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Bridging innovation and sustainability: the rise of porous frameworks in sodium-ion batteries

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The rising demand for sustainable and scalable energy storage systems has positioned sodium-ion batteries (SIBs) as promising alternatives to lithium-ion batteries (LIBs) due to the Earth's abundance, low cost, and favourable redox potential of sodium. However, sodium has an intrinsically larger ionic radius than lithium and sluggish diffusion kinetics, posing significant limitations, including severe volume fluctuations and poor long-term cyclability in conventional electrode chemistries. This review provides a critical analysis of the advanced porous frameworks, including metal–organic frameworks (MOFs), covalent organic frameworks (COFs), porous organic polymers (POPs), porous organic hybrids (POHs), and transition metal chalcogenides (TMCs), that have emerged as compelling solutions to overcome these intrinsic drawbacks. These porous systems provide highly tunable architectures with controllable porosity, chemical functionality, and abundant active sites, offering a promising platform for achieving high specific capacity, enhanced ion transport, and mechanical accommodation of volumetric changes. A discussion is also presented on their structural merits, electrochemical performances and synthesis strategies, along with a comparison of their limitations and challenges. Finally, emerging approaches such as creation of hierarchical porosity, vacancy engineering and solid-state integration are highlighted as pathways to enhance the performance and guide the development of next-generation sodium-based energy storage systems.

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1. Introduction

The accelerating global demand for sustainable, scalable, and affordable energy storage has driven intensive research into alternatives to lithium-ion batteries (LIBs). Although LIBs have dominated portable electronics and electric mobility, concerns

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related to the limited availability of lithium resources, rising costs, and their environmental footprint have necessitated the search for new chemistries. SIBs have emerged as highly attractive candidates, offering the advantages of earth-abundant sodium, low material cost, and comparable intercalation chemistry to lithium systems. However, the commercial translation of SIBs faces persistent challenges.[1] The larger ionic radius of Na^+ (1.02 Å *versus* 0.76 Å for Li^+) results in sluggish ion diffusion, pronounced volume changes upon cycling, and structural instability in conventional layered host materials.[2] Additionally, the electrode materials originally designed for LIBs typically display poor capacity retention, severe mechanical degradation, and irreversible capacity loss when adapted for sodium storage.[3] As a result, the rational design of electrode materials specifically tailored for the unique demands of SIBs remains critical.[4]

Achieving a high reversible capacity is paramount for competing with LIB systems, necessitating materials that can accommodate multiple sodium ions per formula unit without rapid structural degradation. Additionally, excellent rate capability demands open ion transport channels, high electronic conductivity, and defect-tolerant architectures.[5] Mitigating volume change remains one of the most pressing challenges in sodium storage materials, where substantial lattice expansion can induce pulverisation and loss of electrical contact, particularly in alloy-type and conversion-type anodes.[6]

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Presently, the scalable and cost-effective synthesis of electrode materials is non-negotiable to realise their commercialisation.[7] The compatibility of electrode frameworks with conventional carbonate or ether-based electrolytes and increasingly with solid-state electrolytes (SSEs) is also crucial, as side reactions at the electrode and electrolyte interface can trigger capacity fading and safety hazards.[8] Furthermore, safety remains the centre of focus, particularly as sodium dendrites have been reported even at moderate current densities in metallic Na systems, emphasising the need for frameworks that facilitate uniform Na deposition and suppress dendrite formation.[9]

The realisation of practical SIBs hinges on the development of electrode materials that can satisfy a suite of rigorous electrochemical and engineering criteria, as mentioned in Fig. 1. Among them, the most important is a high reversible capacity, which necessitates a material with the ability to host multiple Na^+ ions per formula unit without inducing structural collapse or irreversible phase transformations.[10] Besides, sodium has a larger ionic radius (1.02 Å) and a heavier atomic mass, making it difficult to achieve a greater volumetric and gravimetric energy density. Materials such as layered transition metal chalcogenides and defect-engineered carbon composites have demonstrated capacities exceeding 400 mAh g^{-1}, though maintaining them over long cycles remains challenging.[11] Fig. 1 provides an overview of the fundamental challenges that currently hinder the commercial realization of sodium-ion batteries (SIBs). The large ionic radius of Na^+ inherently causes slower ion diffusion, larger volume expansion, and structural strain during cycling, leading to mechanical instability of the electrode framework. Low energy density remains another critical limitation due to the lower working potential of Na^+ compared to Li^+, resulting in reduced gravimetric and volumetric capacities.[12] This directly impacts the energy-to-weight ratio and restricts the competitiveness of SIBs for high-performance applications. Sodium-ion batteries (SIBs) face several intrinsic and extrinsic challenges that collectively limit their practical deployment despite their cost and abundance advantages over lithium-based systems. The low energy density of SIBs primarily originates from the higher atomic mass and larger ionic radius of Na^+ ions compared to Li^+, which leads to reduced specific capacity and voltage.[13,14] Electrode instability is another major concern, as the repeated insertion and extraction of large Na^+ ions cause significant volume expansion and structural stress, resulting in poor cyclability and mechanical degradation.[15] Furthermore, inhomogeneous pore structures within electrode materials can create non-uniform Na^+ diffusion pathways and irregular electrode–electrolyte interfaces, thereby impairing the ion transport kinetics and compromising the rate performance. From an environmental and sustainability perspective, certain synthetic routes and electrolytes used in SIBs involve toxic solvents, high-temperature processing, and non-recyclable components, which pose ecological and energy-consumption challenges.[16] Finally, the limited Coulombic efficiency and rate capability of SIBs stem from sluggish Na^+ diffusion dynamics and the formation of unstable solid–electrolyte interphases (SEIs), which increase polarization and lead to capacity fading during long-term operation.[17] Thus, addressing these multifaceted challenges through rational materials engineering, particularly *via* porous frameworks with controlled architectures and green synthesis strategies, is crucial for advancing the performance and sustainability of sodium-ion batteries.

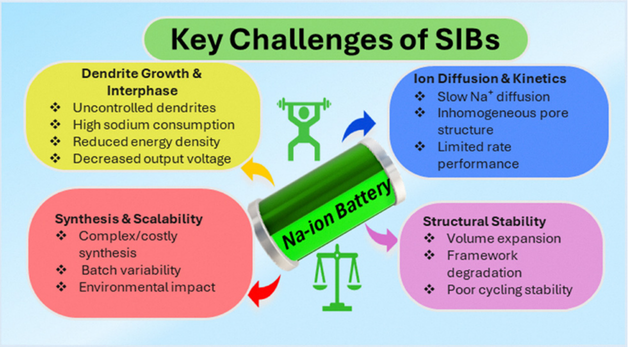

Fig. 1 Schematic of the key challenges in sodium-ion batteries (SIBs): (i) large Na^+ ionic radius, leading to sluggish ion transport and volume expansion, (ii) low energy density relative to Li-ion systems, (iii) structural instability and poor electrode–electrolyte compatibility, (iv) inhomogeneous pore structure, resulting in non-uniform Na^+ diffusion, and (v) environmental impacts associated with solvent toxicity and non-sustainable synthesis.

Furthermore, electrode instability arises from repeated sodiation/desodiation cycles, which can induce pulverization, loss of electrical contact, and unstable solid–electrolyte interphase (SEI) formation. These effects are particularly pronounced in materials with poor mechanical flexibility or mismatched ion diffusion kinetics.[18] Importantly, inhomogeneous pore structures within porous electrodes lead to non-uniform Na^+ distribution and localized stress accumulation, which accelerate degradation and capacity fading.[19] Therefore, achieving uniform pore connectivity and hierarchical architectures is essential for stable ion transport and mechanical durability. From an environmental perspective, sustainability concerns also pose significant challenges. The synthesis of some electrode materials still relies on toxic organic solvents (*e.g.*, DMF and NMP) and energy-intensive processes, contributing to carbon emissions and waste generation.[20] Moreover, improper handling or disposal of chemical precursors can lead to environmental contamination. Addressing these issues requires green synthesis approaches, eco-friendly solvents, and life-cycle management strategies to ensure that sodium-ion technology evolves toward sustainable and circular manufacturing paradigms.

Collectively, these challenges ranging from structural instability and slow ion kinetics to environmental sustainability define the key scientific and engineering frontiers that must be overcome to advance sodium-ion batteries into practical, high-performance, and eco-responsible energy systems.

These interrelated factors collectively limit the electrochemical performance, cycling stability, and environmental viability of current SIB technologies. The subsequent sections discuss material strategies and sustainable design principles to address these multifaceted challenges.

Excellent rate capability is another critical parameter, especially for fast-charging applications. It requires not only open and interconnected Na^+ transport channels but also high electronic conductivity to support rapid redox kinetics.[21] Although crystalline frameworks such as MOFs and COFs offer ordered porosity for ionic diffusion, their poor intrinsic electronic conductivity often hampers their performance at high current densities.[22] Strategies such as heteroatom doping and conductive hybridisation are being actively pursued to address these deficiencies.

Minimal volume expansion during Na^+ insertion and extraction is imperative to preserve the structural integrity of the electrode and prevent pulverisation, a common issue with alloy-type and conversion-type anodes such as Sn, Sb, and TMCs, which can undergo volume changes exceeding 200%.[23] These frameworks, particularly those with hierarchical architectures, can act as mechanical buffers that alleviate stress and maintain electrical contact across cycling.[24]

The cycling stability of SIB electrodes is equally vital. Electrode materials must demonstrate robust structural reversibility, stable solid electrolyte interphase (SEI) formation, and resistance to capacity fading over hundreds to thousands of cycles.[25] Although COFs and POPs have shown promising long-term stability due to their chemically robust backbones, hybrid frameworks incorporating carbonaceous domains or MXenes have achieved enhanced interfacial stability and Coulombic efficiencies.[26]

Scalable, cost-effective synthesis remains a linchpin for commercial viability. Electrode materials must be amenable to low-temperature, environmentally benign processes using inexpensive precursors. MOFs and POPs synthesised *via* aqueous-phase or solvent-free methods, as well as COFs produced through mechanochemistry, are advancing in this regard. These approaches are critical for reducing the environmental footprint and improving the techno-economic competitiveness of SIBs relative to lithium-based systems.[27]

Electrolyte compatibility is another pivotal factor. Electrode materials must remain chemically and electrochemically stable with commonly used carbonate- or ether-based electrolytes. Moreover, as SIB technologies transition to solid-state platforms, interfacial compatibility with solid electrolytes (*e.g.*, Na-β-alumina and NASICON) becomes paramount. Porous materials with tailored surface chemistries or polymeric linkers have shown promise in promoting favourable solid–solid interfacial contact.[28]

Finally, operational safety is of utmost concern, particularly in preventing dendrite formation, thermal runaway, and hazardous side reactions. Frameworks that enable homogeneous Na^+ flux, suppress dendritic growth, and possess high thermal decomposition thresholds can dramatically enhance battery reliability.[29] Hence, TMC-based hybrids and MOF-derived carbons have emerged as promising classes owing to their high thermal stability and ability to regulate the Na^+ deposition morphology.

Collectively, architectures such as MOFs, COFs, POPs, and POHs, and other emerging systems such as TMCs, MXenes, HOFs and others offer distinct advantages in addressing one or more of the above-mentioned performance bottlenecks through tailored chemistry, hierarchical structuring, and hybrid composite engineering. However, no single material class currently satisfies all criteria simultaneously. Therefore, the future of high-performance SIBs will likely depend on rational material design strategies that integrate multiple functionalities, including ion conductivity, redox activity, mechanical stability, and interface compatibility, into synergistic hybrid architectures.

2. Porous frameworks

In this review, porous frameworks are broadly defined as materials possessing an interconnected network of voids, channels, or interlayer spaces that enable efficient ion diffusion and electrolyte accessibility, typically characterized by a specific surface area $>50\ m^2\ g^{-1}$ and well-defined micro-, meso-, or macroporous features, as determined by BET or pore-size distribution analysis. Porous frameworks are defined as crystalline or amorphous materials possessing interconnected voids, channels, or cavities typically ranging from the micro- (<2 nm) to meso- (2–50 nm) and macroporous (>50 nm) scales, which enable rapid mass transport and active site accessibility during electrochemical reactions.[30] The defining parameters are as follows:

1. High surface area ($\geq 100\ m^2\ g^{-1}$), allowing abundant ion-accessible sites.[31]
2. Interconnected pore networks that facilitate ion/electron diffusion.[32]
3. Tunable porosity derived from composition, topology, or synthesis strategy.
4. Mechanical/chemical stability under electrochemical cycling.

