

π -conjugated structures as advanced anion hosts for dual-ion batteries: Mechanistic insights and optimization strategies

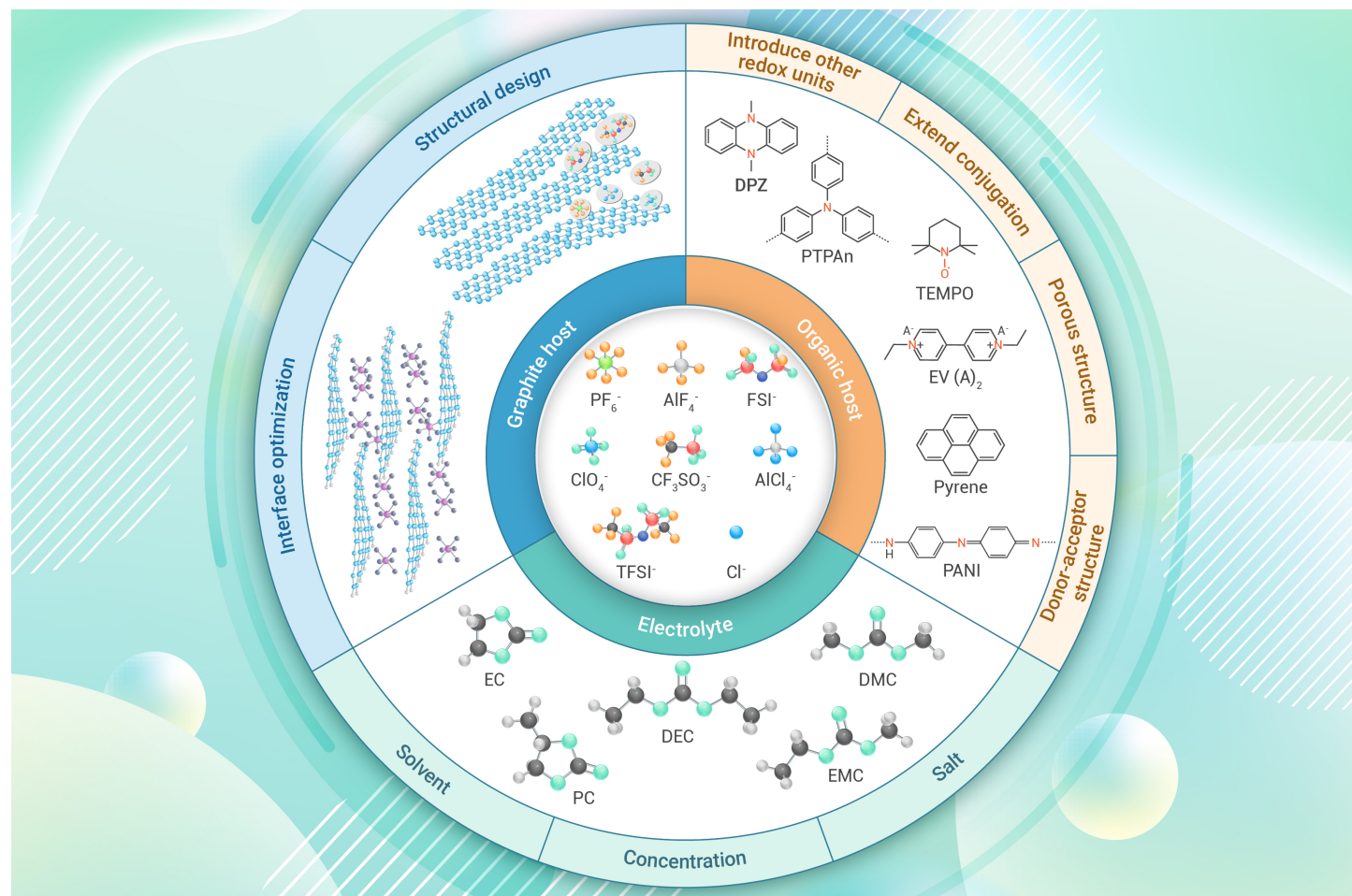
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- The current research status of π -conjugated anion host for dual-ion batteries is introduced.
- Mechanistic insights and optimization strategies of π -conjugated anion-host has been deeply explored.
- Some practical problems have been proposed in order to promote the application of dual-ion batteries.

π -conjugated structures as advanced anion hosts for dual-ion batteries: Mechanistic insights and optimization strategies

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Dual-ion batteries (DIBs) have emerged as a promising energy storage technology due to their cost-effectiveness, environmental friendliness, and potential for high energy and power density. A critical component enabling their performance is the development of efficient anion-hosting cathodes. Among various candidates, π -conjugated structures offer unique advantages, including tunable electronic properties, large π -surfaces for multi-electron transfer, and versatile molecular design. This review comprehensively examines the current progress in π -conjugated materials, like graphite and organic materials, as anion hosts for DIBs, emphasizing the interplay between molecular design and electrochemical performance. We discuss key strategies for enhancing capacity, rate performance, and stability, such as functional group optimization, donor-acceptor architectures, and anion-cation co-storage mechanism. The effects of electrolyte composition, including salt type, concentration, and solvent properties, on anion adsorption and charge transfer processes are critically analyzed. Furthermore, the challenges of achieving high mass loading, improving conductivity, and mitigating side reactions are addressed, alongside innovative approaches such as localized high-concentration electrolytes and interfacial engineering. Lastly, we explore emerging applications of π -conjugated materials in aqueous and low-temperature DIBs, highlighting their potential to expand the operational scope of this technology. The review concludes with perspectives on the future development of π -conjugated anion hosts, including advanced characterization techniques and the integration of computational modeling to unravel fundamental mechanisms. By providing a holistic overview of the design principles and mechanistic insights, this work aims to guide the rational development of high-performance DIBs leveraging π -conjugated materials.

INTRODUCTION

Rechargeable lithium-ion batteries (LIBs) have become indispensable in modern life, powering everything from portable electronics to electric vehicles and grid energy storage systems.^{1,2} Their widespread adoption is owed to their high energy density and excellent cycle stability. However, LIBs face critical challenges, including high costs, resource scarcity, and safety concerns.^{3,4} These limitations are exacerbated by reliance on nickel- and cobalt-based cathodes, which are costly, have limited reserves, and pose environmental challenges during recycling.^{5,6} This underscores the urgent need for alternative, low-cost, and efficient energy storage solutions. Dual-ion batteries (DIBs) have emerged as a promising alternative. Structurally similar to LIBs, DIBs comprise a cathode, anode, electrolyte, and separator (Figure 1). However, their working mechanism is distinct. During charging, electrons are removed from the cathode, causing anions from the electrolyte to intercalate into the cathode as counter-ions. Simultaneously, electrons flow through the external circuit to the anode, where cations deposit. During discharge, this process is reversed, with cations and anions returning to the electrolyte. Thus, both anions and cations actively participate in the redox processes, making them integral components of the electrochemical system. This unique mechanism imparts DIBs with several advantages:

(1) High energy density: Anion intercalation often occurs at higher voltages than cation intercalation, enhancing the energy storage capability.

(2) Improved power density: The concurrent intercalation of anions and cations reduces ion migration distances compared to LIBs, facilitating faster

charge and discharge rates.⁷

(3) Cost and sustainability: DIB cathodes, typically made from graphite or organic materials, avoid the use of expensive noble metals, reducing costs and environmental impact.^{8,9}

(4) Versatility: The anion intercalation mechanism allows DIBs to operate with various cationic electrolytes (e.g., Li^+ , Na^+ , K^+ , Zn^{2+} , Ca^{2+} , and Al^{3+}), enabling the use of diverse, low-cost metal anodes beyond lithium.^{7,10}

These advantages have spurred significant interest in DIBs as a next-generation energy storage solution, characterized by high energy and power densities, cost-effectiveness, and environmental benefits.^{11–14}

Anion host materials are pivotal in determining DIB performance. Structures with large π -conjugated planes are particularly favorable for anion storage due to their unique electronic and structural properties. The extensive delocalization of π -electrons across the conjugated plane creates a high-density negative charge cloud, from where electrons are extracted during oxidation and the anions are adsorbed because of electrostatic force. This facilitates the adsorption or intercalation of anions onto the surface or into the interlayer spaces of the host material. Additionally, large π -conjugated planes exhibit excellent structural stability, allowing them to accommodate significant charge density without substantial deformation or degradation, thereby ensuring long-term cycling performance. Their two-dimensional nature also maximizes the available surface area for anion interactions, contributing to higher storage capacities. Furthermore, the planar structure reduces diffusion barriers for anions, enabling fast and efficient charge transfer processes. These characteristics collectively make π -conjugated materials an ideal platform for developing high-performance anion hosts in dual-ion batteries. Among these, graphite and π -conjugated organic materials have garnered attention for their noble-metal-free composition, low cost, and eco-friendly nature. Graphite, with its long-range ordered structure and appropriate interlayer spacing, enables anion intercalation. In contrast, π -conjugated organic materials offer flexibility and larger internal spaces, favoring surface adsorption of anions. These differences reflect two distinct storage mechanisms: a battery-like intercalation process for high energy density and a capacitor-like adsorption process for high power density.

In this review, we summarize recent advances in the design and modification of anion host materials for dual-ion batteries including graphite and π -conjugated organic materials. For graphite, strategies such as structural optimization, interface engineering, and electrolyte modification address challenges like volume expansion and side reactions at ultra-high voltages. For organic materials, the focus lies on leveraging their structural tunability to develop novel architectures.^{15–20} Additionally, we highlight emerging applications, such as low-temperature DIBs, aiming to inspire the next generation of high-performance dual-ion batteries.

GRAPHITE ANION HOST

Graphite is widely employed as a cathode material in DIBs due to its abundance, low cost, and high working voltage.²¹ Structurally, graphite features a well-ordered, three-dimensional crystalline architecture comprising stacked layers of sp^2 -hybridized graphene sheets held together by weak van der Waals forces.²² This layered configuration provides a uniform interlayer spacing of 3.35 Å (Figure 2A), enabling the accommodation of large anions (Figure 2B).²³ The delocalized π -electrons within the graphene planes grant graphite excellent in-plane electronic conductivity, which supports the rapid transfer of

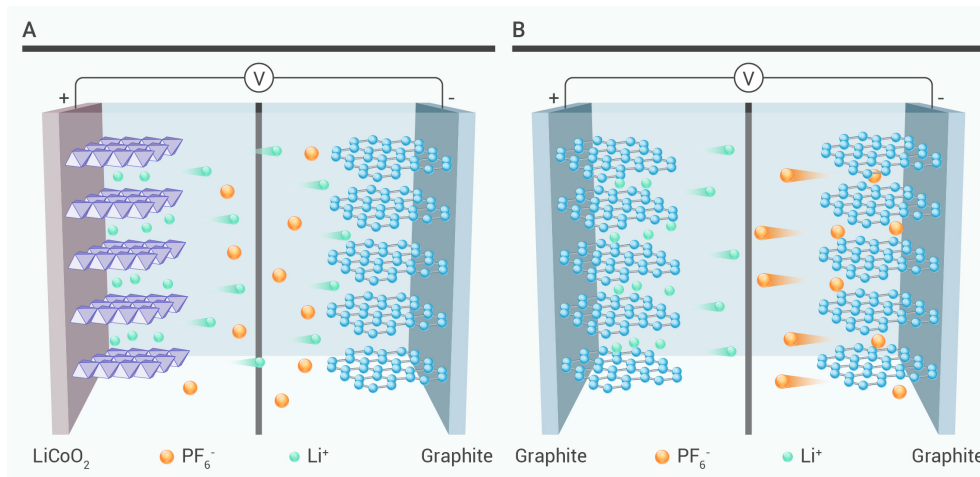


Figure 1. Schematic diagram of the working mechanism of (A) lithium-ion batteries and (B) dual-ion batteries.

lation capacity.²⁷ However, this simplified model does not fully account for the flexibility of graphene layers.²⁸ In response, Daumas and Herold proposed a refined model in which ions can simultaneously intercalate between multiple graphene layers, deforming the surrounding graphene sheets to better accommodate the anions (Figure 2C).^{29,30}

The efficiency of anion intercalation in graphite depends on both the anion type and its solvation structure. During charging, anions must first be desolvated, shedding their

surrounding solvent molecules, before intercalating into the graphite layers. This process needs to overcome the van der Waals forces between graphene sheets.²⁶ Two key energetic factors influence the intercalation process: the desolvation energy, which decreases with increasing anion size, and the intercalation energy, which increases with anion size. Balancing these competing factors is crucial for optimizing graphite cathode performance, as selecting appropriately sized anions can enhance intercalation voltage and overall energy storage efficiency.³¹ These structural and electrochemical characteristics establish graphite as a reliable and versatile anion host in DIBs, paving the way for high-performance energy storage solutions.

