

Covalent Organic Frameworks for Cathode Materials

Subjects: Electrochemistry

Contributor: Chi Wang, Yuchao Tian, Wuhong Chen, Xiaochun Lin, Jizhao Zou, Dongju Fu, Xiao Yu, Ruling Qiu, Junwei Qiu, Shao-Zhong Zeng

Covalent organic frameworks (COFs) are constructed from small organic molecules through reversible covalent bonds, and are therefore considered a special type of polymer. Small organic molecules are divided into nodes and connectors based on their roles in the COF's structure. The connector generally forms reversible covalent bonds with the node through two reactive end groups. The adjustment of the length of the connector facilitates the adjustment of pore size. Due to the diversity of organic small molecules and reversible covalent bonds, COFs have formed a large family since their synthesis in 2005. Among them, a type of COF containing redox active groups such as $-\text{C}=\text{O}-$, $-\text{C}=\text{N}-$, and $-\text{N}=\text{N}-$ has received widespread attention in the field of energy storage. The ordered crystal structure of COFs ensures the ordered arrangement and consistent size of pores, which is conducive to the formation of unobstructed ion channels, giving these COFs a high-rate performance and a long cycle life. The voltage and specific capacity jointly determine the energy density of cathode materials.

Keywords: COFs ; batteries ; cathode ; active sites

1. Introduction

Covalent organic frameworks are new crystalline polymer materials, which are composed of small molecular organic monomers connected by reversible covalent bonds. COF materials were first synthesized in 2005 ^{[1][2][3]}, but it was not until 2015 that Xu et al. proposed a COF with redox activity as a positive electrode for lithium-ion batteries (LIBs) ^[4]. Due to their controllable pore structure, large surface area, simple surface structure modification, high thermal stability, and chemical stability, COFs show great potential as an electrode material with a reversible energy storage function, which has successfully attracted extensive research interest ^{[3][5][6][7][8]}. Since 2019, research on COF material electrodes has shown a significant growth trend ^[9]. In the past, the use of COFs as cathode active materials for metal ion batteries encountered major obstacles ^[10], mainly due to the unstable chemical structure of the synthesized COFs and the lack of redox active sites that can be used for high-voltage reversible charge–discharge. Furthermore, breakthroughs have been made in recent years, and several COF materials with high theoretical capacities, high operating voltages, and high utilization rates for redox active sites have been found. The discovery of these new materials has significantly promoted the research on using COFs in cathode applications.

2. Active Functional Groups of COFs Materials

There are three common functional groups in the COFs which can be used for organic cathodes: $-\text{C}=\text{N}-$, $-\text{C}=\text{O}-$, and $-\text{N}=\text{N}-$. The reaction mechanism of these units is shown in **Figure 1**. According to these three groups, several points and connectors can be derived.

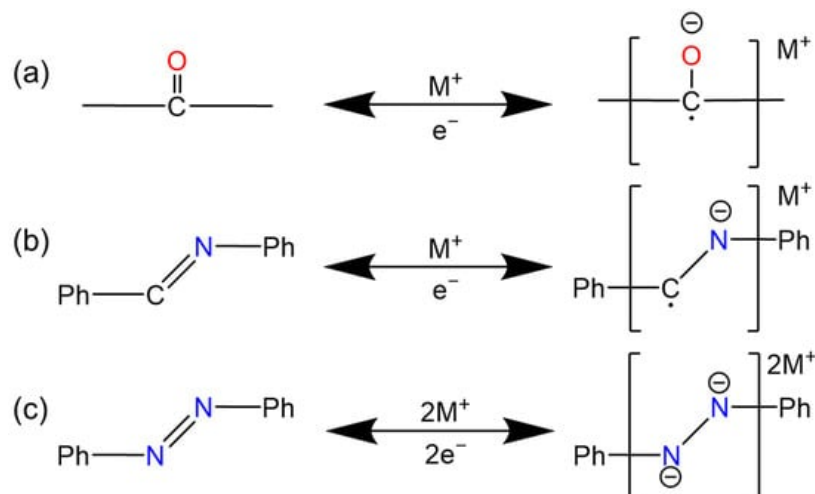


Figure 1. The redox reactions of three typical functional groups: (a) $\text{C}=\text{O}$ -, (b) $\text{C}=\text{N}$ -, and (c) $\text{N}=\text{N}$ -. Where the active functional groups are marked with color and the following are the same.

