

Review

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# Organic cathode materials for aqueous zinc-organic batteries

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## Abstract

Aqueous zinc batteries that utilize metallic Zn as the anode are considered as a promising alternative to lithium-ion batteries due to their intrinsic high safety, low cost, and relatively high energy density. Compared to inorganic cathodes, organic cathodes exhibit several advantages including high theoretical capacity, tunable structure, abundant sources, and environmental friendliness. In this paper, we summarize the recent progress in organic cathodes for aqueous zinc-organic batteries, covering the working mechanisms of three typical types of organic cathodes, their electrochemical performance, and common strategies for further improvement. Finally, we discuss the current challenges and possible future research directions. We hope this review will offer useful information for exploring high-performance organic cathodes.

**Keywords:** Aqueous zinc-organic batteries, organic cathode materials, mechanisms, improvement strategies

## INTRODUCTION

Green energy and new energy storage technologies are vital for addressing the environmental challenges and achieving the carbon neutrality goal. Since Sony introduced the first commercial lithium-ion batteries (LIBs), they have been widely adopted across various fields owing to their high efficiency and decent lifespan<sup>[1,2]</sup>. However, they also have some drawbacks, such as the safety risks, limited lithium reserves and



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high cost<sup>[3,4]</sup>. As a promising alternative to LIBs, aqueous zinc-ion batteries (AZIBs) have garnered significant interest owing to their excellent theoretical capacity (820 mAh·g<sup>-1</sup>), appropriate redox potential (-0.76 V *vs.* standard hydrogen electrode), inherent safety and low cost and demonstrated considerable potential for applications in stationary energy storage systems<sup>[5-9]</sup>.

Cathode materials play a crucial role in the performance of AZIBs. Currently, the main types of inorganic cathode materials are V/Mn/Co/Mo-based compounds<sup>[10-13]</sup> and Prussian blue analogs<sup>[14,15]</sup>. However, these materials often suffer from slow kinetics and structural instability due to the dissolution and/or lattice evolution during the electrochemical process<sup>[16,17]</sup>. Moreover, some inorganic materials contain harmful and toxic elements that would cause negative environmental impacts. On the other hand, organic materials are more suitable for AZIB cathodes, benefiting from their high theoretical capacity, environmental friendliness, designable structure, and wide availability<sup>[18]</sup>.

As research on AZIBs advances, various organic materials have been employed to develop aqueous zinc-organic batteries (AZOBs)<sup>[19-25]</sup>. However, several challenges, including the low conductivity and stability of organic materials and the unclear charge storage mechanisms, impede their further development. There is a pressing need to consolidate and delve deeper insights into these issues to devise effective solutions. In this review, we present a comprehensive overview and future outlook on AZOBs. We explore their history and mechanisms, the recent advancements in organic cathode, and strategies for enhancing their electrochemical performance. Lastly, we discuss the challenges facing organic cathodes and potential future directions.

## DEVELOPMENT HISTORY AND ELECTROCHEMICAL MECHANISMS

### Development history

AZOBs are composed of anodes, electrolytes, separators, and organic cathodes. The anode is mostly commercial high purity zinc foil. The electrolyte is usually a weakly acidic or neutral aqueous solution containing soluble zinc salts. The separator is generally a glass microfiber filter that separates the anode and cathode and prevents short circuits. The organic cathode is generally prepared by mixing organic materials with active functional groups, conductive agents (e.g., acetylene black and ketjen black), and binders (e.g., polyvinylidene fluoride and carboxymethylcellulose) in different proportions. The organic materials, which are abundant on earth and consist mainly of H, C, N, O, and other elements such as F and S, can be synthesized through biomass or artificial synthesis<sup>[26]</sup>.

The organic cathode materials almost determine the electrochemical properties of AZOBs. In the past few decades, substantial advancements have been achieved in investigating organic cathode materials for AZOBs [Figure 1]. In 1985, Macdiarmid *et al.* first used organics (polyaniline) as a cathode for AZIBs<sup>[27]</sup>. Since then, researchers have reported various organic compounds with different redox-active groups as cathodes for AZOBs, such as nitronyl nitroxides<sup>[28]</sup>, organosulfur compounds<sup>[29]</sup>, conjugated carbonyl compounds<sup>[30]</sup>, triphenylamine derivatives<sup>[31]</sup>, imine compounds<sup>[32]</sup>, dual redox groups compounds<sup>[33]</sup>, nitroaromatics<sup>[34]</sup>, and azobenzene compounds<sup>[35]</sup>. Despite these impressive achievements, designing suitable organic materials to construct AZOBs with high capacity, decent rate performance, and excellent long lifespan remains highly challenging.

### Electrochemical mechanisms

Organic cathode materials of AZOBs can be categorized as p-, n-, and bipolar-type materials based on the change of the free radical state of redox-active groups<sup>[24,36,37]</sup>. Figure 2 presents the corresponding redox mechanisms. For p-type organics (e.g., nitronyl nitroxides, triphenylamine derivatives, and organosulfur

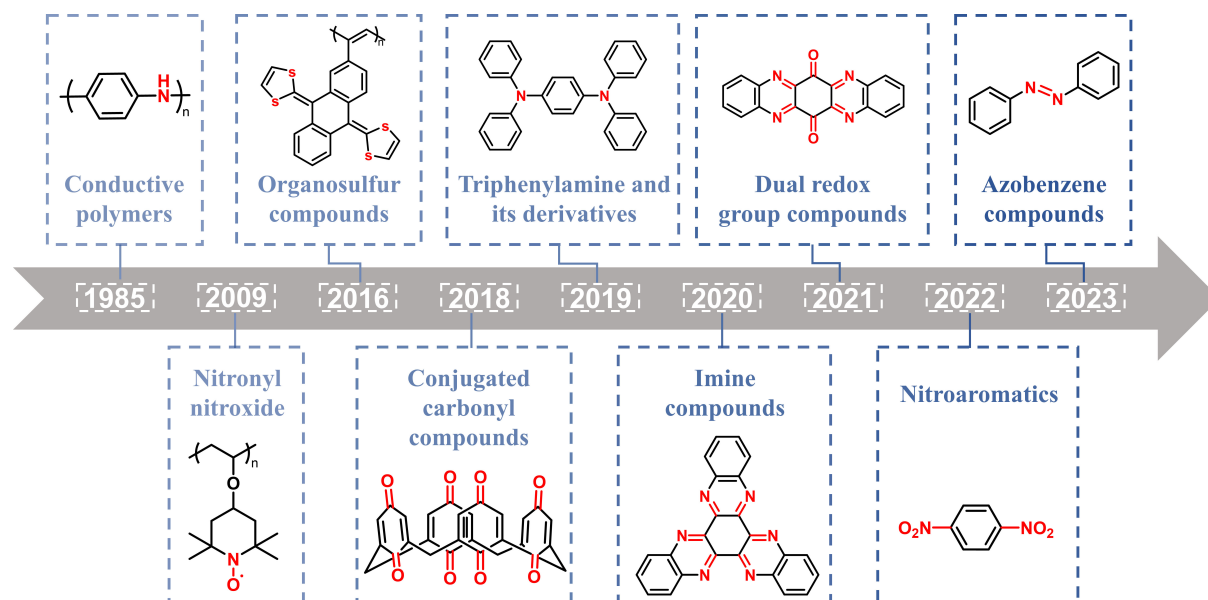


Figure 1. The development of organic cathode materials for AZOBs. AZOBs: Aqueous zinc-organic batteries.

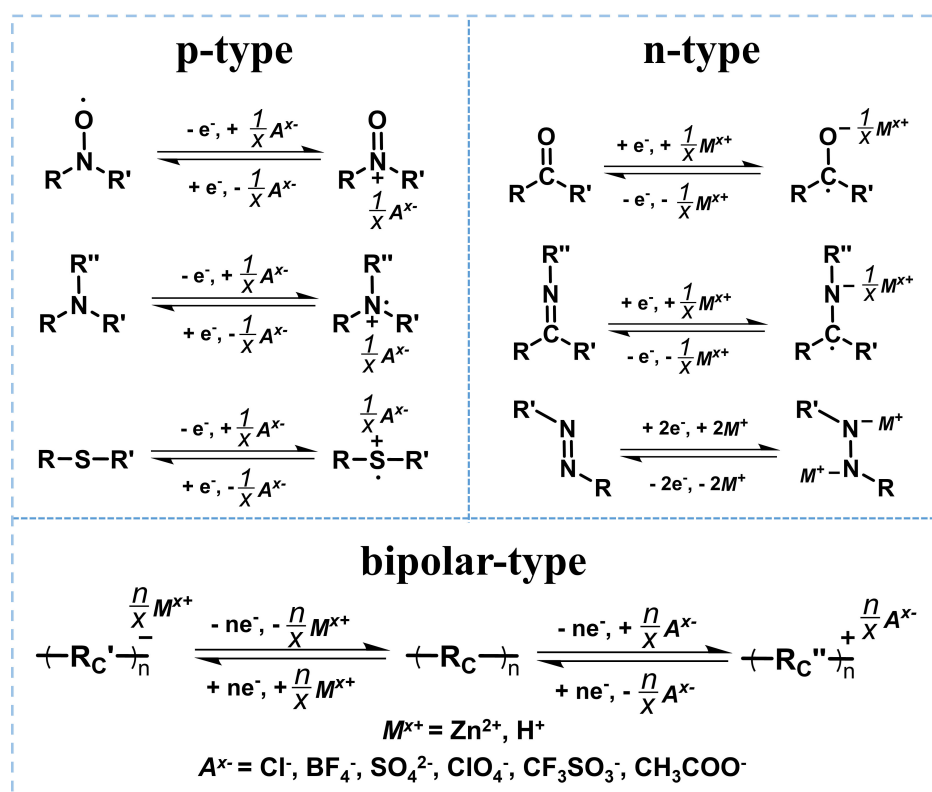


Figure 2. Redox mechanisms of the three types of organics.

compounds), they typically lose electrons and get oxidized; therefore, they must bind to anions in the electrolyte (e.g.,  $\text{Cl}^-$ ,  $\text{BF}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$  or  $\text{CH}_3\text{COO}^-$ ) to remain electric neutrality. On the contrary, n-type organics (such as conjugated carbonyl compounds, imine, and azo compounds) acquire electrons

and convert to anions, which can then be combined with cations (e.g.,  $\text{Zn}^{2+}$  or  $\text{H}^+$ ) to maintain charge balance. Bipolar-type organics exhibit both p- and n-type properties and can be either reduced or oxidized within specific voltage windows<sup>[38]</sup>. In general, p-type organics exhibit low capacities due to limited redox-active molecular structures, whereas n-type organics often possess high specific capacities<sup>[21]</sup>.

Based on the different redox mechanisms, four ion storage mechanisms have been proposed for zinc-organic batteries, i.e.,  $\text{Zn}^{2+}$  storage,  $\text{H}^+$  storage, co-storage of  $\text{H}^+$  and  $\text{Zn}^{2+}$ , and anion storage [Figure 3]. The most reported mechanism is the  $\text{Zn}^{2+}$  storage. Reversible uptake/removal of  $\text{Zn}^{2+}$  takes place during the charging and discharging by coordination with the active center of organics. For example, the active center (C=O) of pyrene-4,5,9,10-tetraone (PTO) can obtain electrons during discharge and convert to anions ( $-\text{C}-\text{O}^-$ ). At the same time, the Zn anode is oxidized to  $\text{Zn}^{2+}$ , combining with  $-\text{C}-\text{O}^-$  of the PTO cathode. On the contrary,  $-\text{C}-\text{O}^-$  loses electrons and is oxidized to the original C=O during charging, while  $\text{Zn}^{2+}$  will be released and reduced on the Zn anode<sup>[39]</sup>. In addition, the hydrated  $\text{Zn}^{2+}$  storage was also confirmed in triangular macrocyclic phenanthrenequinone (PQ- $\Delta$ ) cathode. During the discharge process, PQ- $\Delta$  can capture hydrated  $\text{Zn}^{2+}$ , resulting in a reduced de-solvation energy penalty. The hydrated  $\text{Zn}^{2+}$  ions return to the electrolyte during the subsequent charge process<sup>[40]</sup>.

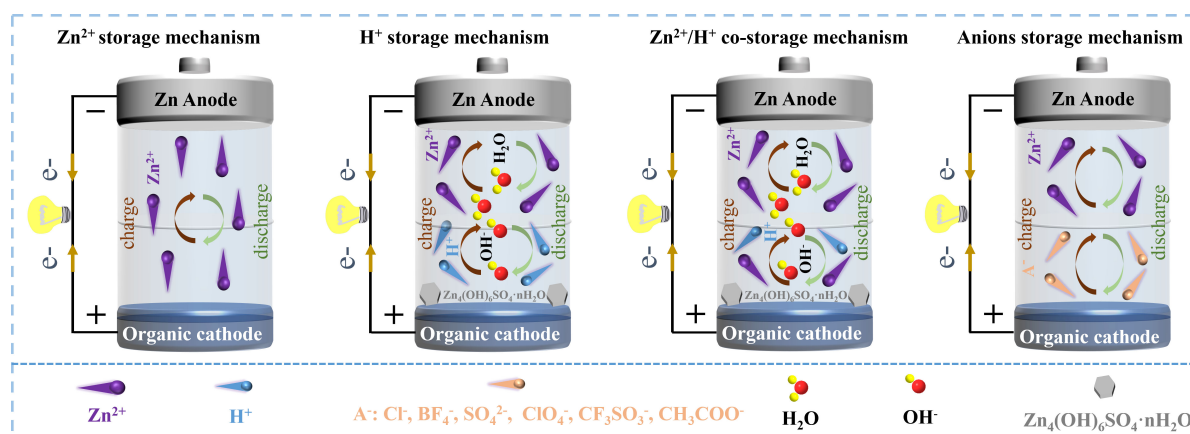
The unique redox mechanism of organic electrodes makes it possible to accommodate various carriers. Compared with  $\text{Zn}^{2+}$ ,  $\text{H}^+$  with a smaller ion radius and lower atomic mass is easier to be inserted into organic cathode materials. Tie *et al.* first observed the reversible uptake/removal of  $\text{H}^+$  in diquinoxalino[2,3-a:2',3'-c]phenazine (HATN) cathode<sup>[32]</sup>. During the discharge process, the C=N functional group in HATN transforms into  $-\text{C}-\text{N}^-$ , combining with  $\text{H}^+$  generated by the decomposition of water in electrolyte. Conversely,  $-\text{C}-\text{N}^-$  is reversibly oxidized to C=N during charging and  $\text{H}^+$  is removed from the HATN cathode. The rapid kinetics of  $\text{H}^+$  uptake/removal endow organic electrodes with excellent electrochemical performance<sup>[41,42]</sup>.

Although the uptake/removal of  $\text{H}^+$  is relatively fast,  $\text{Zn}^{2+}$  may also participate in the storage process together since it has a much higher concentration than  $\text{H}^+$  in the electrolyte. Actually, the phenomenon of  $\text{Zn}^{2+}/\text{H}^+$  co-storage has already been reported in many organic compounds such as dibenzo[b,i]thianthrene-5,7,12,14-tetraone (DTT)<sup>[43]</sup>, diquinoxalino[2,3-a:2',3'-c]phenazine-2,8,14-tricarbonitrile (HATN-3CN)<sup>[44]</sup>, and hexaazatrinaphthalene-quinone (HATNQ)<sup>[45]</sup>. For example, Wang *et al.* confirmed co-storage phenomenon of  $\text{Zn}^{2+}/\text{H}^+$  in the DTT cathode<sup>[43]</sup>. Both experiments and theoretical calculations have proved that  $\text{Zn}^{2+}$  and  $\text{H}^+$  can insert this cathode to form  $\text{DTT}_2(\text{H}^+)_4(\text{Zn}^{2+})$ , improving its stability.

The anion storage mechanism usually occurs in p-type organics, which typically first lose electrons and yield cations, which then bind to anions from the electrolyte. For instance, the nitroxyl radicals of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether) (PTVE) lose electrons and are oxidized to  $-\text{N}^+=\text{O}$  during charging, enabling them to bind with absorbed anions ( $\text{Cl}^-$ ) from electrolyte. In the process of subsequent discharge,  $-\text{N}^+=\text{O}$  reversibly transforms back to nitroxyl radicals, and the anion is removed from the PTVE and released to the electrolyte<sup>[28]</sup>.