These frameworks can be organic, inorganic, or hybrid in nature, each offering distinct structural and electrochemical characteristics. The unifying concept lies in their architectural porosity, governing ion transport, redox site exposure, and electrolyte permeability, which are critical factors in the performance of sodium-ion batteries (SIBs). Porous frameworks such as MOFs, COFs, POPs, and POHs, and other emerging systems such as TMCs, HOFs and MXenes have been increasingly explored to fulfil these stringent requirements, as clearly explained in Fig. 2. This figure provides a comparative overview of how their pore topology, bonding type, and dimensionality influence the sodium-ion storage mechanisms. For instance, MOFs exhibit highly ordered metal–ligand coordination frameworks; COFs display covalently linked π-conjugated networks; POPs possess amorphous interconnected pore structures; TMCs feature layered morphologies with interlayer porosity; and MXenes show 2D lamellar architectures with tunable surface terminations that serve as ion diffusion channels. These frameworks have attracted growing interest for sodium-ion

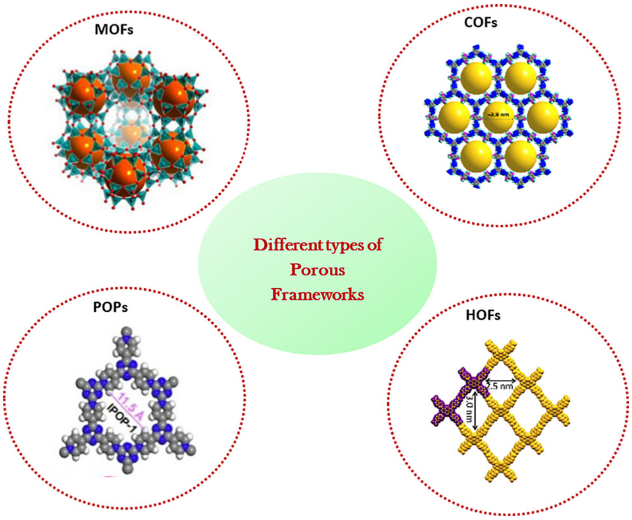

Fig. 2 Schematic of the structural diversity among various porous frameworks employed in sodium-ion batteries, including metal–organic frameworks (MOFs), reproduced from ref. 36 with permission from Springer Nature,[36] Copyright 2022, covalent organic frameworks (COFs), reproduced from ref. 37 with Permission Nature Communication,[37] Copyright 2018, porous organic polymers (POPs), reproduced from ref. 38 with Permission from Elsevier,[38] Copyright 2023, and hydrogen organic frameworks (HOFs), reproduced from ref. 40 with Permission from Elsevier,[40] Copyright 2020.

storage due to their high surface areas, tunable porosity, and structural adaptability. These materials offer intrinsic advantages for addressing Na^+ diffusion limitations, buffering volumetric expansion, and enhancing cycling stability.[33] Recent breakthroughs in defect engineering, hierarchical structuring, and hybridisation with conductive nanostructures have further advanced the performance of these porous systems.[34] MOFs, with their tunable porosity and compositional diversity, can serve as templates for high-capacity carbonaceous or chalcogenide materials, but their poor intrinsic conductivity and moderate mechanical robustness remain limitations.[35] Furthermore, the presence of insulating organic linkers and their limited electronic conductivity restrict their rate performance. COFs, featuring redox-active organic linkers and ordered channels, offer high cycling stability and electrolyte compatibility, but require strategies to overcome their low electronic conductivity.[36] COFs, composed of covalently linked π-conjugated frameworks, overcome this by providing stronger covalent bonding and extended conjugation pathways that enhance electronic transport, but their synthetic complexity and structural fragility under long cycling remain challenges.[37] POPs/POHs exhibit amorphous and flexible frameworks, allowing better mechanical stability and sustainable synthesis from organic precursors. However, their irregular porosity results in less controllable ion diffusion pathways. POPs and POHs are attractive due to their chemical flexibility and scalable synthesis, but their typically amorphous nature and moderate ion diffusion rates demand hierarchical structuring and heteroatom doping.[38,39] HOFs have recently gained attention due to their crystalline order, tunable structures, and solution-processable fabrication. Unlike MOFs and COFs, where coordination or covalent bonds dominate, HOFs are assembled through reversible hydrogen bonding, enabling facile regeneration, recyclability, and defect healing, while maintaining structural porosity. Their intrinsic advantages include lightweight architecture, high porosity, eco-friendly composition, and ability to incorporate redox-active functional groups such as imides, quinones, or heteroatoms. These characteristics provide abundant ion-accessible channels and enhance the Na^+ diffusion kinetics.[40,41]

Therefore, although no single material class perfectly meets all performance criteria, the rational design of hybrid frameworks, vacancy engineering, and creation of hierarchical porosity and conductive composites represent the most promising directions for achieving commercially competitive sodium-ion battery systems. This review critically evaluates the classes of porous materials, benchmarking their electrochemical performance and technological viability against conventional phosphides, oxides, and sulphates, while proposing forward-looking design strategies including hierarchical porosity, conductive hybrid composites, defect modulation, and integration with solid-state systems, to advance sodium-ion battery technology toward practical, sustainable applications. Despite the remarkable advancements achieved across diverse frameworks, each material class still faces intrinsic scientific bottlenecks that constrain its translation from laboratory prototypes to real-world sodium-ion batteries (SIBs). Our analysis highlights both the material-specific and cross-cutting issues that define the current performance landscape and outlines rational strategies for overcoming them.

2.1 Metal–organic frameworks (MOFs)

MOFs have garnered significant attention as one of the most structurally versatile and chemically tunable classes of porous materials for electrochemical energy storage. Constructed from metal ion or cluster nodes interconnected by organic linkers, MOFs offer ultrahigh surface areas (typically 1000–5000 m^2 g^{-1}), customizable pore architectures, and a wide range of metal–ligand combinations that enable molecular-level tuning of their electrochemical behaviour.[42] In SIBs, MOFs are particularly appealing due to their framework flexibility, well-defined channels for ion transport, and abundant coordination sites for Na^+ adsorption and storage. Nevertheless, the direct use of pristine MOFs as electrodes is hindered by their inherent limitations such as low electronic conductivity, structural fragility under cycling stress, and pore collapse during prolonged electrochemical operations. Thus, to address these issues, a major strategy is the transformation of MOFs into derived functional materials such as porous carbons, metal oxides, phosphides, and TMCs through pyrolysis, sulfidation, or phosphorisation. Fig. 3(a) shows the different synthesis strategies and structural evolution of MOF-derived materials, together with the representation of various classes of MOFs. These MOF-derived materials (MDCs) inherit the ordered nanostructure and high surface area of their parent MOFs, while offering enhanced conductivity and mechanical robustness.[43]

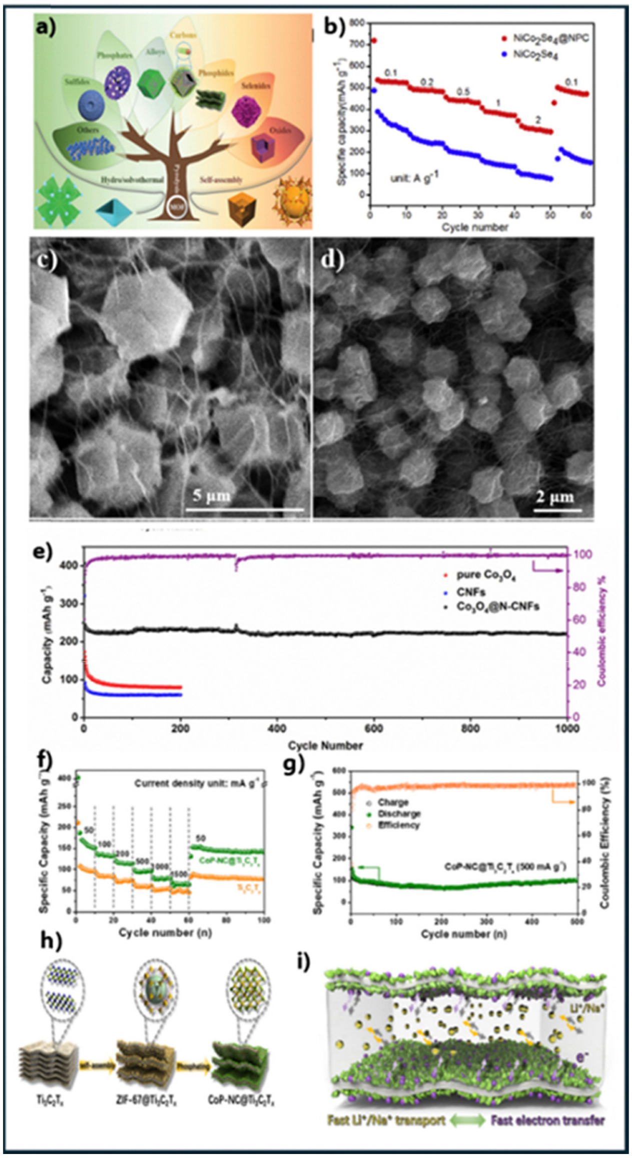

Fig. 3 (a) Schematic of different categories of transition metal-based anode materials (sulphides, phosphates, oxides, selenides, phosphides, alloys, carbons, and others) and synthetic strategies (hydrothermal, MOF-derived, and self-assembly) for sodium-/lithium-ion storage, reproduced from ref. 43 with permission from Wiley,[43] Copyright 2022. (b) Rate capability comparison of the $NiCo_2Se_4$@NPC and pristine $NiCo_2Se_4$ electrodes at various current densities, highlighting the superior electrochemical performance of the composite, reproduced from ref. 45 with permission from Elsevier,[45] Copyright 2022. (c) and (d) SEM images of the Co_3O_4@N-CNF composites showing uniformly distributed microsphere-like structures embedded within interconnected carbon networks at different magnifications, reproduced from ref. 49 with permission from Elsevier,[49] Copyright 2021 (scale bars: 5 μm and 2 μm, respectively). (e) Long-term cycling performance and coulombic efficiency of the pure Co_3O_4, CNFs, and Co_3O_4@N-CNF electrodes, tested over 1000 cycles, showing remarkable cycling stability of the composite electrode, reproduced from ref. 50 with permission from Elsevier,[50] Copyright 2022. (f) Rate performance of $Ti_3C_2T_x$, CoP-NC@$Ti_3C_2T_x$, and the related hybrid electrodes at increasing current densities, demonstrating the improved reversibility and capacity retention of the hybrid system, reproduced from ref. 51 with permission from Elsevier,[51] Copyright 2019. (g) Long-term cycling stability and coulombic efficiency of the CoP-NC@$Ti_3C_2T_x$ electrode at 500 mA g^{-1}, exhibiting high-capacity retention over extended cycles reproduced from ref. 51 with permission from Elsevier,[51] Copyright 2019. (h) Schematic of the synthesis route: preparation of $Ti_3C_2T_x$ MXene, followed by the growth of ZIF-67 on the MXene, and subsequent conversion into CoP-NC@$Ti_3C_2T_x$ hybrid structure, reproduced from ref. 52 with permission from Elsevier,[52] Copyright 2020. (i) Schematic of the electrochemical mechanism for the CoP-NC@$Ti_3C_2T_x$ electrode, highlighting fast Li^+/Na^+ transport and rapid electron transfer through the conductive and porous framework reproduced from ref. 52 with permission from Elsevier,[52] Copyright 2021.

For instance, the direct pyrolysis of zeolitic imidazolate frameworks (ZIF-8) yielded nitrogen-doped porous carbon with hierarchical porosity and fast Na^+ diffusion pathways, achieving a reversible capacity of 600 mAh g^{-1} at 0.15 A g^{-1}.[44] MOF-derived metal sulphides have also shown promise, where sulphidation of Co-MOF and Ni-MOF templates leads to composite electrodes, where nanosized sulphide domains embedded in conductive carbon matrices offer both high capacity and improved rate performance. Li *et al.* demonstrated an $NiCo_2Se_4$/C composite synthesised from a bimetallic MOF, delivering a high specific capacity of 462 mAh g^{-1} at 0.1 A g^{-1}, as shown in Fig. 3(b) and excellent kinetics due to its 3D porous framework and dual-metal synergy.[45] Beyond sulphides, phosphide-based materials derived from MOFs have emerged due to their high theoretical capacities and superior electronic conductivities. However, challenges such as volume expansion and unstable SEI formation persist. Hierarchical nanostructures, such as hollow spheres and yolk–shell architectures, have been effective in mitigating mechanical degradation.

Despite these advancements, several critical limitations remain. The conductivity of MOF-derived carbon frameworks is highly sensitive to the pyrolysis temperature and heteroatom doping levels, often requiring trade-offs between electrical conductivity and structural integrity. Volume changes during Na^+ insertion/extraction in metal-based nanophases also lead to gradual mechanical fatigue, even in well-designed porous structures. Moreover, the scalable synthesis of MOFs is constrained by the high cost of organic linkers, use of toxic solvents, and complex multistep processing, which limit their commercial viability.[46] In recent times, research has started to explore MOFs not just as templates but as multifunctional precursors, redox-active hosts, and interfacial regulators in SIB systems. Defect engineering and heteroatom doping have emerged as powerful tools to modulate their electronic structure and ion transport.[47] The incorporation of nitrogen, sulphur, or phosphorus introduces additional active sites and enhances the conductivity. Mixed-metal MOFs further enable synergistic redox behaviour and improved stability.[48]

Carbonisation and graphitisation strategies have also been employed to improve the conductivity, while preserving the porosity of MOFs. ZIF-67-derived Co_3O_4@N-CNF frameworks demonstrate Na^+ capacities exceeding 380 mAh g^{-1}, retaining stability over 150 cycles at 100 mA g^{-1}, with graphitic nitrogen and mesopores significantly accelerating ion diffusion.[49] As shown in Fig. 3(c) and (d), the SEM images of the Co_3O_4@N-CNF composites show uniformly distributed microsphere-like structures embedded within interconnected carbon networks at different magnifications (scale bars: 5 μm and 2 μm, respectively). Fig. 3(e) shows the long-term cycling performance and coulombic efficiency of pure Co_3O_4, CNFs, and Co_3O_4@N-CNF electrodes, tested over 1000 cycles, showing the remarkable cycling stability of the composite electrode. To further enhance the conductivity, hybrid composites have been developed. Zhao *et al.* fabricated porous $CoFe_2O_4$ nano cube (PCFO-NC) precursors, showing a capacity of 360 mAh g^{-1} after 50 cycles at the current density of 50 mA g^{-1} and superior rate capability owing to its conductive graphene matrix.[50] Other hybrid systems include MOF/CNT and MOF/MXene composites, where conductive networks mitigate resistance and improve the mechanical resilience. For example, Fig. 3(f) shows the rate performance of $Ti_3C_2T_x$, CoP-NC@$Ti_3C_2T_x$, and related hybrid electrodes at increasing current densities, demonstrating the improved reversibility and capacity retention of the hybrid system. Fig. 3(g) shows the long-term cycling stability and coulombic efficiency of the CoP-NC@$Ti_3C_2T_x$ electrode at 500 mA g^{-1}, exhibiting high-capacity retention over extended cycles. Fig. 3(h) shows a schematic representation of the synthesis route, where the $Ti_3C_2T_x$ MXene was prepared, followed by the growth of ZIF-67 on it, resulting in the hybrid structure of MOF@MXene as a CoP-NC@$Ti_3C_2T_x$ composite, achieving 101.6 mAh g^{-1} at a current density of 500 mA g^{-1} after 500 cycles, demonstrating excellent rate retention.[51] Fig. 3(i) shows a schematic illustration of the electrochemical mechanism in the CoP-NC@$Ti_3C_2T_x$ electrode, highlighting fast Li^+/Na^+ transport and rapid electron transfer through its conductive and porous framework. Advances in architecture control *via* self-assembly and 3D printing have enabled the fabrication of scalable MOF-based materials with tailored pore size distributions and compositional gradients.[52] Self-assembled NiCo-MOFs on carbon nanofibers exhibit dual-sublattice redox behaviour, exploiting the synergy between their metal centres and conjugated ligands. There are different types of strategies to incorporate MOF in the fabrication of Na-ion batteries with electronic conductivity and structural stability.