According to the characteristics of these groups, researchers divided the cathode COFs into six categories. The following sections will discuss these six categories and their corresponding COFs.

2.1. Quinones and Ketones

At present, there are more and more studies on carbonyl active groups [11][12][13] (Figure 1a), which are composed of $\text{C}=\text{O}$ bonds (Figure 2). They have fast electrochemical kinetics, a high capacity, and are capable of storing a variety of ions [14][15][16]. Carbonyl compounds are almost completely insoluble in aqueous electrolytes, but their discharge products are highly soluble. The generated free radical intermediates are usually unstable and can be converted into inactive compounds through reactions with other molecules or free radicals in the electrolyte, which inevitably limits their cycle stability [15][17]. For example, the tricarbonyl material dichloroisocyanuric acid (DCCA) has been identified as an irreversible structure because of the formation of inactive precipitates [18]. The highly crystalline π -conjugated structure of COF materials can provide a stable physical and chemical reaction environment, which is conducive to the utilization of carbonyl groups.

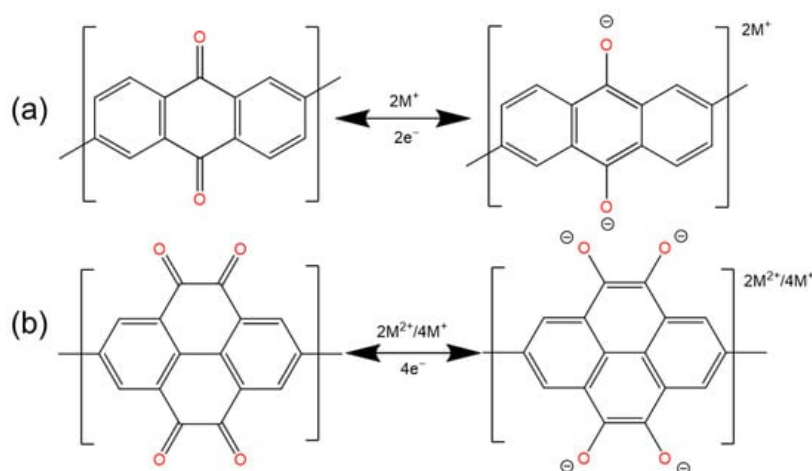


Figure 2. The reaction mechanism of $\text{C}=\text{O}$. (a) Typical monovalent ionic reactions, (b) Typical multivalent ionic reactions.

In terms of a zinc ion battery (ZIB), Ma et al. synthesized carbonyl-rich Tp-PTO-COF (Figure 3a) by condensing 1,3,5-triformylphloroglucinol (Tp) with 2,7-diaminopyrene-4,5,9,10-tetraone (DAPTO) via an acid-catalyzed solvothermal reaction [19]. With multiple active sites, compared to other electrodes, the material delivers a high specific capacity of 301.4 mAh g^{-1} at 0.2 A g^{-1} [20][21]. It also has excellent cycle stability. After 1000 cycles at 2 A g^{-1} , it delivers a capacity of 218.5 mAh g^{-1} with 95% retention of its initial capacity. The coulombic efficiency of the battery is maintained at around 100%.