## DESIGN OF ORGANIC CATHODES

In the above section, we have discussed the working mechanisms of distinct types of organic cathodes. In general, the molecular structure plays an essential role in determining their redox/ion storage mechanism and, thus, the electrochemical performance. Next, we will discuss the properties and applications of these organic cathodes in AZOBs.



**Figure 3.** Schematic diagram of four different types of ion storage mechanisms for AZOBs during discharging and charging. AZOBs: Aqueous zinc-organic batteries.

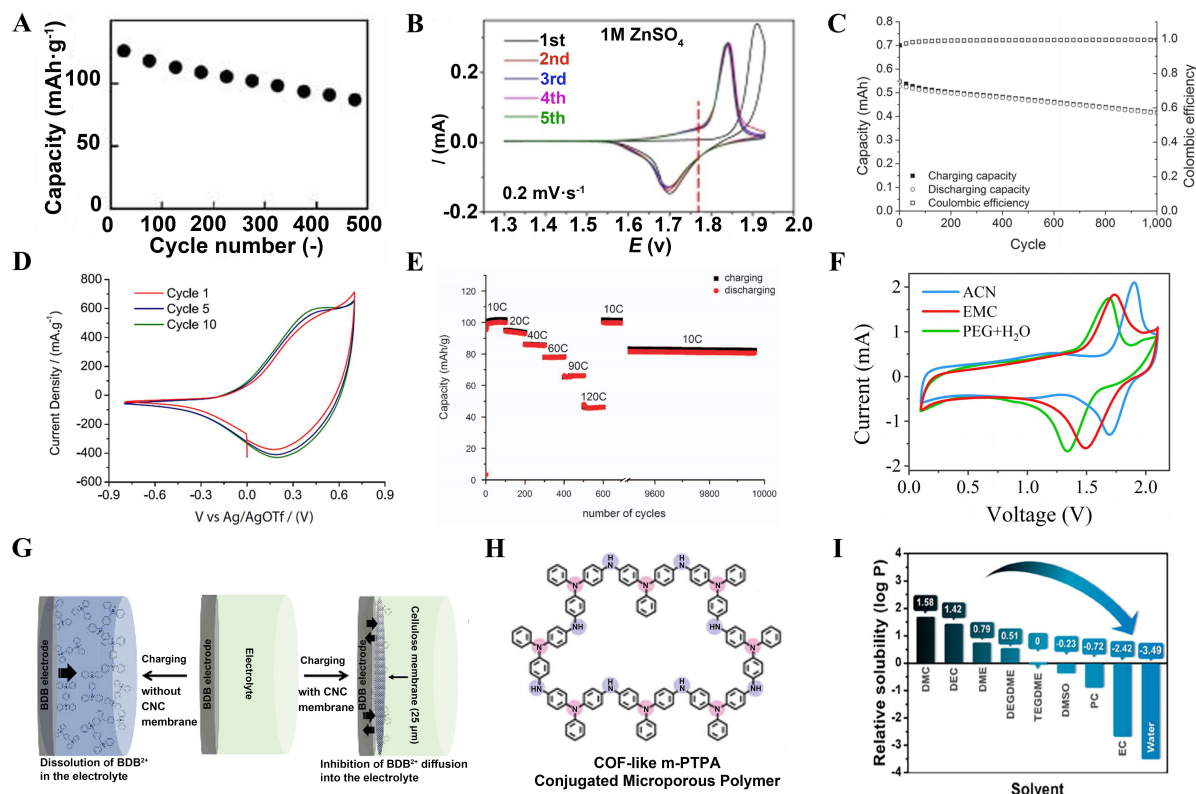
## P-type organic cathodes

### Nitronyl nitroxides

Nitronyl nitroxides typically show fast redox kinetics and high redox voltage<sup>[46]</sup>. In 2009, Koshika *et al.* investigated PTVE with nitroxyl radicals as a cathode for AZOBs<sup>[46]</sup>, which possessed a voltage plateau of 1.7 V and a cycling life of over 500 cycles under 60 C [Figure 4A]. Subsequently, Luo *et al.* found that the anion types can affect the working voltage of PTVE cathodes<sup>[47]</sup>. Benefiting from the strong electrostatic interaction between  $\text{SO}_4^{2-}$  and nitroxyl radicals, the working potential of Zn//PTVE batteries with  $\text{ZnSO}_4$  electrolytes can reach up to 1.77 V [Figure 4B], which is higher than that with  $\text{Zn}(\text{ClO}_4)_2$  electrolytes (1.53 V) and  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  (1.58 V). However, because high voltage would inevitably lead to electrolyte decomposition, the cycling lifespan of Zn//PTVE batteries with  $\text{ZnSO}_4$  electrolytes was comparatively poor with a 21.9% capacity retention over 1,000 cycles under  $1 \text{ A}\cdot\text{g}^{-1}$ . It should be noted that nitronyl nitroxides generally suffer from the dissolution of nitroxyl radicals and exhibit unsatisfactory stability. To solve this problem, Winsberg *et al.* introduced different polymer frameworks to stabilize nitroxyl radicals by synthesizing copolymers of 2,2,6,6-tetramethylpiperidinyl-N-oxyl (TEMPO)<sup>[48]</sup>. The cathode delivered a high voltage window of 2 V and, more importantly, a 78.6% capacity retention after 1,000 cycles [Figure 4C].

### Organosulfur compounds

Organosulfur compounds are also p-type organics, with sulfur as the active site. In 1998, C'iric'-Marjanovic' *et al.* prepared a rechargeable zinc battery based on polythiophene (PT) cathode<sup>[49]</sup>. In non-aqueous electrolytes, PT//Zn batteries can provide a discharge voltage of 1.25 V and a Coulombic efficiency (CE) of over 95% at low current densities ( $10\text{--}50 \mu\text{A}\cdot\text{cm}^{-2}$ ). However, as the current density increased, the CE of PT//Zn batteries significantly decreased. Poly(3,4-ethylenedioxythiophene) (PEDOT) is another common conjugated sulfide compound that can be synthesized using PT. In 2015, Simons *et al.* designed rechargeable PEDOT//Zn batteries using imidazolium-based ionic liquid as the electrolytes<sup>[50]</sup>. The cyclic voltammetry (CV) curves are almost identical under various cycles [Figure 4D], indicating a good structural reversibility of the PEDOT cathode. Subsequently, Häupler *et al.* prepared a poly(acetylene)-based polymer cathode with 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moieties (PexTTF) for AZOBs<sup>[29]</sup>. Thanks to the conjugated skeleton that improves the electron transfer, the battery delivered a remarkable rate capacity ( $111 \text{ mAh}\cdot\text{g}^{-1}$  at 120 C). Additionally, it provided an  $81 \text{ mAh}\cdot\text{g}^{-1}$  capacity after 9,400 cycles under 10 C, with a loss of approximately 14% [Figure 4E]. Recently, Cui *et al.* reported three organic sulfur compounds (thianthrene, phenoxathiine and phenothiazine) as cathodes for zinc metal batteries<sup>[51]</sup>. They



**Figure 4.** (A) Cycling performance of PTV cathode. Reproduced with permission<sup>[46]</sup>. Copyright 2009, Wiley Online Library; (B) CV profiles of Zn//PTVE battery based on 1M ZnSO<sub>4</sub> electrolyte. Reproduced with permission<sup>[47]</sup>. Copyright 2020, Wiley Online Library; (C) Cycling performance of TEMPO cathode. Reproduced with permission<sup>[48]</sup>. Copyright 2016, Wiley Online Library; (D) CV profiles of PEDOT cathode. Reproduced with permission<sup>[50]</sup>. Copyright 2015, Wiley Online Library; (E) Rate capability of PexTTF. Reproduced with permission<sup>[29]</sup>. Copyright 2016, Springer Nature; (F) CV curves of thianthrene cathode. Reproduced with permission<sup>[51]</sup>. Copyright 2022, Wiley Online Library; (G) Diagram of the function of CNC membrane. Reproduced with permission<sup>[31]</sup>. Copyright 2019, American Chemical Society; (H) Synthesis route of m-PTPA. Reproduced with permission<sup>[52]</sup>. Copyright 2021, Wiley Online Library; (I) The relative solubility of DMPZ in different electrolyte solvents. Reproduced with permission<sup>[53]</sup>. Copyright 2022, American Chemical Society. PTV: Poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether); CV: cyclic voltammetry; TEMPO: 2,2,6,6-tetramethylpiperidiny-N-oxyl; PEDOT: poly(3,4-ethylenedioxythiophene); PexTTF: 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moieties; CNC: cellulose nanocrystal; m-PTPA: porous polytriphenylamine; DMPZ: 5,10-dihydro-5,10-dimethylphenazine.

found that electron cloud density is a key factor influencing the voltage of organics. Organics with a uniform distribution of electron clouds are more likely to lose electrons, leading to an increase in electron loss energy, which, in turn, provides a relatively high voltage. The discharge voltage of thianthrene with symmetrically distributed electron clouds can reach 1.5 V in a solution of ethyl methyl carbonate with 1M zinc trifluoromethanesulfonate [Zn(OTF)<sub>2</sub>] as electrolyte, which is higher than that of phenoxathiine and phenothiazine. The operating voltage can be further increased by electrolyte design by manipulating the anionic de-solvation energy. In Zn(OTF)<sub>2</sub> electrolyte using acetonitrile as the solvent, the voltage of the thianthrene cathode can reach 1.7 V [Figure 4F].

### Triphenylamine derivatives

Triphenylamine derivatives with strongly electron-donating N atoms can readily oxidize to form positively charged cationic radicals<sup>[22]</sup>. For example, the tertiary nitrogen of 1,4 bis(diphenylamino)benzene (BDB) molecule undergoes reversible oxidation/reduction in two steps, while anions are inserted/released from high concentration aqueous electrolytes with high oxidative stability<sup>[31]</sup>. However, the BDB discharge products are severely dissolved in the electrolyte, leading to a gradual loss of capacity during cycling. Glatz

*et al.* introduced an additional cellulose membrane and a glass fiber separator to limit the dissolution of BDB discharged products [Figure 4G]. The BDB cathode combined with cellulose nanocrystal (CNC) membrane can maintain an ~82% capacity retention over 500 cycles at  $0.39 \text{ A}\cdot\text{g}^{-1}$  and exhibit decent cycling life. To further enhance the stability of triphenylamine derivatives, Zhang *et al.* prepared a porous polytriphenylamine (m-PTPA) as the cathode of AZOBs [Figure 4H]<sup>[52]</sup>. The m-PTPA with insoluble polymerization skeleton and specific 3D covalent organic framework exhibited a decent electrochemical stability (an 87.6% retention over 1,000 cycles under  $16 \text{ A}\cdot\text{g}^{-1}$ ). In addition to adjusting the molecular structure, electrolyte design can also improve the stability of triphenylamine derivatives. Lee *et al.* found that the solubility of 5,10-dihydro-5,10-dimethylphenazine (DMPZ) in water is significantly lower than that in most non-proton solvents [Figure 4I]<sup>[53]</sup>. A DMPZ cathode can maintain an ~81% capacity retention over 1,000 cycles at  $0.255 \text{ A}\cdot\text{g}^{-1}$  in 17 m NaClO<sub>4</sub> aqueous electrolyte, which proves the decent cycling stability.

### Conductive polymers

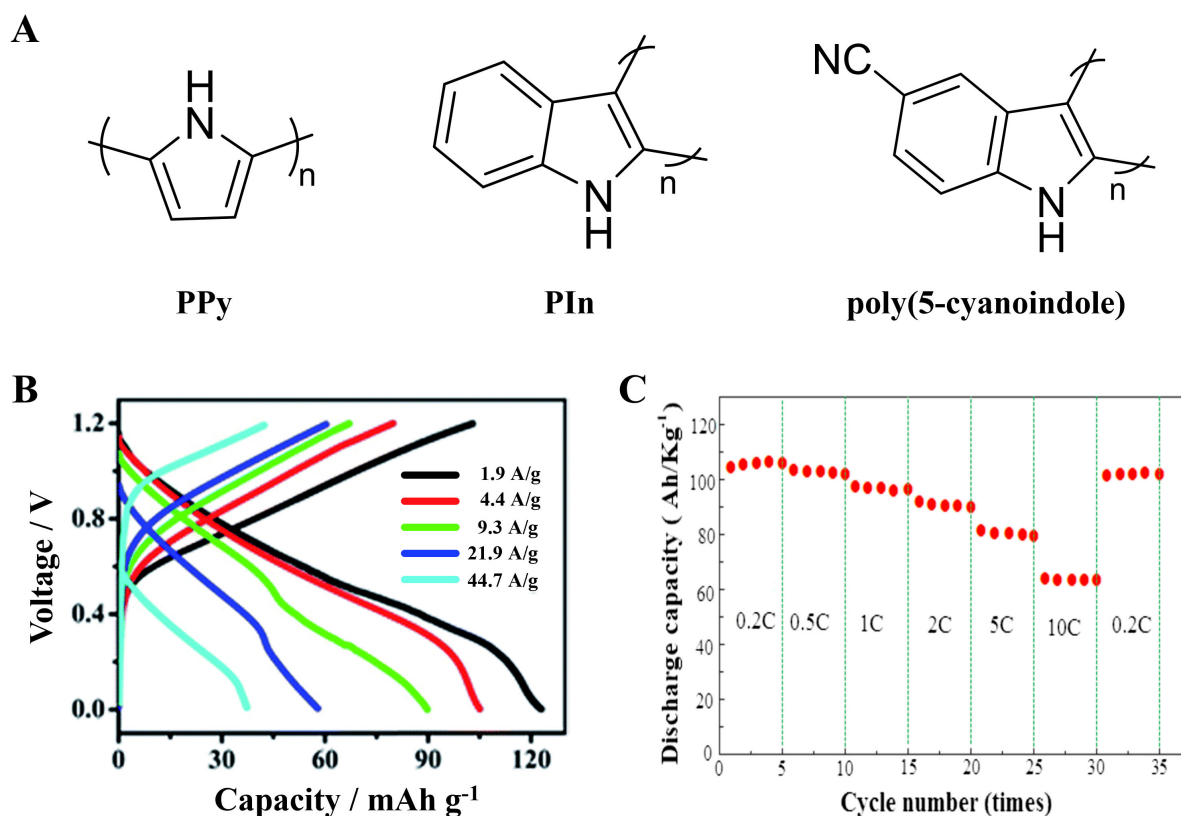
Conductive polymers (CPs) have high conductivities and highly delocalized electron clouds, which would contribute to rapid redox kinetics<sup>[22,54]</sup>. Various polymers, such as polypyrrole (PPy)<sup>[55]</sup>, polyindole (PIn)<sup>[56,57]</sup>, and poly(5-cyanoindole)<sup>[58]</sup>, have been reported as cathodes for AZOBs [Figure 5A]. Among them, PPy has been extensively explored benefiting from its high redox reversibility, non-toxicity, and decent conductivity. Wang *et al.* prepared the Zn//PPy cell based on PPy cathodes and obtained a capacity of  $123 \text{ mAh}\cdot\text{g}^{-1}$  at  $1.9 \text{ A}\cdot\text{g}^{-1}$  [Figure 5B]<sup>[55]</sup>. PIn and its derivatives also have high conductivities. Cai *et al.* synthesized PIn as the cathode for AZOBs, which displayed a capacity of about  $80\text{-}60 \text{ mAh}\cdot\text{g}^{-1}$  at  $200\text{-}1,000 \text{ A}\cdot\text{m}^{-2}$ , demonstrating a good rate capability<sup>[57]</sup>. Subsequently, they used poly(5-cyanoindole) fibers as the cathode of AZOBs<sup>[58]</sup>. Zn//poly(5-cyanoindole) cell showed a voltage of 2.0 V and the highest discharge capacity ( $107 \text{ mAh}\cdot\text{g}^{-1}$ ) at 0.2 C [Figure 5C], much higher than that of Zn//PIn batteries ( $80 \text{ mAh}\cdot\text{g}^{-1}$ ).

