance, electrostatic spinning can be employed to produce large-area, flexible COF membranes with integrated conductive networks, which are suitable for direct use as binder-free electrodes. 3) Optimizing slurry formulation and coating techniques to achieve uniform, robust electrodes that maintain structural integrity and electrochemical performance in large-format cells.

To summarize, COFs possess precisely tunable pore structures, robust covalent frameworks, and versatile functionalization potential, which collectively establish them as highly promising electrode candidates for MVIBs—with the ability to boost ion transport kinetics, improve cycling stability, and optimize interfacial compatibility. While recent studies have validated the value of COFs in topology control, chemical modification, and interface regulation, their practical deployment remains constrained by challenges in large-scale synthesis, long-term cycling mechanisms, and the balance between conductivity and stability. Looking ahead, research efforts should focus on developing cross-scale design methodologies and engineering-driven preparation processes, combining computational predictive guidance, cutting-edge characterization tools, and scalable fabrication technologies to accelerate the transformation of COF-based materials from laboratory prototypes into practical energy storage products.

CRedit authorship contribution statement

Chaohui He: Writing – original draft, Investigation, Data curation. **Zhenyang Zhou:** Data curation. **Liqiang Mai:** Writing – review & editing, Resources, Funding acquisition. **Qinyou An:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Declaration of competing interest

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

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