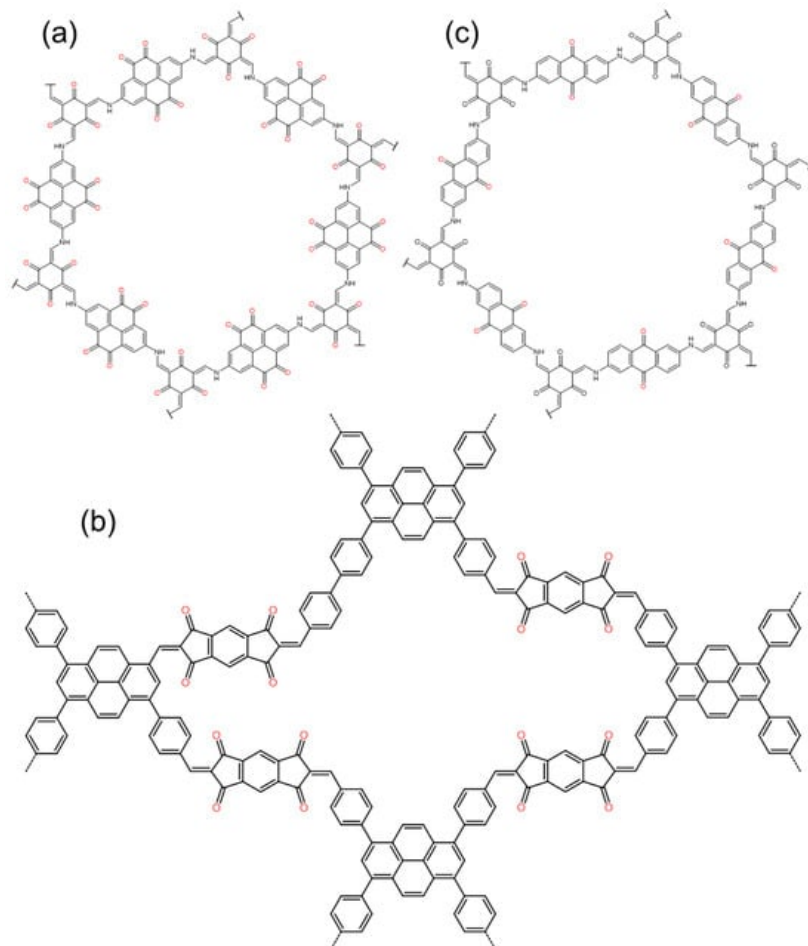


Figure 3. The structure of typical quinones- and ketones-based COFs: (a) Tp-PTO-COF, (b) 2D-COF, (c) TFPPy-ICTO-COF.

Huang Ning's team reported a new Janus dione-based COF (**Figure 3b**) connected to olefin via a Knoevenagel condensation reaction, which was constructed from s-indacene-1,3,5,7(2H,6H)-tetraone (ICTO, Janus dione) as edges and 1,3,6,8-tetrakis(4-formylphenyl) pyrene (TFPPy) [22]. This COF has full sp^2 conjugation throughout its skeleton and delivered a high specific capacity of 338 mAh g^{-1} at a discharge rate of 0.1 C, which ranks as the highest record among COF-based LIBs. It also has excellent stability; after 1000 cycles, the reversible capacity kept a retention of 100%.

It is similar to the structure seen in **Figure 3a**. Researchers prepared 2D-COF (**Figure 3c**) samples with different stacking thicknesses by condensing 1,3,5-triformylphloroglucinol (TFP) with 2,6-diaminoanthraquinone (DAAQ) to study the dependence of redox activity and radical intermediate stability on the thickness of the COF layer [23]. The test showed that, compared to the thickest sample (100–250 nm), which has a 182 mAh g^{-1} capacity (at 50 mA g^{-1}), the thinnest sample (4–12 nm) displays a high capacity of 500 mAh g^{-1} at the same current density, excellent rate capability (198 mAh g^{-1} at 5 A g^{-1}), and excellent cycle stability (at 5 A g^{-1} , the capacity retention is maintained at 99% after 10,000 cycles). It has been successfully demonstrated that the stability of radical intermediates and their contributing capacity can be systematically improved by reducing the thickness of two-dimensional COFs.

Duan et al. synthesized DAAQ-COF@CNT for a potassium ion cathode. It was constructed using 2,6-diaminoanthraquinone (DAAQ) [24], 1,3,5-triformylresorcinol, and carbon nanotubes. By using carbon nanotubes as a conductive network and an auxiliary stripping agent, the material exhibits a reversible capacity of 157.7 mAh g^{-1} (0.1 A g^{-1}), and the capacity retention rate remains at 77.6% after 500 cycles at a current density of 0.5 A g^{-1} .

2.2. Imide

Carbonyl-containing ($-\text{C}=\text{O}-$) imide compounds have attracted much attention due to their high theoretical capacity (two-electron redox per imide center, (**Figure 4a**), high operating voltage ($\approx 2.5 \text{ V}$), rapid redox reaction, and excellent chemical stability [25]). However, imides often have the disadvantage of insufficient utilization of their redox active sites ($-\text{C}=\text{O}-$), especially in the case of a high current rate and a long-term operation [26][27]. The current improvement methods are mainly focused on expanding the conjugation and increasing the conductivity [28].