In summary, p-type organic cathodes generally exhibit high redox potentials, which can be attributed to the nature of their redox reactions. In p-type materials, the redox reactions involve the removal of electrons from the highest occupied molecular orbital (HOMO) or single occupied molecular orbital (SOMO) during oxidation<sup>[59]</sup>. This process typically results in higher redox potentials compared to n-type materials (which will be discussed later). However, high voltages inevitably lead to the decomposition of aqueous electrolytes, which results in poor cycling performance. Using organic electrolytes can effectively solve this problem<sup>[51,60]</sup>, but it suffers from safety hazards and high costs. Introducing electrolyte additives could be a viable way to improve the stability of aqueous electrolytes as their efficacy has already been confirmed in aqueous Zn batteries<sup>[61,62]</sup>. Moreover, some p-type organic cathodes and their discharge products in aqueous electrolytes suffer from severe dissolution and thus poor cycling lifespan, which can be improved by electrolyte and separator design and the structural optimization through co-polymerization<sup>[29,48]</sup>. It is worth mentioning that most p-type organic cathodes suffer from complex preparation processes and low capacity, which hinder their application. In contrast, n-type organic cathodes often possess high capacity, and their preparation is relatively simple. Below, we will discuss the latest progress in n-type organic cathodes for AZOBs.

## N-type organic cathodes

### Conjugated carbonyl compounds

As a typical N-type cathode material, conjugated carbonyl compounds have been widely studied as cathodes for AZOBs owing to their good reversibility, diverse structure, and outstanding theoretical capacity [Figure 6]<sup>[30,63-75]</sup>. In the process of discharge, the carbonyl group (C=O) obtained electrons and converted to enolate (C-O), accompanied by the insertion of cations (Zn<sup>2+</sup> or H<sup>+</sup>) to maintain charge neutrality. Below, we will discuss three typical types of conjugated carbonyl compounds, namely, quinones, ketones and imides.

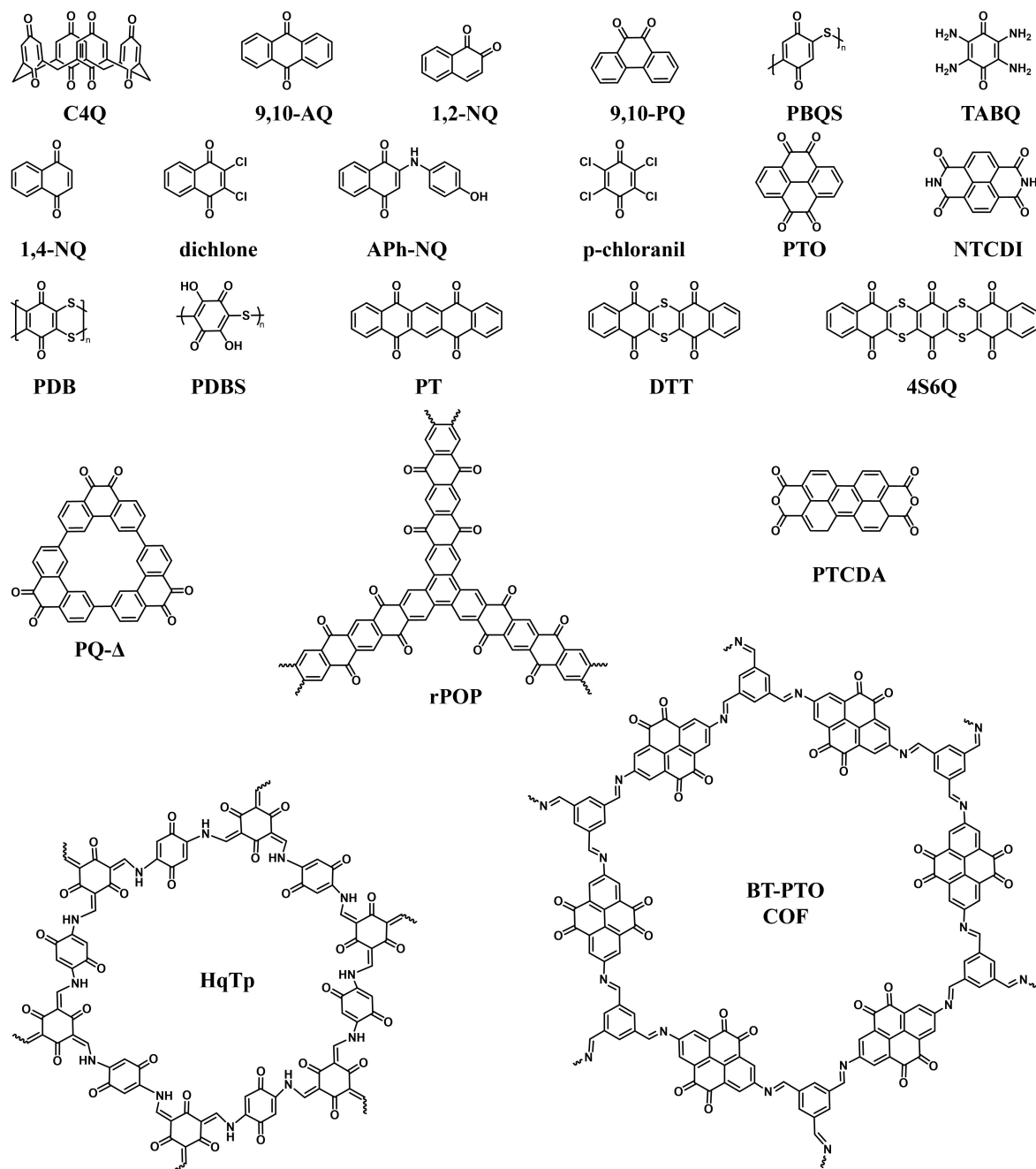


**Figure 5.** (A) The molecular structure of p-type conductive polymers, including PPy, PIn and poly(5-cyanoindole); (B) (Dis-)charge profiles of Zn//PPy battery under different currents. Reproduced with permission<sup>[55]</sup>. Copyright 2018, Royal Society of Chemistry; (C) Rate capability of the Zn//poly(5-cyanoindole) battery. Reproduced with permission<sup>[58]</sup>. Copyright 2015, Elsevier. PPy: Polypyrrole.

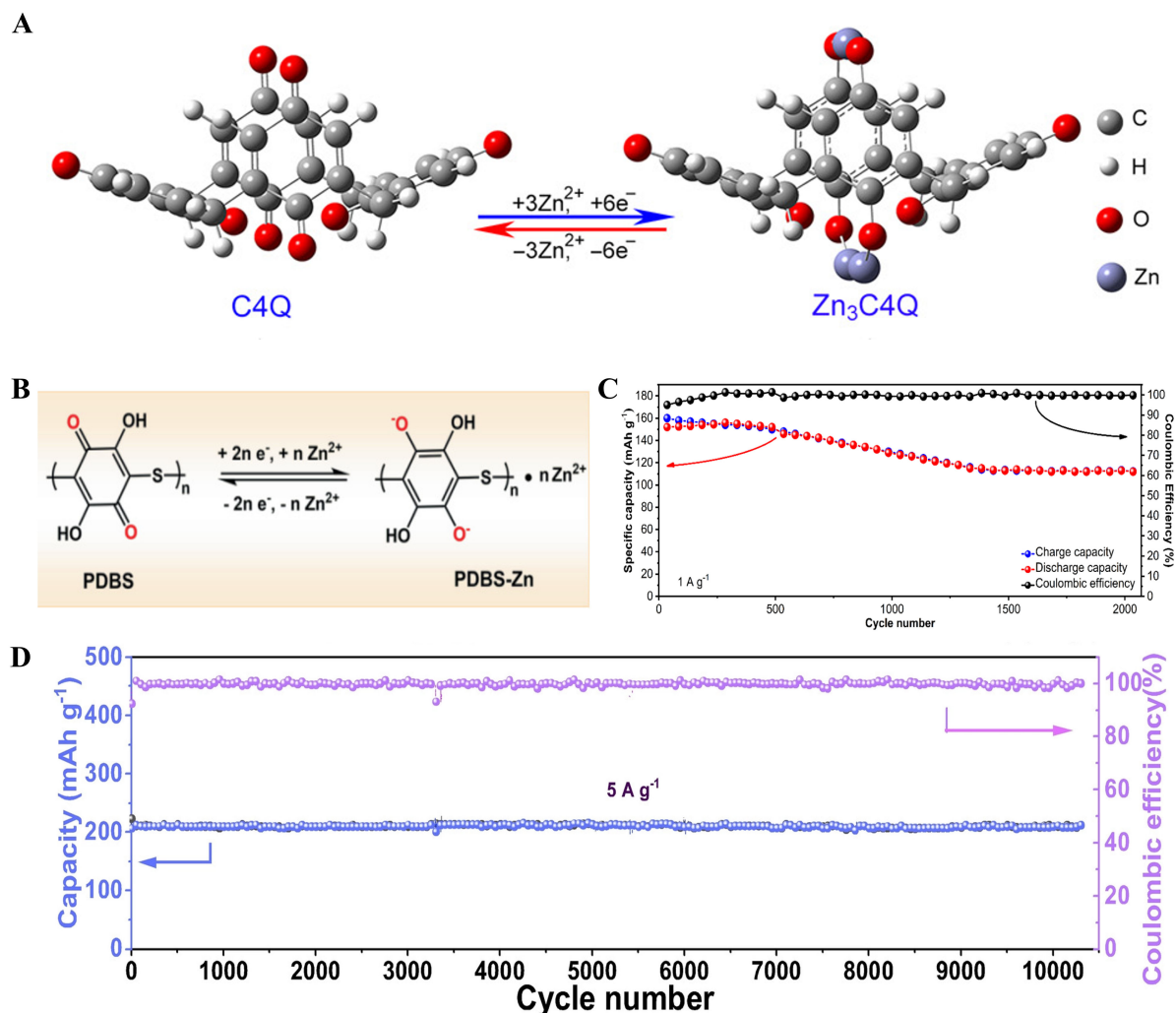
Zhao *et al.* explored for the first time various quinone compounds, including 9,10-anthraquinone (9,10-AQ), calix[4]quinone (C4Q), 9,10-phenanthrenequinone (9,10-PQ), 1,2-naphthoquinone (1,2-NQ), and 1,4-naphthoquinone (1,4-NQ) as cathode materials for AZOBs<sup>[30]</sup>. Among them, the C4Q exhibits a high capacity of 335 mAh·g<sup>-1</sup> thanks to the open bowl structure that possesses a small steric hindrance and thus can accommodate more Zn<sup>2+</sup> [Figure 7A]. However, the discharge product C4Q<sup>2x-</sup> of C4Q can dissolve in the electrolyte, pass through the filter paper, and react with zinc to form byproducts, resulting in poor cycling life, which is a common problem for quinone compounds. Multiple strategies have, therefore, been proposed to address this issue. For instance, Zhao *et al.* used a Nafion membrane to prevent anions from passing through by utilizing the ionic selectivity of the membrane<sup>[30]</sup>. As a result, the battery can be operated for at least 1,000 cycles under 0.5 A·g<sup>-1</sup>, with a capacity decay of only 0.015% per cycle. Hybridizing quinone-based compounds with carbons [such as graphene and carbon nanotubes (CNTs)] is also a common method for enhancing stability and improving conductivity<sup>[65,76]</sup>. Kumankuma-Sarpong *et al.* investigated several composites of naphthoquinone (NQ)-based organics and CNTs for AZOBs<sup>[65]</sup>. They found that during the redox process, the CNT skeleton not only provides electrical and ionic pathways but also minimizes the discharge product dissolved. After 1,500 cycles under 0.339 A·g<sup>-1</sup>, Zn-NQ@CNT batteries can also show a capacity of 137.2 mAh·g<sup>-1</sup>. Additionally, the stability of organic cathodes can be enhanced by small molecule polymerization. Sun *et al.* prepared a poly(2,5-dihydroxy-1,4-benzoquinonyl sulfide) (PDBS) as the cathode in AZOBs<sup>[69]</sup>. The O and S coordination groups exhibit strong electron donor properties during discharge and can be used as the coordination arms of Zn<sup>2+</sup> [Figure 7B]. Hence, PDBS||Zn cell can provide a 79% capacity retention after 2,000 cycles under 2 A·g<sup>-1</sup>.



## Conjugated carbonyl compounds



**Figure 6.** The molecular structure of common carbonyl compounds in AZOBs<sup>[30,63-75]</sup>. AZOBs: Aqueous zinc-organic batteries; C4Q: calix[4]quinone; 9,10-AQ: 9,10-anthraquinone; 1,2-NQ: 1,2-naphthoquinone; 9,10-PQ: 9,10-phenanthrenequinone; PBQS: poly(benzoquinonyl sulfide); TABQ: tetraamino-p-benzoquinone; 1,4-NQ: 1,4-naphthoquinone; APh-NQ: 2-[(4-hydroxyphenyl) amino] naphthalene-1,4-dione; PTO: pyrene-4,5,9,10-tetraone; NTCDI: 1,4,5,8-naphthalene diimide; PDB: 2,5-dihydroxy-1,4-benzoquinonyl; PDBS: poly(2,5-dihydroxy-1,4-benzoquinonyl sulfide); PT: polythiophene; DTT: dibenzo[b,i]thianthrene-5,7,12,14-tetraone; 4S6Q: 6a,16a-dihydrobenzo[b]naphtho[2',3':5,6][1,4]dithiino[2,3-i]thianthrene-5,7,9,14,16,18-hexaone; PQ-Δ: triangular macrocyclic phenanthrenequinone; rPOP: redox-active quinone-based porous organic polymer; PTCDA: perylene-3,4,9,10-tetracarboxylic dianhydride; HqTp: Hq-2,5-diaminohydroquinone, Tp-1,3,5-triformylphloroglucinol; BT-PTO: benzenetricarboxaldehyde pyrene-4,5,9,10-tetraone; COF: covalent organic frameworks.



**Figure 7.** (A) The  $\text{Zn}^{2+}$  storage mechanism of the C4Q cathode. Reproduced with permission<sup>[30]</sup>. Copyright 2018, AAAS; (B) The  $\text{Zn}^{2+}$  storage mechanism of the PDBS-Zn. Reproduced with permission<sup>[69]</sup>. Copyright 2021, Wiley Online Library; (C) Cycling performance of NTCDI cathode. Reproduced with permission<sup>[67]</sup>. Copyright 2019, Wiley Online Library; (D) Cycling performance of BT-PTO COF cathode under  $5 \text{ A g}^{-1}$ . Reproduced with permission<sup>[75]</sup>. Copyright 2022, Wiley Online Library. C4Q: Calix[4]quinone; PDBS: poly(2,5-dihydroxy-1,4-benzoquinonyl sulfide); NTCDI: 1,4,5,8-naphthalene diimide; BT-PTO: benzenetricarboxaldehyde pyrene-4,5,9,10-tetraone; COF: covalent-organic frameworks.

Compared with quinone compounds, ketone compounds usually exhibit good stability in electrolytes. For instance, PTO cathodes can maintain an  $\sim 70\%$  capacity retention after 1,000 cycles under  $3 \text{ A g}^{-1}$ , which verifies a decent cycling life<sup>[39]</sup>. Compared with quinones and ketones, nitrogen atoms in imide compounds have lone pair electrons, which can improve the storage capacity of  $\text{Zn}^{2+}$  by enhancing the redox ability of carbonyl groups. Wang *et al.* prepared 1,4,5,8-naphthalene diimide (NTCDI) as the cathode for AZOBs<sup>[67]</sup>. The large  $\pi$ -conjugated structure makes NTCDI flexible and guarantees its durability during continuous discharge and charge, maintaining a 73.7% capacity retention under  $1 \text{ A g}^{-1}$  after 2,000 cycles [Figure 7C]. Covalent-organic frameworks (COF) containing carbonyl groups are also popular cathode materials for AZOBs. Zheng *et al.* synthesized the BT-PTO COF cathode using a benzenetricarboxaldehyde (BT) node and PTO monomer<sup>[75]</sup>. Thanks to the ordered channel structure that promotes the ion transfer, the cathode provided a prominent cycle lifespan, with a 98.0% capacity retention over 10,000 cycles under  $5 \text{ A g}^{-1}$  [Figure 7D]. However, the synthesis of COFs is usually complicated and tedious, and the inactive node components in these frameworks would increase molecular weight and reduce their theoretical capacity.