Beyond electrode design, MOFs play a role in enhancing the ionic conductivity through integration with solid electrolytes and ion-conducting polymers. Sulfonated UiO-66 combined with PEO-based electrolytes exhibited an order-of-magnitude improvement in Na^+ conductivity at room temperature.[53] Additionally, functionalization of organic linkers with Na^+-chelating groups such as carboxylates and sulfonates has been shown to lower the interfacial impedance and promote the formation of a stable SEI. *Operando* XPS and EIS studies confirm that MOF-derived carbons containing fluorinated linkers form NaF-rich passivation layers, improving the electrochemical stability. In solid-state SIBs, MOF-derived interphases composed of oxides and sulphides provide mechanical cushioning and chemical compatibility with solid electrolytes.[54] A dual-functional ZnO-C interphase derived from MOFs, when applied with NASICON electrolytes, demonstrated over 98% Coulombic efficiency for 500 cycles.

More recently, emerging classes such as MOF glass amorphous analogues with flexible, solvent-processable networks have shown promise in flexible SIB designs due to their intrinsic self-healing properties. Additionally, hydrogen-bonded organic frameworks (HOFs) and conductive MOFs with π-conjugated linkers are under investigation for their potential to simultaneously conduct ions and electrons.[55]

Despite the considerable advancements in the development of MOFs for SIBs, several critical challenges continue to limit their widespread application. One major limitation is the chemical instability of MOF structures under prolonged Na^+ cycling, which often leads to framework degradation or pore collapse, ultimately reducing their long-term electrochemical performance. Additionally, the trade-off between maintaining high porosity and achieving sufficient electronic conductivity remains a significant barrier. Although pyrolysis and heteroatom doping can enhance the conductivity, they frequently result in partial pore collapse or reduced surface area, thereby diminishing the ion accessibility and active site exposure. Scalability is another persistent issue, as the synthesis of high-quality MOFs typically requires expensive organic linkers, toxic solvents, and energy-intensive processing, raising concerns about the economic and environmental viability of their large-scale production.[56]

Several strategies hold promise for overcoming these limitations. The rational design of mixed-metal MOFs and defect-rich frameworks can modulate the redox behaviour of MOFs and introduce additional active sites, thereby improving their capacity and stability. Incorporating MOFs with highly conductive matrices such as MXenes, graphene, and carbon nanotubes (CNTs) can significantly enhance their charge transport, while maintaining their structural integrity. Moreover, adapting MOF-derived materials for solid-state sodium batteries offers a promising avenue to address safety and energy density challenges, especially using interfacial MOF layers or solid-state compatible derivatives that accommodate volume changes and enhance ionic contact.[57] Overall, MOFs represent a highly tunable and multifunctional class of materials for the fabrication of next-generation SIBs, and through synergistic structural engineering and compositional tailoring, they are poised to become vital components in the development of high-performance, sustainable energy storage systems.

2.2 Covalent organic frameworks (COFs)

Covalent organic frameworks represent a distinct class of crystalline porous polymers constructed by light-element backbones (C, H, N, O, and B) and highly ordered, tunable porous structures *via* strong covalent bonds. The well-defined one-dimensional (1D) and two-dimensional (2D) channels in COFs facilitate rapid ion diffusion, while their abundant sites available for functionalization offer immense potential for tailored Na^+ storage mechanisms. Their 2D or 3D architectures offer exceptional structural regularity, modular tunability, and extensive π-conjugation, making them highly promising candidates for sodium-ion battery (SIB) applications.

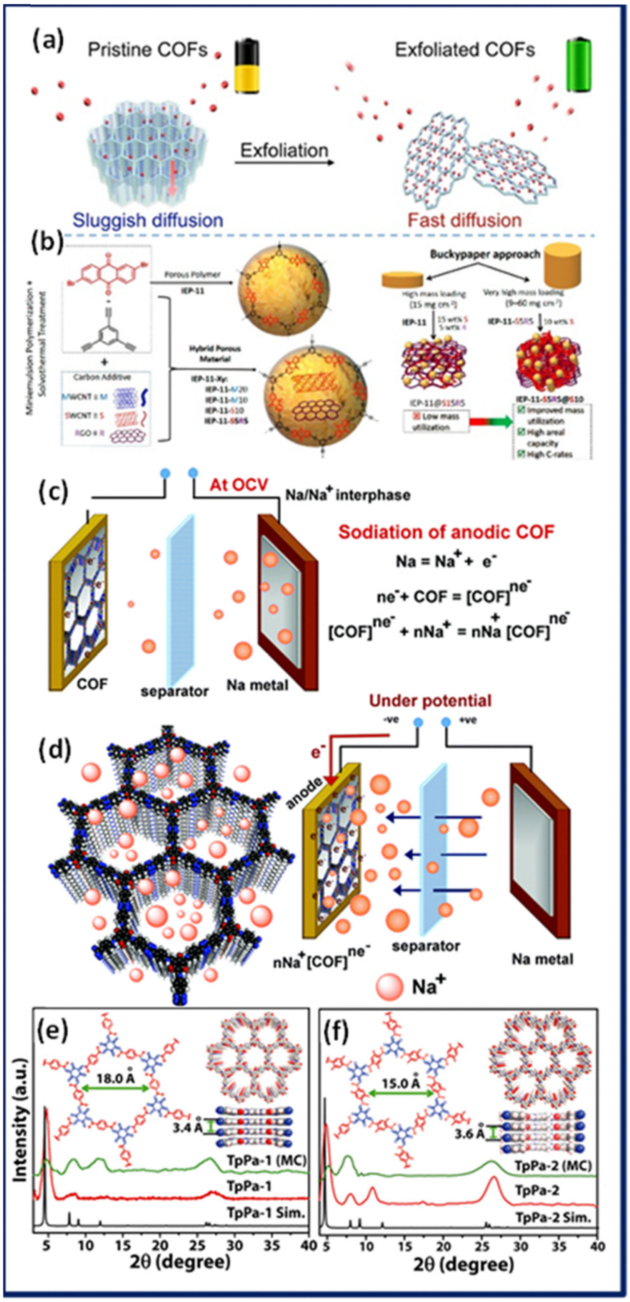

Fig. 4 (a) Exfoliation of pristine COFs into few-layer nanosheets enhances ion transport, shifting from sluggish diffusion in bulk COFs to fast diffusion in their exfoliated counterparts, reproduced from ref. 60 with permission from the American Chemical Society,[60] Copyright 2022. (b) Bucky paper-inspired strategy for hybrid porous polymer (IEP-11) electrodes, illustrating synergistic integration with carbon additives (MWCNTs, rGO, and acetylene black) and tunable high-mass-loading architectures to achieve superior rate capability, reproduced from ref. 61 with permission from Elsevier,[61] Copyright 2020. (c) Mechanistic illustration of sodiation at the Na/Na$^+$ interphase: at open-circuit voltage (OCV), Na metal oxidises to Na$^+$, which inserts into the COF, while under an applied potential, electron flow drives reversible Na$^+$ intercalation, reproduced from ref. 65 with permission from The Royal Society of Chemistry,[65] Copyright 2019. (d) Molecular-level view of the Na$^+$ accommodation within COF pores, emphasising the ordered 1D channels that facilitate Na$^+$ diffusion and electrochemical redox reproduced from ref. 65 with permission from The Royal Society of Chemistry,[65] Copyright 2019. (e) and (f) X-ray diffraction (XRD) patterns of TpPa-1 and TpPa-2 COFs, respectively, showing experimental and simulated profiles with corresponding pore size distributions ($\sim$18.0 Å for TpPa-1 and $\sim$15.0 Å for TpPa-2), validating the periodicity and crystallinity of the frameworks. Insets highlight atomic arrangements and Na$^+$ transport pathways, Reproduced from ref. 70 with permission from the American Chemical Society,[70] Copyright 2021.

Unlike MOFs, which rely on metal nodes, COFs are entirely metal-free, offering low mass density and potential for high theoretical capacities when appropriately functionalized. The core of COF functionality in SIBs is their tunable architecture. Strategic monomer design allows the integration of redox-active units (*e.g.*, imine, hydrazone, phenazine, and carbonyl) within the framework, thus enabling reversible Na$^+$ storage through faradaic mechanisms.[58] Hu *et al.* demonstrated a phenazine-based COF with capacity of 265 mAh g^{-1} and 92% capacity retention over 500 cycles, attributing its performance to its N-rich aromaticity and strong Na$^+$ affinity.[59] However, despite these structural advantages, pristine COFs typically suffer from poor intrinsic electrical conductivity and suboptimal mechanical robustness under repeated electrochemical cycling. This has spurred a range of materials innovations aimed at enhancing their conductivity and long-term stability. Fig. 4(a) shows a schematic representation of the structural engineering and electrochemical behaviour of COF-based electrodes for sodium-ion batteries. Exfoliation of pristine COFs into few-layer nanosheets effectively improves their ionic accessibility and charge storage kinetics. In bulk COFs, the dense stacking of layered frameworks hinders ion mobility, leading to sluggish Na$^+$ diffusion. Upon exfoliation, the exposure of more active sites and shortened ion-diffusion pathways enable rapid transport and better utilisation of the intrinsic porosity of the COFs. These design strategies underline the growing emphasis on structural and interfacial engineering of COFs for sodium-ion battery electrodes. Exfoliation not only maximises the utilisation of their extended π-conjugated frameworks but also enhances electrolyte infiltration, leading to improved cycling stability.[60] As shown in Fig. 4(b), a bucky paper-inspired electrode design demonstrates how hybrid porous polymer structures (*e.g.*, IEP-11) can be integrated with conductive carbon additives such as MWCNTs, rGO, and acetylene black. The bucky paper approach exemplifies a scalable route toward the practical fabrication of electrodes by achieving a high areal mass loading without compromising ionic diffusion or electronic conductivity, which are key bottlenecks in translating COFs from laboratory prototypes to industry-relevant energy storage systems. Together, these advances highlight that future COF-based electrodes will likely rely on the synergistic integration of nanoscale structural tailoring and macro-level electrode engineering to bridge the gap between fundamental materials chemistry and real-world sodium-ion battery applications.[61]

One promising approach involves heteroatom doping (*e.g.*, N, S, and P), which improves both electron delocalisation and sodium binding. Specifically, nitrogen, sulphur, or phosphorus species are incorporated into the COF skeleton to improve its electrical conductivity and enrich active sites.[62] Heteroatom-rich COFs exhibit improved electron mobility and increased redox-active centres, enhancing both the capacity and rate performance. COFs doped with electron-rich moieties exhibit enhanced electrochemical activity, with increased specific capacities and reduced overpotentials. The appeal of COFs in energy storage stems from their predictable channels for ion transport, high surface areas (>1000 m^2 g^{-1}), and redox-active sites that can be tailored *via* rational monomer design.[63]

Researchers found that COFs often suffer from low intrinsic electrical conductivity and relatively limited volumetric stability, especially under high current densities. The lack of extended π-conjugation in early COF systems restricted charge transport, while cycling-induced stress and poor wettability with conventional electrolytes led to framework degradation and capacity fading. Electrochemical impedance spectroscopy (EIS) typically revealed high charge-transfer resistance (R_{ct}), and *ex situ* structural analysis (*e.g.*, PXRD and TEM) showed partial collapse of the crystalline framework after long-term cycling.[64] These limitations spurred a wave of innovations aimed at overcoming the above-mentioned bottlenecks through rational design strategies.