As cation-intercalated graphite, the type of anion in DIBs is directly related to the theoretical specific capacity, voltage, and rate performance of anion-

intercalated graphite. However, large size anion embedding may result in structural deterioration of graphite (Figure 2B). The mechanism of anion intercalation in graphite was first described in 1940 by Rüdorff and Hofmann, who proposed that anions intercalate into graphite layers to form ionic graphite intercalation compounds (GICs) via a staging process.²⁶ In this model, anion insertion occurs between graphene layers without significant structural distortion, with the staging number reflecting the number of graphite layers separating intercalated anion layers. A higher staging number corresponds to lower interca-

lation capacity.²⁷ However, this simplified model does not fully account for the flexibility of graphene layers.²⁸ In response, Daumas and Herold proposed a refined model in which ions can simultaneously intercalate between multiple graphene layers, deforming the surrounding graphene sheets to better accommodate the anions (Figure 2C).^{29,30}

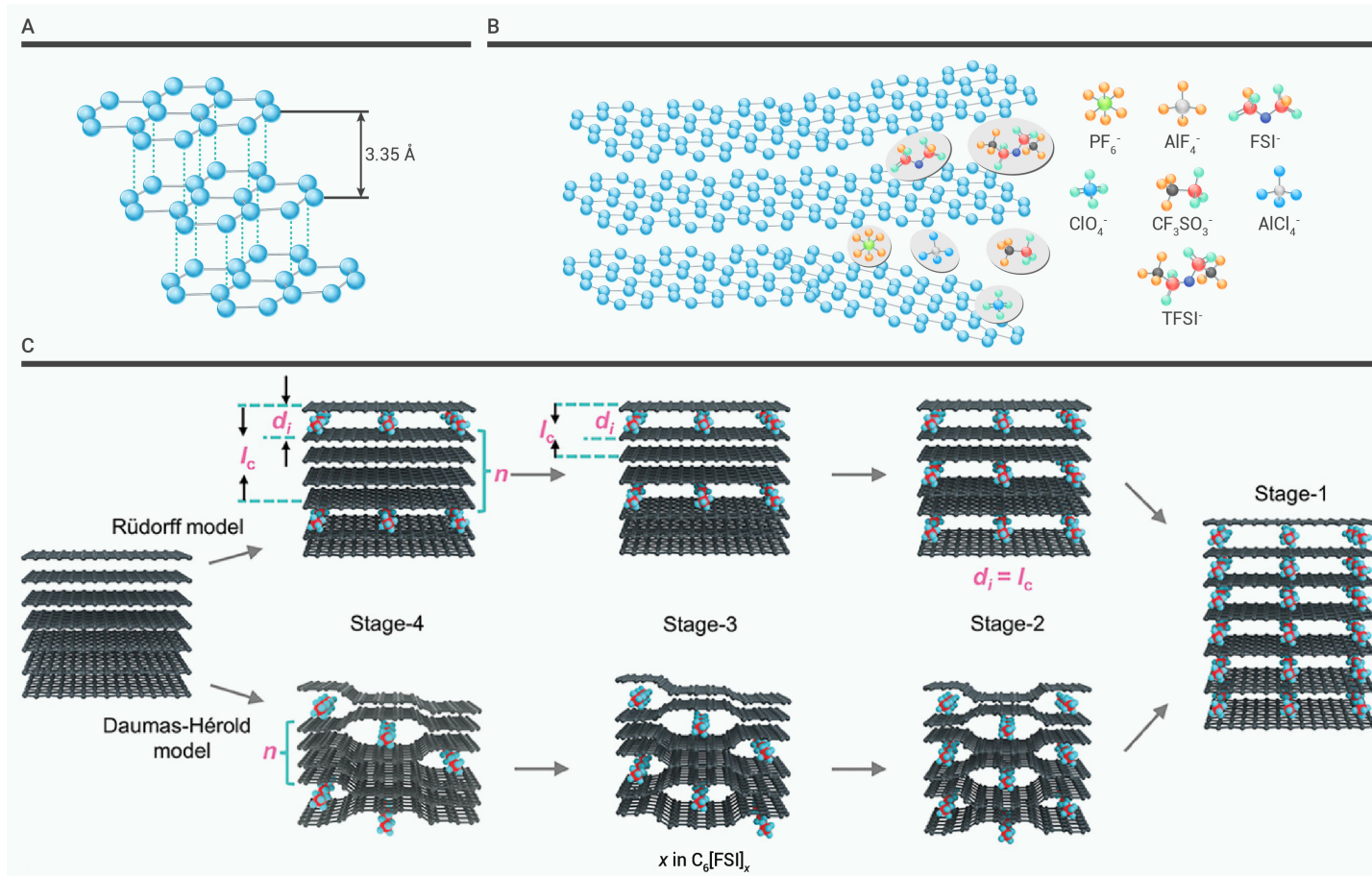


Figure 2. Graphite structure and staging mechanism (A) Typical structures of graphite. (B) Schematic of cation intercalation into graphite structure, where the intercalation of large-sized anions leads to graphite structural deterioration. (C) Schematic illustration of the staging mechanism described by Rüdorff and Daumas-Herold models for anion intercalation into a graphite cathode. Reproduced with permission.³¹ Copyright 2023, Wiley-VCH.

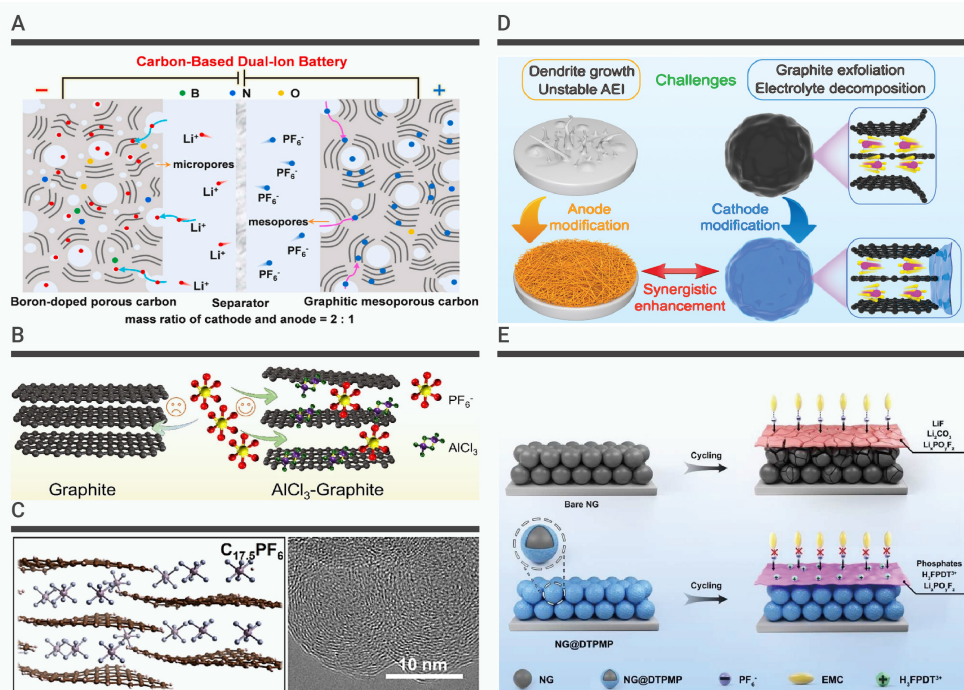


Figure 3. Graphite optimization strategies (A) Diagram of ion transport mechanisms in micropores and mesopores of carbon-based dual-ion battery. Reproduced with permission.⁴⁷ Copyright 2022, Elsevier. (B) The structure and PF_6^- intercalation process of graphite and AlCl_3 -graphite. Reproduced with permission.⁵⁹ Copyright 2023, Elsevier. (C) Schematic for anion storage mechanism in LOGC with its HRTEM image. Reproduced with permission.⁶¹ Copyright 2021, Wiley-VCH. (D) The modification process of Al_2O_3 -coated graphite cathode. (E) The optimization mechanism of DTPMP on the surface of graphite. Reproduced with permission.⁷³ Copyright 2022, Wiley-VCH.

These approaches provide a foundation for improving the capacity, rate capability, and longevity of graphite cathodes, ensuring their viability in high-performance dual-ion batteries.

Structural design of graphite for anion hosting

The structural attributes of graphite, including particle size, morphology, interlayer spacing, and composite design, significantly influence its performance as an anion host in DIBs.^{40–44} These parameters govern key properties

intercalated graphite cathodes.³² The number of anions that can be intercalated in the graphite interlayers directly determines the theoretical specific capacity of the graphite cathode. Taking the widely studied anion PF_6^- as an example, Read investigated through theoretical and experimental studies that the GIC formed by PF_6^- completely embedded in graphite layers is C_{20}PF_6 , which corresponds to the theoretical specific capacity of about 112 mAh/g and the volume expansion rate of about 130%.³³ Moreover, bis(trifluoromethanesulfonyl)imide (TFSI)-based electrolytes with better chemical stability and lower sensitivity to hydrolysis than PF_6^- have also been widely used in DIBs.²³ Balabajew *et al.* found that the GIC of TFSI completely intercalated graphite at 20°C was about $\text{C}_{26}(\text{TFSI})$ (corresponding to 86 mAh g⁻¹), and at 60°C about $\text{C}_{20}(\text{TFSI})$ (corresponding to 112 mAh g⁻¹). This indicates that the theoretical capacity of anion-intercalated graphite is temperature dependent.³⁴ Considering the severe volume expansion associated with large-sized anion-intercalated graphite, smaller halide anions such as Cl^- , Br^- and I^- have also been developed as anion charge carriers. These anions tend to be easier to insert into graphite cathodes due to their small size, resulting in a higher theoretical specific capacity.³⁵ Gao *et al.* even achieved an intercalation capacity of 605.7 mAh g⁻¹ for the anions in graphite by using concentrated $\text{ZnCl}_2/\text{ZnBr}_2/\text{Zn}(\text{OAc})_2$ solutions.³⁶ However, despite the smaller sized halide anions provide a higher theoretical capacity, their coulombic efficiency (CE), operating voltage, and cycle life are unsatisfactory. There are many other anions (e.g. ClO_4^- and BF_4^-) that have been extensively studied and the actual discharge capacity of graphite cathodes is also related to the type of solvent, the concentration of electrolyte and the voltage window, which are discussed in detail in the Electrolyte Optimization section.

The anion intercalation mechanism enables the graphite cathode to achieve exceptionally high operating voltages (3.0–5.3 V vs. Li^+/Li).³⁷ However, this advantage is offset by several challenges. The insertion of large-sized anions causes significant volume expansion, leading to poor cycling stability. Additionally, the size mismatch between the anions and the graphite's interlayer spacing impedes ion diffusion, resulting in sluggish kinetics. This limitation adversely affects both capacity (<100 mAh g⁻¹) and rate performance (~2 A g⁻¹).^{38,39} To overcome these challenges and optimize the performance of graphite cathodes, two key strategies have been proposed:

(1) Structural Optimization: Adjusting the degree of graphitization and tuning the interlayer spacing to better accommodate large anions, thereby mitigating volume expansion and enhancing ion diffusion.

(2) Protective Layer Construction: Developing artificial cathode electrolyte interphase (CEI) layers to stabilize the graphite structure, suppress side reactions, and improve cycling stability.

ties such as capacity, rate performance, and cycling stability.

Particle size and morphology. Reducing the particle size and increasing the specific surface area of graphite have been shown to enhance both capacity and rate performance.⁸ Smaller particles shorten ion diffusion pathways, while higher surface area increases the availability of electrochemical active sites. Incorporating microporous structures further enhances performance by promoting charge accumulation within confined nanopores, which facilitates the adsorption of large anions.^{45,46} For example, Wang *et al.* synthesized a 3D multimodal carbonaceous micro-nanocomposite through nitrogen and sulfur co-doping. The interconnected mesoporous and macroporous structure enabled a reversible specific capacity of 172.1 mAh g⁻¹ at a current density of 0.05 A g⁻¹.⁴⁴ Similarly, Li *et al.* demonstrated that a mesoporous graphite cathode exhibited excellent rate performance, retaining 78% of its capacity at a high current density of 5 A g⁻¹ (Figure 3A).⁴⁷

Interlayer spacing. The interlayer spacing of graphite is a critical parameter affecting anion intercalation kinetics and capacity.⁴⁸ Since most anions (e.g., PF_6^- , 4.36 Å; TFSI⁻, 3.9 Å) are larger than the typical 3.35 Å spacing of graphite, slow diffusion and significant volume expansion often degrade performance.^{49–51} Expanding the interlayer spacing promotes faster ion diffusion and provides more active sites for electrochemical reactions.²³ This can be achieved through: (1) Heteroatom doping (e.g., oxygen, nitrogen, fluorine) introduces functional groups that increase layer spacing.^{52–56} For instance, N-doped graphite synthesized by Chen *et al.* exhibited expanded interlayer spacing (0.39–0.51 nm), achieving a high specific capacity of 240 mAh g⁻¹ at 0.1 A g⁻¹.⁵⁷ (2) Inserting ions or molecules between graphite layers can further enhance spacing and stability. Zheng *et al.* demonstrated that pre-inserting Li^+ ions expanded the interlayer spacing to 3.67 Å, significantly improving the cathode's performance under high currents.⁵⁸ Similarly, AlCl_3 pre-intercalation not only expanded the spacing to 3.52 Å but also acted as a structural stabilizer, enabling a high specific capacity of 100.8 mAh g⁻¹ with PF_6^- anions (Figure 3B).⁵⁹

Graphite-disordered carbon composites. Blending graphite with disordered carbon in optimized proportions enhances capacity, rate capability, and cycling stability. Disordered carbon provides fast anion adsorption kinetics and additional storage sites while mitigating anion repulsion within graphite layers. It also alleviates the volume expansion associated with intercalation, improving stability.^{35,60–64} Mechanical mixing is a straightforward method for creating such composites. For example, Martha *et al.* achieved improved performance in lithium-based DIBs by mixing graphite and disordered carbon in a 3:1 ratio.⁶⁰ However, localized graphitization of disordered carbon can further enhance interfacial compatibility. Tang *et al.* compared various carbon

materials as cathodes for potassium-based DIBs, demonstrating that locally ordered graphitized carbon (ketjen black) significantly outperformed both fully ordered graphite and fully disordered activated carbon, achieving a specific capacity of 232 mAh g⁻¹ at 50 mA g⁻¹ (Figure 3C).⁶¹ Additionally, porous microcrystalline carbon designed by Tang *et al.* for sodium-based DIBs exhibited enhanced capacity due to the increased specific surface area provided by its porous structure.⁶⁴

By tailoring the structural characteristics of graphite, including particle morphology, interlayer spacing, and composite configurations, researchers can address the limitations of graphite as an anion host, enabling its broader application in high-performance DIBs. These strategies collectively improve capacity, rate performance, and cycling stability, paving the way for the next generation of energy storage materials.

Interface design

In addition to structural optimization, constructing artificial protective layers on graphite surfaces has emerged as an effective strategy to enhance the performance of graphite cathodes.^{65–70} During the initial charge/discharge cycle, an in-situ cathode/electrolyte interface layer forms naturally on the graphite surface. While this layer improves cathode stability, it also reduces the first-cycle coulombic efficiency. Artificial CEI layers, which mimic the in-situ formation mechanism, offer controllable thickness and superior electrochemical properties compared to their naturally formed counterparts.⁴⁰

Inorganic coatings. Inorganic materials, such as Al₂O₃, are commonly used to coat graphite cathodes due to their rigidity and chemical inertness.^{71,72} These coatings suppress the deposition of electrolyte decomposition products, contributing to improved cycling stability. For example, DIBs with Al₂O₃-coated graphite cathodes demonstrate ultra-long cycle life over a broad temperature range (–25 to 40°C), highlighting the robust nature of this approach (Figure 3D).⁶⁹ However, the poor electrical conductivity of Al₂O₃ can limit its performance under high-power conditions. Moreover, these inorganic coatings tend to be attached to the graphite surface as discrete microcrystals. The limited interaction forces between the metal oxide particles and their ease of detachment from the graphite surface mean that they do not provide comprehensive and effective protection for the graphite cathode.