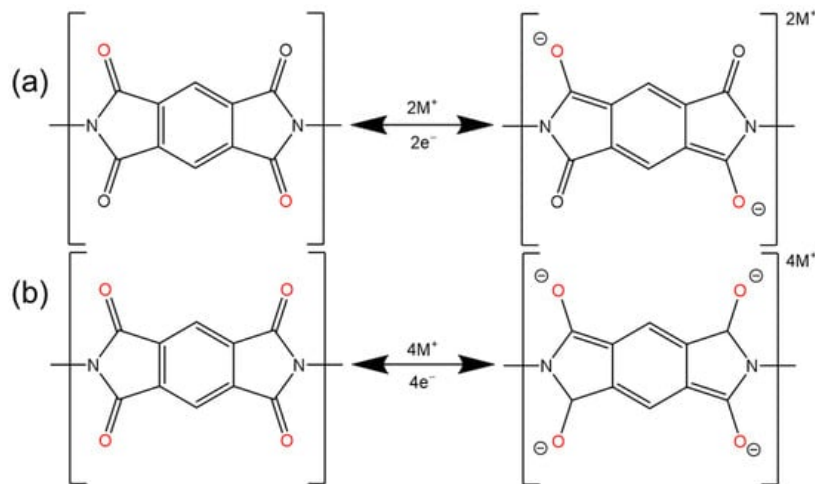


Figure 4. The (a) $2e^-$ and (b) $4e^-$ reactions of imide functional groups.

In order to pursue the plane structure, Luo selected naphthalimide (NTCD) as a monomer, which has a large conjugated structure and is condensed with hexaketocyclohexane (HKH) to synthesize NTCDI-COF [29], aiming this large conjugated system to improve the stability and conductivity of COFs. The material shows a specific capacity of 210 mAh g^{-1} at 0.1 A g^{-1} . At a current of 2 A g^{-1} , after 1500 cycles, NTCDI-COF still has a capacity of 125 mAh g^{-1} , and the capacity retention rate is 86%. Yang et al. synthesized Tb-DANT-COF using 1,3,5-triformylbenzene (Tb) as the reactant instead of 1,3,5-triformylphloroglucinol (Tp) [30]. By changing the conjugated backbone, the charge transfer and lithium-ion diffusion in the material were improved, and the initial discharge capacity increased from 93.4 to 144.4 mAh g^{-1} . It also shows a good rate performance and cycle stability.

In terms of enhanced π - π conjugation, Shehab et al. chose pyromellitic dianhydride (PMDA) and 1,3,6,8-tetra (4-aminophenyl) pyrene (TAPP) as raw materials to synthesize a highly conjugated crystalline PICO-1 (Figure 5a) material through a linker-exchange mechanism [31]. Each repeating unit of the material consists of 16 redox-active imide sites. Under the influence of high π conjugation, each carbonyl group can be effectively utilized (Figure 4b), thereby maximizing the specific capacity and allowing it to approach the theoretical capacity. PICO-1 produced a specific capacity of $\approx 230 \text{ mAh g}^{-1}$ in the first few cycles at 0.1 C . At a rate of 0.3 C , 99% coulombic efficiency was maintained over 175 cycles.

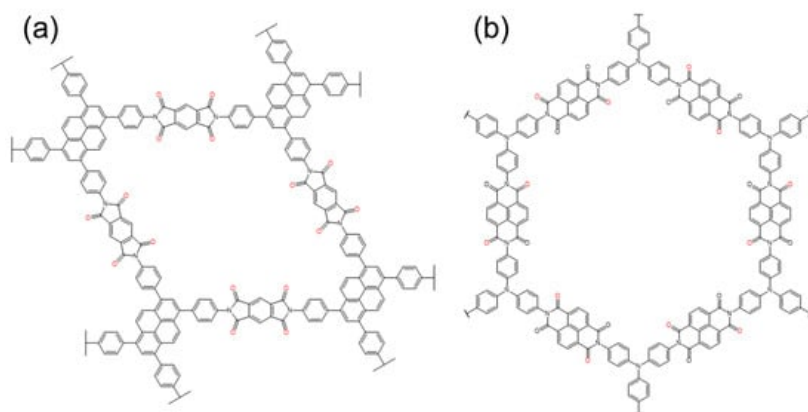


Figure 5. The structure of typical imide-based COFs, (a) PICO-1, (b) 2D-PAI.

The use of a conductive agent is also particularly important. Wang et al. reported the synthesis of a crystalline 2D-PAI (Figure 5b) via a polycondensation reaction between tris (4-aminophenyl) amine (TAPA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) [26]. Driven by the π - π stacking interaction, the crystal 2D-PAI can easily be integrated with carbon nanotubes (CNT) to prepare 2D-PAI@CNT. This material has a unique porous structure and can provide a short diffusion path for ions; the charge storage process is a fast surface-controlled pseudocapacitive process. Therefore, although the initial capacity is only 104 mAh g^{-1} , it has a high rate capability and ultra-stable cycle stability. After 8000 cycles, the capacity retention is still as high as 100%.