One prominent direction is the design of COFs incorporating redox-active linkers, such as phenazine, imine, hydrazone, and carbonyl functionalities, which directly participate in reversible Na^+ storage reactions. Recent developments have focused on integrating redox-active and π-conjugated building blocks into the COF backbone. For example, benzothiadiazole- and pyrene-based linkers have been used to introduce delocalized electron pathways, improving the charge mobility and electrochemical responsiveness. Chen *et al.* synthesised a benzothiadiazole-linked COF, which delivered 290 mAh g^{-1} with 88% capacity retention after 400 cycles at 1 A g^{-1}, owing to its high electron density and optimised pore accessibility. Moreover, Schiff-base COFs with hydrazone and β-ketoenamine linkages provide redox-active centres that reversibly interact with Na^+ through enolization and tautomerism mechanisms.[65] These systems exhibited flatter and more defined charge–discharge plateaus, with EIS showing significantly reduced R_{ct} values, demonstrating faster charge-transfer kinetics. Cyclic voltammetry (CV) confirmed the pseudocapacitive contributions from their redox-active linkers, while *operando* FTIR and Raman spectroscopy verified their reversible bond switching mechanisms (*e.g.*, $C{=}N \leftrightarrow C{-}NH$) during Na^+ insertion/extraction.[66] Furthermore, many different linkages formed by diverse building blocks with different physical and chemical properties, geometric features and bond chemistries are shown in Fig. 4.

The formation of hybrid composites has proven to be another pivotal strategy. By integrating COFs with conductive matrices such as graphene, carbon nanotubes (CNTs), and MXenes, researchers have achieved significant improvements in charge transport kinetics and cycling durability. The interfacial compatibility between the COF shell and the rGO core enabled uniform Na^+ diffusion and suppressed polysulphide dissolution. The synergy between the high electronic conductivity of rGO and the ordered porous structure of COFs significantly enhanced the charge transfer kinetics and Na^+ ion accessibility. Sun *et al.* reported the preparation of a COF–MXene hybrid, where imine-linked COFs were *in situ* grown on Ti_3C_2 sheets. The hybrid anode delivered an outstanding reversible capacity of 365 mAh g^{-1} at 0.05 A g^{-1} with a stable performance over 500 cycles, which is attributed to the synergistic effects between the porous COF matrix and highly conductive MXene layers.[67,68] The synergy between the high electrical conductivity of MXene and the porosity of COFs was confirmed by the suppressed IR drop in the galvanostatic profiles and the uniform Na^+ distribution visualised through electron energy loss spectroscopy (EELS). Fig. 4(c) presents a mechanistic illustration of sodiation at the Na/Na^+ interphase. At open-circuit voltage (OCV), metallic sodium spontaneously undergoes oxidation, releasing Na^+ ions and electrons. These Na^+ ions migrate across the separator and insert into the π-conjugated framework of the COF, where the redox-active sites act as hosts for charge storage. The charge transfer can be described as $ne^- + COF \rightarrow [COF]^{n-}$ enabling the reversible coordination of Na^+ within the framework. Under an applied potential, electron flow between the anode and cathode drives the dynamic intercalation/deintercalation process, highlighting the role of COFs as efficient anodic hosts. This mechanism underscores how the ordered porosity, abundant heteroatoms, and extended conjugation of COFs create a favourable Na^+ adsorption and storage environment, thereby reducing polarisation and enhancing the coulombic efficiency. Fig. 4(d) presents a molecular-level view of Na^+ accommodation within COF pores. The crystalline frameworks of COFs provide uniform, tunable 1D channels that act as directional highways for Na^+ transport. The periodicity and nanoscale pore environment ensure efficient ionic diffusion, while the high density of binding sites (*e.g.*, imine linkages and heteroatom functionalities) supports stable and reversible electrochemical interactions. During the sodiation/desodiation cycle, Na^+ ions intercalate into these channels, and the extended π-conjugated skeleton facilitates electron delocalisation, improving the overall charge transfer kinetics.[69] This ordered pore geometry not only mitigates volume fluctuations during cycling but also preserves the structural integrity of the electrode, a critical factor for long-term cycling stability. This framework-driven ion accommodation highlights the advantage of COFs over amorphous carbons or disordered porous polymers, making them promising platforms for high-performance sodium-ion storage.[70]

Recent innovations have shown a breakthrough in ionic conductivity, which is considered a bottleneck in COFs. Incorporating functional groups into COFs such as sulphonated COFs, carboxyl-functionalized pores, or those doped with sodium-conducting polymers (*e.g.*, PEO or PVDF) resulted in enhanced ionic mobility by providing continuous ion-transport channels. An imine-linked COF integrated with a solid polymer electrolyte exhibited ionic conductivity of 2.1×10^{-4} S cm^{-1} and stable interfacial contact in all-solid-state cells. Interface engineering has also been critical for realising stable SEI formation and mitigating electrolyte degradation. Functional linkers such as catechol, thiophene, and azobenzene have been incorporated to modulate the surface energy, Na^+ affinity, and interfacial reactivity. *Operando* FTIR and Raman studies have confirmed that these linkers stabilise the interfacial layers and reduce irreversible capacity loss.[71]

In terms of synthesis, traditional solvothermal methods often rely on toxic, high-boiling solvents such as mesitylene and 1,4-dioxane, raising concerns regarding environmental sustainability and scalability. Thus, to address these issues, alternative routes such as microwave-assisted synthesis, mechanochemical milling, and interfacial polymerisation are gaining attention. Mechanochemically synthesised COFs, previously limited by crystallinity challenges, have now demonstrated capacities exceeding 280 mAh g^{-1} with 92% capacity retention over 600 cycles.[62] Fig. 4(e) and (f) present the X-ray diffraction (XRD) patterns of TpPa-1 and TpPa-2 COFs, respectively, showing their experimental and simulated profiles with corresponding pore size distributions ($\sim$18.0 Å for TpPa-1 and $\sim$15.0 Å for TpPa-2), validating the periodicity and crystallinity of the frameworks. The insets highlight their atomic arrangements and Na^+ transport pathways. Solvent-free processes also offer a more environmentally friendly and industrially viable pathway to produce COFs on a large scale. Furthermore, the mechanical stability of COFs under repeated cycling has been improved through framework interlocking, flexible linker integration, and elastic polymer backbones. These advances are critical for the fabrication of flexible and wearable sodium-ion energy devices. In addition, dual-function COFs serving as both electrode materials and solid-state electrolytes are gaining attraction for integrated system miniaturisation.

COFs, with their tunable pore channels and crystalline 2D/3D architectures, provide controllable and predictable sodium-ion transport pathways. Their ordered frameworks composed of light elements (C, H, N, O, and B) enable the precise integration of electroactive moieties directly into the skeleton, offering tailored Na^+ diffusion and redox activity. Recent studies demonstrate that incorporating redox-active units such as anthraquinone, benzothiadiazole, and imine/hydrazone linkages can substantially enhance the charge-storage performance by providing faradaic reaction sites within the π-conjugated backbone.

However, the intrinsic limitations of COFs, including low electronic conductivity and limited structural robustness under repeated sodiation/desodiation, remain significant obstacles. Thus, to overcome these issues, hierarchical structural engineering and nanoscale exfoliation have emerged as effective solutions. Few-layer COF nanosheets with open edge sites exhibit markedly faster ion transport compared with bulk frameworks. The construction of COF–carbon hybrids (*e.g.*, COF/rGO, COF/CNT, and COF/MXene composites) creates interconnected electron pathways and reduces interfacial resistance, thereby improving both their rate capability and capacity retention.

Further, the introduction of heteroatom dopants (N, S, and P) into COF linkers enhances the electron density, promotes Na^+ binding, and improves the redox reversibility. Emerging research also focuses on COF-on-substrate architectures and conductive polymer intergrowth, which mitigate stacking issues and improve the mechanical integrity of the electrode. These strategies are guiding the use of COFs in the preparation of practical, flexible sodium-ion electrodes with outstanding stability and fast-charge performance.

However, despite these strides, achieving volumetric energy densities comparable to commercial electrodes remains difficult due to the low packing density of COFs. Additionally, their long-term interfacial stability with liquid and solid electrolytes under high-voltage conditions is still underexplored. Future directions include novel/hybrid monomer design, COF-on-metal growth for improved interface conductivity, and incorporation of self-healing linkers for long-life cycling.

2.3 Porous organic polymers (POPs) and porous organic hybrids (POHs)

POPs have emerged as a compelling class of amorphous, covalently linked porous materials for SIBs, owing to their inherent structural versatility, synthetic tunability, and scalable fabrication routes. Unlike their crystalline counterparts, such as MOFs and COFs, POPs are typically constructed *via* dynamic covalent chemistry (*e.g.*, Schiff-base condensation and click chemistry) or irreversible coupling reactions (*e.g.*, Friedel–Crafts alkylation), enabling the modular design of pore structures, surface functionalities, and framework topologies. Their large specific surface areas (typically 500–2000 m^2 g^{-1}), low density, and abundant organic functionalities offer fast Na^+ diffusion, high ion-accessible surface areas, and multiple interaction sites for reversible sodium storage.[72]

However, their amorphous nature, while advantageous for scalable synthesis and defect tolerance, also poses intrinsic limitations such as poor electrical conductivity, irregular pore connectivity, and moderate structural rigidity during prolonged cycling. These drawbacks often limit their rate performance and capacity retention, particularly at high current densities. Thus, to overcome these challenges, significant efforts have been devoted to heteroatom doping, redox-functional monomer design, and composite hybridisation strategies that engineer both ionic and electronic pathways within the polymer matrix.[73]

One of the most effective approaches to boost the sodium storage capability of POPs is the incorporation of redox-active functional moieties into their backbones. Functional groups such as carbonyls, imides, azo, and thiophene units introduce reversible redox centres, while facilitating π-conjugation, which support electronic delocalization and improve the conductivity. For example, a thiophene-based bipyridine POP, 2,2′-dithiophene-linked bipyridine polymer (P-DTBPY), demonstrated a high reversible capacity of 260 mAh g^{-1} at 0.1 A g^{-1} and 93.6% capacity after 2000 cycles at 5 A g^{-1}. This enhancement was attributed to the synergistic interaction among multiple Na^+ binding sites and fast charge transport across the conjugated skeleton.[74] Similarly, hydrophilic POPs containing ether or carboxyl groups have shown enhanced Na^+ affinity and efficient SEI formation, improving the first-cycle coulombic efficiency.

Doping POP frameworks with electron-rich heteroatoms such as nitrogen, sulphur, and phosphorus can significantly enhance their redox activity and electrical conductivity. Nitrogen-doped POPs exhibit high sodiophilicity and charge delocalisation through lone-pair interactions with Na^+ ions.[75] Li *et al.* synthesised a nitrogen-doped POP, which achieved a reversible capacity of 275 mAh g^{-1} at 0.1 A g^{-1}, maintaining excellent cycling stability over 500 cycles.[76] These doped frameworks also promote uniform SEI formation and enhance the mechanical resilience during volume fluctuations.[77]

To mitigate the inherently low conductivity of pure POPs, composite strategies have been widely adopted. POHs are formed by integrating POPs with conductive nanostructures such as graphene, CNTs, MXenes, and TMCs. These hybrid materials combine the chemical tunability of POPs with the superior electronic conductivity and mechanical strength of inorganic scaffolds.[78] For instance, Fu *et al.* developed a POP–MoS_2 composite, which delivered a high capacity of 361 mAh g^{-1} at 5.0 A g^{-1} and demonstrated an enhanced rate performance.[79] The conductive MoS_2 sheets facilitated fast electron transfer, while the porous POP matrix provided Na^+-accessible channels.[69] Similarly, a 3D POP-MXene hybrid electrode with interpenetrated conductive pathways achieved 365 mAh g^{-1} at 0.05 A g^{-1} and retained over 90% of its capacity after prolonged cycling.[80] The MXene nanosheets buffered volume changes and provided continuous electrical percolation, which are crucial for maintaining the electrode integrity under repeated Na^+ insertion/extraction cycles.

Beyond compositional tuning, architectural design plays a critical role in optimising POP-based materials. Interconnected 2D/3D networks and yolk–shell nanostructures have been explored to enhance their mechanical robustness and multidirectional ion/electron transport. These architectures not only mitigate stress-induced degradation but also facilitate faster ion kinetics. Hierarchical POP-CNF (carbon nanofiber) composites, with *in situ*-grown POP layers, have shown improved tensile strength and long-life performance, making them suitable for flexible SIB configurations.[81] The performance of POPs in SIBs is also closely tied to their interfacial behaviour with liquid and solid electrolytes. Functionalized POPs containing sulfonic acid, carboxyl, or ether groups have demonstrated enhanced ionic conductivity ($\sim 10^{-4}$ S cm^{-1}) by forming continuous ion-transport channels and promoting stable SEI formation. Incorporating ionic liquids or sodium salts into the framework or electrolyte matrix further reduces the interfacial resistance and improves the wettability.[82] These attributes are particularly advantageous for emerging quasi-solid-state and gel-based SIB configurations to realise a high coulombic efficiency of almost 100%.

To align with sustainable manufacturing principles, recent advances have focused on solvent-free, energy-efficient synthesis routes for POPs. Mechanochemical ball milling and thermal polymerisation techniques have enabled the formation of redox-active POPs from biomass-derived monomers (*e.g.*, phloroglucinol and lignin) without the use of toxic solvents or high reaction temperatures. These green approaches preserve the framework porosity and maintain its high electrochemical activity, while offering pathways for industrial-scale production. POHs integrating inorganic functional clusters (*e.g.*, SiO_2, TiO_2, and polyoxometalates) extend the performance envelope of POPs by providing mechanical reinforcement, pseudocapacitive behaviour, and enhanced ion-electron dual transport.[83] A recent study demonstrated a flexible solid-state SIB using a POM-based POH, which delivered 300 mAh g^{-1} and retained $>90\%$ capacity over 800 cycles, even under mechanical bending. These multifunctional systems are increasingly relevant for wearable and high-power sodium-ion energy applications.[84]

Despite the remarkable progress, several obstacles remain in the practical deployment of POPs and POHs for SIBs. Achieving a high volumetric energy density remains challenging due to the low tap density of highly porous frameworks. Additionally, balancing their porosity with electrical conductivity is non-trivial, as excessive carbonisation or doping can collapse their pore structure. Also, realising long-term interfacial stability under high-voltage and solid-state operating conditions requires deeper investigation. Future strategies should include the molecular-level design of redox-active monomers and interface engineering with advanced electrolytes. The integration of multifunctional POPs into flexible and quasi-solid-state systems represents an exciting frontier for the next generation of sodium-ion energy storage technologies.