Organic coatings. Organic coatings, in contrast, are flexible and exhibit strong affinity for graphite surfaces. Zheng *et al.* developed a method to implant unsaturated organic sulfonates onto graphite particles through a cost-effective and environmentally friendly process. The sulfonate coating, stabilized by π - π interactions with the graphite layers, effectively prevents electrolyte decomposition and structural degradation. This significantly reduces interfacial resistance and enhances the cycling stability of DIBs.⁶⁵ Organic coating can also promote the desolvation of the anion. Zhang *et al.* implanted diethylenetriaminepenta (DTPMP) on the surface of natural graphite particles by in situ electrochemical reaction, and the resulting interfacial phase not only improved the antioxidant stability of the electrolyte, but also facilitated the desolvation of the PF₆⁻ anion because of the strong ion-ion interaction between PF₆⁻ and H₃FPDT³⁺, which led to the improvement of the fast-charging and ultralong-cycling performances of the graphite cathodes in dual-ion batteries (Figure 3E).⁷³

In general, stabilized and uniform CEI can significantly improve energy density, coulombic efficiency and rate performance. A well-developed CEI need to have high ionic conductivity, low electronic conductivity, resistance to mechanical and chemical changes, and suitable thickness. For CEI formed in situ, it tends to have self-healing properties.⁷⁴ However, in high-pressure DIB systems, spontaneously formed CEIs tend to be inhomogeneous and unstable. Artificial CEI is superior to the original CEI layer in terms of mechanical stability. It can effectively mitigate the repetitive rupture and reconstruction of CEI caused by volume expansion during anion insertion/withdrawal, thereby improving battery performance. Although artificial CEI layers effectively improve the cycling stability of graphite cathodes, their fabrication often requires sophisticated techniques. Simplifying the preparation process without compromising performance is essential for the broader application of interface design in DIBs. Further research should focus on scalable and cost-efficient methods to construct high-performance artificial CEI layers, enabling the development of next-generation energy storage systems.

Electrolyte optimization strategy

The electrolyte in DIBs must meet several critical requirements to ensure optimal performance. It should possess a wide electrochemical stability window to support high-voltage operation while being chemically compatible with both electrodes to prevent side reactions. High ionic conductivity and selective anion transport are essential for efficient redox processes, with small, mobile anions often providing better reversibility and faster kinetics. High-concentration electrolytes (HCEs) and localized high-concentration electrolytes (LHCEs) can suppress side reactions and improve stability, though their viscosity must be managed to maintain ion mobility. Additionally, the electrolyte impacts voltage and capacity through desolvation processes, ion pairing, and charge transfer dynamics, necessitating careful optimization of solvent and salt combinations. It should also function effectively across a broad temperature range, with low viscosity and favorable desolvation-free processes for low-temperature applications. Finally, environmental sustainability, low toxicity, and cost-effectiveness are crucial for scalability and practical use.

In DIBs, the electrolyte plays a dual role: facilitating ion transport and serving as a reservoir for anion and cation carriers.^{75,76} The electrolyte's composition and properties directly influence the anion storage capacity of graphite cathodes, which depends on the size, structure, and electrochemical stability of the anions. Various anions, including PF₆⁻, ClO₄⁻, BF₄⁻, FSI⁻, TFSI⁻, NO₃⁻, AlCl₄⁻, [ZnCl₄]²⁻, have been demonstrated to intercalate reversibly into graphite.^{33,77–80} Smaller anions generally exhibit lower intercalation potentials and higher theoretical capacities due to easier accommodation in the graphite lattice. For instance, BF₄⁻ (ionic radius: 0.229 nm) typically offers better capacity than PF₆⁻ (ionic radius: 0.254 nm).⁸¹ However, exceptions arise when solvation effects significantly alter intercalation behavior.⁸²

Solvent optimization. The solvent is a critical component of the electrolyte, as its interaction with anions shapes the solvation structure, influencing desolvation energy and intercalation dynamics. An ideal solvent should provide high ionic conductivity, a broad electrochemical stability window, low toxicity, low viscosity, excellent thermal stability, and the ability to form stable cathode electrolyte interphases (CEIs).^{23,83}

Organic electrolytes dominate DIB research due to their high dielectric constants and robust electrochemical stability. Carbonate-based solvents, including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC), are widely used (Figure 4A).^{84–86,87} The choice of solvent often depends on the anion's binding characteristics and solvation preferences. For instance, EMC works well with PF₆⁻,⁸⁸ whereas PC solvents with high receptor numbers are more suitable for ClO₄⁻ and BF₄⁻.^{89,90} Cyclic carbonates offer superior ionic conductivity and foster stable CEI formation but suffer from high viscosity. Chain carbonates, by contrast, provide lower viscosity and excellent electrochemical stability. Practical applications often involve mixing cyclic and chain carbonates to balance these properties.

The high operating voltages of graphite cathodes pose challenges to electrolyte stability, as oxidation and decomposition become significant concerns. Sulfone-based solvents, known for their high oxidative resistance, are promising candidates for high-voltage applications. For example, a mixture of ethyl methyl sulfone (EMS) and sulfolane (SL) combined with LiBF₄ as a solute enables stable operation up to 5.5 V, delivering a reversible capacity of 90 mAh g⁻¹.⁹¹ However, the high viscosity and strong anion affinity of sulfone solvents necessitate their combination with carbonates to improve capacity and rate performance.^{92–94} Due to their low viscosity and high ionic conductivity, Ether-based solvents have also been investigated in DIBs. Xia *et al.* used ether-based electrolytes to construct Na-DIB combining cationic solvent co-embedding and anionic storage chemistry. This approach essentially eliminated the slow desolvation process in Na-DIB, allowing for fast kinetics of 10 A g⁻¹ and ultra-low temperature of –70 °C.⁹⁵ However, dilute ether-based electrolytes have poor oxidation resistance and are difficult to withstand high-voltage anodes above 4.0 V. Lu *et al.* proposed a co-solvent electrolyte design strategy to overcome the high-voltage limitations of the electrolyte chemistry in K-DIB. This approach significantly enlarges the anion-rich solvated clusters and helps to form an effective electrode-electrolyte interface, thus enhancing compatibility with high-voltage electrodes.⁹⁶ Furthermore, the use of high-concentration electrolytes, gel polymer electrolyte, and

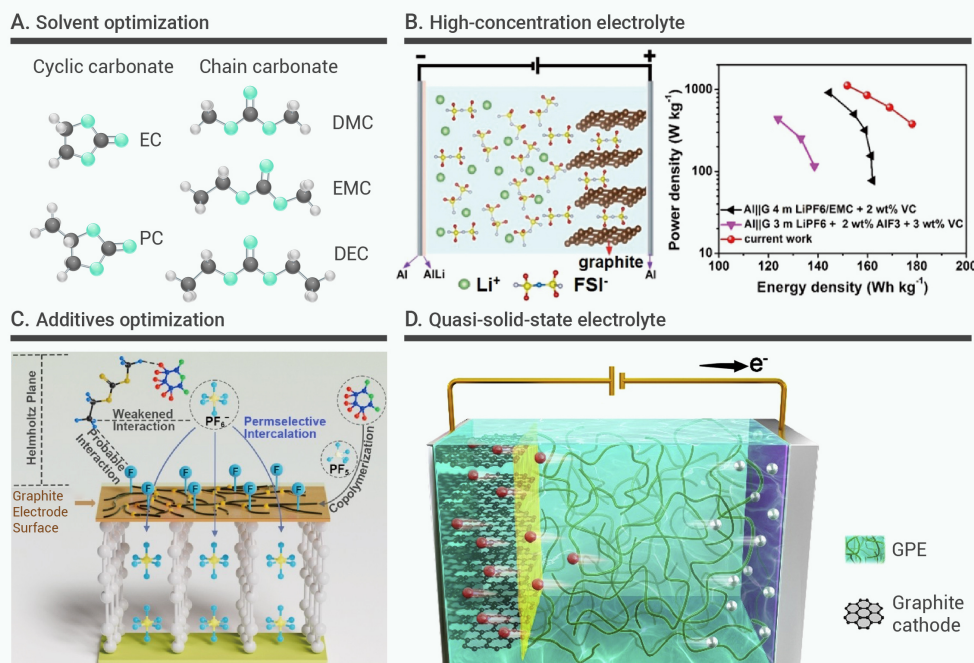


Figure 4. Electrolyte optimization strategies (A) The structures of carbonate electrolytes used in common DIBs. (B) The application of localized highly concentrated electrolyte (LHCE) in DIBs. Reproduced with permission.¹⁰⁷ Copyright 2020, Wiley-VCH. (C) The anionic solvation structure within the Helmholtz plane optimized by HFGA. Reproduced with permission.¹²⁹ Copyright 2024, Wiley-VCH. (D) Schematic illustration of the DIBs using GPE. Reproduced with permission.¹³⁵ Copyright 2020, Elsevier.

chlorinated or fluorinated ether-based electrolytes can also be an effective solution to this problem.^{97,98}

Fluorinated solvents are gaining traction for their oxidative stability and their ability to facilitate the formation of fluorinated CEIs. For instance, methyl 2,2,2-trifluoroethyl carbonate drives the formation of a beneficial secondary CEI, enhancing cycling stability and suppressing self-discharge.⁹⁹ By optimizing solvent selection and composition, researchers can significantly enhance the performance, stability, and efficiency of DIBs, paving the way for more robust and versatile energy storage systems.

High-concentration electrolytes. High-concentration electrolytes (HCEs) have emerged as a compelling strategy to enhance the stability and electrochemical performance of DIBs.^{100–109} By significantly reducing the proportion of solvent molecules, HCEs decrease the solvation number of anions, leading to lower desolvation energy and intercalation potential. This reduction also minimizes the co-intercalation of solvent molecules, thereby improving Coulombic efficiency and cycling stability. Additionally, the elevated ion concentration inherent in HCEs boosts anion availability, enhancing intercalation capacity as predicted by the Nernst equation.^{110,111} The effectiveness of HCEs has been demonstrated across various DIB systems. For example, Kovalenko *et al.* employed a 5 M potassium bis(fluorosulfonyl)imide in alkyl carbonate electrolyte to construct a lithium-free graphite DIB, achieving an energy density of 207 Wh kg^{−1} with an average discharge voltage of 4.7 V.¹⁰⁹ Tang *et al.* developed a graphite/aluminum DIB using a 7.5 M LiFSI/EC-DMC electrolyte, which exhibited an ultra-high energy density of 180 Wh kg^{−1} (Figure 4B).¹⁰⁷ HCEs have also advanced aqueous DIBs, where low operating potentials have traditionally been a barrier. For instance, Cervenka *et al.* applied a highly concentrated Zn(ClO₄)₂ electrolyte in a Zn-graphite DIB. This “water-in-salt” approach expanded the electrochemical window to 2.80 V and achieved a mean discharge voltage of 1.95 V.¹⁰³

Despite these successes, HCEs face significant challenges. Their high salt concentration increases costs, complicating large-scale applications. Moreover, elevated viscosity and reduced interfacial compatibility led to poor rate performance. Localized high-concentration electrolytes (LHCEs) offer a promising alternative. With the addition of the inert diluent, LHCEs combine the advantages of low cost and moderate ionic conductivity of dilute electrolytes while retaining the favorable solvation structure found in highly concentrated electrolytes.^{112,113} Unlike conventional HCEs, the solvation structure of the electrolyte, rather than salt concentration alone, governs anion intercalation behavior.¹⁰⁰

LHCEs show great promise in low-temperature DIB applications, where electrolyte viscosity and interfacial compatibility become critical.¹¹⁴ At low temperatures, traditional electrolytes face significant kinetic and stability

challenges due to reduced ionic mobility and interfacial degradation.^{114–120} LHCEs address these issues by retaining favorable solvation structures while lowering the viscosity. For instance, Tang *et al.* developed a unique variant of LHCE (v-LHCE) by introducing a weak-solvating solvent with low energy levels, enabling phase stability. A DIB constructed with this v-LHCE demonstrated capacity retention of 51.6% at −60°C, highlighting its potential for extreme temperature applications.¹¹⁵ While LHCE research has primarily focused on the solvation structure of cations, understanding anion solvation remains an

underexplored yet crucial area for advancing DIB performance.^{121–123}

Continued investigation into tailored solvation environments for anions may further unlock the potential of LHCEs in diverse operational contexts.

Additive optimization. Additives are widely used in DIB electrolytes as an effective strategy for improving performance and modifying electrolyte properties.¹²⁴ Among these, fluorinated additives are the most common, as their mechanisms align closely with those of fluorinated solvents. These additives enhance the cycling stability of DIBs by facilitating the formation of robust cathode-electrolyte interfaces (CEIs) on graphite cathodes.^{125–128} Fluorinated ethylene carbonate (FEC) is a notable example. Chou *et al.* demonstrated that adding FEC to the electrolyte of Na-based DIBs significantly improved cycling stability. The preferential decomposition of FEC led to the formation of a NaF-rich interface, which suppressed side reactions and mitigated cathode pulverization during electrochemical cycling.¹²⁷

In addition to stabilizing CEIs, additives can modify the solvation structure of anions and cations in the electrolyte. Cui *et al.* introduced hexafluoroglutaric anhydride (HFGA) as an additive based on a Helmholtz plane modulation strategy. HFGA's strong H–F affinity with ethyl methyl carbonate (EMC) optimized the anionic solvation structure within the Helmholtz plane. This reduced EMC-related co-intercalation and oxidative decomposition during charging, significantly enhancing the performance of DIBs (Figure 4C). Furthermore, HFGA promoted the formation of a stable CEI on the graphite cathode, enabling high-voltage operation of up to 5.5 V with improved electrochemical reversibility.¹²⁹ The concentration of additives plays a crucial role in determining the performance of DIBs. Insufficient additive levels fail to deliver the desired benefits, while excessive amounts can reduce overall Coulombic efficiency.¹³⁰ Striking an optimal balance in additive concentration is therefore essential for achieving the best performance outcomes.

While fluorinated and functional additives have demonstrated substantial potential, future research should aim at designing multifunctional additives that not only promote robust CEI formation but also optimize solvation structures. Such advances could unlock improvements in voltage ranges, cycle stability, and energy densities, thereby addressing key challenges in the development of high-performance DIBs.