Wang used rGO for compositing; he adopted PMDA as the dianhydride and tris (4-aminophenyl) amine (TAPA, for PI-COF-1) [32]. To significantly enhance the capacity and rate performance, he prepared a PI-ECOFs/rGO cathode material by mechanical grinding PI-COF and chemically reducing graphene oxide (rGO). By enhancing the activity of the redox active sites buried deep inside the channel, the capacity of PI-ECOF-1 reaches 112 mAh g^{-1} , which is equivalent to 79%

of the theoretical capacity (142 mAh g^{-1}), while PI-COF-1 only provides a capacity of 85 mAh g^{-1} , which is equivalent to 60% of its theoretical capacity.

2.3. Imine and Azo

The --C=N-- and --N=N-- functional groups are crucial for charge storage in COF cathode materials. Both of them can accept two units of electrons and simultaneously adsorb two charge units of metal ions.

Using independent imine and azo bonds as active sites is relatively rare in cathode COF materials, mainly due to their comparatively low redox potentials. Most studies prefer to combine them with other functional groups to enhance performance, rather than using imine or azo bonds alone.

The --C=N-- group in a COF is derived from the Schiff base reaction [33][34][35], which plays a dual role in connecting the molecular monomers and acting as a redox active site. Its flatness and conjugated structure exert a significant influence on the electrochemical activity of the group [34][36][37][38][39]. COFs containing --C=N-- always accumulate tightly and usually need to grow in situ on materials with a high conductivity and a high specific surface area such as carbon nanotubes [7][40]. The work by Lei et al. has demonstrated the lithium-ion adsorption process in these types of COFs [40]. During the first step of discharge, only nitrogen atoms are involved in lithium adsorption, with an oxidation–reduction potential above 1.5 V [5], meeting the requirements for cathode materials. However, the potentials of the subsequent four lithium adsorption steps are all below 1.5 V, which does not meet the requirements for cathode materials. Thus, for COFs used as cathode materials, only the reaction shown in **Figure 1b** typically occurs.

As for COFs containing --N=N-- , the azo bonds not only connect the molecular framework structurally but also functionally provide active sites. The conjugation with adjacent aromatic rings further enhances the conductivity of the azo bonds. The rapid charge–discharge capability and relatively longer cycle life of aromatic azo compounds can be attributed to the extension of the π -conjugated structure and the strong affinity between azo groups and metal ions [2][34][41][42].

2.4. Pyrazine

Pyrazine (1,4-diazabenzene) possesses two carbon–nitrogen bonds within its hexagonal ring that serve as active sites for multivalent metal ion cathode materials (**Figure 6a**). These pyrazine active sites are frequently found within hexaazatrinaphthylene (HATN) groups (**Figure 6b**). HATN, a widely used organic cathode material, boasts a high theoretical capacity due to its abundance of active sites. However, its application is significantly impeded by low redox stability and high solubility in electrolytes, leading to a diminished lifespan.