2.4 Other emerging systems

Although transition metal chalcogenides (TMCs) and MXenes are not intrinsically porous frameworks like MOFs or COFs, they are included in this review as emerging systems with functional or pseudo-porous characteristics. Their 2D layered architectures inherently contain interlayer voids, edge defects, and tunable surface terminations, which collectively generate accessible pathways for ion diffusion and electrolyte penetration. These structural features impart high ion-accessible surface areas and enable efficient charge transport, mimicking the electrochemical behavior of porous materials. These properties emphasize their porosity-driven electrochemical performance rather than crystallographic porosity.

2.4.1. Transition metal chalcogenides (TMCs). TMCs comprising sulphides, selenides, and tellurides of transition metals have emerged as a highly promising family of anode materials for SIBs due to their high theoretical capacities, rich redox chemistry, and diverse structural tunability. Unlike traditional oxide or phosphate-based materials, TMCs offer flexible layered configurations and multivalent transition metal centres that enable conversion and alloying reactions, thus achieving superior sodium storage capability.[85] For instance, MoS_2 and VS_4, with layered and chain-like structures respectively, exhibit Na^+ intercalation potential combined with metallic or semi-metallic conductivity, enabling fast redox kinetics and favourable rate performances. Although transition metal chalcogenides (TMCs) are traditionally regarded as 2D layered materials, recent studies have demonstrated that engineering their porosity and

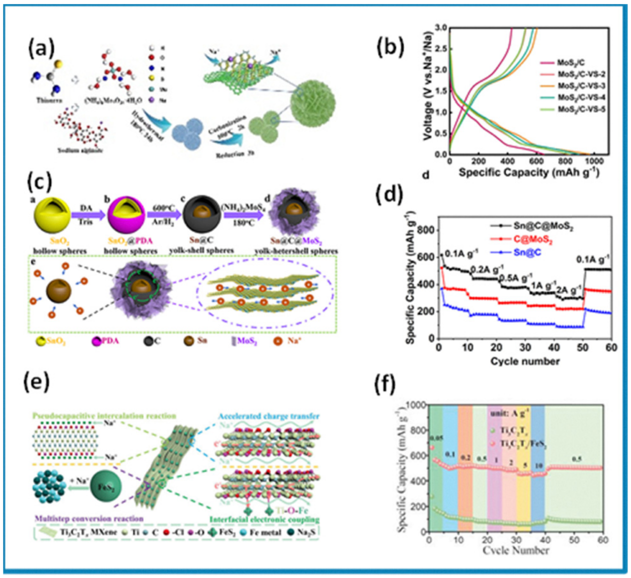

Fig. 5 (a) Schematic of the synthetic route toward the MoS_2/C composites from molecular precursors. (b) Charge–discharge profiles of MoS_2/C prepared under different conditions, reproduced from ref. 87 with permission from Wiley,[87] Copyright 2021. (c) Stepwise construction of the Sn@C@MoS_2 yolk–shell heterostructures from SnO_2 hollow spheres *via* PDA coating, carbonisation, and MoS_2 growth, with the schematic Na^+ storage mechanism, reproduced from ref. 90 with permission from Elsevier,[90] Copyright 2019. (d) Comparison of the rate performance of the Sn@C@MoS_2, C@MoS_2, and Sn@C electrodes, reproduced from ref. 90 with permission from Elsevier,[90] Copyright 2019. (e) Illustration of pseudocapacitive intercalation, multistep conversion, and interfacial electronic coupling in MXene–FeS_2 hybrids, reproduced from ref. 93 with permission from Wiley,[93] Copyright 2022. (f) Cycling performance of the composite electrode at varying current densities, demonstrating its high reversible capacity and robust stability, reproduced from ref. 93 with permission from Wiley,[93] Copyright 2022.

structural modification transform them into functional porous frameworks. TMCs (*e.g.*, MoS_2, $FeSe_2$, and WS_2) naturally form layered architectures that can be exfoliated or templated into porous nanosheets, hollow spheres, or hierarchical nanoflakes. These morphologies yield large surface areas, short Na^+ diffusion paths, and efficient electrolyte infiltration properties consistent with porous frameworks.

The primary strength of TMCs lies in their high theoretical capacities, which frequently exceed 400–600 mAh g^{-1} depending on their stoichiometry and crystal structure. For example, layered 2H-MoS_2 allows the intercalation of Na^+ between S–Mo–S layers and subsequent conversion reactions to form Na_2S and metallic Mo, resulting in theoretical capacities up to 670 mAh g^{-1}.[86] Fig. 5(a) presents a schematic illustration of the synthesis route for hierarchical nanostructured electrode materials for sodium-ion storage, employing precursors such as thiourea, sodium alginate, and ammonium molybdate, *via* hydrothermal/carbonisation/reduction steps, leading to the formation of MoS_2/carbon composite architectures. Also, it highlights Na^+ storage within the layered MoS_2 lattice. Fig. 5(b) compares the charge–discharge curves of MoS_2/C composites prepared under different conditions (VS-2, VS-3, VS-4, and VS-5), where the voltage plateaus correspond to the conversion and intercalation reactions of MoS_2 with Na^+, showing a variation in reversible capacity. Similarly, FeS_2 undergoes full conversion and alloying reactions with sodium to deliver capacities of around 600 mAh g^{-1}. These materials also possess favourable Na^+ diffusion pathways, which is attributed to their weak interlayer van der Waals forces and large interplanar spacing (typically >6 Å), which can be further expanded by doping or exfoliation.[87] In the case of VS_4, its quasi-1D chain structure facilitates Na^+ insertion along its aligned vanadium–sulphur chains, enhancing the capacity and cycling behaviour.

However, despite their advantages, TMCs suffer from several critical limitations, which hinder their practical application. Among them, the main issue is their drastic volumetric expansion (often $>200\%$) during conversion reactions, which leads to mechanical stress, pulverisation of the electrode, and rapid capacity fading. Furthermore, the formation of unstable solid electrolyte interphases (SEI) and the poor reversibility of the Na_2S/Na_2Se formation/decomposition process compromise their coulombic efficiency and long-term cyclability. TMCs also tend to exhibit sluggish reaction kinetics for complete conversion and reformation of chalcogenide phases, particularly under high current densities.[88] Environmental concerns related to toxic chalcogen precursors and difficulty in their large-scale, safe processing also need to be addressed. To overcome these limitations, researchers have developed nanoscale TMC architectures that buffer volume expansion and improve the kinetics. Hollow and yolk–shell MoS_2, FeS_2, and SnS_2 structures, often encapsulated in conductive carbon matrices, are particularly effective in maintaining their structural integrity during cycling.[89]

Defect and vacancy engineering has also been employed to modulate the electronic structure and facilitate Na^+ storage. Introducing sulphur vacancies in MoS_2 or selenium vacancies in $MoSe_2$ generates high-energy adsorption sites, increases the Na^+ diffusivity, and accelerates pseudocapacitive storage. For instance, VS_4 nanorods with rich S-vacancy sites delivered fast kinetics and 93% retention over 300 cycles. Doping TMCs with heteroatoms such as N, P, and O has also been shown to enhance their conductivity and structural robustness. In addition, researchers are exploring phase engineering of TMCs, especially transitioning from semiconducting 2H to metallic 1T phases. Metallic 1T-MoS_2 provides superior conductivity, more active sites, and improved ion mobility. Mao *et al.* reported that Sn@N-doped C@MoS_2 nanospheres exhibited a reversible capacity of 480 mAh g^{-1} at 0.5 A g^{-1} and 85% retention over 500 cycles.[90] Fig. 5(c) shows the stepwise synthesis of Sn@C@MoS_2 yolk–shell heterostructures, including (a) SnO_2 hollow spheres. (b) SnO_2@PDA hollow spheres after polydopamine coating. (c) Sn@C yolk–shell spheres obtained after carbonisation in Ar/H_2. (d) Sn@C@MoS_2 yolk–shell heterostructures after MoS_2 growth. (e) Schematic of Na^+ transport and buffering in the yolk–shell design. Fig. 5(d) shows a comparison of the cycling performance at different current densities (0.1 to 2 A g^{-1}) of the Sn@C@MoS_2, C@MoS_2, and

Sn@C electrodes. Among them, Sn@C@MoS_2 shows the highest capacity retention and superior rate performance, evidencing the synergistic effect of the yolk–shell and heterointerface design.[90]

Another widely adopted strategy involves hybridisation with conductive materials such as graphene, reduced graphene oxide (rGO), MXenes, and MOF-derived porous carbons. For instance, MoS_2/rGO nanocomposites exhibit high capacities and excellent rate performances due to their synergistic electron conduction pathways and uniform Na^+ diffusion.[91] Liu *et al.* synthesised an FeS_2@rGO composite with a highly interconnected conductive matrix, which retained 420 mAh g^{-1} after 500 cycles at 1 A g^{-1}. The incorporation of carbon not only increased its conductivity but also confined polysulphide intermediates and enhanced the SEI formation.[92] Similarly, Fig. 5(e) shows a schematic of the mechanism of MXene–FeS_2 hybrids, demonstrating the pseudocapacitive intercalation reaction with Na^+, and multistep conversion reactions involving $Ti_3C_2T_x$ MXene and FeS_2 (TiO_2, Fe, and Na_2S intermediates), and then interfacial electronic coupling with accelerated charge transfer. Overall, it emphasises how MXene-based hybrids exhibit improved conductivity and stabilise the conversion reactions. Fig. 5(f) shows the long-term cycling stability as specific capacity *vs.* cycle number at different current densities (0.1–0.5 A g^{-1}), where the coloured bands mark the applied current density. The composite electrode maintained a high reversible capacity ($\sim$600–700 mAh g^{-1}) with stable cycling and excellent Coulombic efficiency.[93]

Despite these advances, open challenges remain. The full reversibility of TMC conversion reactions is still not well understood, and side reactions involving Na_2S/Na_2Se often lead to irreversible capacity loss. The volumetric energy density of TMC electrodes is also lower than the theoretical value due to the porosity introduced during nano-structuring. Moreover, the integration of TMCs with solid-state electrolytes (SSEs) is complicated by the interfacial instability and incompatibility between sulphide-rich electrodes and oxide SSEs. Finally, the scalability of environmentally benign, low-cost synthesis methods (*e.g.*, molten salt synthesis and mechanochemical routes) must be improved for industrial applications. Transition metal chalcogenides, encompassing sulphides, selenides, and tellurides of transition metals, have gained significant attention as high-capacity anode materials for SIBs due to their multielectron redox reactions and diverse structural topologies.[94] Their intrinsic advantages include high theoretical capacities (often $>$500 mAh g^{-1}), favourable layered structures, and metallic or semi-metallic conductivity in certain phases, particularly 1T-phase dichalcogenides (*e.g.*, MoS_2 and VS_2).[95]

Further, TMCs operate primarily *via* conversion and alloying reactions, which deliver high capacity but accompanied by severe volume expansion (typically $>$150–200%), leading to mechanical degradation, poor cycling stability, and unstable SEI formation. For example, FeS_2 can theoretically deliver $\sim$894 mAh g^{-1}, but its capacity drops significantly without structural reinforcement. Additionally, TMCs such as MoS_2 and SnS_2exhibit sluggish kinetics and low initial Coulombic efficiency due to irreversible intermediate phase formation and polysulphide dissolution. To counteract volume effects and poor kinetics, researchers have developed hollow, yolk–shell, and core–shell nanostructures using templates or self-assembly techniques.

A yolk–shell Sn@N-doped C@MoS_2 composite retained 488 mAh g^{-1} at 0.1 A g^{-1} after 300 cycles, benefiting from its internal void space, which accommodated strain and preserved electrical contact.[96] Similar strategies using CoS_2, Ni_3S_2, and VS_4 have demonstrated substantial improvements in both rate capability and cycle retention. Hybridising TMCs with conductive substrates such as graphene, MXenes, and MOF-derived carbon has yielded marked performance enhancements. A VS_4/rGO nanocomposite showed 430 mAh g^{-1} over 500 cycles with $>$95% capacity retention at 1 A g^{-1}. These composites exhibited improved electron transport, buffered volume changes, and suppressed polysulphide migration. Doping with heteroatoms (*e.g.*, N, O, and P) can further enhance the conductivity and Na^+ adsorption.[97]

Recent studies have focused on sulphur/selenium vacancy engineering to enhance the electrochemical activity and pseudocapacitive behaviour. For instance, S-vacancy-rich MoS_2 delivered a capacity of $\sim$520 mAh g^{-1} due to its improved Na^+ diffusion kinetics and increased active site density. Furthermore, phase modulation from 2H (semiconducting) to 1T (metallic) structures in MoS_2 or VS_2 dramatically boosts the conductivity.[98] TMCs often suffer from unstable SEI layers, especially in carbonate-based electrolytes. Designing TMC-based electrodes with fluorinated interfaces or integrating them with fluorine-rich binders results in improved interfacial passivation and excellent electrochemical performance.