Quasi-solid-state electrolyte. The development of quasi-solid-state electrolytes (QSSEs) offers a promising pathway to enhance the performance of DIBs, particularly in terms of electrochemical stability at high voltages.^{131–135} QSSEs integrate the benefits of both liquid and solid electrolytes, combining high ionic conductivity with robust solid-liquid interfacial properties and excellent mechanical flexibility. For instance, Wang *et al.* designed a multifunctional gel polymer electrolyte for sodium-based DIBs by in situ polymerizing ethoxylated pentaerythritol tetraacrylate monomers in an optimized

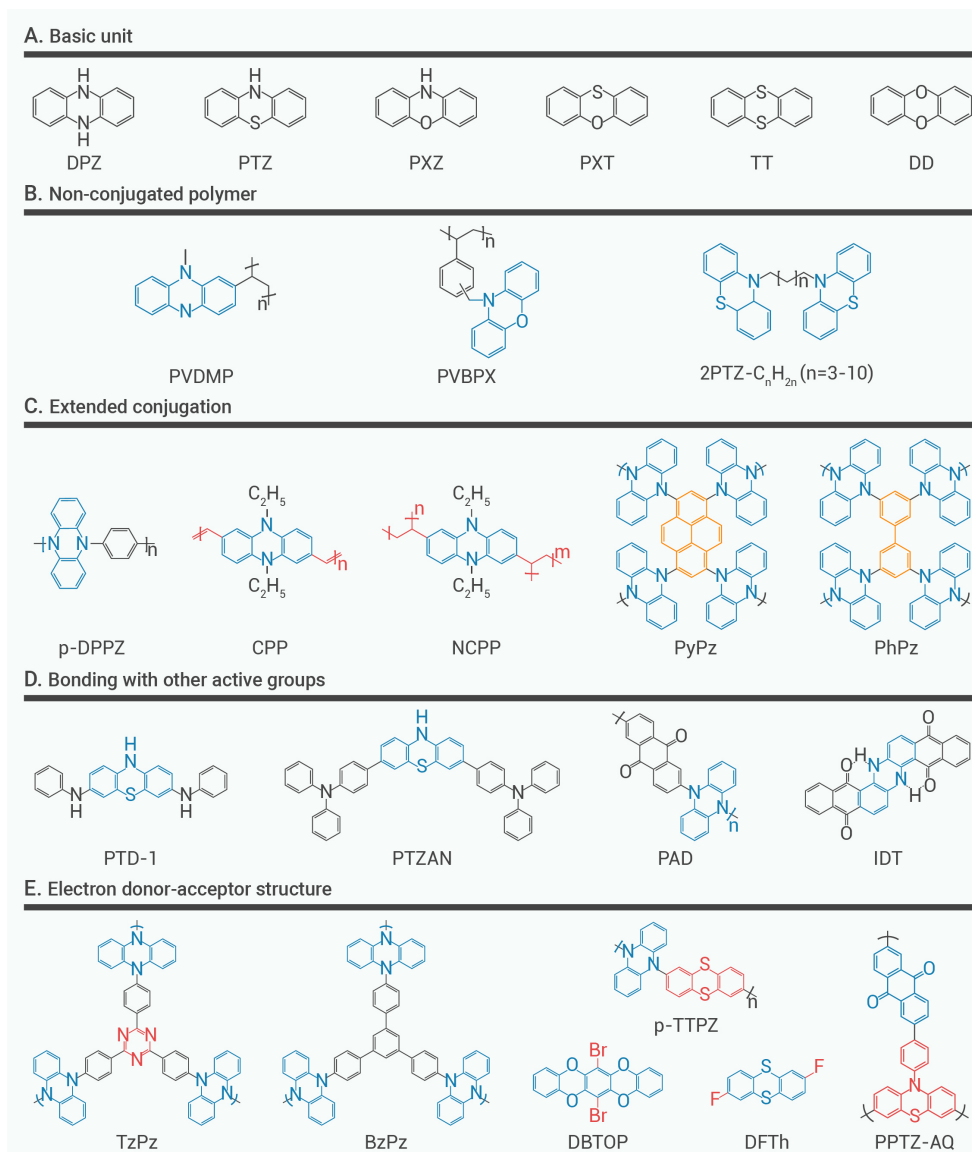


Figure 5. Molecular structural and modification strategy of heterocyclic compounds.

groups or heteroatoms to optimize anion interactions, further improving capacity and stability. Together, these features make large conjugated planes in organic structures provide a stable and adaptable environment for the storage of anions, making them ideal for high-capacity and high-performance anion storage applications in devices like DIBs.

OEMs are broadly classified into p-type, n-type, and bipolar categories based on their redox processes. P-type OEMs, which are oxidized firstly and adsorb anions during the redox reaction, have garnered significant attention due to their approximately 1V higher potential compared to n-type materials in LIBs.¹³⁶ Unlike graphite, where anions intercalate, p-type OEMs adsorb anions at surface redox-active sites, enabling higher capacity and rate performance through multiple redox centers and large interior spaces. They also exhibit moderate voltage, reducing stress on the electrolyte compared to graphite. These advantages make p-type OEMs promising low-cost cathodes for DIBs.

A key benefit of p-type OEMs is their tunable molecular structure, which allows optimization of voltage, capacity, and rate performance. Their versatility extends applications from alkali metal batteries to multivalent systems like Mg²⁺, Ca²⁺, Zn²⁺, Al³⁺ ion batteries. Additionally, the range of compatible electrolytes has expanded from organic to aqueous systems. The following sections explore p-type OEMs based on their structural units, electrochemical properties, modification strategies, and emerging applications. In this part, organic anion hosts are classified into the following categories: heterocyclic, aniline, nitroxide radical, viologen, polycyclic

liquid electrolyte. This QSSE demonstrated high oxidation resistance and effectively facilitated uniform ion transport while suppressing sodium dendrite formation. The resulting DIBs achieved a remarkable energy density of 484 Wh kg⁻¹ with excellent cycling stability over 1,000 cycles, positioning them as a cost-effective option for energy storage (Figure 4D).¹³⁵

Furthermore, QSSEs can expand the operational temperature range of DIBs, enhancing their adaptability in various environments. Tang *et al.* developed a QSSE based on poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) crosslinked with Al₂O₃ nanoparticles for flexible sodium-based DIBs. The QSSE exhibited a 3D porous structure with an ionic conductivity of 1.3 × 10⁻³ S cm⁻¹, enabling the DIBs to maintain excellent flexibility and electrochemical performance across a broad temperature range from -20 to 70 °C.¹³³ QSSEs thus represent a versatile solution for overcoming limitations associated with conventional liquid electrolytes, providing enhanced stability, operational flexibility, and durability for advanced DIB systems.

ORGANIC ANION HOST

Organic electrode materials (OEMs) with large conjugated planes are highly favorable for anion storage due to their ability to delocalize positive charges across the extended π-electron system, which stabilizes intercalated anions. The planar geometry facilitates strong π-π interactions and reduces steric hindrance, flexible and large interior space allowing efficient accommodation of anions of various sizes and shapes. These structures also enhance charge transfer kinetics during intercalation and deintercalation processes. Additionally, the conjugated framework can be chemically tailored with functional

aromatic hydrocarbons and their derivatives. The current modification strategies are introduced, such as extending conjugation, bonding with other active groups and building electron donor-acceptor structure, they have a significant impact on stability, capacity and rate performance, respectively. Based on the flexibility of organic synthesis methods, this has also inspired novel molecular design strategies.

Molecular structural and modification strategy

Heterocyclic compounds. Heterocyclic compounds, initially derived from natural sources, have become foundational materials for DIBs due to their diverse electrochemical properties.^{137,138} Representative examples include dihydrophenazine (DPZ), phenothiazine (PTZ), phenoxazine (PXZ), phenoxathiine (PXT), thianthrene (TT), and dibenzo-1,4-dioxin (DD), arranged by increasing voltage (Figure 5). The detailed electrochemical performances of those materials are shown in Table 1. The high voltage of DD, reaching 4.1 V in LIBs, surpasses commercial inorganic materials due to the strong electron-withdrawing effect of oxygen heteroatoms compared to nitrogen (DPZ) and sulfur (TT).¹³⁹ In aqueous zinc-ion batteries (ZIBs), TT demonstrates a highest discharge voltage of 1.5 V versus Zn²⁺/Zn compared with PXT (1.3 V vs. Zn²⁺/Zn) and PTZ (0.85 V vs. Zn²⁺/Zn) which can be further enhanced to 1.7 V by solvent optimization from polyethylene glycol (PEG)/H₂O to acetonitrile.¹⁴⁰ Carbazole¹⁴¹ and its derivatives, such as indolo-carbazole¹⁴² and azatruxene¹⁴³, exhibit high discharge voltages up to 4.09 V versus Li⁺/Li.

They have the potential for high capacity due to two-electron transfer. Ning

Table 1. Summary on electrochemical performance of heterocyclic compounds as electrode materials in DIB.

Electrode	Electrolyte	Counter electrode	Discharge voltage (V)	Capacity (mAh g ⁻¹)	Rate capability (mAh g ⁻¹)	Cycle number (Current density or/and capacity retention)	Ref.
DD	5 M LiClO ₄ in EC/EDC (v/v, 1:1)	Li	4.1	90	40 (1.5 A/g)	–	139
TT	1 M Zn(OTf) ₂ in EMC	Zn	1.5	103	–	–	140
PTZ	1 M Zn(OTf) ₂ in EMC	Zn	0.85	140	–	–	140
PXT	1 M Zn(OTf) ₂ in EMC	Zn	1.3	96	–	–	140
PXZ	3 M Zn(OTf) ₂ in H ₂ O	Zn	0.98/1.18	215	83 (10 A g ⁻¹)	3,500 (2 A g ⁻¹)	144
PVDMP	1 M LiClO ₄ in EC/DMC/EMC (v/v/v, 1:1:1)	Li	3.0/3.6	220	131 (20 C)	3,900 (5 C)	149
PVBPX	AlCl ₃ in [EmIm]Cl (molar ratio = 1.3:1)	Al	1.07/1.81	126	60 (10 A g ⁻¹)	50,000 (5 A g ⁻¹ , 99.8%)	150
2PTZ-C ₇ H ₁₄ @YP-80F CPP	1 M LiPF ₆ in EC/EDC (v/v, 1:1)	Li	3.4-3.6	93.6	48.4 (100 C)	10,000 (100 C, 81.5%)	151
NCP	1 M LiPF ₆ in EC/EDC (v/v, 1:1)	Li	2.9/3.8	184	156 (1 A g ⁻¹)	500 (1 C, 92%)	159
NCP	1 M LiPF ₆ in EC/EDC (v/v, 1:1)	Li	2.9/3.6	149	81 (1 A g ⁻¹)	500 (1 C, 63%)	159
PyPz	AlCl ₃ in [EmIm]Cl (molar ratio = 1.3:1)	Al	0.89	231	116 (30 A g ⁻¹)	1,000 (0.2 A g ⁻¹ , 93.9%)	160
PhPz	AlCl ₃ in [EmIm]Cl (molar ratio = 1.3:1)	Al	0.7	137	61 (10 A g ⁻¹)	1,000 (0.2 A g ⁻¹ , 74.7%)	160
PTD-1	2 M ZnSO ₄ in H ₂ O	Zn	~0.8	145.6	48.9 (30 A g ⁻¹)	4,000 (1 A g ⁻¹ , 82.5%)	162
PTZAN	0.5 M Zn(OTf) ₂ in TMP/EC/DEC (v/v/v, 1:1:1)	Zn	~1.2	145	77 (5 A g ⁻¹)	2,000 (1 A g ⁻¹ , 77%)	167
TzPz	1 M LiPF ₆ in EC/EDC (v/v, 1:1)	Li	3.11/3.95	192	108 (30 A g ⁻¹)	400 (0.2 A g ⁻¹ , 99%)	174
BzPz	1 M LiPF ₆ in EC/EDC (v/v, 1:1)	Li	3.03/3.79	148	44 (10 A g ⁻¹)	400 (0.2 A g ⁻¹ , 79.2%)	174
p-TTPZ	1 M LiClO ₄ in EC/EDC (v/v, 1:1)	Li	3.16/3.82	135	124 (10 A g ⁻¹)	1,000 (2 A g ⁻¹)	175
DBTOP	LiFSI in DMC (molar ratio=1:1.1)	Li	3.87/4.3	108.1	71.4 (6 A g ⁻¹)	–	177

et al. unveil the reversible two-electron redox properties of PXZ in aqueous electrolytes, which is originating from the stability and heightened aromaticity of redox intermediates.¹⁴⁴ Smaller-sized anions in electrolyte facilitate the two-electron redox process, realizing remarkably high specific capacity of 215 mAh g⁻¹ and 100 % capacity retention over 3500 cycles. Besides, the two-electron process of PXZ is limited in organic solvents because the highly selective to solvents and salts. Despite their potential for two-electron redox reactions, many heterocyclic compounds utilize only the first oxidation step due to the high voltage of the second step exceeding the electrolyte's electrochemical stability window.^{145,146} Structural modifications, such as alkyl or phenyl substitution, have been shown to fine-tune redox voltages.¹⁴⁶

Polymerization. To address the solubility issues of small organic molecules, polymerization has emerged as an effective strategy to enhance stability.^{147,148} Polythylidimethylphenazine (PVDMP) showed a high capacity of up to 220 mAh g⁻¹, which approaching to a stable value of 150 mAh g⁻¹ after 100 cycles and prolonged cycles (3,900 cycles) without obvious capacity fade.¹⁴⁹ Poly(vinylbenzyl-N-phenoxazine) (PVBPX) exhibited a high capacity of 133 mAh g⁻¹ at 0.2 A g⁻¹ in aluminum-ion batteries (AIBs), and polymerization endowed with ultra-long lifetime of 50,000 cycles.¹⁵⁰ Covalent bonding of PTZ units with varied alkyl chain lengths has also shown a correlation between chain length and electrochemical performance, with optimized designs achieving minimal voltage drop and high capacity retention (74.5%) after prolonged cycling (10,000 cycles).¹⁵¹

Extend conjugation. Since it was discovered that p-DPPZ was beneficial for capacity improvement,^{152,153} a series of modification methods to expand the conjugation degree have emerged. Compared to the alkyl group, the conjugated skeleton facilitates the rapid transfer of electrons,¹⁵³ which allows heterocyclic compounds to exhibit higher capacity and stability.¹⁵⁴⁻¹⁵⁸ For example, the comparison between conjugated (CPP) and unconjugated poly(diethyldihydrophenazine vinylene) (NCP) demonstrate that enhanced electron delocalization enables two-electron reaction and promote the redox process in the high-potential region.¹⁵⁹ Hence, CPP showed a higher reversible specific capacity of 184 mAh g⁻¹ and better cyclic stability. PyPz was designed with larger conjugate planes than PhPz, the co-planar polymer

design offer higher redox activity (231 mAh g⁻¹ vs. 137 mAh g⁻¹) and good stability of 100,000 cycles, the fast redox kinetics allows the battery to operate at low temperatures (–30° C).¹⁶⁰

Introduce other redox units. The presence of inactive linking groups in polymers increases molecular mass, thereby reducing the density of active sites and lowering the theoretical capacity. To address this limitation, researchers have developed strategies that incorporate multiple redox-active units into large conjugated planes, minimizing capacity loss.^{141,161-167} Wang's research group connected PTZ with diphenylamine (PTD-1)¹⁶² or triphenylamine (PTZAN),¹⁶⁷ respectively, achieving capacities around 150 mAh g⁻¹ and an average voltage of ~1 V vs. Zn²⁺/Zn in aqueous ZIBs. By integrating p-type building blocks such as 5,10-dimethyl-5,10-dihydrophenazine-2,7-dicarbaldehyde with bipolar-type semiconductors, capacities exceeding 300 mAh g⁻¹ were realized.¹⁶⁵ Additionally, polymerization with carbonyl-based units such as PAD and IDT has shown promise for constructing symmetrical cells due to the voltage difference of over 1 V between n-type and p-type active sites.¹⁶⁸⁻¹⁷³ This approach not only enhances the energy density but also ensures efficient charge transfer and electrochemical stability, advancing the performance of organic electrode materials for dual-ion batteries.