### *Imine compounds*

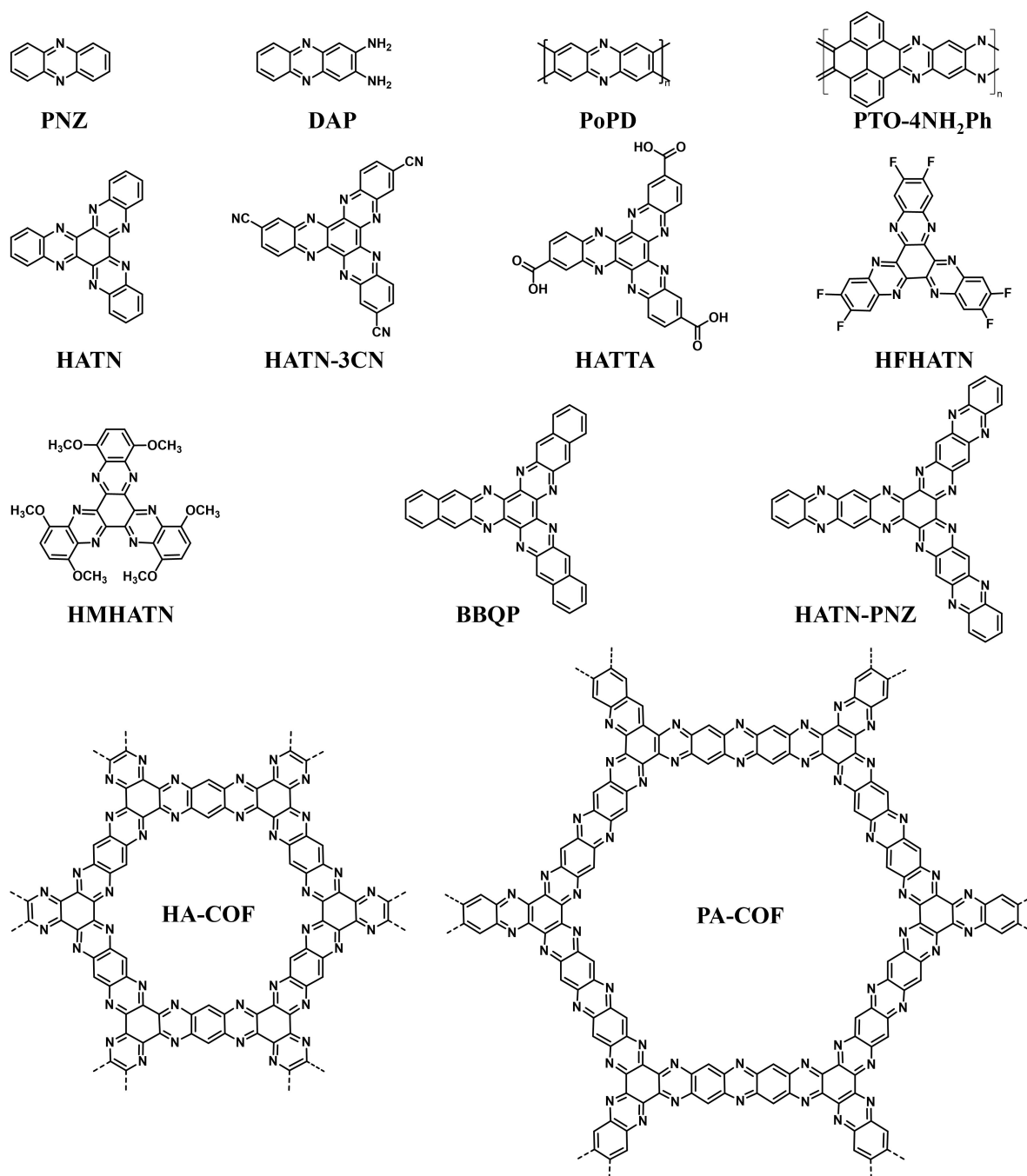
The active functional group (C=N) of imine compounds can obtain electrons and convert to anions (-C-N<sup>-</sup>) during discharging, accompanied by the insertion of cations (Zn<sup>2+</sup> or H<sup>+</sup>) to maintain charge neutrality. Additionally, the presence of N atoms can improve the electron conductivity and increase the redox potential<sup>[20]</sup>. In recent years, imines have shown broad applications in AZOBs [Figure 8]<sup>[32,44,77-87]</sup>.

Small organic 2,3-diaminophenazine (DAP) has been widely used as cathode materials for AZOBs. However, the amino groups in the molecular structure of DAP increase the possibility of hydration by forming hydrogen bonds [Figure 9A], promoting the dissolution in aqueous electrolytes, resulting in poor cycling performance (a 29% capacity retention under 0.1 A·g<sup>-1</sup> over 200 cycles)<sup>[77]</sup>. Liang *et al.* used a CNTs-modified glass fiber membrane to suppress the dissolution of DAP [Figure 9B] and achieved a decent cycling lifespan (an 80% capacity retention over 10,000 cycles under 25.5 A·g<sup>-1</sup>)<sup>[78]</sup>. In addition to the membrane modification, extending the  $\pi$ -conjugated structure of organics is an effective method to suppress dissolution and enhance the electrochemical performance. Tie *et al.* prepared the HATN with a  $\pi$ -conjugated aromatic structure as a cathode for AZOBs<sup>[32]</sup>. They claimed that the capacity contribution of the HATN comes from H<sup>+</sup> insertion [Figure 9C]. Thanks to the fast proton uptake kinetics, the Zn-HATN batteries delivered an extremely high capacity of 405 mAh·g<sup>-1</sup> under 0.1 A·g<sup>-1</sup>. Moreover,  $\pi$ -conjugated structure enhances the  $\pi$ - $\pi$  intermolecular interactions and inhibits the dissolution in mild electrolytes. Therefore, Zn//HATN batteries possessed a super lifespan with a 93.3% capacity retention after 5,000 cycles under 5 A·g<sup>-1</sup>. Introducing electron-withdrawing groups (-CN) into HATN can further promote the dispersion of negative charges on N atoms [Figure 9D], stabilizing the reaction intermediates to obtain rapid reaction kinetics<sup>[44]</sup>. Therefore, HATN-3CN displayed an outstanding capacity of 190 mAh·g<sup>-1</sup> under 20 A·g<sup>-1</sup>. Similarly, introducing electron-withdrawing conjugated groups (-COOH) to obtain 5,6,11,12,17,18-hexaazatrinaphthylene-2,8,14-tricarboxylic acid (HATTA) cathode also shows excellent rate ability (136.1 mAh·g<sup>-1</sup> under 25 A·g<sup>-1</sup>) and superior lifespan (an 84.07% capacity retention after 10,000 cycles under 25 A·g<sup>-1</sup>)<sup>[79]</sup>. Recently, Li *et al.* prepared a hexaazatrinaphthalene-phenazine (HATN-PNZ) as the cathode material of AZOBs<sup>[80]</sup>. Due to the conjugation elongation of aromatic rings and phenazine, HATN-PNZ with large charge delocalization area can effectively transfer electrons in molecules and lead to rapid reaction kinetics. Based on this, HATN-PNZ cathodes showed an exceptional rate capability of 144 mAh·g<sup>-1</sup> under 100 A·g<sup>-1</sup>. Besides, molecular polymerization is also a common method for limiting the dissolution of small molecular organics. Zhang *et al.* developed a poly(o-phenylenediamine) (PoPD) cathode for AZOBs, where the Zn<sup>2+</sup> reversibly coordinates with adjacent C=N bonds in the PoPD structure [Figure 9E]<sup>[81]</sup>. This coordination mechanism sustains a stable conjugated structure (a 66.2% capacity retention under 1 A·g<sup>-1</sup> over 3,000 cycles). COF compounds containing C=N bonds also offer excellent electrochemical properties. Wang *et al.* designed the phenanthroline-COF (PA-COF) through the solvothermal condensation reaction between 2, 3, 7, 8-phenazinetetramine and hexaketocyclohexane. It has rich active sites, an electron-rich backbone, and abundant pores with sizes of 2-5 nm, which can better promote reversible ion intercalation. Therefore, PA-COF can provide a capacity of 247 mAh·g<sup>-1</sup> under 0.1 A·g<sup>-1</sup>, and its capacity decay is only 0.38% per cycle within 10,000 cycles under 1.0 A·g<sup>-1</sup> [Figure 9F]<sup>[87]</sup>. However, only the HATN units in PA-COF molecules can host Zn<sup>2+</sup>, and the components connecting the active groups are inactive, reducing the capacity of PA-COF cathode material to a certain extent.

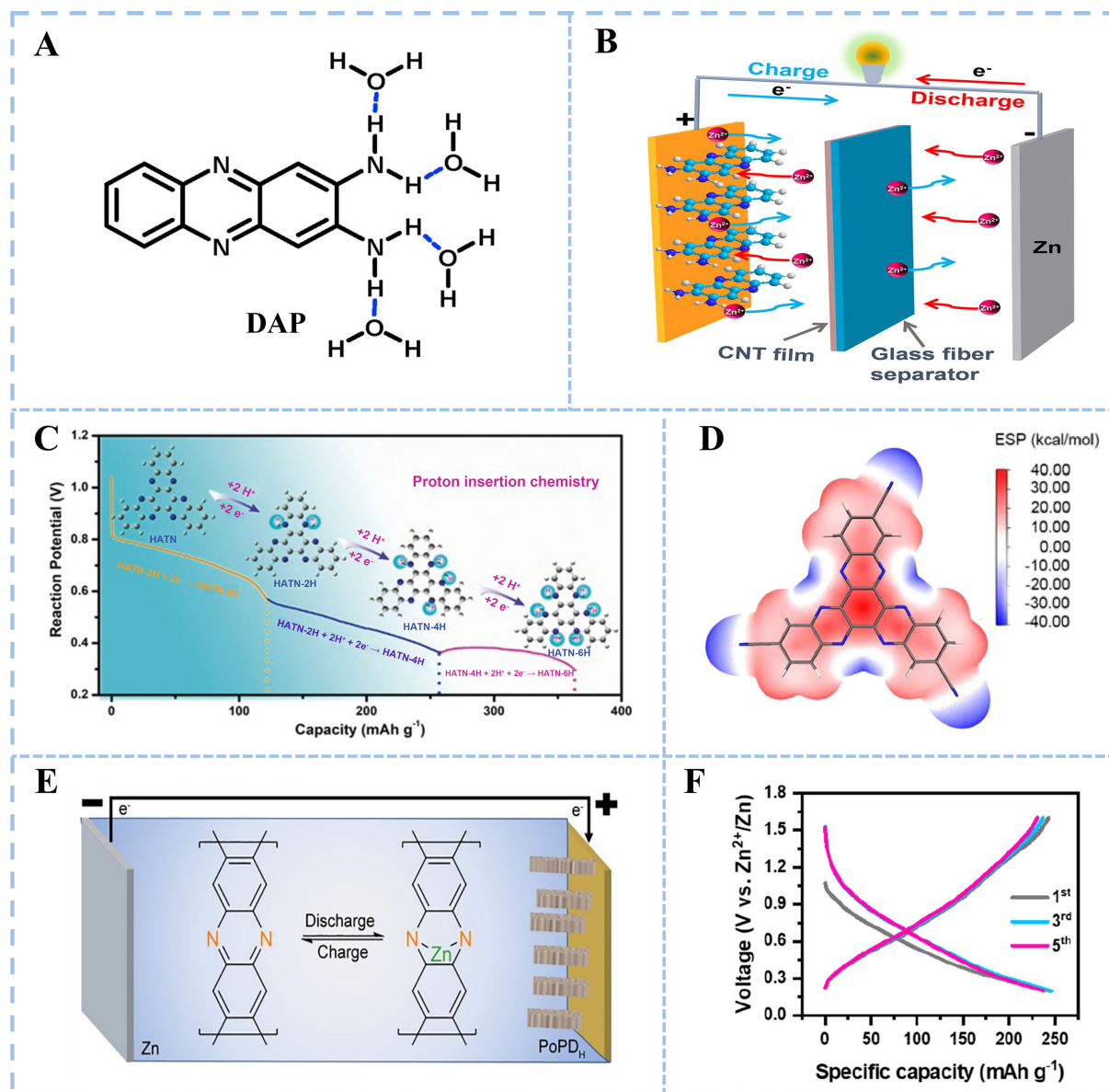
### *Compounds with dual redox groups*

Organic materials with a single redox group (C=O or C=N) have been extensively explored, but their specific capacity is usually limited. Designing organic compounds with multiple redox groups can achieve

## Imine compounds



**Figure 8.** The molecular structures of common imine compounds in AZOBs<sup>[32,44,77-87]</sup>. AZOBs: Aqueous zinc-organic batteries; PNZ: phenazine; DAP: 2,3-diaminophenazine; PoPD: poly(o-phenylenediamine); PTO: pyrene-4,5,9,10-tetraone; HATN: hexaazatriphthalene; HATN-3CN: diquinoxalino[2,3-a:2',3'-c]phenazine-2,8,14-tricarbonitrile; HATTA: 5,6,11,12,17,18-hexaazatriphthalene-2,8,14-tricarboxylic acid; HFHATN: hexafluorohexaazatriphthalene; HMHATN: hexamethoxy hexaazatriphthalene; BBQP: benzo[a]benzo[7,8]quinoxalino[2,3-i]phenazine-5,6,8,14,15,17; HA-COF: hexaazatriphenylene-based covalent-organic frameworks; PA-COF: phenanthroline covalent-organic frameworks.

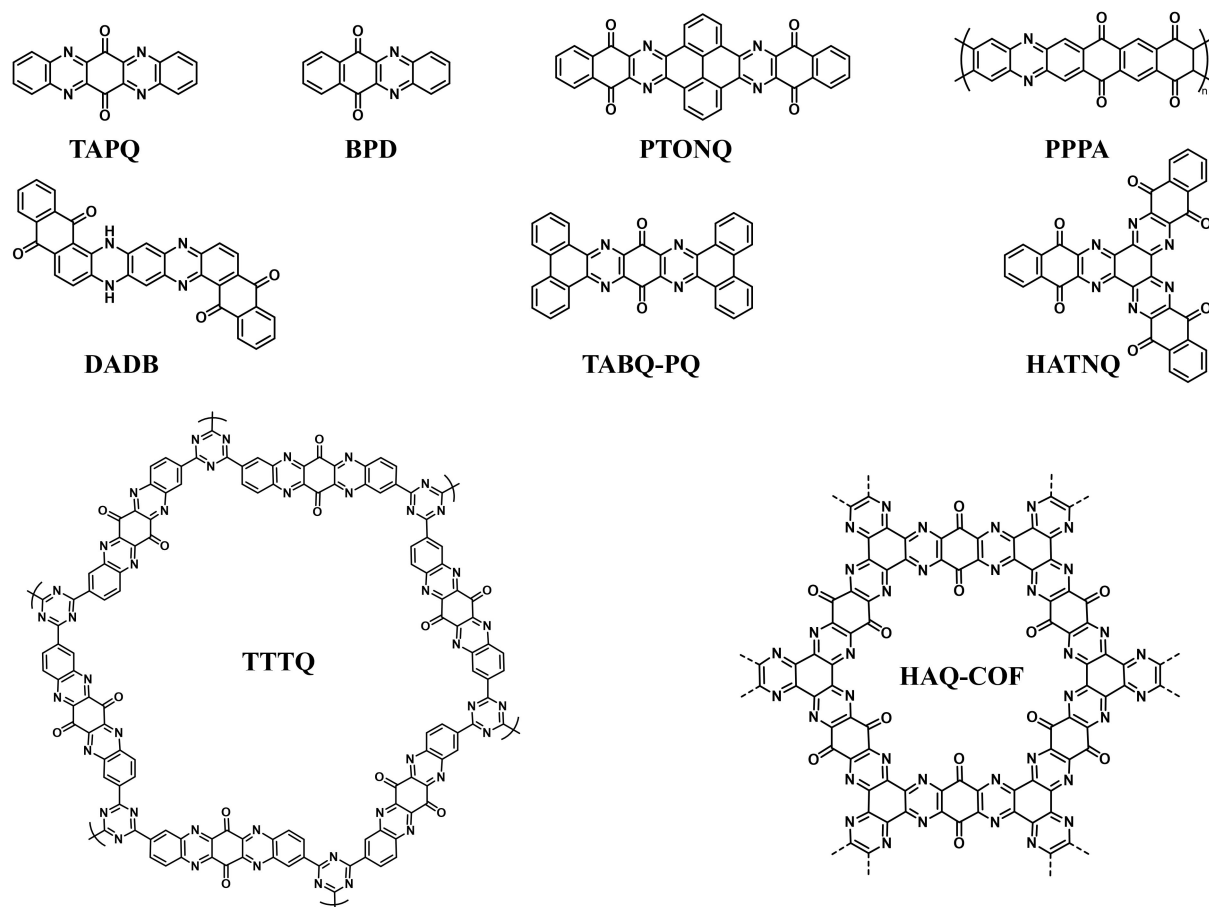


**Figure 9.** (A) Hydration mechanisms of DAP in aqueous electrolytes. Reproduced with permission<sup>[77]</sup>. Copyright 2020, Elsevier; (B) Schematic diagram of Zn/DAP battery. Reproduced with permission<sup>[78]</sup>. Copyright 2022, Elsevier; (C) Calculated structural evolution and protonation pathway at discharging process of HATN. Reproduced with permission<sup>[32]</sup>. Copyright 2020, Wiley Online Library; (D) Calculated molecular electrostatic potential distribution of HATN-3CN molecule. Reproduced with permission<sup>[44]</sup>. Copyright 2021, Elsevier; (E) Zinc storage mechanism of PoPD. Reproduced with permission<sup>[81]</sup>. Copyright 2020, Elsevier; (F) (Dis-)charge profiles of PA-COF cathode under  $1.0 \text{ A g}^{-1}$ . Reproduced with permission<sup>[87]</sup>. Copyright 2020, American Chemical Society. DAP: 2,3-diaminophenazine; HATN: diquinoxalino[2,3-a:2',3'-c]phenazine; HATN-3CN: diquinoxalino[2,3-a:2',3'-c]phenazine-2,8,14-tricarbonitrile; PoPD: poly(o-phenylenediamine); PA-COF: phenanthroline covalent-organic frameworks.

higher energy density and working voltage. In recent years, some compounds with dual redox groups (C=O and C=N) have recently been developed as cathodes for AZOBs [Figure 10]<sup>[33,45,86,88-94]</sup>.