Operando TEM and XPS studies show that incorporating F-containing ligands leads to more uniform and thinner SEI layers composed of NaF and organic components, which stabilise Na^+ cycling. In solid-state SIBs, TMCs can serve as flexible, redox-active hosts that are compatible with sulphide or NASICON-type solid electrolytes.[18] An SnS_2-gel composite demonstrated over 350 mAh g^{-1} with excellent rate performance in a solid-state configuration, where the soft gel electrolyte buffered the volume expansion and ensured ionic contact. Furthermore, dual-function composites such as $MoSe_2$@polymer matrices act as both electrode and interface regulators.[99]

Recent reports highlight 3D-printed TMC scaffolds, electrospun nanofibers, and binder-free flexible films for wearable applications. TMC–MXene hybrids with vertically aligned channels delivered $>$90% capacity retention at 5 A g^{-1}, showing their viability for fast-charging SIBs.[100] Mechanochemical and molten salt syntheses are also advancing as scalable, green methods for the production of TMCs. Although TMCs offer compelling electrochemical advantages, the key to their future lies in precise defect control, hierarchical composite engineering, and electrolyte interface optimisation. A deeper mechanistic understanding of sodiation-induced phase transitions, SEI dynamics, and ion transport under solid-state conditions is crucial. Integration of TMCs with multifunctional frameworks and adaptive polymeric binders will be instrumental in realizing durable, high-performance SIBs. TMCs encompassing sulfides, selenides, and tellurides, are among the most promising anode materials due to their high theoretical capacities, metallic/semi-metallic conductivity, and multivalent redox activity. Nevertheless, their application is hindered by their large volume variation during cycling, unstable SEI formation, and sluggish conversion kinetics. Introducing meso/macroporosity and embedding TMCs into conductive carbon matrices have proven effective in buffering their volume expansion and maintaining electrical contact. Porous TMC–carbon composites (*e.g.*, MoS_2/rGO, FeS_2@C, and VS_4/CNFs) offer abundant surface-active sites and short ion-diffusion pathways, resulting in enhanced Na^+ kinetics and improved Coulombic efficiency. Future breakthroughs will likely arise from defect and vacancy engineering, which modulate electronic structures and introduce high-energy Na^+ adsorption sites. Moreover, multi-anion chemistry combining sulfide, selenide, and phosphide species offers new opportunities to tune the reaction potentials and mechanical flexibility. Interface optimisation through fluorine-rich or polymeric coatings has also been shown to stabilise SEI formation and suppress side reactions.

From our perspective, the rational integration of TMCs with porous conductive scaffolds and controlled anion/vacancy design will be pivotal for achieving long-term cycling stability and high coulombic efficiency in next-generation SIB anodes.

2.4.2. MXenes.

MXenes possess layered 2D structures with surface terminations (–O, –OH, and –F), which can be tailored to create ion-accessible channels and abundant active sites. Surface etching and pillaring techniques generate hierarchical porosity, significantly enhancing Na^+ diffusion and their mechanical resilience. Their high electrical conductivity ($>10^3$ S cm^{-1}) makes them ideal conductive backbones for MOF, COF, and TMC hybrids, forming multi-functional architectures with improved energy density and cycling life. MXenes, a family of two-dimensional transition metal carbides, nitrides, and carbonitrides, offer extraordinary electrochemical potential due to their high electrical conductivity, mechanical robustness, and tailorable surface terminations. MXenes such as $Ti_3C_2T_x$ and Nb_2CT_x have been shown to accommodate Na^+ ions both between their layers and *via* surface redox reactions.[101] MXenes, derived from MAX-phase precursors, exhibit interlayer voids, surface terminations (–O, –OH, and –F), and tunable spacing, which collectively enable engineered porosity. Surface etching, pillaring, and chemical intercalation introduce abundant channels and open diffusion pathways, which support their classification as 2D porous frameworks for ion storage.

Although MXenes are primarily known as two-dimensional (2D) layered materials rather than conventional porous frameworks, they can effectively function as porous-like architectures in sodium-ion batteries due to their interlayer spacing, tunable surface terminations, and large specific surface area. The unique $M_{n+1}X_nT_x$ structure (where M = transition metal, X = C/N, and T = surface terminations such as –O, –OH, and –F) forms ion-accessible nanochannels, which facilitate rapid Na^+ diffusion and charge transport. Moreover, chemical etching, intercalation, or heteroatom doping can expand their interlayer gaps, further enhance their pseudo-porous nature and improve their electrolyte wettability. When integrated with other porous matrices such as MOFs, COFs, or carbon frameworks, MXenes act as conductive scaffolds that stabilize the structural integrity and prevent restacking of the electrode. This synergistic design combines the high electrical conductivity of MXenes with the ion diffusion advantages of porous frameworks, leading to improved capacity retention, rate capability, and cycling stability in sodium-ion batteries.[102] For example, Na^+ intercalation in $Ti_3C_2T_x$ MXene delivered capacities of $\sim$300 mAh g^{-1} and ultrafast charge/discharge rates owing to its electronic conductivity $>$10 000 S cm^{-1}. The surface functionalization (–O, –OH, and –F) of MXenes enhances their Na^+ affinity but often leads to hydrophilic swelling and restacking, which limit their performance. Solutions such as interlayer expansion *via* polymer pillaring, COF intercalation, and 3D assembly strategies have improved the their active site accessibility and suppressed their restacking. MXenes also show promise in hybrid frameworks, acting as electron-conducting backbones for MOFs, COFs, and TMCs. For instance, a $Ti_3C_2T_x$/COF hybrid demonstrated a reversible capacity of 350 mAh g^{-1} and improved cycling stability due to its complementary ion and electron transport pathways. MXene–polymer gels and composite solid electrolytes have also emerged as mechanically compliant, ion-conductive materials for solid-state SIB configurations.

2.4.3. Bridging frameworks.

Beyond conventional porous frameworks, several novel material classes have emerged as transformative components in sodium-ion battery (SIB) systems. Although traditional porous materials such as MOFs, COFs, and POPs have dominated the SIB landscape, emerging systems including Prussian blue analogues (PBAs), hydrogen-bonded organic frameworks (HOFs), MOF-derived glasses, and organosulphur-based networks offer unconventional strategies to overcome key limitations in energy density, rate capability, and solid-state compatibility. These materials exhibit distinctive advantages in electrical conductivity, structural flexibility, and sustainable processability, positioning them as next-generation candidates for high-performance and durable sodium-ion batteries.

Prussian blue analogues (PBAs) are another emerging class, especially for SIB cathodes. Their rigid open-cube framework allows fast Na^+ intercalation with minimal volume change, and they are composed of abundant, low-cost metals such as Fe, Mn, and Ni. $Na_2Fe[Fe(CN)_6]$ is the conventional PBA with an operating voltage of $\sim$3.4 V *vs.* Na/Na^+ and capacity of $\sim$140 mAh g^{-1}. However, its low electronic conductivity and water-induced lattice distortion remain concerns. Strategies to improve its stability include controlled dehydration, polymer coating, and composite formation with carbon matrices. Recent efforts have achieved $>$90% retention over 1000 cycles with optimised electrolyte and particle morphology. PBAs feature open-framework Na^+-rich cubic lattices based on transition metal cyanides. $Na_2Fe[Fe(CN)_2]$, the most studied PBA, offers fast diffusion paths and excellent cycling stability. However, its low conductivity and water sensitivity reduce its practical energy density. Strategies including vacancy control, dehydration, and carbon coating have improved its stability. An Fe–Mn PBA@carbon hybrid was reported to achieve 150 mAh g^{-1} and

85% retention over 1000 cycles. Additionally, PBAs are compatible with aqueous electrolytes, paving the way for safer, low-cost large-scale SIBs. Advanced synthetic techniques such as spray-drying and flow synthesis are enhancing their scalability. Prussian blue analogues (PBAs), featuring open cubic frameworks and tunable metal–cyanide coordination, enable rapid and reversible Na^+ intercalation with minimal structural distortion. Their advantages of low cost, aqueous synthesis, and environmental benignity make them particularly attractive for grid-scale sodium storage. Ongoing research is focused on vacancy control, dehydration tuning, and carbon hybridisation to enhance their electronic conductivity and structural stability.

Finally, organic–inorganic hybrids have attracted attention owing to their synergistic properties. These materials combine redox-active organic units (*e.g.*, quinones, Schiff bases, and phthalocyanines) with conductive inorganic phases (*e.g.*, SnS_2 and MoS_2) or porous carbon. COF–MoS_2 composites, for example, exploit Na^+ diffusion through COF channels and the high redox capacity of MoS_2. In another study, a benzoquinone–SnS_2 hybrid delivered a reversible capacity of 320 mAh g^{-1} and improved stability under high current loads. The flexibility of these hybrids makes them ideal for flexible/wearable energy storage applications.

HOFs, self-assembled *via* directional hydrogen bonding, offer lightweight, flexible, and solution-processable structures. Despite their relatively low stability compared to COFs, certain HOFs maintain integrity in organic electrolytes and enable Na^+ diffusion through their functionalized pores. Recent work on HOFs with pyrazole and triazine cores showed reversible capacities of 220–260 mAh g^{-1} with moderate rate performance. Their solution-phase compatibility makes them attractive for printable/flexible electronics.

MOF-derived glasses represent a novel class combining amorphous flexibility with the chemical tunability of MOFs. The short-range ordered networks of these materials facilitate isotropic ion transport and mechanical resilience, resulting in stable cycling even under mechanical deformation. Furthermore, their solvent-free fabrication and recyclability align with sustainable energy principles. MOF glasses, thermally or mechanically amorphised MOFs, combine the porosity of MOFs with the processability and robustness of glasses. They exhibit high mechanical flexibility, isotropic ion transport, and unique non-crystalline coordination environments. A recent ZIF-glass anode demonstrated a capacity of 280 mAh g^{-1} and excellent mechanical tolerance, making it promising for wearable SIBs. The structural adaptability of MOF glasses also makes them ideal for interfacial integration in solid-state batteries. However, further development is needed to balance their conductivity and porosity.

Organosulphur polymers and networks offer high theoretical capacities *via* multielectron sulphur redox reactions. These frameworks, including thiophene-based COFs and sulphur–phenylene polymers, exhibit reversible capacities >400 mAh g^{-1} and strong pseudocapacitive behaviour. A recent study incorporated redox-active S–S motifs into a porous polymer, which retained >300 mAh g^{-1} over 500 cycles. The key challenges include polysulphide dissolution and electronic passivation, which can be mitigated *via* covalent tethering and encapsulation strategies. Collectively, these emerging systems act as bridging frameworks that unify the structural order of MOFs/COFs with the flexibility of amorphous polymers or glasses. Future efforts should focus on synergistic hybridisation among these frameworks of MXene/COF, PBA/MOF glass, or COF/MXene composites to achieve the optimal balance among ion mobility, mechanical robustness, and sustainability.[103] We believe that the future of porous energy materials lies in hybridisation, where structural diversity, hierarchical porosity, and defect-engineering principles are synergistically applied across material systems. By integrating crystalline precision (COFs and MOFs) with conductive and flexible domains (MXenes, PBAs, and glasses), researchers can design multifunctional electrodes that bridge the gap between theoretical potential and real-world application.

MOFs and COFs feature ordered, crystalline pore geometries, whereas POPs exhibit amorphous, interconnected networks with hierarchical porosity. In contrast, TMCs and MXenes derive their porosity from layered nanosheet architectures with engineered voids and expanded interlayer gaps. Despite their structural differences, all these materials share a common functional goal, to create efficient ion diffusion pathways, expose abundant redox-active sites, and enhance interfacial contact with the electrolyte. The combination of micro-, meso-, and macropores ensures balanced kinetics between ion transport and electron conduction.[104] Hence, this unified framework definition encompasses both crystalline and amorphous systems, underlining the versatility of porous frameworks in sustainable sodium-ion energy storage. The integration of emerging materials such as PBAs and organic–inorganic hybrid structures presents a powerful path forward for next-generation SIBs. These systems combine the advantages of high electronic and ionic transport, structural flexibility, and mechanical resilience. However, the fundamental understanding of their electrochemical mechanisms, interface chemistry, and compatibility with full-cell architectures remains unclear. Future research should aim to design multifunctional hybrid electrodes that harness the unique features of these emerging systems, while maintaining processability and scalability for commercial viability. These emerging frameworks exhibit unique advantages including conductivity, flexibility, and redox activity. However, their success depends on understanding their structural evolution under Na^+ cycling, tailoring their interface dynamics, and designing multifunctional hybrids. Future work should leverage *in situ* characterisation and machine learning to guide the rational design of next-generation hybrid frameworks for high-performance and multifunctional SIBs.

3. Comparative analysis of porous framework classes

A rigorous comparison of the performance, synthesis scalability, safety, and material compatibility across porous framework

Table 1 Comparison of the strengths, limitations, challenges, and proposed strategies of different frameworks

Frameworks	Strengths	Limitations	Key challenges	Recommended solutions
MOFs	High porosity, chemical tunability	Poor conductivity, fragile structure	Electronic conductivity	Carbonisation, conductive hybridisation (*e.g.*, graphene and MXene)[106]
COFs	Ordered ion channels, redox-active linkers	Low tap density, limited conductivity	Rate capability and density	π-conjugated units, heteroatom doping, thin-film growth[107]
POPs/POHs	Structural flexibility, scalable synthesis	Low conductivity, amorphous porosity	Na^+ diffusion kinetics	Hybrid systems, hierarchical pore design[108]
TMCs	High capacity, conductive layers	Severe volume changes, poor SEI stability	Mechanical degradation	Yolk–shell structures, conductive matrix integration[109]
MXenes, Prussian blue analogues	Fast ion transport, stable host lattices	Limited chemical diversity	Surface stability and integration	Surface functionalization, hybrid electrode design[110]

classes is indispensable for identifying the most promising candidates for SIBs. Table 1 presents a consolidated overview of MOFs, COFs, POPs, POHs and TMCs, juxtaposing their key electrochemical metrics, major challenges, and recommended material engineering solutions.