Donor-acceptor structure. The design of electron donor-acceptor structure would accelerate the electron transfer along the conjugated skeleton, contributing to the high conductivity, which is achieved by narrowing the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Jiang's group synthesized CMPs with DPZ donor and 2,4,6-triphenyl-1,3,5-triazine acceptor (TzPz).¹⁷⁴ Compared to the 1,3,5-triphenylbenzene acceptor (BzPz), the stronger electron withdrawing effect of the TzPz promotes electron transfer and increases the capacity to 192 mAh g⁻¹ with excellent rate performance (108 mAh g⁻¹ at 30 A g⁻¹). Similarly, D-A conjugated polymer (pTTPZ) with DPZ electron donor and TT acceptor significantly improved the rate performance compared to polymers without D-A structure, realizing a high capacity of 124.2 mAh g⁻¹ at 10 A g⁻¹.¹⁷⁵ In addition, the electron withdrawing effect could rise up anion insertion voltage.¹⁷⁶ When Br and F substituents were introduced on conjugated plane, respectively, the discharge plateaus of the heterocyclic

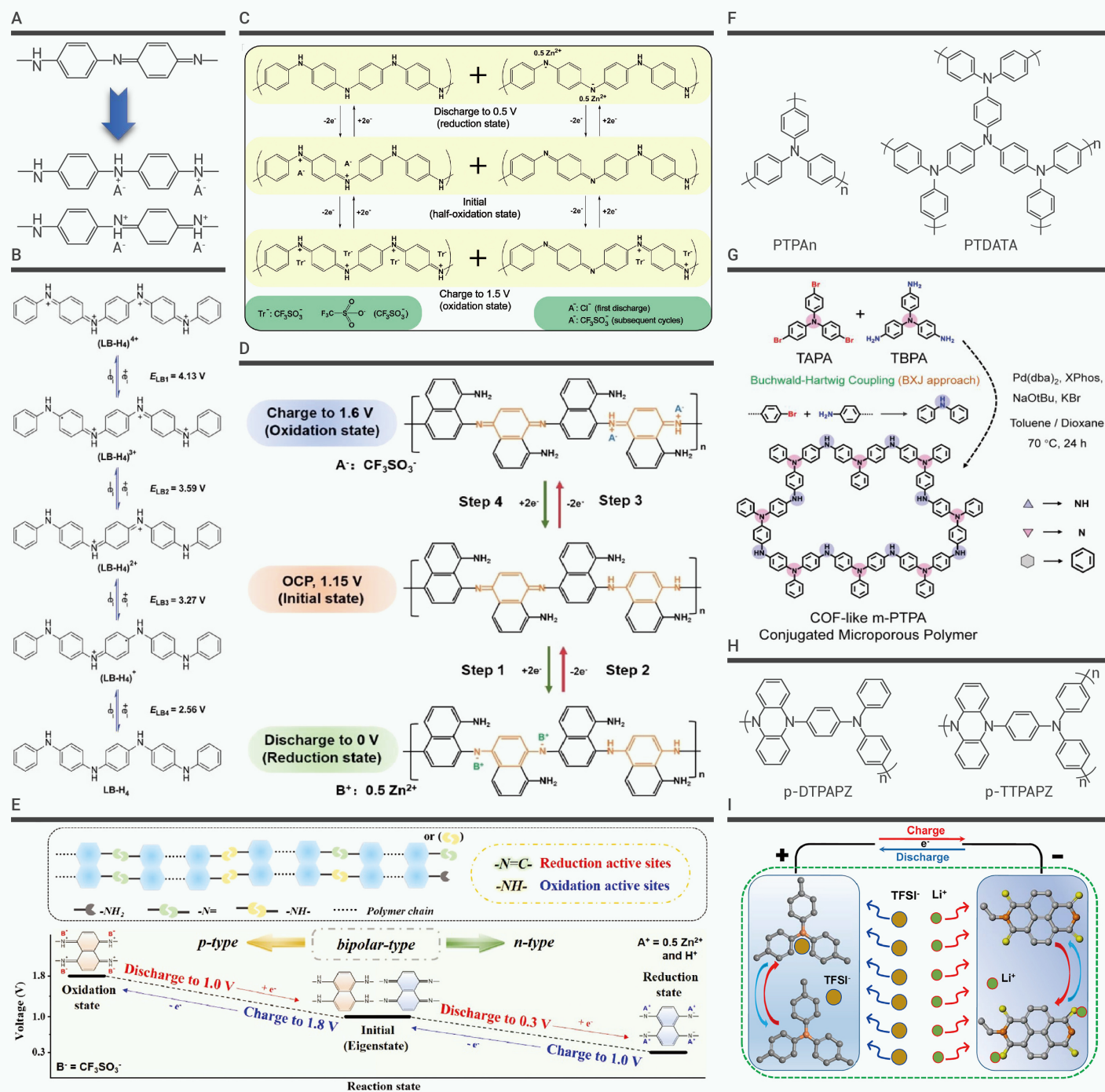


Figure 6. Polyaniline and its derivatives (A) The protonation process of polyaniline. (B) The energy storage mechanism of leucoemeraldine base (LB) in LIBs. Reproduced with permission.¹⁸⁵ Copyright 2023, Wiley-VCH. (C) The energy storage mechanism of polyaniline in aqueous zinc-ion batteries. Reproduced with permission.¹⁸⁷ Copyright 2018, Wiley-VCH. Bipolar properties of (D) polymer PDAN and (E) PDAN/activated carbon composite electrodes. Reproduced with permission.¹⁹¹ Copyright 2022, Wiley-VCH. Reproduced with permission.¹⁹² Copyright 2024, Wiley-VCH. (F) Molecular structure of triphenylamine polymers PTPAn and PTDATA. Reproduced with permission.²⁰⁹ Copyright 2021, Wiley-VCH. (H) Molecular structure of p-DTPAPZ and p-TTPAPZ. Reproduced with permission.²¹⁴ Copyright 2018, Elsevier.

compounds DBTOP and DFTh exceed the limitation to up to 4.4¹⁷⁷ and 4.10 V vs. Li^+/Li .¹⁷⁸ Recent innovations include solvent-free ionic liquid systems, which enable simultaneous cation and anion doping in D-A structure (PPTZ-AQ).¹⁷⁹ This design improves the electrical conductivity and ion diffusion dynamics, achieving capacities exceeding 200 mAh g⁻¹ with excellent rate and low-temperature performance, even at high mass loadings.

These advances in the structure and modification strategies of heterocyclic compounds underscore their versatility and potential as high-performance, cost-effective materials for next-generation DIBs. In general, extending conjugated surfaces is beneficial to reduce solubility and improve

reversibility, promoting long cycle performance. The introduction of other active sites is conducive to improving the capacity, but it should be noted that the theoretical capacity of the known active groups is still relatively low. The further discovery of novel active sites and storage mechanisms should be encouraged. The construction of D-A structure is helpful to enhance the conductivity, thus reducing the conductive carbon and enhancing the rate performance, which is a promising development direction. Similarly, these strategies are applicable to other organic anion hosts discussed later.

Aniline and its derivatives. Polyaniline. PANI is among the most promising organic electrode materials due to its high electrical conductivity and a

theoretical specific capacity of 294 mAh g⁻¹ within the high-voltage region when fully activated by p-type doping. Initially developed for alkali metal-ion batteries, PANI demonstrated low capacity and poor stability in its unmodified form.¹⁸⁰⁻¹⁸² However, protonated PANI (P-PANI) shows significantly improved electrochemical performance in both EC/DEC electrolytes¹⁸³ and ionic liquid electrolytes¹⁸⁴ (Figure 6A). Song's group pioneered the use of leucoemeraldine base (LB) as an organic electrode material, incorporating 30% conductive carbon to ensure adequate electron conduction. The energy mechanism was shown in Figure 6B. In the voltage range of 2.0–4.2 V versus Li⁺/Li, the electrode delivered a reversible specific capacity of up to 277 mAh g⁻¹ and excellent cycling stability, retaining 84% capacity after 1,000 cycles.¹⁸⁵ The high proportion of -NH- groups in LB facilitates anion adsorption, while irreversible deprotonation at high potentials limits long-term capacity. Fluoridized-polyaniline-H⁺/carbon nanotube composites (FPHC) further enhance PANI's performance, with fluorine atoms narrowing the HOMO-LUMO gap to improve electron conductivity and increase charge/discharge voltages.¹⁸⁶

PANI's application in aqueous multivalent metal-ion batteries has gained attention in recent years. In situ polymerization on carbon fiber surfaces yielded a PANI cathode with a capacity of 200 mAh g⁻¹ and an average operating voltage of 1.1 V versus Zn²⁺/Zn.¹⁸⁷ Chen *et al.* revealed a bipolar energy storage mechanism for PANI in aqueous ZIBs, involving the insertion and extraction of Zn²⁺ and CF₃SO₃⁻ ions (Figure 6C). Generally, PANI exhibits significant activity only in strong acid solutions to avoid deprotonation. Some strategies like sulfo-self-doped PANI (S-PANI)¹⁸⁸ and composite with nitrogen-doped carbon¹⁸⁹ were explored to maintain proton concentration in weakly acidic ZnSO₄ electrolytes. Employing a saturated aqueous Mg(NO₃)₂ electrolyte suppresses irreversible deprotonation, enabling the Mg/PANI battery to achieve long lifespans and power densities akin to supercapacitors.¹⁹⁰

Wang *et al.* synthesized poly(1,8-diaminonaphthalene) (PDAN) as a ZIB cathode material, achieving a capacity of 140 mAh g⁻¹ at 0.1 A g⁻¹ and outstanding cycle stability over 1,000 cycles without capacity fading (Figure 6D).¹⁹¹ PDAN exhibits a bipolar energy storage mechanism with -NH- units providing ion storage sites. Composite electrodes of poly(1,8-diaminonaphthalene) and activated carbon, prepared via in situ electropolymerization, delivered an exceptional capacity of 479.5 mAh g⁻¹, with 91.6% utilization of reaction sites due to the high surface area and conductivity of activated carbon (Figure 6E).¹⁹² Bipolar non-doped polydiphenylamine (PDPA) has been introduced as a high-conductivity organic cathode material for lithium and potassium dual-ion batteries. With 80% active material loading, PDPA achieved impressive energy densities of 523 Wh kg⁻¹ and 462 Wh kg⁻¹ for lithium and potassium half-cells, respectively. However, its poor cycling stability, caused by partial dissolution, remains a challenge.¹⁹³

Polytriphenylamine. PTPAn offers a theoretical capacity of 109 mAh g⁻¹ and a high-voltage plateau at 3.6 V versus Li⁺/Li. As a p-type material, PTPAn primarily relies on anion carriers, making cations in the electrolyte relatively insignificant to its electrochemical properties.¹⁹⁴ This has enabled PTPAn's application across a variety of battery systems, including those based on Li,¹⁹⁵⁻¹⁹⁸ Na,¹⁹⁹ K,²⁰⁰⁻²⁰² Zn,^{203,204} Ca.²⁰⁵⁻²⁰⁷ However, the high activity of water restricts PTPAn to organic or "water-in-salt" electrolytes to prevent side reactions.^{203,208}

To overcome PTPAn's limited theoretical capacity and its aggregated morphology, structural modifications have been developed. Su *et al.* synthesized a nanofiber-packed mesoporous polytriphenylamine derivative (PTDATA), increasing its specific surface area from 5.6 m² g⁻¹ to 560.58 m² g⁻¹, which enhanced its capacity to 133.1 mAh g⁻¹, achieving 92.8% of its theoretical value (143.5 mAh g⁻¹) (Figure 6F).¹⁹⁵ Zhang *et al.* developed COF-like porous polytriphenylamine cathode (m-PTPA) by Buchwald-Hartwig cross-coupling of triphenylamine monomers (Figure 6G).²⁰⁹ The surface area was improved from 32 m² g⁻¹ (PTPAn) to 655 m² g⁻¹ (m-PTPA), which is beneficial to stimulate redox activity. Due to the introduction of -NH- active sites and porous structure, the capacities of PTPAn and m-PTPA cathodes are measured to be 99.8 mAh g⁻¹ and 210.7 mAh g⁻¹ in aqueous ZIBs.

Further improvements in PTPAn involve copolymerization with active redox units to enhance capacity. Xu *et al.* synthesized p-DTPAPZ and p-TTPAPZ polymers by combining triphenylamine and dihydrophenazine (DPZ) units, achieving high specific capacities of up to 160.1 mAh g⁻¹ through multi-electron redox processes (Figure 6H).¹⁹⁸ However, most studies focus on enhanc-

ing capacity through molecular bonding with n-type redox groups, which adsorb cations in low-voltage regions, exhibiting limited progress in increasing operating voltage.^{197, 204, 210-213}

Low-Temperature Applications. The dual-ion battery mechanism, which involves separate cation and anion adsorption on opposing electrodes, minimizes carrier migration distance. Additionally, the anion-doping mechanism in organic electrodes bypasses desolvation, lowering ion diffusion barriers and enabling high-rate capabilities, even at low temperatures. In anti-freezing ethyl acetate (EA) electrolyte, rechargeable batteries with PTPAn and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA)-derived polyimide (PNTCDA) as cathode and anode material (Figure 6I), can function well at ultra-low temperatures (-70°C), while battery systems based on inorganic materials cannot work. This all-organic battery exhibits a capacity retention rate of ~70% at -70°C compared that at room temperature, it is due to the rapid charge storage dynamics in surface groups and large spaces in organic solids.²¹⁴ Qin *et al.* reported a similar system using a solvent-free ionic liquid electrolyte, which retained 79% capacity at -80°C.²¹⁵ Sodium dual-ion batteries utilizing PTPAn as the cathode and graphite as the anode also demonstrated 89% and 61% of their room-temperature capacities at -40°C and -70°C, respectively, highlighting their potential for ultra-low-temperature operation.⁹⁵

In summary, the detailed electrochemical performances of aniline and its derivatives are shown in Table 2. As a conductive polymer, PANI is expected to solve the problems of high content of carbon additives and low mass load of electrode in practical applications. At present, it is still necessary to solve the problem of poor cyclic stability caused by deprotonation, and the release of more anion storage sites to increase its capacity will be attractive. Polytriphenylamine has a lower capacity than polyaniline, but its distorted structure hold potential for ultra-low-temperature applications through combination with other organic anodes. In addition, trianiline groups could act as a building block for porous organic hosts, thus facilitating ion transport.