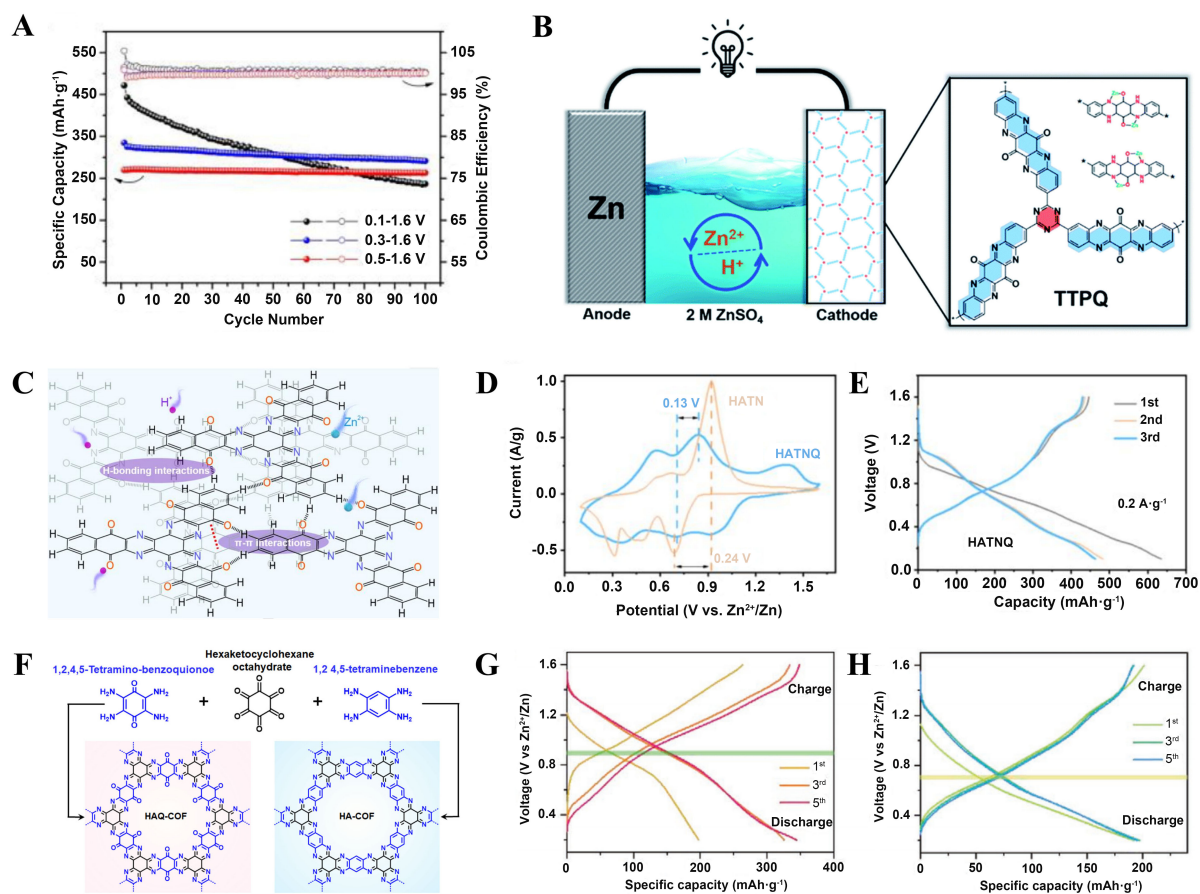
Gao *et al.* combined the structures of quinone and pyrazine to synthesize a novel organic cathode material for AZOBs, named 5,7,12,14-tetraaza-6,13-pentacenequinone (TAPQ)<sup>[33]</sup>. TAPQ with abundant C=N and C=O groups provides a significant reversible specific capacity of  $443 \text{ mAh g}^{-1}$ . However, the poor

## Dual redox groups compounds



**Figure 10.** The molecular structures of commonly reported compounds with dual redox groups in AZOBs<sup>[33,45,86,88-94]</sup>. AZOBs: Aqueous zinc-organic batteries; TAPQ: 5,7,12,14-tetraaza-6,13-pentacenequinone; BPD: benzo[b]phenazine-6,11-dione; PTONQ: benzo[i]benzo[6',7']quinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine-5,10,16,21-tetraone; PPPA: poly(phenazine-alt-pyromellitic anhydride); DADB: 8,21-dihydronaphtho[2,3-a]naphtha[2',3':7,8]quinoxalino[2,3-i]phenazine-5,11,16,22-tetraone; TABQ-PQ: dibenzo[a,c]dibenzo[5,6:7,8]quinoxalino[2,3-i]phenazine-10,21-dione; HATNQ: hexaazatrinaphthalene-quinone; TTPQ: poly(triazine-5,7,12,14-tetraaza-6,13-pentacenequinone); HAQ-COF: quinone-functionalized covalent-organic frameworks.

reversibility of excessive  $H^+$  insertion leads to the collapse of TAPQ cathode structure and unsatisfactory cycling lifespan in 0.1-1.6 V [Figure 11A]. Subsequently, Wang *et al.* enhanced the cycling lifespan of TAPQ by polymerization<sup>[93]</sup>. They synthesized poly(triazine-5,7,12,14-tetraaza-6,13-pentacenequinone) (TTPQ) based on TAPQ monomers as cathodes for AZOBs [Figure 11B]. The TTPQ provided a decent cycle stability, with an  $\sim 94\%$  capacity retention under  $0.5 \text{ A}\cdot\text{g}^{-1}$  over 250 cycles. Recently, Li *et al.* prepared a hydrogen-bonded organic framework, benzo[a]benzo[7,8]quinoxalino[2,3-i]phenazine-5,6,8,14,15,17-hexane (BBQPH), as the cathode for AZOBs<sup>[95]</sup>. The intermolecular hydrogen bonding enhances the structural stability of BBQPH, and the abundant C=N and C=O groups trigger multi-electron redox chemistry with super delocalization. Therefore, BBQPH cathodes demonstrated a high reversible capacity of  $498.6 \text{ mAh}\cdot\text{g}^{-1}$  and a high energy density of  $355 \text{ Wh}\cdot\text{kg}^{-1}$  under  $0.2 \text{ A}\cdot\text{g}^{-1}$ . Similarly, Chen *et al.* designed HATNQ as cathode material for AZOBs. The two-dimensional layered supramolecular structure of HATNQ is conducive to rapid charge transfer and ion transport [Figure 11C]. Compared with HATN, the



**Figure 11.** (A) Cyclic performance of TAPQ cathode under  $0.05 \text{ A}\cdot\text{g}^{-1}$ . Reproduced with permission<sup>[33]</sup>. Copyright 2021, Elsevier; (B) Schematic diagram of Zn//TTPQ battery. Reproduced with permission<sup>[93]</sup>. Copyright 2022, Royal Society of Chemistry; (C) Diagram of two-dimensional layered supramolecular structure of HATNQ. (D) The cyclic voltammetry curves of HATN and HATNQ at  $0.2 \text{ mV}\cdot\text{s}^{-1}$ ; (E) (Dis-)charge profiles of the HATNQ cathode at  $0.2 \text{ A}\cdot\text{g}^{-1}$ . Reproduced with permission<sup>[45]</sup>. Copyright 2022, Wiley Online Library; (F) Synthesis route of HAQ-COF and HA-COF; (Dis-)charge profiles of HAQ-COF (G) and HA-COF (H) cathode under  $0.1 \text{ A}\cdot\text{g}^{-1}$ . Reproduced with permission<sup>[86]</sup>. Copyright 2021, Wiley Online Library. TAPQ: 5,7,12,14-tetraaza-6,13-pentacenequinone; TTPQ: poly(triazine-5,7,12,14-tetraaza-6,13-pentacenequinone); HATN: diquinoxalino[2,3-a:2',3'-c]phenazine; HATNQ: hexaazatrinaphthalene-quinone; HAQ-COF: quinone-functionalized covalent-organic frameworks; HA-COF: hexaazatriphenylene-based covalent-organic frameworks.

HATNQ electrode had a lower polarization and higher operating voltage [Figure 11D]<sup>[45]</sup>. Impressively, the HATNQ cathode displayed a magnificent capacity of  $482.5 \text{ mAh}\cdot\text{g}^{-1}$  under  $0.2 \text{ A}\cdot\text{g}^{-1}$  [Figure 11E]. In addition, introducing additional redox groups can increase the capacity of COF cathodes. For example, Wang *et al.* obtained quinone-functionalized COF (HAQ-COF) by introducing quinone groups to replace the inactive components in hexaazatriphenylene-based COF (HA-COF), significantly improving their electrochemical performance<sup>[86]</sup>. As presented in Figure 11F, HAQ-COF and HA-COF were prepared through solvent thermal condensation of 1,2,4,5-tetraaminobenzene and 1,2,4,5-tetraamino-benzoquinone with hexaketocyclohexane octahydrate, respectively. Compared with HA-COF, HAQ-COF showed better uptake ability for  $\text{Zn}^{2+}$  and  $\text{H}^{+}$  due to the existence of quinone groups. Therefore, HAQ-COF delivered a superb capacity of  $344 \text{ mAh}\cdot\text{g}^{-1}$  under  $0.1 \text{ A}\cdot\text{g}^{-1}$  [Figure 11G], higher than that of HA-COF ( $195 \text{ mAh}\cdot\text{g}^{-1}$ , Figure 11H). The preparation of organics with dual redox groups is still complex and costly. In addition, the ion storage mechanisms of dual redox groups are controversial and need further exploration.

### Other n-type compounds

In addition to organics with the most common C=O or C=N groups, several n-type organics with other functional groups (e.g., nitro groups, azo groups, and hydroxyl groups) have also demonstrated the capability of storing  $\text{Zn}^{2+}$  and/or  $\text{H}^+$  ions. Song *et al.* found that para-dinitrobenzene (*p*-DB) can be used as redox-active molecules in AZOBs [Figure 12A]<sup>[34]</sup>. They found the nitro groups possessed strong redox activity that enables two consecutive two-electron  $\text{Zn}(\text{OTF})^+$  (triflate,  $\text{OTF}^- = \text{CF}_3\text{SO}_3^-$ ) reaction mechanisms, which shared  $\text{Zn}^{2+}$  with adjacent nitro groups. Impressively, *p*-DB encapsulated in carbon nanoflower (CF) provided an excellent cycling lifespan under  $5 \text{ A}\cdot\text{g}^{-1}$  over 25,000 cycles [Figure 12B]. Although many organic cathodes have shown promising performance, their recycling process often faces the problem of complete destruction or decomposition of electrode materials. To this end, Chen *et al.* proposed a low-cost, recyclable Zn// azobenzene organic battery [Figure 12C]<sup>[35]</sup>. *In situ* characterizations and quantitative analyses proved that azobenzene can be transformed into hydro-azobenzene by storing protons. Because azobenzene and the discharge product hydro-azobenzene can exist stably in air, and they have very good solubility in organic solvents, the battery can be efficiently recovered under any charge and discharge state, and the average yield of recycled active material in different solvents is as high as 89.1% [Figure 12D]. Interestingly, some originally inert groups can become active centers after proper electrochemical activation. For example, Sun *et al.* reported a hydroxyl polymer polytetrafluorohydroquinone (PTFHQ) as a cathode for AZOBs<sup>[96]</sup>. The part of hydroxyl groups in PTFHQ can be oxidized to active carbonyl groups through an *in-situ* activation process; thereby,  $\text{Zn}^{2+}$  can be stored/released. Additionally, the Z-fold structure of PTFHQ is essential for rapid ion diffusion [Figure 12E]. As a result, the PTFHQ cathode offered an outstanding rate capacity ( $196 \text{ mAh}\cdot\text{g}^{-1}$  under  $20 \text{ A}\cdot\text{g}^{-1}$ , Figure 12F). This work expands the understanding of the working mechanism of AZOBs and offers a constructive method for applying polymer cathode materials.