Despite the remarkable advancements achieved across diverse frameworks, each material class still faces intrinsic scientific bottlenecks that constrain its translation from laboratory prototypes to real-world sodium-ion batteries (SIBs). Our analysis highlights both the material-specific and cross-cutting issues that define the current performance landscape and outlines rational strategies for overcoming them.

Among them, MOFs offer unparalleled tunability and serve as precursors for highly porous carbonaceous or sulphide-based anodes. However, their poor intrinsic conductivity and mechanical fragility necessitate their transformation into conductive hybrids or derivative materials to realise practical SIB performances. Strategies such as *in situ* carbonisation, hierarchical architecture design, and hybridisation with MXenes or graphene have proven effective in mitigating these issues.[105]

Despite the significant progress achieved with MOF-based electrodes for sodium-ion batteries, several key scientific bottlenecks remain unresolved. Their intrinsic low electrical conductivity and structural instability during repeated Na^+ insertion/extraction still limit their rate capability and long-term cycling performance. Additionally, the large ionic radius of Na^+ often leads to sluggish diffusion kinetics and incomplete ion insertion within confined MOF channels. Comparative studies indicate that framework design, particularly the choice of metal nodes, organic linkers, and degree of porosity, plays a decisive role in governing the charge-storage mechanisms and overall reversibility.[111] To overcome these limitations, future breakthroughs are expected to emerge from multi-dimensional strategies, including defect engineering, heteroatom doping, and formation of conductive MOF-derived hybrids or composites. Introducing hierarchical porosity and optimized electronic pathways can simultaneously enhance the Na^+ transport and charge transfer efficiency. Moreover, *in situ*/*operando* characterization and theoretical simulations should be increasingly integrated to elucidate the sodium storage mechanisms at the atomic level. From a sustainability standpoint, green synthesis routes, scalable processing, and recyclability of precursors will be essential for practical deployment. Overall, integrating structural precision, conductivity enhancement, and eco-efficient fabrication offers a promising roadmap toward next-generation MOF-based sodium-ion storage systems.

COFs provide well-ordered ion channels and functional redox-active moieties, making them ideal for high-capacity, structurally stable electrodes. However, their limited conductivity and low tap densities restrict their rate capability and energy density.[112] Overcoming this requires the incorporation of π-conjugated building blocks, heteroatom doping, and synthesis on conductive substrates to promote charge delocalisation and ion transport. In contrast, POPs and POHs are chemically diverse and synthetically accessible, offering scalable fabrication and mechanical adaptability under cycling stress. However, their amorphous structure limits their Na^+ diffusion efficiency.

Current research is focused on designing hierarchical architectures and hybrid systems to balance structural integrity, conductivity, and ion transport properties. Although COFs exhibit remarkable structural tunability and well-defined ion transport channels, their practical implementation in sodium-ion batteries still faces several critical challenges. Their intrinsic poor electronic conductivity and limited structural flexibility during Na^+ insertion often restrict their rate performance and capacity retention. Moreover, their complex synthesis procedures and limited scalability hinder their widespread adoption. Comparative studies reveal that Na^+ storage in COFs strongly depends on their degree of π-conjugation, heteroatom doping (*e.g.*, N, O, B, and S), and interlayer spacing, which collectively influence their redox activity and ion diffusion. Future progress requires rational molecular design to integrate redox-active building blocks with conductive linkages to enhance their charge transport pathways. Introducing metal nodes or conductive polymer networks into COFs can synergistically improve both their structural stability and electronic conductivity.[108] Furthermore, developing flexible and thin-film COF electrodes may pave the way for high-performance, solid-state Na-ion storage devices. In addition, sustainable synthesis routes, such as solvent-free and microwave-assisted methods, should be pursued to align COF fabrication with environmental goals. The combination of precise structural control, improved conductivity, and green synthesis represents a promising route for achieving durable and efficient COF-based sodium-ion batteries.

Porous organic polymers (POPs) and their hydroxyl-functional analogues (POHs) offer unique advantages such as low density, tunable porosity, and chemical robustness, but they continue to face significant limitations in sodium-ion storage applications. Their amorphous nature often leads to irregular pore distribution and non-uniform ion diffusion, while their limited intrinsic conductivity impedes efficient charge transport. Comparative analysis indicates that the sodium storage performance of POPs/POHs is primarily dictated by the density of redox-active sites, pore connectivity, and heteroatom functionality within the polymer backbone. Thus, to advance this class of materials, future efforts should focus on rational monomer selection to achieve higher redox activity and controlled polymerization strategies to tune their porosity and connectivity.[113] Hybridization with conductive nanostructures (graphene, CNTs, or MXenes) and introduction of hierarchical porosity can enhance both their ion diffusion and electronic pathways.[114] Although POPs and POHs offer scalability, chemical tunability, and low density, they suffer from amorphous porosity, irregular connectivity, and modest electronic transport. We identify their bottleneck as a lack of hierarchical organisation that balances mechanical integrity with ion mobility. From our perspective, the development of redox-active monomers and heteroatom-enriched frameworks can convert these materials into multifunctional, flexible electrodes. Hybrid POP–inorganic systems (*e.g.*, POP–MXene and POP–TMC composites) provide a pragmatic solution by combining the design flexibility of organics with the high conductivity of inorganics. Moreover, designing bio-derived POPs/POHs using renewable precursors aligns well with the sustainability aspect of the current energy storage paradigm. Integrating green synthesis, structural optimization, and multifunctional doping will be essential for unlocking the full potential of POPs/POHs as stable, sustainable, and high-capacity sodium-ion battery electrodes.

Transition metal chalcogenides (TMCs) have emerged as promising anode materials owing to their high theoretical capacities and favourable redox activity, but they are still constrained by their severe volume expansion, structural pulverization, and poor cycling stability during repeated sodiation/desodiation. Mechanistic studies reveal that conversion and alloying reactions in TMCs induce substantial stress, leading to electrode degradation and loss of electrical contact. In addition, slow Na^+ diffusion kinetics and unstable solid electrolyte interphase (SEI) layers remain major performance bottlenecks. TMCs stand out for their high theoretical capacities and fast redox kinetics but suffer severely from volumetric expansion and unstable SEI formation, especially in sulphides and selenide systems. These drawbacks have been partly addressed through nanoscale engineering, yolk–shell architectures, and conductive carbon integration, but their conversion reaction reversibility and safety remain key concerns.[115] TMCs, particularly sulphides and selenides, are well-known for their high theoretical capacities and metallic conductivity, but they undergo large volume expansion ($>200\%$) and suffer from unstable SEI formation during cycling. These problems lead to rapid capacity fading and poor Coulombic efficiency. In our view, the most promising solutions involve hierarchical nanoarchitecture engineering, creating yolk–shell, core–shell, or hollow structures that can buffer mechanical stress and accommodate volume changes.[116]

Additionally, vacancy and phase engineering (*e.g.*, stabilising metallic 1T phases and introducing S/Se vacancies) can enhance their electronic conductivity and Na^+ diffusion kinetics. Hybridisation with conductive carbon or MXene matrices can suppress polysulphide dissolution and improve their interfacial stability. These multi-scale designs represent the next frontier in achieving high-performance, long-life TMC-based anodes. Future breakthroughs are likely to arise from nanostructural engineering, such as hollow or layered architectures, heterointerface modulation, and composite formation with conductive carbon frameworks to buffer mechanical stress and enhance electron transport. The integration of defect-rich surfaces, heteroatom doping, and surface coatings can further stabilize the structure and SEI formation.[117] Coupled with *in situ* characterization techniques and theoretical modeling, a deeper understanding of the sodiation mechanism will accelerate material optimization. From a sustainability perspective, the eco-friendly synthesis of TMCs using mild precursors and scalable methods will be critical for translating lab-scale advances into practical sodium-ion technologies.

A critical distinction emerges between crystalline (MOFs and COFs) and amorphous (POPs and POHs) frameworks in terms of structure–property relationship. Although MOFs and COFs exhibit defined porosity and ordered ion channels, which are advantageous for Na^+ kinetics, their intrinsic electrical resistance poses challenges. In contrast, POPs and POHs, though disordered, offer ease of synthesis, abundant active sites, and tunable flexibility.

TMCs, especially sulphides and selenides, achieve some of the highest reported capacities (often exceeding 500 mAh g^{-1}) but suffer from mechanical degradation due to severe volume expansion.[118] Hybrid frameworks such as MOF-derived CoS_2@C or COF/MoS_2 composites have demonstrated how interfacial synergy can yield performances surpassing that of individual phases. To facilitate rational design and material selection in SIBs, a comparative matrix of porous frameworks is essential.

Building upon the insights gained from conventional porous frameworks such as MOFs, COFs, POPs/POHs, and TMCs, recent research has shifted toward emerging systems that integrate the complementary advantages of these earlier materials, while addressing their intrinsic limitations. Materials such as MXenes, Prussian blue analogues (PBAs), and MOF-derived glasses represent a new generation of sodium-ion battery electrodes that combine high conductivity, open frameworks, and structural adaptability. MXenes, for instance, offer metallic conductivity and tunable surface chemistry that overcome the electronic limitations of COFs and MOFs. PBAs, with their robust open frameworks and facile ion diffusion channels, share structural similarities with MOFs but demonstrate improved cycling stability and environmental friendliness.

Meanwhile, MOF-derived glasses bridge the gap between crystalline precision and amorphous flexibility, offering interconnected pathways for both ion and electron transport.

These emerging materials demonstrate how evolution from ordered frameworks to hybrid and amorphous systems can yield synergistic improvements in electrochemical performance and sustainability. Furthermore, combining MXenes or PBAs with MOFs/COFs in hybrid architectures has shown promising results by leveraging their hierarchical porosity, strong interfacial bonding, and rapid Na^+ kinetics. This convergence of traditional and emerging porous systems signifies a vital step toward integrating structural innovation with environmental sustainability in next-generation sodium-ion battery research.

Across all porous frameworks, three recurring scientific challenges persist, as follows: (i) interfacial ion transport, stabilising the electrode–electrolyte interface to prevent degradation and uncontrolled SEI formation.[119] (ii) Electrode–electrolyte compatibility, ensuring chemical and mechanical coherence, especially in solid-state systems. (iii) Scalable, sustainable synthesis, developing cost-effective, environmentally benign production pathways compatible with industrial standards.[120]

We believe that bridging these gaps through rational design, defect modulation, and sustainable synthesis will be decisive in transforming design from conceptual model systems into deployable, high-performance sodium-ion electrodes. The convergence of materials chemistry, nano-architecture design, and green manufacturing offers a tangible roadmap toward scalable, safe, and sustainable energy storage technologies.

3.1 Advantages of porous frameworks in SIBs

a. High surface area and porosity: MOFs, COFs, and related frameworks offer exceptionally high specific surface areas and well-defined pore structures, which facilitate efficient ion transport and provide abundant active sites for electrochemical reactions.[121]

b. Tunable chemistry and functionalization: the chemical composition and pore environment can be precisely engineered, enabling optimisation for sodium-ion insertion, extraction, and storage.

c. Stability and mechanical properties: COFs, for example, exhibit excellent thermal and mechanical stability, and their regular pore structures help prevent battery short-circuiting and promote uniform current distribution.[122]

d. Suppression of side reactions and dendrite growth: advanced architectures, such as fluorinated versions, can provide superior sodiophilicity (affinity for sodium ions) and minimise unwanted side reactions, leading to dendrite-free sodium deposition and enhanced cycling stability.[123]

3.2 Advanced performance, hybridisation and scalable integration

The evaluation of frameworks for sodium-ion batteries must begin with a comprehensive comparison of their electrochemical performance, including specific capacity, rate capability, and long-term cycling stability. Frameworks such as MOF-derived carbonaceous materials and TMC hybrids consistently demonstrate high specific capacities exceeding 400 mAh g^{-1}, while COFs and POPs often exhibit moderate capacities (250–350 mAh g^{-1}) but superior structural retention across extended cycling.[124] The rate performance of these materials is closely related to their ion/electron transport pathways, with π-conjugated COFs, MXene hybrids, and MOF-derived hollow structures achieving fast kinetics even under high current densities.[125] The energy density–power density trade-off is particularly evident, where high-capacity materials such as TMCs deliver excellent gravimetric energy density but suffer from diminished power density due to their sluggish Na^+ diffusion and volume changes, whereas porous organics with capacitive behaviour offer rapid charge–discharge capabilities but limited storage capacity.[126]

Beyond these baseline metrics, reproducibility and performance consistency across synthesis batches are gaining attention. Crystalline frameworks such as COFs and MOFs offer structural uniformity yet may be sensitive to subtle changes in precursor purity, solvent quality, or thermal processing, impacting their electrochemical reproducibility. Amorphous systems such as POPs, while less crystalline, provide better defect tolerance and process robustness, often yielding more consistent performance in scaled-up syntheses. Furthermore, practical assessments increasingly involve full-cell configurations and lean-electrolyte conditions to validate whether high capacity and rate metrics translate under realistic operating scenarios.[127] Understanding the interplay among framework structure, redox site accessibility, and interface stability is critical for achieving not just a high initial performance, but reliable, scalable electrode behaviour suitable for commercial deployment. The consolidated SIB performances of MOFs/MOF-derived materials, COFs, POPs/POHs, TMCs, MXenes, HOFs, PBAs and representative hybrids are listed clearly in Table 2.