Nitroxide radical compound and its derivatives. Organic radical polymers have attracted much attention because of their high redox activity.^{216,217} Nitroxide radical (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), is a typical representative with high voltage (3.6 V vs. Li⁺/Li) and rapid electron transfer kinetics. It needs to be introduced into a polymeric backbone as redox active pendant groups, owing to their solubility in the electrolyte.²¹⁸⁻²²⁰ Though the two-electron redox reaction of nitroxide can be realized containing reversible oxidation and reduction (Figure 7A),²²¹ oxidation process with anions adsorption is more widely applied. The detailed electrochemical performances of those materials are shown in Table 3.

Unlike other organic electrodes, nitroxide radical compounds are one of the most reversible p-type compounds even in aqueous batteries. Luo *et al.* firstly applied the organic radical polymer poly(2,2,6,6-tetramethylpiperidinyloxy-4-ylvinylether) (PTVE) to the aqueous ZIBs (Figure 7B).²¹⁸ Equilibrium voltages of the Zn/PTVE batteries are 1.77, 1.58, and 1.53 V in ZnSO₄, Zn(CF₃SO₃)₂ and Zn(ClO₄)₂ aqueous electrolytes, respectively, with a capacity of ~80 mAh g⁻¹. In AIBs, the presence of water circumvents irreversible disproportionation of TEMPO in organic Al(OTf)₃ electrolyte (Figure 7C).²²² Assembled aqueous AIBs delivered a stable voltage output of 1.25 V with a capacity of 110 mAh g⁻¹. More importantly, a long lifespan of 800 cycles was realized with 0.028% loss per cycle. These indicate that nitroxide radical compounds may be a favorable candidate for future aqueous dual-ion batteries.

Unfortunately, non-conjugated polymer backbone is unfavorable to electron transport, and the inactive polymer chains will result in a decrease in capacity. Therefore, a variety of conjugate and electrochemically active polymeric backbone chains have been developed, their molecular structure are list in Figure 7D, such as thiophene²²³, polyene²²⁴ and PEDOT²²⁵. Fan *et al.* utilized "π-π" conjugated imidazolium and "p-π" conjugated acetylamino co-functionalized TEMPO (MIACNH-TEMPO) as catholyte for aqueous zinc hybrid flow batteries, an open circuit voltage of 1.71V and good stability is achieved because the conjugated chains allow positive charge delocalization of N to reduce side reactions.²²⁶ Ou *et al.* prepared a conjugated radical copolymer by covalent crosslinking of 2,2,5,5-tetramethyl-1-pyrrolidinoxy (PROXYL) radicals and triphenylamine radicals. Conjugated backbone and the radical pendants both exhibited redox activity, delivering a capacity of

Table 2. Summary on electrochemical performance of aniline and its derivatives as electrode materials in DIB.

Electrode	Electrolyte	Counter electrode	Discharge voltage (V)	Capacity (mAh g ⁻¹)	Rate capability (mAh g ⁻¹)	Cycle numbers (Current density or/ and capacity retention)	Ref.
P-PANI	1 M NaClO ₄ in EC/EDC (v/v, 1:1)	N-PDHC	~2.9	97	30 (5 A g ⁻¹)	2,000 (2 A g ⁻¹)	183
PANI@SWCNT	AlCl ₃ in [EmIm]Cl (molar ratio = 1.3:1)	Al	1.65/1.05	~200	75 (40 A g ⁻¹)	8,000 (10 A g ⁻¹ , 87.6%)	184
PANI (Leucoemeraldine base)	1 M LiClO ₄ in EC/EDC + 1% FEC	Li	~3.4	277	166 (2 A g ⁻¹)	1,000 (0.5 A g ⁻¹ , 84%)	185
FPHC	1 M NaPF ₆ in PC	NLHC	~2.67	116	78 (3 A g ⁻¹)	5,000 (2 A g ⁻¹ , 55%)	186
PANI/CF	1 M Zn(OTf) ₂ in H ₂ O	Zn	1.07/0.85/0.65	~200	95 (5 A g ⁻¹)	3,000 (5 A g ⁻¹ , 92%)	187
PANI-S	1 M ZnSO ₄ in H ₂ O	Zn	1.1 V	184	130 (10 A g ⁻¹)	2,000 (10 A g ⁻¹)	188
PANI	4.5 M Mg(NO ₃) ₂ in H ₂ O	PDI-EDA	—	45	~25 (200 C)	2,000 (50 C, 67.5%)	190
PDAN	0.5 M Zn(OTf) ₂ in H ₂ O	Zn	~0.71	171	54 (100 A g ⁻¹)	10,000 (5 A g ⁻¹ , 82.3%)	191
1,8-DAN/AC	0.5 M Zn(OTf) ₂ in H ₂ O	Zn	~0.75	411.3	~270 (60 A g ⁻¹)	50,000 (20 A g ⁻¹ , 68.1%)	192
PTPAn	1 M LiTFSI in DME	Li	3.87	~110	—	—	194
PTPAn	1 M NaTFSI in DME	Na	3.67	~110	—	—	194
PTPAn	1 M KTFSI in DME	K	3.87	~110	—	—	194
PTDATA	1 M LiPF ₆ in EC/DMC (v/v, 1:1)	Li	3.8/3.4/3.2/2.5	133.1	90.9 (0.5 A g ⁻¹)	100 (0.02 A g ⁻¹)	195
m-PTPA	2 M ZnCl ₂ in H ₂ O	Zn	~1.15 V	210.7	~100 (6 A g ⁻¹)	1,000 (6 A g ⁻¹ , 87.6%)	209
p-DTPAPZ	1 M LiPF ₆ in EC/DMC/EMC (v/v/v, 1:1:1)	Li	~3.8/2.95 V	141.3	~137.7 (1 A g ⁻¹)	100 (0.03 A g ⁻¹ , 96.2%)	198
p-TTPAPZ	1 M LiPF ₆ in EC/DMC/EMC (v/v/v, 1:1:1)	Li	~3.8/2.95 V	126.8	94.4 (1 A g ⁻¹)	100 (0.03 A g ⁻¹ , 93.2%)	198
PTPAn	2 mol kg ⁻¹ LiFSI in EA	PNTCDA	~1.1 V	91	84 (10 C)	—	214
PTPAn	EmITFSI in MA/AN (v/v, 1:1)	PI5	~1.1 V	108	76.7 (500 C)	2,000 (5 C, 86%)	215
PTPAn	0.5 M NaPF ₆ in DEGDMC	AG	2.95 V	100	76.7 (10 A g ⁻¹)	800 (1 A g ⁻¹ , 98%)	95

131 mA h g⁻¹ with high discharge voltage of 3.7 V.²²⁷ Due to the stability of the conjugate skeleton, the capacity retention rate is 72% after 3000 cycles. Subsequently, this research group further designed and prepared new conjugated radical polymers P(DATPAPO-TPA), with a conjugated nitrogen-rich triphenylamine derivative as the backbone (Figure 7E).²²⁸ The polymer with multiple redox sites showed a capacity of 143.3 mAh g⁻¹ and a high charge/discharge plateau at ~3.75 V vs. Li⁺/Li. More importantly, it still exhibits a high of 139.4 mAh g⁻¹ and a high flat discharge plateau of ~3.7 V versus Li⁺/Li at 0°C. Because of the distorted structure, the exposed free radicals accelerate the reaction kinetics at low temperatures. Some nitroxide polymers are also compounded with carbon materials to improve their electron conductivity, which facilitates the two-electron process and releases electrochemical activity at a lower voltage range (~2 V vs. Li⁺/Li).²²⁹⁻²³²

Viologen compounds. Viologen compounds are promising due to their high theoretical capacities, though their redox potentials are relatively low (≤ 2.5 V vs. Li⁺/Li). This makes them suitable primarily as anion storage anodes in battery applications.^{233,234} Their high solubility in organic electrolytes also positions them as ideal candidates for flow batteries.²³⁵⁻²³⁷ The detailed electrochemical performances of those materials are shown in Table 4. In LIBs, Chen's research group prepared ionic crystals of ethyl viologen iodide (EVI₂) and ethyl viologen diperchlorate [EV(ClO₄)₂] as cathode (Figure 8A).²³⁸ EVI₂ exhibited a higher specific capacity (~230 mAh g⁻¹) and operating voltage compared to EV(ClO₄)₂, and the latter demonstrated superior rate performance. EVI₂ has also been applied in potassium-ion batteries, where it achieved a reversible capacity of 308 mAh g⁻¹ and a high working potential of nearly 3.5 V.²³⁹

The extended conjugated structure of these polymers contributes to improved stability and capacity. Song *et al.* synthesized poly(butylviologen dichloride) (PBV-Cl₂), achieving a capacity of 183 mAh g⁻¹ in DMSO electrolyte, with two voltage plateaus at 2.8 V and 2.4 V vs. Li⁺/Li (Figure 8B).²⁴⁰ Further enhancement was achieved by integrating viologen units with electrochemically active groups, such as pyrene-4,5,9,10-tetraone and

anthraquinone (Figure 8C). This approach yielded a viologen-based polymer, PVPTOCl₂, with a capacity of 235 mAh g⁻¹.²⁴¹

The low anion storage voltage of viologen compounds makes them suitable for designing bipolar compounds capable of storing both cations and anions within the same voltage range. This design minimizes Coulombic repulsion between like ions, thereby enhancing ion transfer efficiency. Sun *et al.* incorporated p-type viologen groups into an n-type triazine framework (Figure 8D). This composite exhibited a power density comparable to supercapacitors (~28 kW kg⁻¹) through the co-intercalation of cations and anions.²⁴² This dual-ion storage strategy addresses the inherent trade-offs between capacity and rate performance in organic electrodes. It also enables high mass-loading electrodes and robust performance at low temperatures by facilitating ion transfer. As such, viologen compounds represent a versatile and promising avenue for future organic electrode material development.¹⁷⁹

Polycyclic aromatic hydrocarbons and their derivatives. Polycyclic aromatic hydrocarbons (PAH) are composed of a small conjugate structure, such as benzene (C₆H₆), naphthalene (C₁₀H₈), anthracene (C₁₄H₁₀), pyrene (C₁₆H₁₀), perylene (C₂₀H₁₂), and coronene (C₂₄H₁₂). Unlike organic materials containing heteroatoms, PAHs stabilize positive charges through their conjugated planes, enabling anion adsorption.²⁴³ Although lacking traditional energy storage sites like nitrogen, the energy storage performance of PAH derivatives has improved significantly in recent years, becoming competitive with other organic electrodes (Figure 9A and Table 5).

Coronene. Ji's research group demonstrated that coronene exhibits highly reversible anion storage properties in LIBs. It delivered a high discharge plateau of ~4.0 V and excellent cycle stability (Figure 9B).²⁴⁴ Subsequently, coronene was applied as a cathode material in sodium-ion batteries. Despite the high discharge voltage, its specific capacity remained low (~40 mAh g⁻¹).²⁴⁵

Pyrene. Pyrene-based polymers have been shown to significantly enhance the capacity of PAH derivatives. For instance, poly(nitropyrene-co-pyrene)

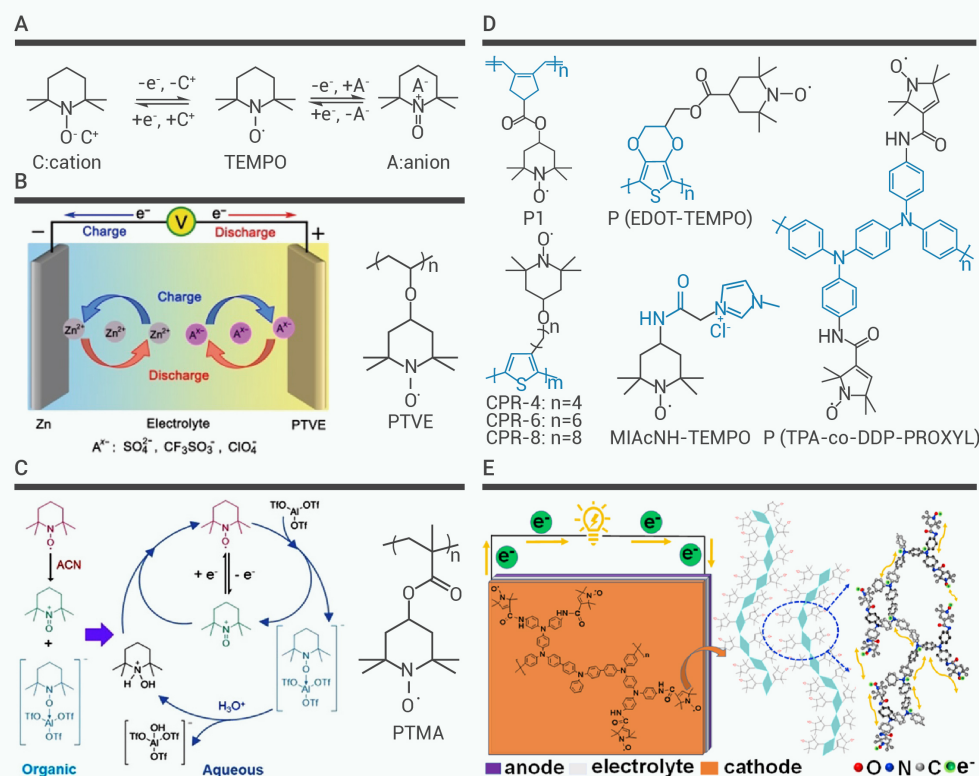


Figure 7. Nitroxide radical compound and its derivatives (A) The molecular structure and two-electron energy storage process of TEMPO. (B) The constructure of Zn//PTVE battery with different anions in electrolyte. Reproduced with permission.²¹⁸ Copyright 2020, Wiley-VCH. (C) Reversible conversion process of PTMA in aqueous aluminum-ion batteries. Reproduced with permission.²²² Copyright 2023, American Chemical Society. (D) Summarized modification of conjugate skeleton in nitroxide radical compounds. (E) Application of P(DATPAPO-TPA) in lithium-ion batteries and schematic diagram of conjugated skeleton promoting electron transfer. Reproduced with permission.²²⁸ Copyright 2024, American Chemical Society.

In summary, PAHs and their derivatives, particularly coronene and pyrene-based materials, exhibit great potential in energy storage applications due to their unique conjugated structures and tunable properties. Strategies such as tailored linkage patterns and functional group modifications are critical for improving capacity, voltage, and stability.