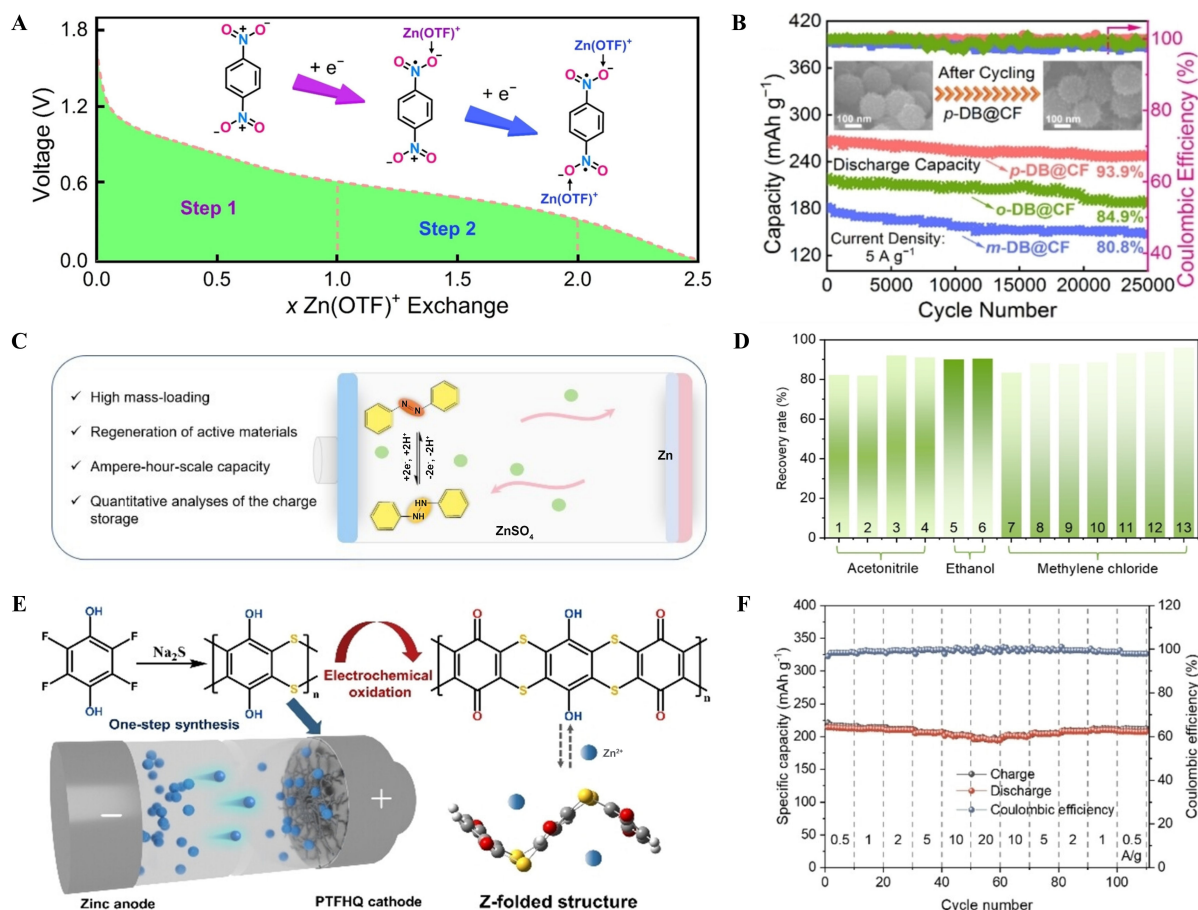
As discussed above, n-type organics exhibit high specific capacity and outstanding rate capacity. However, similar to p-type organics, some n-type organics and their discharge products dissolve severely in aqueous electrolytes, resulting in poor cycle life. This can be improved through structural optimization (such as copolymerization and expanding  $\pi$ -conjugated structures of molecules) and separator design<sup>[45,69,78]</sup>. Hybridizing organics with carbons can also enhance the stability and improve conductivity<sup>[65]</sup>. Additionally, the low working voltage of n-type organics results in a lower energy density of the battery. Introducing electron-withdrawing conjugated groups can increase the working voltage, but its improvement is generally limited<sup>[32,44]</sup>. Organics integrating carbonyl and imine compounds exhibit relatively high voltage and capacity, with high energy density, which can be further explored in future work.

### Bipolar-type organic cathodes

Bipolar organic molecules contain n-type and p-type redox components that can serve as either electron acceptors or electron donors. Bipolar organics combine the advantages of p-type organics and n-type organics and, therefore, often show improved capacity and operating voltage [Figure 13]<sup>[97-103]</sup>.

At present, various bipolar polymers [e.g., polyaniline (PANI)<sup>[97]</sup>, poly(*p*-phenylene) (PPP)<sup>[98]</sup>, *etc.*] are reported as cathodes for AZOBs, among which PANI is the first reported one. The PANI-Zn battery in earlier research was operated in  $\text{ZnCl}_2/\text{NH}_4\text{Cl}$  electrolyte<sup>[27]</sup>. In order to evidently explain the electrochemical mechanism, Wan *et al.* designed and synthesized PANI/carbon felt (PANI/CF) electrodes and explored the mechanism by *ex situ* spectroscopy<sup>[97]</sup>. During the initial discharging process,  $\text{Cl}^-$  was removed from PANI, and  $\text{Zn}^{2+}$  may interact with PANI. During the charging process,  $\text{Zn}^{2+}$  was removed from PANI and  $\text{CF}_3\text{SO}_3^-$  was embedded [Figure 14A]. This dual-ion insertion/extraction mechanism is conducive to fast transfer of charge carriers. Therefore, PANI/CFs exhibited decent rate ability ( $95 \text{ mAh}\cdot\text{g}^{-1}$  under  $5 \text{ A}\cdot\text{g}^{-1}$ ). Noteworthy, the mass loading of most reported AZOB organic cathodes is relatively low (about  $2 \text{ mg}\cdot\text{cm}^{-2}$ ), far away from the requirements for commercial use ( $10 \text{ mg}\cdot\text{cm}^{-2}$ , as referred to LIBs).



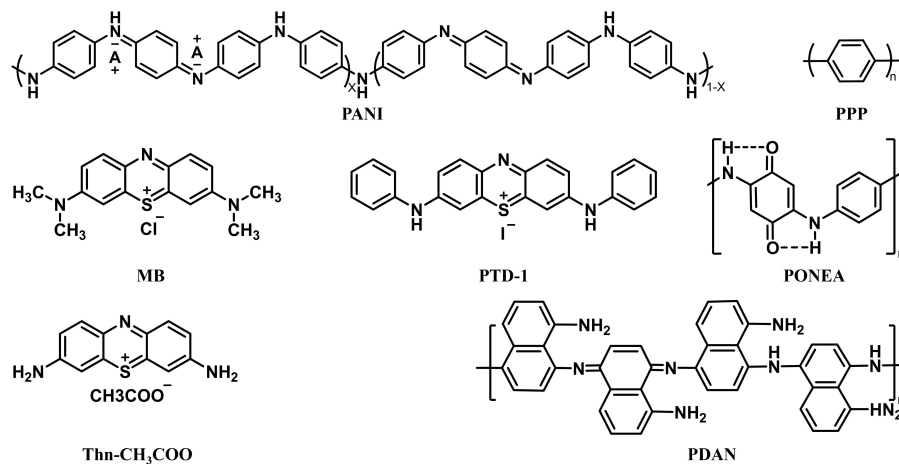


**Figure 12.** (A) Proposed redox reaction of *p*-DB; (B) Cycling performance of *p*-DB@CF cathode under  $5 \text{ A g}^{-1}$ . Reproduced with permission<sup>[34]</sup>. Copyright 2022, Wiley Online Library; (C) Diagram of a recyclable and scalable Zn//AZOB battery; (D) Recovery rate of active substances in different solvents. Reproduced with permission<sup>[35]</sup>. Copyright 2023, Wiley Online Library; (E) The synthesis of PTFHQ and proposed redox mechanism; (F) Rate capability of PTFHQ cathode. Reproduced with permission<sup>[96]</sup>. Copyright 2023, Wiley Online Library. *p*-DB: Para-dinitrobenzene; AZOB: aqueous zinc-organic battery; PTFHQ: hydroxyl polymer polytetrafluorohydroquinone.

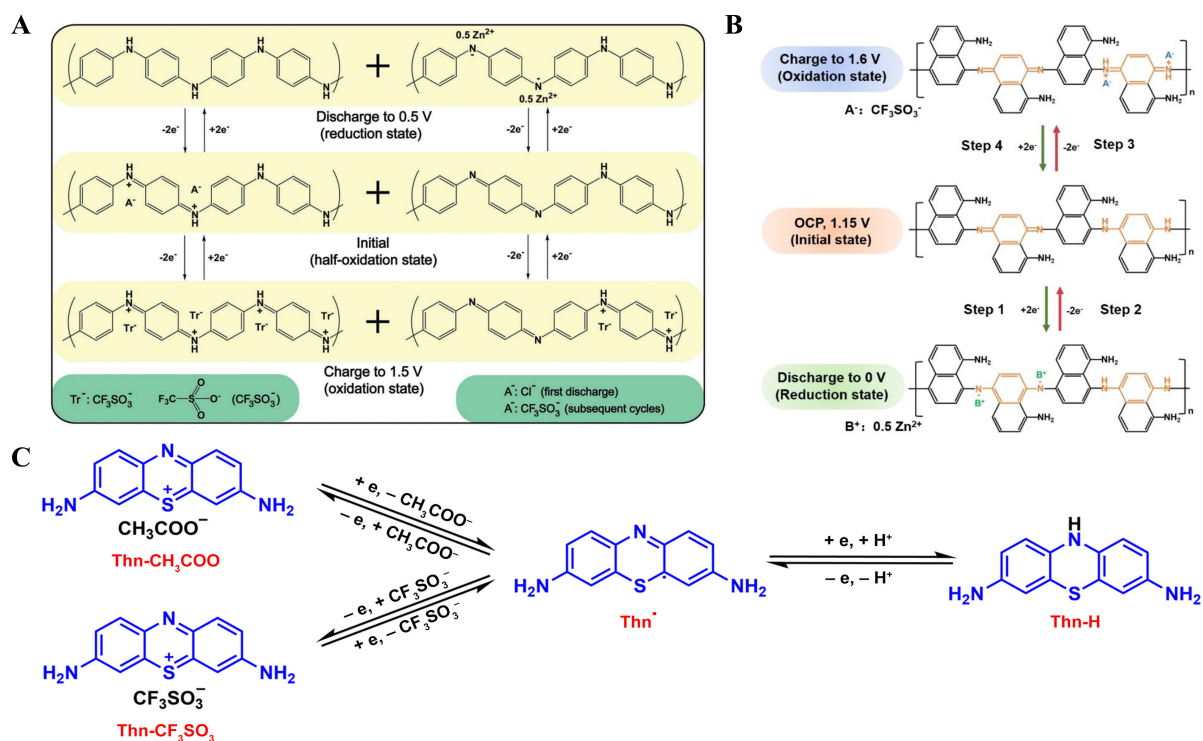
Yan *et al.* reported a polymer poly(1,8-diaminonaphthalene) (PDAN) as a cathode for AZOBs, showing a reaction mechanism similar to that of PANI [Figure 14B]<sup>[103]</sup>. Benefiting from the bipolar-type reaction mechanism and semi-conductive property of PDAN, Zn//PDAN batteries with high-quality load ( $10 \text{ mg cm}^{-2}$ ) of PDAN cathodes demonstrated a good capacity of  $140 \text{ mAh g}^{-1}$  under  $0.1 \text{ A g}^{-1}$ . In addition to polymers, some small molecules such as methylene blue (MB)<sup>[99]</sup> and thionin ( $\text{Thn-CH}_3\text{COO}$ )<sup>[102]</sup> have also been investigated. Compared with MB,  $\text{Thn-CH}_3\text{COO}$  demonstrates a higher theoretical capacity ( $186/235 \text{ mAh g}^{-1}$  for the moiety with/without anions)<sup>[102]</sup>. Extensive characterization and DFT calculations proved that  $\text{H}^+$  cations and  $\text{CF}_3\text{SO}_3^-$  and  $\text{CH}_3\text{COO}^-$  anions were involved in n-type and p-type reactions, respectively [Figure 14C]. Thanks to the dual electron bipolar redox mechanism,  $\text{Thn-CH}_3\text{COO}$  cathodes delivered a good cycling lifespan (a 65% capacity retention under  $1 \text{ A g}^{-1}$  after 500 cycles).

In general, the redox process of bipolar-type organic cathodes involves the insertion/extraction of cations and anions. They often show superior performance than n- or p-type organic cathodes. It should be noted that most bipolar-type organics are polymers that require many inactive components to stabilize the structures, which compromises the specific capacity. In addition, the synthesis of bipolar-type organics is generally much more complex, and thus, they have been considerably less explored as cathodes for AZOBs.

## Bipolar-type organic compounds



**Figure 13.** The molecular structure of common bipolar-type organics in AZOBs<sup>[97-103]</sup>. AZOBs: Aqueous zinc-organic batteries; PANI: polyaniline; PPP: poly(p-phenylene); MB: methylene blue; PTD-1: PONEA: poly quinone phenylenediamine; PDAN: polymer poly(1,8-diaminonaphthalene).



**Figure 14.** (A) Redox mechanism of PANI/CFs. Reproduced with permission<sup>[97]</sup>. Copyright 2018, Wiley Online Library; (B) Redox mechanism of PDAN. Reproduced with permission<sup>[103]</sup>. Copyright 2022, Wiley Online Library; (C) Bipolar ion storage mechanism of Thn-CH<sub>3</sub>COO. Reproduced with permission<sup>[102]</sup>. Copyright 2023, Wiley Online Library. PANI/CFs: Polyaniline/carbon nanoflower; PDAN: polymer poly(1,8-diaminonaphthalene).

In future research, it may be considered to maximize the specific capacity of bipolar-type organic cathodes while ensuring high voltage and conductivity, such as developing bipolar-type organics with low molecular weight and solubility.

The characteristics of three types of organic cathodes are shown in Figure 15 (also see a detailed comparison of the electrochemical performance of various organic cathodes in Table 1). To summarize, p-type organic cathodes necessitate a substantial amount of salt from the electrolyte during the charging process, which escalates the assembly cost of the battery<sup>[38]</sup>. Despite demonstrating high voltages and conductivity, their limited active center results in unsatisfactory capacity and low energy density. However, their high electron affinity and excellent biocompatibility make them promising candidates for wearable medical devices. In contrast, n-type organic cathodes have a relatively straightforward preparation process and typically offer higher capacity, energy density, and longer cycling lifespan<sup>[45,95]</sup>, albeit at a lower operating voltage. Given these characteristics, n-type organic cathodes are well-suited for energy storage systems that demand high energy density and long cycle life, such as those used in residential and commercial settings. Furthermore, bipolar-type organic cathodes amalgamate the advantages of both n- and p-type organic cathodes, exhibiting high operating voltage, high conductivity, and robust cycle life. They are ideal for energy storage systems that require high electrical conductivity and stability, such as medical devices and sensor equipment.

## IMPROVEMENT STRATEGIES FOR HIGH PERFORMANCE

Although organic cathodes have shown significant advantages for AZOB application, some issues remain unsolved, such as the dissolution of small molecular compounds, low operating voltage, poor conductivity, *etc.*, which lead to poor cycling lifespan and low energy density of the AZOBs. This chapter will discuss strategies to improve the voltage, specific capacity, cycling lifespan and rate capability of organic cathodes [Figure 16], which are crucial parameters for evaluating battery performance.

### Voltage

The cathode voltage ( $E_{cathode}$ ) is determined by the Gibbs free energy change ( $\Delta G$ ) during the electrochemical reactions, as formulated in

$$E_{cathode} = \frac{\Delta G}{nF} \quad (1)$$

where  $F$  and  $n$  represent the Faraday constant and the number of transferred electrons, respectively<sup>[104]</sup>. Therefore, high-voltage organic cathodes can be identified by screening their corresponding  $\Delta G/n$  values. Cui *et al.* explored the effect of electron cloud distributions on the voltage of organic sulfur compounds (thianthrene, phenoxathiine and phenothiazine)<sup>[51]</sup>. The electronegativity of thianthrene (-13.30) with a symmetrically distributed electron cloud distribution is greater than that of phenoxathiine (-16.72) and phenothiazine (-20.21). Due to the difference in electronegativity, the  $\Delta G$  of thianthrene is greater than that of phenoxathiine and phenothiazine, and the discharge voltage of thianthrene (1.5 V) is notably higher than that of phenoxathiine (1.3 V) and phenothiazine (0.85 V). Optimization of electrolyte composition can also increase  $\Delta G/n$ , which is an efficacious method to enhance the working voltage. For example, DFT calculation results show that  $\Delta G/n$  of  $[2(PTVE^+)SO_4^{2-}]$  is higher than that of  $(PTVE^+ClO_4^-)$  and  $(PTVE^+CF_3SO_3^-)$ <sup>[47]</sup>. Therefore, the voltage of Zn//PTVE cells using  $ZnSO_4$  electrolyte (1.77 V) is higher than that using  $Zn(CF_3SO_3)_2$  electrolyte (1.58 V) or  $Zn(ClO_4)_2$  electrolyte (1.53 V). In addition, the working voltage of AZOBs is closely related to the energy level of the lowest unoccupied molecular orbital (LUMO) in n-type organic cathodes or the HOMO in p-type organic cathodes<sup>[105]</sup>. A lower HOMO/LUMO energy level suggests that the potential of electrons exiting or entering it is higher, given their negative charge<sup>[106]</sup>. For instance, thianthrene cathodes, which have a low HOMO energy (-5.7 eV), exhibit a higher working