Beyond standard electrochemical metrics and synthesis scalability, several emerging criteria further differentiate porous framework classes in sodium-ion battery systems. A key aspect lies in their underlying sodium storage mechanism. MOFs and TMCs often utilise conversion-type reactions, yielding high capacities but suffering from structural degradation, whereas COFs and POPs favour intercalation or pseudocapacitive behaviour, offering improved rate performance and longevity.[136] Frameworks that exhibit capacitive-dominated kinetics, such as π-conjugated COFs and N-doped MOF-derived carbons, enable rapid charge–discharge operations with enhanced surface reactivity. Composite strategies, including MXene/COF or MOF/rGO hybrids, have shown superior synergistic effects by combining ion diffusion channels with conductive backbones, effectively overcoming the limitations of individual classes.[137]

Sustainability and device integration considerations further shape the viability of these frameworks. Mechanochemical or solvent-free synthesis routes, particularly for COFs and POPs, minimise environmental impact and enable scalable production using green chemistry principles.[138] The ease of

Table 2 Consolidated SIB performances of MOFs/MOF-derived materials, COFs, POPs/POHs, TMCs, MXenes, HOFs, PBAs and representative hybrids

Framework	Materials	Template	Initial DC/CC (mAh g^{-1})	RC/rate (C or mA g^{-1})	Cycle number/retention
MOF-derived carbon	ZIF-8-N-doped porous carbon P@N-MPC	ZIF-8	600 mAh g^{-1}	0.15 A g^{-1}	—[44]
MOF-derived sulphide	$NiCo_2Se_4$@NPC	Bimetallic MOF	462.1 mAh g^{-1}	0.1 A g^{-1}	—[45]
MOF-derived sulphide	Hollow NiCo-MOF-sulphide nanospheres	NiCo-MOF	360 mAh g^{-1}	—	200[128]
MOF–MXene hybrid	3D MXene@Ni-MOF hybrid $NiSe_2$@C@MXene	Ni-MOF	327 mAh g^{-1} after 4000 cycles	10 A g^{-1}	4000 cycles[129]
Conductive MOF	ZIF-67-derived Co–N–C	ZIF-67	380 mAh g^{-1} after 150 cycles	100 mA g^{-1}	500 cycles[49]
COF-pyrene-imidazole based	PyIm-COF	—	250 m Ah g^{-1}	5 A g^{-1}	97.2% retention over 2000 cycles[130]
COF (phenazine)	Phenazine-based COF	—	265	—	500 92% retention[59]
COF@disordered carbon	COF@carbon	—	1000 mA g^{-1}	100 mA g^{-1}	1000 cycles[131]
POP (redox-active)1	Thiophene-based bipyridine polymer	—	260 mAh g^{-1}	0.1 A g^{-1}	93.6% capacity after 2000 cycles at 5 A g^{-1}[132]
N-doped POP	N-doped POP	—	275	0.1 A g^{-1}	500 (stable)[76]
POH (POP–MoS_2)	POP–MoS_2 composite	—	387.9 mAh g^{-1}	10 c rate	Capacity retention of 78% over 200 cycles[69]
POH (POP–MXene)	3D POP–MXene hybrid	—	365	0.05 A g^{-1}	>90% long-term[80]
POH (POM based)	POM-based POH (flexible SSB)	—	300	—	800 (>90% retention)[84]
TMC (Sn@N-doped C@MoS_2)	Yolk–shell Sn@N-doped C@MoS_2	—	488 mAh g^{-1}	0.1 A g^{-1}	300 (85% retention)[90]
TMC (SnO@rGO)	SnO@rGO composite	—	391.9 mAh g^{-1}	100 mA g^{-1}	Capacity retention of 96.2%[91]
TMC (VS_4@rGO)	VS_4/rGO nanocomposite	—	100 mAh g^{-1}	1.6 C	2000 cycles[97]
MXene ($Ti_3C_2T_x$)	$Ti_3C_2T_x$ MXene (pristine)	—	~300 mAh g^{-1}	—	—[101]
PBA (cathode)	$Na_2Fe[Fe(CN)_6]$	—	~140 mAh g^{-1}	—	>90% retention over 1000 cycles[133]
HOF	Pyrazole/triazine-core HOFs	—	220–260 mAh g^{-1}	—	—[134]
MOF glass	ZIF-glass anode	—	280 mAh g^{-1}	—	—[135]

post-synthetic modification through linker exchange, heteroatom doping, or polymer grafting adds another layer of tunability for targeted applications.[139] From a manufacturing standpoint, the compatible of these frameworks with additive techniques such as 3D printing (*e.g.*, MOF-derived porous carbons and POP–CNF hybrids) opens new avenues for constructing high-performance electrodes at the device level.[140]

Safety and electrolyte compatibility remain central to framework design. MOFs and COFs functionalized with fluorinated or sulfonated groups exhibit improved interfacial stability, facilitating the formation of an NaF-rich SEI, which suppresses dendrite growth and enhances the long-term reliability. Thermally stable frameworks such as imine-linked COFs and organophosphorus POPs demonstrate decomposition temperatures exceeding 350 °C, supporting their suitability in high-temperature or abuse-tolerant systems.[141] Furthermore, emerging frameworks such as MOF glasses and HOFs present flexible, self-healing architectures that buffer thermal stress and support uniform sodium flux, which are critical in both solid-state and wearable energy systems. These advanced design features position framework materials as multifunctional, adaptable candidates for next-generation SIBs.

3.3 Sustainability and green pathways in sodium-ion batteries

The transition toward sustainable electrochemical energy storage demands materials and processes that balance high performance with environmental responsibility and economic feasibility. As sodium-ion batteries (SIBs) move closer to large-scale deployment, evaluating sustainability beyond laboratory metrics becomes crucial. Genuine sustainability in this context encompasses energy density, resource availability, toxicity, process scalability, and end-of-life management. These frameworks such as MOFs, COFs, POPs, and TMC-derived hybrids offer an inherently sustainable materials platform due to their structural tunability, compositional diversity, and potential for green synthesis.

3.3.1. Green and scalable synthesis. Modern porous structures can be synthesised using aqueous, ethanol-based, or solvent-free routes, which eliminate the need for hazardous solvents such as DMF and DMSO. Mechanochemical milling, microwave-assisted polymerisation, and room-temperature self-assembly techniques drastically reduce the reaction time, energy consumption, and chemical waste.[142] These synthetic routes align with the principles of green chemistry and promote industrial scalability, while maintaining structural precision.

3.3.2. Use of abundant and non-critical elements. Sodium-ion batteries inherently benefit from the abundance and low cost of sodium, a resource over 1000 times more plentiful than lithium in the Earth's crust. Similarly, these architectures primarily composed of earth-abundant elements such as Fe, C, B, N, and O reduce the dependency on critical metals (*e.g.*, Co and Ni). This elemental sustainability significantly lowers both the material cost and geopolitical risks associated with supply chains.

3.3.3. Non-toxic and environmentally benign constituents. Many organic frameworks (COFs and POPs) utilise biobased or recyclable monomers (*e.g.*, phloroglucinol, lignin derivatives, and imines) and can be processed without heavy metals or halogenated compounds. Moreover, MOF- and TMC-derived materials can be modified to exclude toxic precursors or use benign alternatives (*e.g.*, Fe, Mn, and Zn nodes).[143] The minimisation of hazardous by-products during synthesis and their disposal reduces the overall environmental footprint of SIB components.

3.3.4. Low-temperature and energy-efficient fabrication. Conventional high-temperature treatments (>800 °C) used for carbonisation or chalcogenide conversion can be replaced by low-temperature pyrolysis, photothermal activation, or templated self-assembly approaches. These processes minimise the energy input and preserve the micro-/mesoporous structures crucial for ion transport. Life-cycle energy assessments have shown that lowering the fabrication temperatures by even 200 °C can reduce total carbon emissions by over 30%.

3.3.5. Recycling and circular manufacturing. To achieve circular sustainability, it is vital to design electrode materials that allow easy recovery and reusability of the active components. Porous structures provide this opportunity through their open architectures and modular bonding chemistry, enabling the dissolution, regeneration, or reactivation of spent electrodes. MOF-derived carbons and TMC composites can be directly reprocessed or refunctionalised after cycling.[144] Furthermore, employing binders and electrolytes compatible with water-based recycling facilitates the sustainable recovery of Na-based electrodes, minimising waste and chemical contamination.

3.3.6. Energy density and environmental performance. Although sustainability often emphasises cost and toxicity, energy density is equally critical from a resource-efficiency standpoint. These high-performance frameworks that deliver >350 mAh g^{-1} at stable voltage profiles improve the overall energy-per-resource ratio, thus enhancing energy sustainability.[145] Lightweight organic frameworks (COFs and POPs) also contribute to higher gravimetric energy densities, compensating for the lower cell voltage compared to Li-ion systems.

3.3.7. Integrating sustainability across the design hierarchy. From our perspective, sustainable SIB development requires integrating eco-design principles at every stage from precursor selection and synthesis to cell fabrication and recycling. Combining abundant, low-toxicity elements with energy-efficient synthesis and recyclable electrode architectures embodies the next generation of sustainable battery chemistry.

Collectively, these strategies position materials with a porous nature as holistic green materials capable of fulfilling both performance and sustainability goals. By embedding sustainability metrics such as energy per material cost, life-cycle recyclability, and carbon footprint reduction into the design of porous materials, the sodium-ion battery field can progress toward true environmental and economic viability.

4. Conclusion

The development of high-performance electrode materials for SIBs is a cornerstone in the pursuit of sustainable, scalable, and economically viable energy storage technologies. The design of frameworks has emerged as indispensable in advancing sodium-ion batteries (SIBs), offering unique combinations of high surface area, tunable porosity, and chemical versatility. Across MOFs, COFs, POPs/POHs, TMCs, and emerging systems such as MXenes, PBAs, HOFs, and MOF glasses, remarkable progress has been made in overcoming the challenges of sluggish Na^+ diffusion, large ionic radii, and severe volume fluctuations. Although each class provides distinct strengths ranging from the ordered ion channels of COFs to the high redox activity of TMCs, no single material satisfies all commercial criteria. The path forward clearly lies in rationally engineered hybrid architectures that integrate multiple functionalities, including hierarchical porosity for efficient ion transport, defect/vacancy engineering for enhanced reactivity, conductive networks for rapid charge transfer, and mechanically adaptive scaffolds to buffer volumetric strain. Equally critical are scalable and green synthesis approaches, rigorous *operando* characterisation, and adoption of realistic testing protocols (full cells, high areal loading, and lean electrolytes), which will accelerate translation from academic prototypes to practical devices. Moreover, interface stability with liquid and solid-state electrolytes, chemical safety of high-capacity chemistries, and reproducibility across synthesis batches must be systematically addressed. In essence, the strategic convergence of these materials, defect engineering, interfacial design, and sustainable synthesis provides a powerful roadmap to unlock high-performance, durable, and safe sodium-ion batteries. With continued interdisciplinary innovation, porous framework–based electrodes will not only bridge innovation and sustainability but also establish sodium-ion batteries as a commercially viable, scalable, and environmentally responsible alternative to lithium systems. These materials, when fused with smart defect engineering and green hybrid design, pave the way for sustainable, high-capacity, and industry-ready sodium-ion batteries.

5. Future design strategies and perspective

Achieving commercial-grade sodium-ion batteries requires multifunctional materials that unite resilience, conductivity, stability, and sustainable synthesis. Six key directions chart the way forward, as follows:

1. Hierarchical porosity – designing micropores for storage and meso/macropores for diffusion enables high capacity, fast kinetics, and volume buffering *via* core–shell, yolk–shell, and hollow architectures.

2. Defect/vacancy engineering – introducing controlled defects (*e.g.*, S, O, and N vacancies) boosts the number of active

sites, shortens the Na^+ pathways, and enhances the pseudocapacitive behaviour, while tuning conductivity.

3. Ionic conductivity enhancement – embedding Na^+-conductive domains, polar groups, or polymeric linkers accelerates ion mobility, particularly in solid-state systems.

4. Hybridisation with conductive frameworks – coupling porous hosts with rGO, CNTs, MXenes, or MOF-derived carbons provides synergistic ion/electron pathways, structural buffering, and high-rate capability.

5. Scalable & green synthesis – transitioning to mechanochemical, aqueous, and solvent-free routes with biomass-derived precursors ensures environmental sustainability and industrial viability.

6. Solid-state integration – frameworks must deliver interfacial stability, mechanical compliance, and dendrite suppression to enable next-generation solid-state sodium batteries.

Collectively, these strategies outline a roadmap where hybrid porous materials integrating tunable porosity, defect control, conductive scaffolds, and eco-friendly synthesis will transform SIBs from laboratory promise into sustainable, high-performance energy storage solutions.

Author contributions

Sujatha Dhavamani: conceptualisation, investigation, writing – original draft. Muhammad Waqas Khan: conceptualisation, writing – original draft, review and editing. Babar Shabbir: writing – review and editing. Asif Mahmood: writing – review and editing. Subhendu K. Panda: supervision, writing – review and editing. Nasir Mahmood: conceptualisation, supervision, writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included. The data supporting this feature review article can be found in the respective articles of the journals. The details of permissions acquired for the respective figures have been clearly stated in the article.

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