Other types. Porphyrins and phthalocyanines are large aromatic molecules with an 18 π -electron configuration, featuring conjugated skeletons with nitrogen atoms, central metal ions, and peripheral substituents. These structures enable these compounds to act as elec-

trons donors (16 π -electrons) or acceptors (20 π -electrons).²⁵⁰ The electrochemical properties of porphyrins and phthalocyanines are significantly influenced by the choice of central metal ions and peripheral substituents.²⁵¹⁻²⁵⁴ They are generally utilized as bipolar compounds in batteries, where they store anions at high potential and cations at low potential.^{168,255-258} However, their widespread application is hindered by complex synthesis and relatively limited exploration compared to other organic electrodes.

Triazine groups can stabilize charge through π -conjugated plane.²⁵⁹⁻²⁶² Covalent triazine frameworks (CTFs) exhibit promising energy storage capabilities, with capacities of up to 240 mAh g⁻¹ in sodium-ion batteries. These frameworks enable both p-type and n-type doping, although the p-type doping capacity remains relatively low (~50 mAh g⁻¹). The asymmetry in doping capacities presents a challenge for further optimization and application.

Ferrocene, a metallocene compound, has been studied for its potential in anion energy storage. Despite its intriguing redox properties and stability, its application has been limited due to challenges in molecular modification and insufficient scalability.^{256,263} These alternative organic electrode materials, while less extensively studied, offer unique electrochemical characteristics. Porphyrins and phthalocyanines provide tunable redox behavior through central metal ions and substituents, while triazine-based frameworks demonstrate high capacities

Table 3. Summary on electrochemical performance of nitroxide radical compound and its derivatives as electrode materials in DIB.

Electrode	Electrolyte	Counter electrode	Discharge voltage (V)	Capacity (mAh g ⁻¹)	Rate capability (mAh g ⁻¹)	Cycle numbers (Current density or/and capacity retention)	Ref.
PTVE	1 M ZnSO ₄ in H ₂ O	Zn	1.77	~80	58 (10 A g ⁻¹)	–	218
PTVE	1 M Zn(OTf) ₂ in H ₂ O	Zn	1.58	~80	52 (10 A g ⁻¹)	1,000 (1 A g ⁻¹ , 77%)	218
PTVE	1 M Zn(ClO ₄) ₂ in H ₂ O	Zn	1.53	~80	50 (10 A g ⁻¹)	–	218
PTMA	1 M Al(OTf) ₃ in H ₂ O	Al	1.0–1.1	120	90 (8 C)	1,000 (4 C, 77%)	222
MIACNH-TEMPO PROXYL	1 M LiPF ₆ in EC/DMC/EMC (v/v/v, 1:1:1)	Li	3.7	131	103 (2 A g ⁻¹)	3,000 (0.5 A g ⁻¹ , 93.6%)	226
MIACNH-TEMPO PROXYL	1 M LiPF ₆ in EC/DMC/EMC (v/v/v, 1:1:1)	PAQS	1.8	81.6	49 (0.5 A g ⁻¹)	1,500 (0.02 A g ⁻¹ , 82.1%)	226
P(DATPAPO-TPA)	1 M LiPF ₆ in EC/DMC/EMC (v/v/v, 1:1:1)	Li	3.75	143.3	113.2 (10 C)	2,000 (50 C, 83%)	228

Table 4. Summary on electrochemical performance of viologen compounds as electrode materials in DIB.

Electrode	Electrolyte	Counter electrode	Discharge voltage (V)	Capacity (mAh g ⁻¹)	Rate capability (mAh g ⁻¹)	Cycle numbers (Current density or/and capacity retention)	Ref.
EVI ₂	2 M LiClO ₄ in Tetraglyme	Li	–	230	149 (5 C)	200 (0.5 C, 96%)	238
EVI ₂	1 M KFSI in EC/EDC	K	2.2/2.6/3.4	308	128.1 (0.5 A g ⁻¹)	1,000 (0.3 A g ⁻¹ , 60.7%)	239
PBV-Br ₂	1 M LiPF ₆ in EC/EDC	Li	2.5/2.0	153	–	50 (64%)	240
PBV-Cl ₂	1 M LiPF ₆ in EC/EDC	Li	2.5/2.0	197	–	50 (54%)	240
PBV-(PF ₆) ₂	1 M LiPF ₆ in EC/EDC	Li	2.5/2.0	118	–	50 (66%)	240
PBV-Cl ₂	1 M LiCl in DMSO	Li	2.15	177	132.7 (5 A g ⁻¹)	200 (0.2 A g ⁻¹ , 72%)	240
PBV-Cl ₂	1 M LiCl in DMSO + 2 wt% FEC	Li	2.8/2.4	172	41.3 (0.5 A g ⁻¹)	300 (0.2 A g ⁻¹ , 88%)	240
PVAQCl ₂	1 M LiTFSI in DOL/DME (v/v, 1:1)	Li	–	113	75.8 (5 A g ⁻¹)	–	241
PVPTOCl ₂	1 M LiTFSI in DOL/DME (v/v, 1:1)	Li	–	235	150.3 (5 A g ⁻¹)	3,000 (66.8%)	241

through dual-doping mechanisms. Ferrocene, although promising, requires breakthroughs in molecular design to realize its potential in practical energy storage applications. Further research into these structures could diversify the toolbox of organic electrodes and address specific challenges in modern battery technologies.

In conclusion, the diverse structures of organic electrodes and their flexibility in design have attracted extensive attention from researchers. Thus, heterocyclic compounds with a relatively large number of heteroatoms are calculated to have a high theoretical capacity (close to 300 mAh g⁻¹) and are currently the most extensively studied organic anion hosts. The high conductivity of PANI and the extreme low temperature resistance of polytrianiline also make it a potential candidate. Nitroxide radical compounds suffer from low capacity and have high solubility in organic solvents because of the lack of a rigid structure. Combining them with conjugated chains can improve this situation to some extent. Viologen-based materials have the lowest voltage among organic hosts, which is caused by the grafting of carbon chains at the energy-storage sites and the lack of electron-withdrawing groups. Since energy storage usually relies on heteroatom sites in organic hosts, this leads to an upper limit of the capacity, restricting capacity improvement, and defect sites are detrimental to electrical conductivity. Polycyclic aromatic hydrocarbons have a highly delocalized π -electron structure and usually store energy through conjugated planes, which is not limited by the number of heteroatoms. Therefore, they are more ideal host materials. However, current research on them is still at a preliminary stage and requires more in-depth and extensive studies.

Despite having many advantages, organic hosts still face a number of practical problems in practical applications. First and foremost is the issue of their stability during long-term use. In the organic electrolyte system, the main source of structural instability is the dissolution of the electrode material. Therefore, covalent polymerization or modification of the solvent is helpful to enhance the cycle stability. Especially for some porous organic hosts, such as conjugated microporous polymers (CMP), covalent organic frameworks (COF), covalent triazine frameworks (CTF), etc., they often exhibit higher cycle stability. For organic hosts in aqueous electrolytes, small molecules also show relatively high cycle stability due to their insolubility. Strategies such as increasing the conjugated surface, covalent polymerization, and constructing a porous structure are still applicable for further improvement. Since most of them conform to the surface reaction mechanism rather than internal deintercalation, the adsorption and desorption of ions usually do not damage the structure and electrochemical stability of the material, which is also the source of the high power density and high cycle stability of organic hosts. In addition, because organic hosts have anion selectivity, attention should be paid to selecting appropriate anions.

In addition to their respective challenges, organic hosts also face two common challenges: (1) Organic hosts generally have poor electrical conductivity, which leads to the extensive use of conductive carbon and hinders the preparation of high-loading electrodes. To enhance their electrical conductivity, a donor-acceptor (D-A) structure can be introduced to form an

intramolecular heterojunction, thereby narrowing the band gap and enhancing conductivity. Co-storage of anions and cations is also a solution. By utilizing the Coulomb force between them, ion transport can be enhanced. Although this has been preliminarily verified, more experimental confirmation and theoretical explanations are still needed. (2) The synthesis methods are cumbersome and it is difficult to prepare them in large quantities. Currently, the production scale of organic hosts is small, and the production process is cumbersome, being limited to laboratory synthesis and difficult to meet future large-scale applications. Therefore, it is necessary to develop new structures that are easy to prepare in large quantities, or directly use current chemical products. This aspect needs to be paid attention to in future research.

Electrolyte optimization

Unlike graphite anion hosts, organic anion hosts generally have a moderate voltage, so there is less stress on the electrolyte and it is less likely to cause decomposition. During the oxidation process of organic hosts, anions are adsorbed in the structure as counter-ions, forming a doping-like state. Therefore, organic hosts are selective towards the types of anions, which is commonly reported in some studies. Anion species with stronger adsorption electrostatic forces often result in higher voltages. However, the capacity and cycle performance usually decrease due to the reduced reversibility of anion adsorption and desorption. Selecting an appropriate anion species is an effective means to balance its performance. In addition, the solvent has a significant impact on the redox voltage of organic hosts, which stems from the change in the desolvation energy of anions. Due to differences in solubility, the choice of solvent may also reduce the cycle stability of small-molecule electrodes, especially solvents with high polarity. Covalent polymerization can effectively reduce the dissolution of electrode materials by the solvent. Currently, there are few studies on the effect of electrolyte concentration on organic hosts. However, high-concentration electrolytes are conducive to the application of organic hosts in aqueous electrolytes. We have analyzed the two types of organic hosts that have been most extensively studied, namely heterocyclic compounds and polyaniline. They are characterized by high performance and ease of preparation.

Influence on heterocyclic compounds. For heterocyclic compounds, anion selectivity plays a crucial role in the two-electron redox process: The ionic radius order is $\text{BF}_4^- < \text{ClO}_4^- < \text{PF}_6^- < \text{TFSI}^-$. As the anion size increases, the polarization between oxidation and reduction peaks increases, indicating that smaller anions favor faster electron transfer.⁸⁹ Duan *et al.* reported that the electrochemical behavior of poly(2-vinyl-5,10-dimethyl-dihydrophenazine) (PVDMP) varies with PF_6^- , ClO_4^- , and TFSI^- electrolytes. Among these, TFSI^- owns the largest Stokes radius and the most positive molecular electrostatic potential (Figure 10A), representing the weakest ability to form ion pairs with oxidized active groups, followed by PF_6^- and ClO_4^- . The strong ability of forming ion pair can promote the oxidation of PVDMP, thereby reducing the redox potential (Figure 10B).⁸³

The solvent choice also affects voltage significantly, as seen in zinc-ion

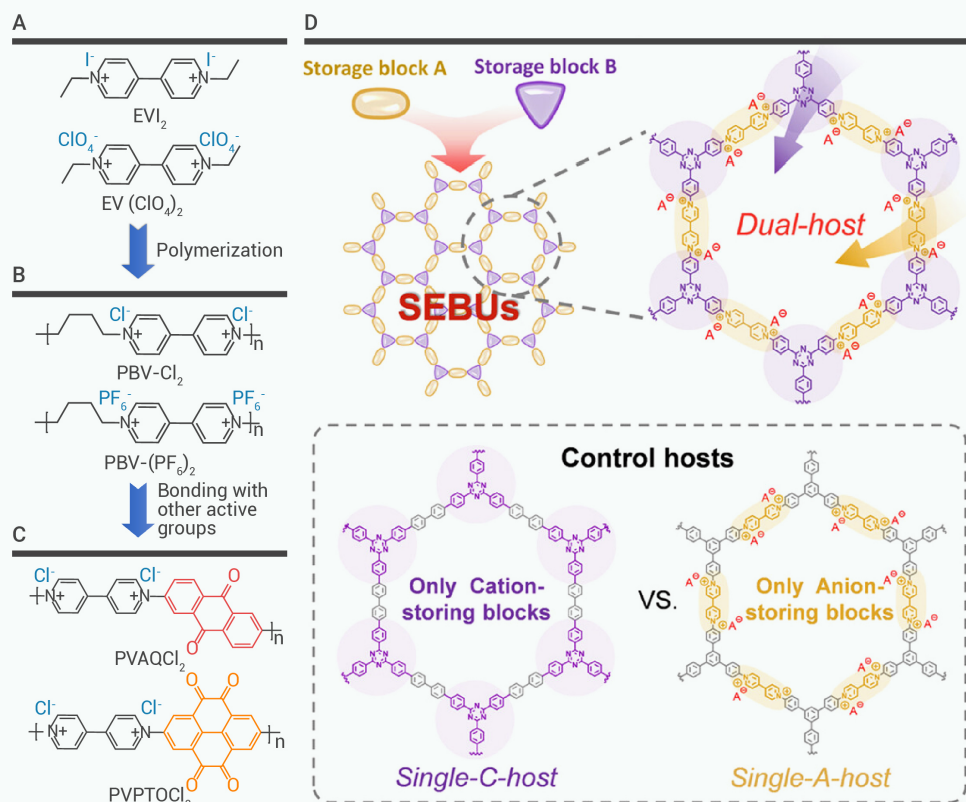


Figure 8. Viologen compounds. Structural development of viologen compounds: (A) Small molecules, (B) non-conjugated polymer, (C) conjugated polymer with other active groups, (D) Design principles of bipolar compounds with cation and anion co-storage. Reproduced with permission.²⁴² Copyright 2023, Wiley-VCH.

batteries. The redox potential of p-type organic materials involves two thermodynamic steps: Oxidation of the organic material (removal of electrons from π -conjugated structures) is associated with an energy change, ΔG_1 . Neutralization of positive charges through anion adsorption, involving desolvation energy (ΔG_2) and coordination energy (ΔG_3). The total Gibbs free energy change, $\Delta G_4 = \Delta G_1 + \Delta G_2 - \Delta G_3$, determines the cathode potential (Nernst equation, $E = -\Delta G_4/nF$) (Figure 10C&D). For example, in Zn//TT batteries, the desolvation energy of Zn(OTF)₂ in various solvents followed the order polyethylene glycol (PEG) + H₂O < ethylmethyl carbonate (EMC) < acetonitrile (ACN), resulting in voltage outputs of 1.3V, 1.5V, and 1.7V, respectively.⁷⁴

Influence on PANI Electrodes. As is well known, as the organic electrode that has been applied earliest and most widely, the deprotonation of PANI (polyaniline) significantly affects its stability. Therefore, the electrolyte needs to provide a proton environment. In addition, the electrolyte concentration significantly impacts PANI electrodes: In low-concentration electrolytes, PANI undergoes irreversible deprotonation, forming pernigraniline, which degrades stability.¹²⁴ High-concentration electrolytes mitigate side reactions, improving cycling performance. Better reversibility can be obtained using NaClO₄ electrolyte compared to NaPF₆ electrolyte in sodium-ion based dual-ion battery.¹¹⁷

At present, the capacity of polyaniline is relatively lower compared with other organic electrodes, and the adjustment of the electrolyte has limited influence on the electrochemical performance of polyaniline. However, a large number of low-temperature resistant electrolytes^{264,265} and gel electrolytes^{266,267} have good compatibility with polyaniline electrodes. This significantly expands its application scope and also makes organic electrodes a favorable candidate for energy supply devices in extreme environments or flexible wearable devices.