**Table 1. Electrochemical performance of organic cathodes for AZOBs**

Cathode	Type	Electrolyte	Capacity (mAh·g <sup>-1</sup> /A·g <sup>-1</sup> )	Rate capacity (mAh·g <sup>-1</sup> /A·g <sup>-1</sup> )	Cycling stability (%/no. cycle/A·g <sup>-1</sup> )	Ref.
PTVE	p	1M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	83/0.2	52/10	77.0/1,000/1	[47]
Thianthrene		1M Zn(OTF) <sub>2</sub> -acetonitrile	112/0.5	66/20	82/8,000/1	[51]
BDB		1M Zn(OTF) <sub>2</sub> -19M LiN(SO <sub>3</sub> CF <sub>3</sub> )	125/0.026	80/0.78	75/1,000/0.78	[31]
m-PTPA		2M ZnCl <sub>2</sub>	210.7/0.5	107.5/6	87.6/1,000/6	[52]
DMPZ		17M NaClO <sub>4</sub>	231/0.051	107/1.275	81/1,000/0.255	[53]
PPy		-	123/1.9	40/44.7	38/200/4.4	[55]
Poly(5-cyanoindole)		1M ZnCl <sub>2</sub>	107/0.2C	61/10C	63/800/2C	[58]
C4Q	n	3M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	335/0.02	172/1	87/1,000/0.5	[30]
NQ@CNT		2M ZnSO <sub>4</sub>	333.5/0.34	129.7/0.68	41/1,500/0.339	[65]
PDBS		2M ZnSO <sub>4</sub>	260/0.01	161.25/5	79/2,000/2	[69]
PTO		2 M ZnSO <sub>4</sub>	336/0.04	113/20	70/1,000/3	[39]
NTCDI		2 M ZnSO <sub>4</sub>	240/0.1	140/2	73.7/2,000/1	[67]
BT-PTO COF		3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	225/0.1	108/500	98/10,000/5	[75]
DAP		3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	219.1/0.255	77/127.5	80/10,000/25.5	[78]
HATN		2 M ZnSO <sub>4</sub>	405/0.1	123/20	93.3/5,000/5	[32]
HATN-3CN		2 M ZnSO <sub>4</sub>	320/0.05	190/20	90.7/5,800/5	[44]
HATTA		1M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	225.8/0.05	136.1/25	84.07/10,000/25	[79]
HATN-PNZ		2 M ZnSO <sub>4</sub>	226/5	159/30	92.7/30,000/30	[80]
PoPD		2 M ZnSO <sub>4</sub>	318/0.05	95/5	66.2/3,000/1	[81]
PA-COF		1 M ZnSO <sub>4</sub>	247/0.1	68/10	62/10,000/1	[87]
TAPQ		1 M ZnSO <sub>4</sub>	443/0.05	15/5	50.2/100/0.05	[33]
TTPQ		2 M ZnSO <sub>4</sub>	404/0.3	204/5	94/250/0.5	[93]
HATNQ		3 M ZnSO <sub>4</sub>	482.5/0.2	177.5/9	80/11,000/5	[45]
HA-COF		2 M ZnSO <sub>4</sub>	164/0.1	35.4/10	75.3/10,000/5	[86]
HAQ-COF		2 M ZnSO <sub>4</sub>	344/0.1	95.6/10	85/10,000/5	[86]
p-DB@CF		3 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	402/0.1	214/20	93.9/25,000/5	[34]
PTFHQ		2 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	215/0.1	145/50	92/3,400/20	[96]
PANI/CFs	bi	1 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	200/0.05	95/5	92/3,000/5	[97]
PDAN		0.5 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	171/0.1	54/100	82.3/10,000/5	[103]
Thn-CH <sub>3</sub> COO		2 M Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	162/0.1	113.4/5	65/500/1	[102]

AZOBs: Aqueous zinc-organic batteries; PTVE: poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl vinyl ether); OTF: trifluoromethanesulfonate; BDB: 1,4-bis(diphenylamino)benzene; m-PTPA: porous polytriphenylamine; DMPZ: 5,10-dihydro-5,10-dimethylphenazine; PPy: polypyrrole; C4Q: calix[4]quinone; NQ@CNT: naphthoquinone@carbon nanotube; PDBS: poly(2,5-dihydroxy-1,4-benzoquinonyl sulfide); PTO: pyrene-4,5,9,10-tetraone; NTCDI: 1,4,5,8-naphthalene diimide; BT-PTO COF: benzenetricarboxaldehyde pyrene-4,5,9,10-tetraone covalent-organic frameworks; DAP: 2,3-diaminophenazine; HATN: diquinoxalino[2,3-a:2',3'-c]phenazine; HATN-3CN: diquinoxalino[2,3-a:2',3'-c]phenazine-2,8,14-tricarbonitrile; HATTA: 5,6,11,12,17,18-hexaazatrinaphthylene-2,8,14-tricarboxylic acid; HATN-PNZ: hexaazatrinaphthalene-phenazine; PoPD: poly(o-phenylenediamine); PA-COF: phenanthroline covalent-organic frameworks; TAPQ: 5,7,12,14-tetraaza-6,13-pentacenequinone; TTPQ: poly(triazine-5,7,12,14-tetraaza-6,13-pentacenequinone); HATNQ: hexaazatrinaphthalene-quinone; HA-COF: hexaazatrinaphthalene-based covalent-organic frameworks; HAQ-COF: quinone-functionalized covalent-organic frameworks; p-DB@CF: para-dinitrobenzene@carbon nanoflower; PTFHQ: hydroxyl polymer polytetrafluorohydroquinone; PANI/CFs: polyaniline carbon nanoflowers; PDAN: polymer poly(1,8-diaminonaphthalene).

voltage compared to phenothiazine (-4.68 eV) and phenoxathiazine (-5.47 eV). The HOMO or LUMO energy levels can be adjusted by changing the position of functional groups or introducing electron-withdrawing/donating groups. For example, due to the lower LUMO energy of 1,2-NQ compared to that of 1,4-NQ, the average discharge potential of 1,2-NQ is approximately 0.17 V higher than that of 1,4-NQ<sup>[30]</sup>. Introducing electron-withdrawing groups (e.g., -CN, -COOH) can also reduce the LUMO energy and thus increase the operating voltage. Compared to HATN-3CN (-3.87 eV), the discharge voltage of HATN with high LUMO energy (-2.78 eV) is 0.16 V lower than that of HATN-3CN<sup>[44]</sup>.

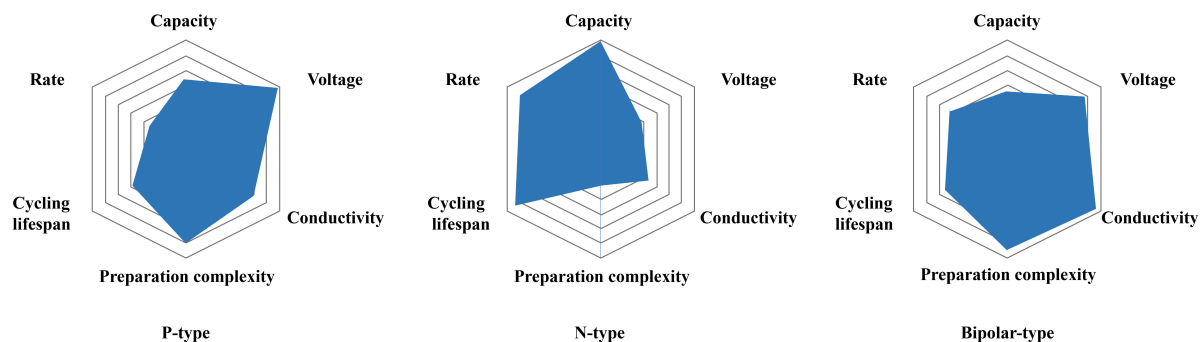
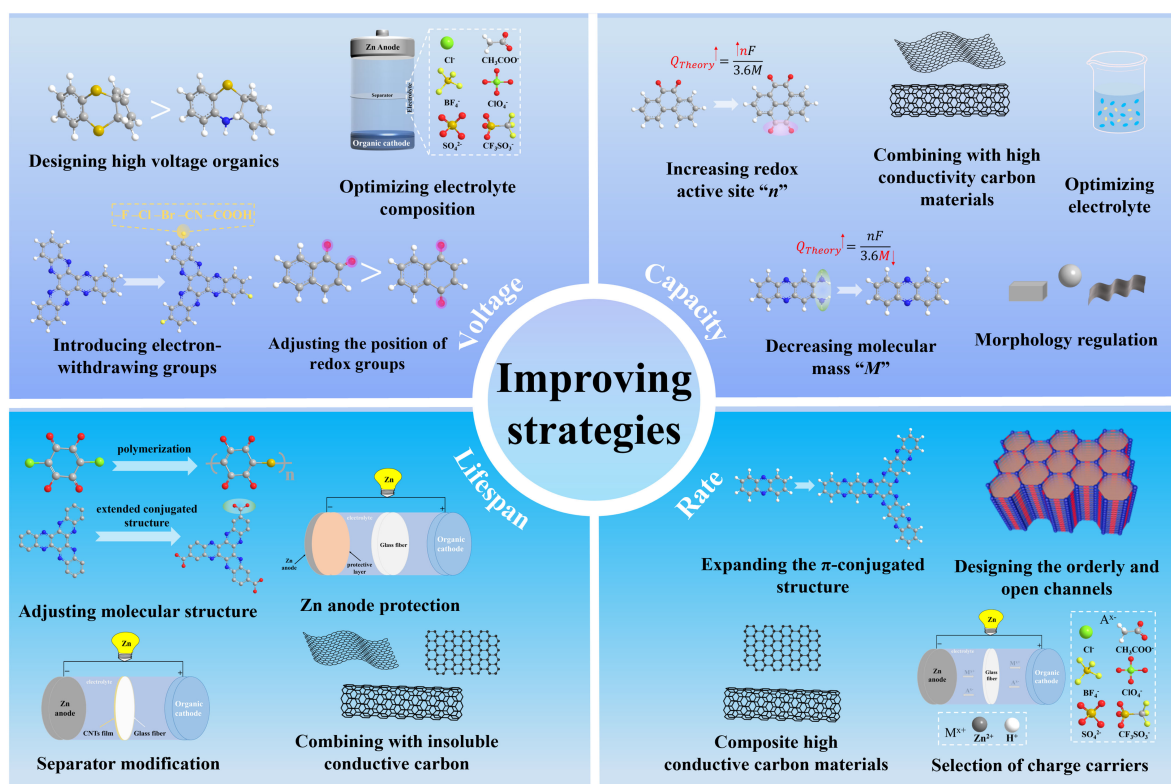


Figure 15. The characteristics of three types of organic cathodes.



Strategies for improving the voltage, specific capacity, cycling lifespan and rate capability.

Figure 16.

### Specific capacity

The theoretical capacity ( $Q_{Theory}$ ) of organic cathodes is obtained as

$$Q_{Theory} = \frac{nF}{3.6M} \tag{2}$$

where  $n$ ,  $F$ , and  $M$  represent the theoretically maximal number of electrons transferred during charging/discharging, Faraday constant, and relative molecular mass, respectively. Therefore, increasing the “ $n$ ” and decreasing the “ $M$ ” of organics are conducive to obtaining high theoretical specific capacity. Increasing the redox-active sites of organics can increase the “ $n$ ” value, thereby increasing the theoretical specific capacity. For example, PTO, obtained by introducing two carbonyl groups in 9,10-PQ, has a theoretical capacity of  $409 \text{ mAh}\cdot\text{g}^{-1}$ <sup>[39]</sup>, higher than 9,10-PQ ( $258 \text{ mAh}\cdot\text{g}^{-1}$ )<sup>[30]</sup>. Similarly, compared to HATN ( $419 \text{ mAh}\cdot\text{g}^{-1}$ ), HATNQ has six more carbonyl groups and a higher theoretical capacity of  $515 \text{ mAh}\cdot\text{g}^{-1}$ <sup>[32,45]</sup>. Removing inactive components from organics can reduce the “ $M$ ”; it is also a method to enhance theoretical specific capacity. For example, PNZ can be obtained by removing the inactive amino components in DAP molecules, and the theoretical specific capacity is increased from 255 to  $297 \text{ mAh}\cdot\text{g}^{-1}$ <sup>[77,78]</sup>. However, dissociating some small molecular organics in aqueous electrolytes usually leads to poor cycle lifespan. Cycling stability needs to be considered when the “ $M$ ” is reduced.

The above two approaches can enhance the theoretical specific capacity of organics. However, the actual specific capacity is influenced by many factors, such as electrolytes, conductivity, and morphology. Combining organics with highly conductive carbon materials is the most direct method to improve the conductivity. For instance, the initial capacity of NQ@CNT composite cathodes is  $333.5 \text{ mAh}\cdot\text{g}^{-1}$ , close to their theoretical capacity ( $339.0 \text{ mAh}\cdot\text{g}^{-1}$ )<sup>[65]</sup>. Similarly, the actual specific capacity of the PANI/graphene composite cathode ( $184.5 \text{ mAh}\cdot\text{g}^{-1}$ ) is also higher than that of the PANI cathode ( $163.1 \text{ mAh}\cdot\text{g}^{-1}$ )<sup>[107]</sup>. Besides, the morphology of organics also affects their actual specific capacity. For instance, the specific capacity of “pebble-like” PANI is half that of “sponge-like” PANI because electrolytes and solvents can more easily enter the porous structure<sup>[108]</sup>. Moreover, the m-PTPA conjugated microporous polymer (CMP) cathode with a conjugated microporous structure exhibits a discharge capacity of  $210.7 \text{ mAh}\cdot\text{g}^{-1}$  at  $0.5 \text{ A}\cdot\text{g}^{-1}$ , which is higher than the nonporous conjugated PTPA cathode ( $99.8 \text{ mAh}\cdot\text{g}^{-1}$ )<sup>[52]</sup>. In addition, Zhang *et al.* synthesized cuboid, sphere, and narrow strip-shaped PoPD (PoPD<sub>H</sub>, PoPD<sub>N</sub> and PoPD<sub>A</sub>) in acidic, neutral, and alkaline solvents as cathodes for AZOBs, respectively<sup>[81]</sup>. The cuboid PoPDH cathode, due to its higher conductivity compared to the spherical PoPDN and narrow strip PoPDA cathodes, has a higher discharge capacity at  $0.05 \text{ A}\cdot\text{g}^{-1}$ . The capacities are as follows: cuboid PoPDH ( $318 \text{ mAh}\cdot\text{g}^{-1}$ ), spherical PoPDN ( $124 \text{ mAh}\cdot\text{g}^{-1}$ ), and narrow strip PoPDA ( $101 \text{ mAh}\cdot\text{g}^{-1}$ ). Besides, different types of electrolytes also affect the specific capacity of AZOBs<sup>[47,97,102,109]</sup>. For example, due to the weaker electrostatic interaction between thionin cation (Thn<sup>+</sup>) and  $\text{CF}_3\text{SO}_3^-$  compared to  $\text{CH}_3\text{COO}^-$  and  $\text{SO}_4^{2-}$ , the specific capacity of the Thn- $\text{CH}_3\text{COO}$  cathode using  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  electrolytes is higher than that using  $\text{Zn}(\text{CH}_3\text{COO})_2$  electrolytes and  $\text{ZnSO}_4$  electrolytes<sup>[102]</sup>. The specific capacity can also be significantly influenced by the concentration of the electrolyte used. It is, therefore, vital to select an optimal electrolyte concentration, which could be either super- or low-concentrated, to boost the capacity of AZOBs<sup>[110]</sup>. A case in point is the polycatechol cathode, which, when used with a  $3\text{M ZnSO}_4$  electrolyte, yields a higher specific capacity ( $204 \text{ mAh}\cdot\text{g}^{-1}$ ) compared to when it is used with a  $0.2 \text{ M ZnSO}_4$  electrolyte ( $\sim 142 \text{ mAh}\cdot\text{g}^{-1}$ ), at a discharge rate of  $0.05 \text{ A}\cdot\text{g}^{-1}$ <sup>[109]</sup>.

### Cycling lifespan

The cycle lifespan of AZOBs is significant for their practical application, which is determined by their components, including the organic cathodes, Zn anodes, electrolytes, and separators. Some of the organic materials suffer from dissolution issues and, consequently, unsatisfactory cycling lifespan in liquid electrolytes, mainly because of the intrinsic instability of the molecular structure due to the weak intermolecular van der Waals forces. In addition, they may also be detached from the electrode by the solvation of solvent molecules in electrolytes<sup>[111]</sup>. Molecular polymerization can expand the molecular size of monomers and hinder the solvation process, thereby suppressing the dissolution and enhancing structural stability. For example, the serious dissolution of 2,5-dichloro-3,6-dihydroxy-p-quinone (CLA) monomers in aqueous electrolytes leads to rapid capacity decline. To solve this problem, Sun *et al.* prepared PDBS based

on CLA monomers as the cathode for AZOBs<sup>[69]</sup>. Compared with CLA, the stability of PDBS cathodes was significantly enhanced (a 79% capacity retention under  $2 \text{ A}\cdot\text{g}^{-1}$  after 2,000 cycles). Additionally, COFs connected by covalent bonds to form a spatial network structure reveal good stability. For example, compared to PTO, BT-PTO COF has a remarkable cycle lifespan, with a 98% capacity retention under  $5 \text{ A}\cdot\text{g}^{-1}$  over 10,000 cycles<sup>[75]</sup>. Expanding the  $\pi$ -conjugated system of organics is beneficial for  $\pi$  electron delocalization, leading to improved electrochemical stability. For example, the large  $\pi$ -conjugated framework of HATTA enhances  $\pi$ - $\pi$  intermolecular interaction, resulting in enhanced stability of HATTA in  $1 \text{ M Zn}(\text{CF}_3\text{SO}_3)_2$  aqueous electrolytes, which is conducive to long cycle lifespan (an 84.07% capacity retention under  $25 \text{ A}\cdot\text{g}^{-1}$  over 10,000 cycles)<sup>[79]</sup>. Combining organics with insoluble conductive carbon materials (e.g., CNTs<sup>[65]</sup>, CMK-3<sup>[66]</sup> and CF<sup>[34]</sup>) is another efficient strategy. For example, NQ@CNTs composite cathodes exhibited a decent cycling lifespan ( $137.2 \text{ mAh}\cdot\text{g}^{-1}$  for 1,500 cycles under  $0.339 \text{ A}\cdot\text{g}^{-1}$ ) as the NQ was captured within the CNTs framework, and consequently, the dissolution was inhibited<sup>[65]</sup>.

As a part of the AZOBs structure, separators also significantly influence the cycle lifespan. Through delicate separator design, the dissolution of active substances and the shuttle of dissolved substances to the counter-electrode could be effectively suppressed. Liang *et al.* used a modified glass fiber membrane with CNTs film to inhibit the dissolution of DAP, providing an outstanding cycling lifespan (an 80% capacity retention under  $25.5 \text{ A}\cdot\text{g}^{-1}$  over 10,000 cycles)<sup>[78]</sup>. With a cation-selective membrane (Nafion membrane), Zn//C4Q batteries can provide a cycling lifespan of 1,000 cycles under  $0.5 \text{ A}\cdot\text{g}^{-1}$  (87% capacity retention)<sup>[30]</sup>. Similarly, Zn//copper-tetracyanoquinodimethane (CuTCNQ) batteries using a graphene-modified glass fiber membrane showed high rate performance and decent cycling lifespan, as the modified membrane can inhibit the dissolution of CuTCNQ and the shuttle effect in aqueous electrolytes<sup>[112]</sup>. However, ion-selective membranes and graphene-modified membranes cannot fundamentally solve the dissolution problem, and their cost is generally much higher than that of commonly used glass fiber membranes. In addition, different types and concentrations of electrolytes can affect the cycling lifespan of AZOBs. For example, the cycling lifespan of the PANI/CFs in  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  electrolytes is better than that in  $\text{ZnSO}_4$  electrolytes because the  $\text{CF}_3\text{SO}_3^-$  can stabilize the oxidized PANI by reducing the number of water molecules around oxidized PANI<sup>[97]</sup>. The number of free solvent molecules in high-concentration electrolytes greatly decreases with changes in solvation structure, which can alleviate the dissolution of organics. For example, 3,4,9,10-perylenetetracarboxylic dianhydride exhibited excellent cycling lifespan in high concentration electrolytes, with an 87% capacity retention under  $1 \text{ A}\cdot\text{g}^{-1}$  over 1,000 cycles<sup>[113]</sup>. In addition, electrolytes can also be optimized from the perspectives of ionic liquids<sup>[114-116]</sup>, electrolyte additives<sup>[117-119]</sup>, organic solvents<sup>[120-122]</sup>, and quasi/all-solid electrolytes<sup>[123-125]</sup>. Additionally, 5,7,12,14-pentacenetetrone cathodes were found to be more stable in  $1 \text{ M Zn}(\text{CF}_3\text{SO}_3)_2$  electrolytes containing trimethyl phosphate (TMP) additives (with a 61.86% capacity retention under  $0.1 \text{ A}\cdot\text{g}^{-1}$  after 550 cycles) than in  $1 \text{ M Zn}(\text{CF}_3\text{SO}_3)_2$  electrolytes<sup>[126]</sup>, due to the strong interaction between  $\text{Zn}^{2+}$  and TMP that changes the solvation structure and inhibits parasitic reactions. As an important component of batteries, Zn anodes also restrict the cycling lifespan of AZOBs to a certain extent. During the cycling process, Zn anodes typically face issues such as hydrogen evolution reaction, zinc dendrites growth, corrosion, and byproduct formation, leading to a decrease in cycling lifespan<sup>[127-131]</sup>. At present, the protection of Zn anodes is mainly achieved through strategies such as artificial surface coatings, controllable synthesis, advanced separators, and electrolyte engineering<sup>[132-136]</sup>. For instance, a  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  (NZSP) coating was shown to effectively suppress the hydrogen evolution and the formation of zinc dendrites, resulting in a prolonged lifespan of NZSP-Zn// $\text{V}_2\text{O}_5$ @PEDOT batteries compared to Zn// $\text{V}_2\text{O}_5$ @PEDOT<sup>[136]</sup>. Overall, in addition to designing structurally stable organic cathode materials, separator modification, electrolyte optimization, and Zn anode protection are also promising strategies for improving the long cycle lifespan of AZOBs.

### Rate capability

The rate capability is a key indicator for evaluating the fast-charging capacity of batteries, mainly related to the mobility of ions and electrons. In general, the electronic conductivity of most organic compounds is relatively poor, and their rate capability is often unsatisfactory. Expanding the  $\pi$ -conjugated structures in organics is an efficacious way to enhance its intrinsic conductivity, which can increase  $\pi$ -electron delocalization and thus improve electron migration and further the conductivity of organics<sup>[44,137]</sup>. For example, HATTA cathodes obtained by introducing electron-withdrawing conjugative groups (-COOH) into the HATN molecule delivered a capacity of 136.1 mAh·g<sup>-1</sup> under 25 A·g<sup>-1</sup>, higher than HATN cathodes (123 mAh·g<sup>-1</sup> under 20 A·g<sup>-1</sup>)<sup>[79]</sup>. Besides, HATN-PNZ with large charge delocalization area can effectively transfer electrons in molecules due to the conjugation elongation of aromatic rings and phenazine, leading to rapid kinetic reactions. Compared with PNZ (97 mAh·g<sup>-1</sup> under 100 A·g<sup>-1</sup>), HATN-PNZ offered a superior rate capacity of 144 mAh·g<sup>-1</sup> under 100 A·g<sup>-1</sup><sup>[80]</sup>.

Optimizing synthesis methods and conditions to control the crystal structure and morphology of organic materials is also a viable strategy to enhance conductivity. For instance, Luo *et al.* prepared organic cathodes of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) with varying degrees of crystallinity. Compared to pure PTCDA, the variant with higher crystallinity expands the  $\pi$ - $\pi$  conjugated system, leading to more delocalized electrons. This facilitates the transfer of electrons and ions, thereby improving the conductivity and providing superior rate capability<sup>[138]</sup>. Given that protons can serve as charge carriers, the conductivity of PoPD synthesized under acidic conditions significantly surpasses that of its counterpart synthesized under neutral/alkaline conditions. This results in a high capacity of 318 mAh·g<sup>-1</sup> at 0.05 A·g<sup>-1</sup> and decent rate performance (95 mAh·g<sup>-1</sup> at 5 A·g<sup>-1</sup>)<sup>[81]</sup>. Doping organic polymers with metal ions or organic molecules can alter the structure and carrier concentration of the organics, thereby enhancing their conductivity. For example, Gong *et al.* designed a Zn<sup>2+</sup>-doped polyaniline (PAZ) organic cathodes using a re-doping method, which resulted in high conductivity. Consequently, with the current density increasing from 1.0 to 10 A·g<sup>-1</sup>, the Zn//PAZ battery can deliver a capacity of 285.4 to 134.1 mAh·g<sup>-1</sup><sup>[139]</sup>. Similarly, Ma *et al.* leveraged the semi-self-doping properties of phytic acid to effectively boost the conductivity of PANI cathode by doping it with phytic acid. This resulted in a superior rate capacity, with a specific capacity of ~150/114 mAh·g<sup>-1</sup> at 1/10 A·g<sup>-1</sup><sup>[140]</sup>. Besides, the orderly and open channels and well-defined porosity of COFs allow cations to move quickly and facilitate the penetration of electrolyte ions, providing superior rate performance. Based on this, BT-PTO COF delivered a decent rate capability (108 mAh·g<sup>-1</sup> under 500 A·g<sup>-1</sup>)<sup>[75]</sup>.

The most used strategy for improving conductivity is to composite organics with conductive carbon materials. These materials typically have superior conductivity and large specific surface area, allowing electrons to quickly transfer along the network, thereby improving rate capability. For example, the poly quinone phenylenediamine (PONEA)/graphene composite cathodes can exhibit a splendid capacity of 277 mAh·g<sup>-1</sup> under 20 A·g<sup>-1</sup>, higher than PONEA cathodes<sup>[101]</sup>. In addition, different charge carriers (e.g., SO<sub>4</sub><sup>2-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Zn<sup>2+</sup> or H<sup>+</sup>) can also affect the rate capability. For example, the rate capability of Zn//PTVE batteries in Zn(ClO<sub>4</sub>)<sub>2</sub> and Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> electrolyte is lower than that in ZnSO<sub>4</sub> electrolyte<sup>[47]</sup>. The small size and high ion migration of H<sup>+</sup> ensure fast kinetics. Organic cathodes that can store H<sup>+</sup> typically provide better rate capability than those that can only store Zn<sup>2+</sup><sup>[32,44]</sup>.

### CONCLUSIONS AND PERSPECTIVES

In recent years, organic cathode materials have shone in the field of aqueous zinc ion batteries because of their advantages of environmental friendliness, wide sources, adjustable structure, and high capacity. In this review, we first introduced the development history of AZOBs and then summarized the recent progress in three typical types of organic cathodes, namely the p-, n-, and bipolar-type organics, in terms of both the



working mechanisms and electrochemical performance. These organic materials have their pros and cons. For instance, n-type organic materials have drawn increasing attention due to their high capacity, fast rate capability, environmental friendliness, and abundance. However, they still suffer from low electrical conductivity and high solubility in electrolytes. P-type organic materials, on the other hand, offer different advantages and challenges. While they can also exhibit high redox voltage and fast rate capability, they may face issues related to stability and reversibility of the redox reactions. Bipolar-type organic materials can potentially combine the advantages of both p-type and n-type materials, offering a balance between performance, stability, and cost. However, the design and synthesis of bipolar-type materials can be more complex. In this regard, we further discussed the developed strategies for improving the performance of AZOBs based on the voltage, specific capacity, cycling lifespan and rate capability.

Though the research of organic cathodes in AZOBs has made great progress, the commercial application of AZOBs still faces many challenges: (1) The energy density is relatively low. Due to using aqueous electrolytes, the working voltage of the AZOBs is normally less than 2.0 V. Moreover, additional conducting additives are often required to enhance the conductivity of organic cathodes, which, however, might reduce the energy density; (2) Working mechanism is not fully understood. Currently, it is proposed that these materials may store  $Zn^{2+}$  and/or  $H^+$  ions. However, it remains unclear which mechanism dominates. Furthermore, the regulation of the reaction mechanism is also not well understood; (3) Unexpected side effects. During the charging and discharging process, some small organics and discharge products are often dissolved in aqueous electrolytes, resulting in a poor cycling lifespan.

In response to the above challenges, we propose the following prospects for the future development of organic cathodes.

(1) Improving the energy density of organic cathodes. Many organic materials suffer from low conductivity and thus require a lot of conductive carbon during the electrode fabrication process, which, in turn, would reduce the active materials and, consequently, the energy density of the battery. Several strategies could be considered to address this issue.

(a) Advanced manufacturing techniques. Techniques such as nanostructuring or creating composite materials could be used to improve the distribution of conductive carbon in the electrode, which could enhance conductivity without significantly reducing the proportion of active materials.

(b) Surface modification. Surface modification of active materials could be another way to improve their conductivity. This could involve coating the surface of the active materials with a thin layer of conductive material or altering the surface chemistry to improve its interaction with conductive carbon.

(c) Structural optimization. The structure of the active materials could be optimized to improve their interaction with conductive carbon, thereby enhancing the overall conductivity of the electrode without needing to add excessive amounts of conductive carbon.

(d) Developing new materials: research could focus on developing new organic materials with higher intrinsic conductivity, which would reduce the need for additional conductive carbon.

These are just a few potential strategies, and research in this area is ongoing. The goal is to find a balance that allows for high conductivity while maintaining a high proportion of active materials, thereby maximizing the energy density of the battery. It is also worth mentioning that machine learning could be a

very promising approach to facilitating the discovery of new and high-performance organic cathodes. By analyzing the electrochemical data of known organic materials and furthering the structure-property relationship, key elements that affect the battery performance can then be identified. Consequently, new organic structures with these key elements can be predicted and further experimentally verified. It is noted that the application of machine learning in new organics design is still in its early stages, requiring high-quality and diverse data and algorithm support.

(2) Understanding the charge storage and capacity decay mechanisms of organic cathodes. Previous studies reveal that both  $Zn^{2+}$  and  $H^+$  storages contribute to the capacity of organic cathodes of AZOBs. The diffusion of protons is kinetically smoother and is beneficial to high-rate performance, but it also induces local pH changes and promotes the generation of byproducts. Therefore, understanding the reaction mechanism and furthering its regulation are essential to achieving high-performance AZOBs. It should be noted that organic cathodes containing carbon elements are often quite sensitive and easy to decompose under certain characterization conditions, such as the high voltage electron beams. This brings about additional difficulty in tracking the dynamic structural evolution of the material during charging and discharging. Some advanced characterization techniques (e.g., *in situ* Fourier transform infrared spectroscopy, nuclear magnetic resonance, and electrochemical quartz crystal microbalance), together with theoretical simulations, provide approaches to comprehending the detailed energy storage mechanism of organic cathodes and, consequently, the performance optimization.

(3) Enhancing the stability of organic cathodes. The stability and lifespan of organic cathodes in aqueous zinc batteries can be compromised due to the dissolution of some organic materials in aqueous electrolytes. This dissolution is closely tied to the structure and composition of the organic materials. As such, optimizing these aspects could potentially decrease their solubility in the electrolyte, thereby enhancing the cycling lifespan of batteries. Additionally, applying protective layers or coatings on the cathode material can prevent the organic materials from directly contacting the electrolyte, further improving the stability of the organic cathodes. Modifying the electrolyte formula or incorporating specific electrolyte additives may also help minimize the dissolution of the organic materials. However, the key to devising effective mitigation strategies lies in a thorough understanding of the dissolution process.

(4) Exploring other avenues for organic cathodes. Organic cathodes have good flexibility and elasticity, and flexible batteries based on organic cathodes have broader application prospects in wearable devices. Based on their good biocompatibility, organic cathodes can be used in medical devices such as pacemakers to provide continuous electrical energy. In addition, the degradability of organic cathodes is also conducive to the construction of biodegradable batteries, making them easier to handle and recover after the end of battery life, thereby reducing the impact on the environment.

In summary, there is still a long way to go in developing sustainable, economical, and high-performance organic cathodes for AZOBs. We aspire that this review will offer valuable inspiration for the mechanism research and construction of high-performance AZOBs.

## DECLARATIONS

### Authors' contributions

Proposed the topic of this review: Liang H

Prepared the manuscript: Li J

Collectively discussed and revised the manuscript: Li J, Liang H

### Availability of data and materials

Not applicable.

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### Conflicts of interest

Both authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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