CONCLUSION AND PERSPECTIVES

In recent years, through unceasing exploration, enhancement, and refinement, certain promising progress has been achieved in dual-ion batteries (DIBs). However, when contrasted with the well-established technology and remarkable triumphs of lithium-ion batteries (LIBs) in the energy-storage market, the development of DIBs is yet in an early stage. In comparison to LIBs, the development of DIBs encounters several major constraints. Firstly, the theoretical capacity of DIBs is relatively low. This is ascribed to the

restricted quantity of active centers within the π -conjugated cathodes. Secondly, issues such as poor cycling stability and low Coulombic efficiency (CE) plague DIBs. In actual commercial applications, the low CE of DIBs gives rise to continuous energy dissipation during the charging procedure. This not only substantially escalates the costs borne by users but also leads to a significant amount of energy waste, thus impeding the wide-scale adoption of DIBs in the market.

Despite these challenges, DIBs represent a promising direction in energy storage technology, offering cost-effective and environmentally friendly solutions. In contrast to LIBs and sodium-ion batteries (SIBs), DIBs possess a distinct edge in terms of high power density. This is due to the fact that they utilize both cations and anions for concurrent charge transport. As a result, it is anticipated that the issue of inconvenient recharging for electric vehicles can be resolved, and the charging

time of electric vehicles can be significantly cut down. Furthermore, DIBs function at relatively high voltages, and with the evolution of novel materials and technologies, their energy density is likely to be enhanced further. Amidst the global pursuit of sustainable development, the eco-conscious attributes of DIBs have garnered considerable market interest. DIBs are capable of employing a range of non-rare elements, including organic material and graphite, as electrode materials, which underscores their sustainable resource utilization and environmental compatibility. These benefits are particularly accentuated in the realm of large-scale energy storage, where DIBs demonstrate their superior potential. To promote the large-scale and commercial application of DIBs, it is still necessary to actively conduct in-depth exploration and innovative practices in the following aspects:

Graphite and π -conjugated organic anion hosts have emerged as viable cathode materials, but key challenges remain. Graphene-based materials continue to dominate as cathodes in DIBs. However, their low capacity and structural collapse during cycling demand innovative strategies for improvement. The poor cycle stability of graphite is mainly caused by the co-intercalation of large-sized anions and solvent molecules, which leads to the collapse of its structure. One effective approach is modulating micro-morphology and expanding interlayer spacing, with the integration of disordered carbon showing the most significant promise. Locally ordered graphitized carbon alleviates anion repulsion and introduces pseudocapacitance, positioning it as a leading candidate for future optimization. Interfacial modifications, such as constructing artificial cathode electrolyte interphase (CEI) membranes, can mitigate electrolyte decomposition and enhance graphite cathode stability. Streamlining the fabrication of CEI membranes will be critical for advancing this strategy.

Organic anion hosts have also gained traction as potential positive electrodes for DIBs, driven by their structural tunability. However, current limitations include restricted active sites in functional groups, poor electrical conductivity, and high dependence on conductive additives ($\geq 30\%$), often tested at low areal loads (1–2 mg cm⁻²). Addressing these issues requires the development of novel functional groups to enhance theoretical capacity. Polycyclic aromatic hydrocarbons (PAHs), with their extensive π -conjugated surfaces, offer significant potential for multi-electron transfer, presenting a promising avenue for capacity breakthroughs. Moreover, donor-acceptor (D-A) structures and anion-cation co-storage mechanism could enhance

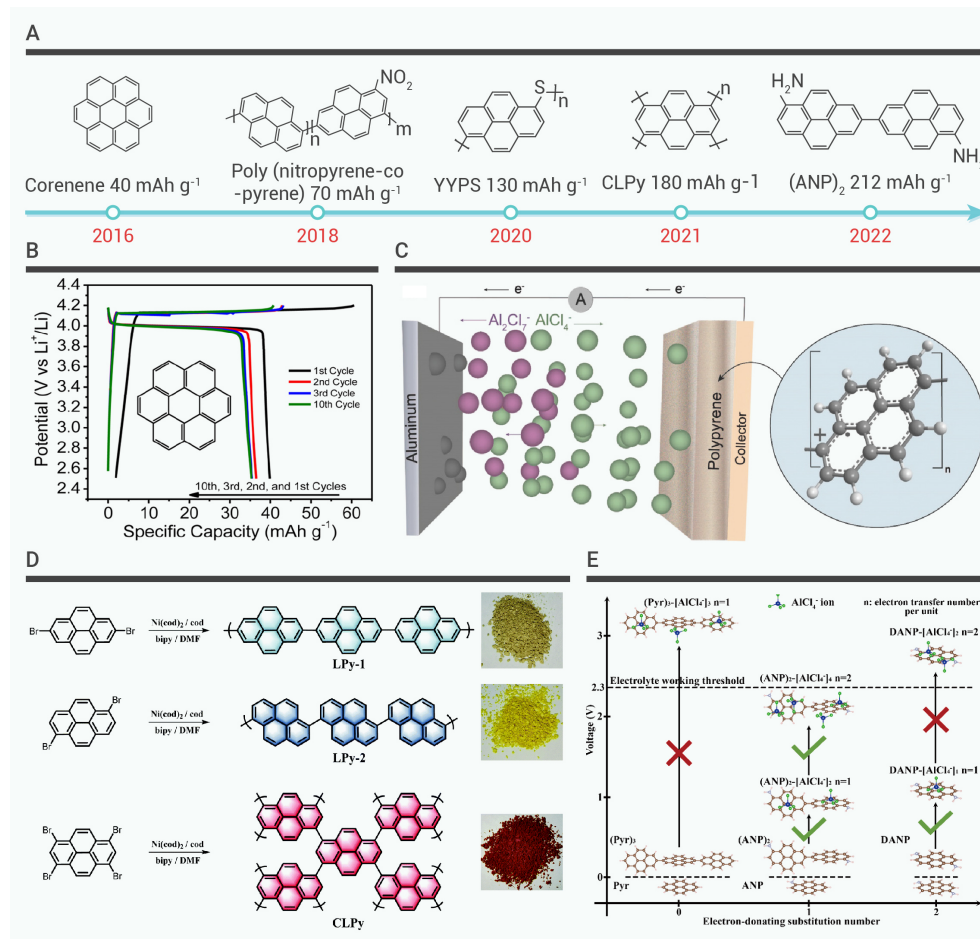


Figure 9. Polycyclic aromatic hydrocarbons (PAHs) and their derivatives

nisms, and desolvation-free processes position them as excellent candidates for low-temperature batteries. However, current organic electrodes for such applications are primarily phenylamine derivatives, which offer limited capacity. Expanding the library of p-type organic materials tailored for low-temperature conditions and enhancing compatibility with low-temperature electrolytes could drive significant advancements in this field.

Finally, while DIBs have made notable strides, their development lags behind traditional LIBs. Beyond designing high-performance DIBs, advancing in situ and operando characterization techniques is critical to elucidating their energy storage mechanisms, such as electrochemical in-situ quartz crystal microbalance technology (EQCM). EQCM is an in situ characterization technique founded on the piezoelectric effect of quartz crystals. In this technique, when the mass of the electrode material varies, the oscillation frequency of the quartz crystal alters correspondingly. Through precise measurement of this frequency change, researchers are able to monitor in real-time the mass variation of the electrode material during the adsorption and desorption processes of fluoride ions. This, in turn, enables a profound understanding of the adsorption behavior and

internal electron transport, reducing the reliance on conductive carbon and enabling higher-load electrodes.

The electrolyte system plays a pivotal role in optimizing DIB performance. High-concentration electrolytes (HCEs) are effective in broadening the electrochemical stability window and minimizing side reactions. However, their high viscosity and cost hinder practical application. Localized high-concentration electrolytes (LHCEs) provide a feasible alternative by balancing stability and cost. For organic hosts, tailored electrolyte formulations—considering solvent type, salt composition, and concentration—are essential to maximize voltage, capacity, and cycling stability. Despite some progress, the integration of organic hosts in aqueous DIBs remains limited due to compatibility challenges. While “water-in-salt” electrolytes can mitigate some issues, their high viscosity and low ion diffusion restrict rate capabilities.²⁶⁸ Future efforts should focus on refining aqueous electrolyte designs to unlock the potential of organic hosts in new applications.

Organic materials' large internal space, surface anion adsorption mecha-

anism of fluoride ions on the electrode surface.^{269–271} The mass change of the electrode per mole of electrons transferred is utilized to monitor the battery charge-discharge process. As such, it can offer insights into both ion and electron transport, rendering it a potent instrument for clarifying the charge-storage mechanism of novel electrode materials. EQCM has been applied to verify the anion-transfer mechanism at the cathode of dual-ion batteries.^{272,273} EQCM also can be employed to investigate the interaction between the electrolyte and the anionic host. This application enables the comprehensive screening of electrolytes.²⁷⁴ Furthermore, computational modeling represents a crucial approach for researching the energy-storage mechanism of dual-ion batteries. Computational models established via first-principal calculations and molecular dynamics simulations are capable of unveiling the microscopic intercalation mechanism, diffusion behavior, and reaction kinetics of anions within electrode materials. Moreover, with the continuous advancement and maturation of high-throughput computing and machine learning^{275,276}, the integration of advanced characterization tech-

Table 5. Summary on electrochemical performance of polycyclic aromatic hydrocarbons and their derivatives as electrode materials in DIB.

Electrode	Electrolyte	Counter electrode	Discharge voltage (V)	Capacity (mAh g ⁻¹)	Rate capability (mAh g ⁻¹)	Cycle numbers (Current density or/and capacity retention)	Ref.
Coronene	1 M LiPF ₆ in EC/DEC (v/v, 1:1)	Li	4 V	40	21 (0.5 A g ⁻¹)	960 (0.02 A g ⁻¹ , 92%)	244
Coronene	1 M NaPF ₆ in EC/DEC (v/v, 1:1)	Na	3.75	43	15 (0.2 A g ⁻¹)	1,000 (0.1 A g ⁻¹ , 85%)	245
Poly(nitropyrene-co-pyrene)	AlCl ₃ in [EmIm]Cl (molar ratio = 1.3:1)	Al	1.7	100	—	300 (0.2 A g ⁻¹)	246
polypyrrole	AlCl ₃ in [EmIm]Cl (molar ratio = 1.3:1)	Al	1.7	70	—	1,000 (0.2 A g ⁻¹)	246
PPYS	1 M LiClO ₄ in PC	Li	2.8	140	90 (1 A g ⁻¹)	1,000 (1 A g ⁻¹)	247
CLPY	30 M ZnCl ₂ in H ₂ O	Zn	0.82	180	105 (3 A g ⁻¹)	38,000 (3 A g ⁻¹ , 96.4%)	248
ANP/MC	AlCl ₃ in [EmIm]Cl (molar ratio = 1.3:1)	Al	1.55	249	107 (10 A g ⁻¹)	12,000 (10 A g ⁻¹ , 90%)	249

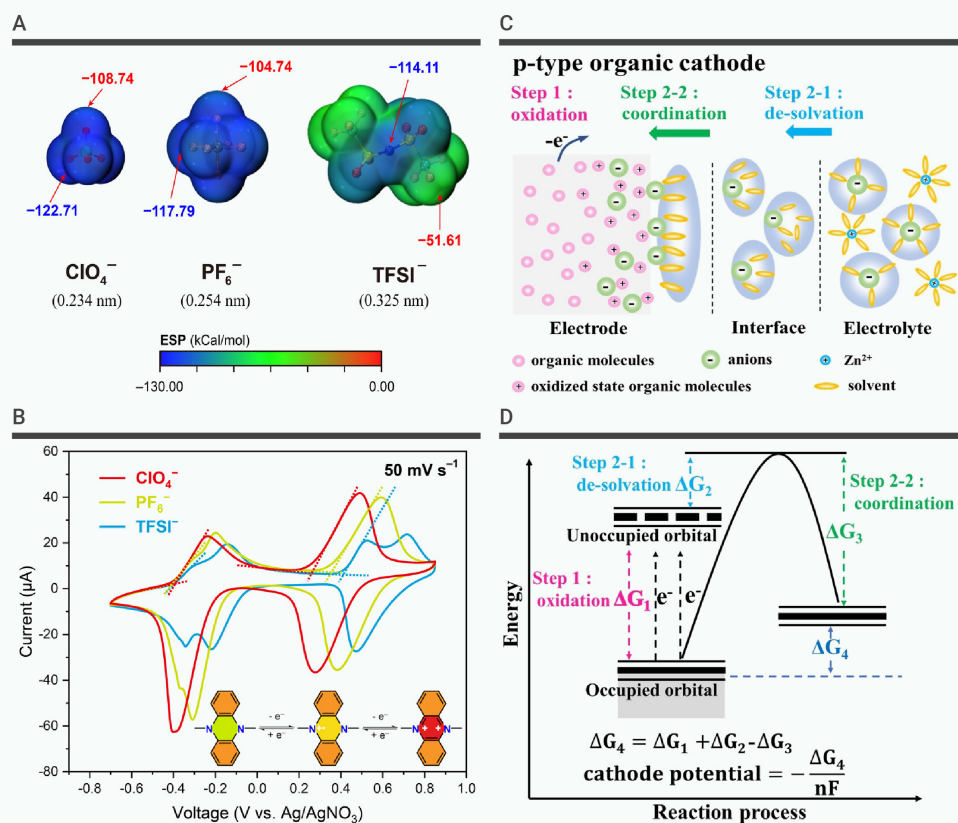


Figure 10. Electrolyte optimization of organic anion hosts (A) Molecular electrostatic potential and Stokes radius of PF₆⁻, ClO₄⁻ and TFSI⁻. (B) Cyclic voltammograms of PVDMP with different anions PF₆⁻, ClO₄⁻ and TFSI⁻ in the electrolyte. Reproduced with permission.¹⁴⁹ Copyright 2023, Wiley-VCH. (C) Scheme of the reaction process of organic p-type materials in zinc-ion batteries. (D) Scheme of the composition of the cathode potential. Reproduced with permission.¹⁴⁹ Copyright 2022, Wiley-VCH.

niques holds promise for application in the screening of electrode materials and electrolytes in dual-ion batteries. This deeper understanding will accelerate the evolution of DIB technology, paving the way for a broader spectrum of applications.

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AUTHOR CONTRIBUTIONS

Shicong Zhang collected the data and literature necessary for this work. Shicong Zhang and Chenyu Wei wrote the original manuscript and made the figures. Tianquan Lin supervised all the tasks and revised the manuscript. All authors contributed to the final edition of this article and approved the final submitted version.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

The data that support the plots within this paper and other finding of this study are available from the corresponding author upon request.