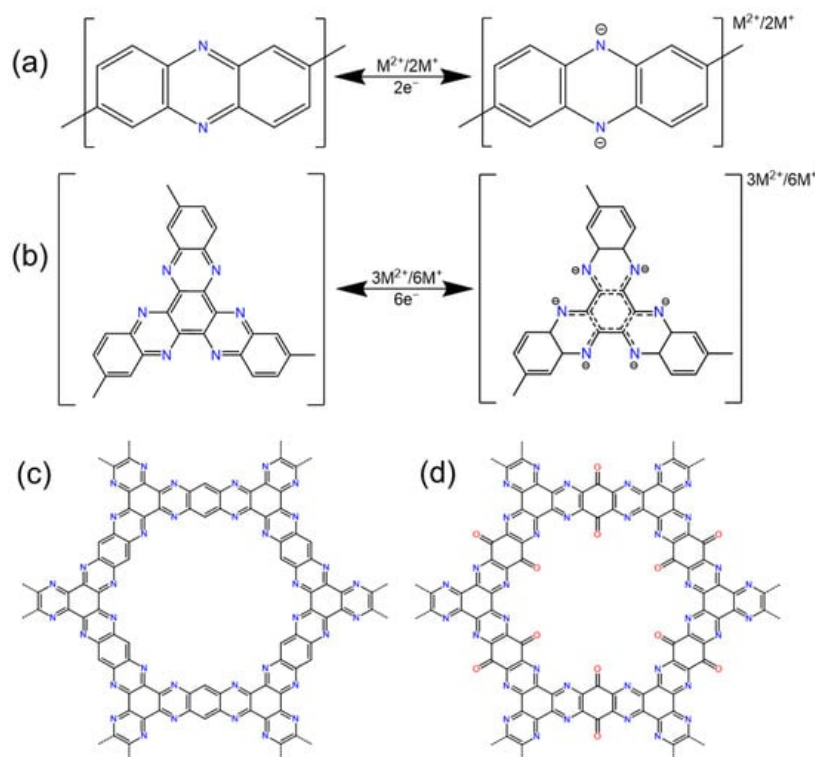


Figure 6. (a) The redox reaction mechanism of pyrazine, (b) the redox reaction mechanism of HATN, (c) the structure of HAQ-COF, (d) the structure of HA-COF.

In 2017, Peng and colleagues first proposed the utilization of N-heteroaromatic triquinolinamine subunit small molecules, referred to as 3Q (**Figure 6b**) [43], which are also known as HATN, as the cathode in rechargeable organic batteries, achieving excellent electrochemical performance. Therefore, Xu et al. thought of connecting HATN molecules and different connectors to the COF to achieve better stability [44]. They connected HATN-6CHO with PDAN and PDA, respectively, to prepare 2D CCP-HATN and 2D C=N HATN. These two substances were grown in situ on carbon nanotubes, and the obtained 2D CCP-HATN@CNT core-shell hybrid exhibited a high capacity of 116 mAh g⁻¹ and a high utilization rate of HATN's redox active sites. It has excellent cycle stability (91% capacity retention after 1000 cycles) and rate capability (82%, 1.0 A g⁻¹ vs. 0.1 A g⁻¹) as a cathode material for LIBs.

Researchers produced HAQ-COF (**Figure 6c**) and HA-COF (**Figure 6d**) via the solvothermal reaction of hexacyclohexanone (HKC) with Tetraaminobenzoquinone (TABQ) and 1,2,4,5-tetraaminobenzene (TAB) [45], respectively, and applied them as cathodes for ZIB with excellent cycle stability. Through a combination of ex situ spectral analyses and density functional theory (DFT) calculations, the zinc-ion storage mechanisms of the two materials were elucidated. Wu et al. [46] synthesized the same COF by mixing the two substances in proportion and dissolving them in NMP with a small amount of sulfuric acid for 12 h. And it exhibited excellent and long cycle stability and a high rate capacity. At a current density of 2 C (1.54 A g⁻¹), it maintained a capacity of 198.4 mAh g⁻¹ after 1000 cycles, and the capacity retention rate was 81%. At a high current density of 5 C (3.87 A g⁻¹), it can still provide a capacity of 158 mAh g after 1500 cycles.

A two-dimensional polyimide-linked HATN-AQ-COF was synthesized by using 2,3,8,9,14,15-hexacarboxyhexaazatrinaphthalic anhydride (HATN-AP) and 2,6-diaminoanthraquinone (DAAQ) [47]. This COF showed an excellent rate capability and high active site utilization. The reaction pathway of lithium-ion storage was revealed by a series of ex situ spectral analyses and DFT calculations.

Many similar COFs using HATN have been prepared. The main methods can be roughly attributed to two ways. One is to prepare the COF through the condensation of HKC and a monomer with an ortho-amino group [45][46][48][49]. The second is to use a certain group that can be condensed on the periphery of HKC to react with other substances [44][47][50][51]. For example, Chu et al. grafted cyano groups onto the periphery of HKC and synthesized HATN-CTF through a trimerization strategy [52].

There are also several COFs which use other structural pyrazine groups, such as the DAPH-TFP COF which uses diaminophenazine as a connector [53]. Compared with a DAPH-TFPF COF with diaminoanthraquinone as the connector, the DAPH-TFP COF provides higher energy density and power density due to its higher lithium-ion diffusion coefficient. CTF-TTPQ was directly synthesized using 2,9-dicyano-5,7,12,14-tetraaza-6,13-pentabenzquinone (DCTPQ) for aqueous zinc-ion batteries [54], which utilized multiple redox sites. It provided a high-rate capability (82% of the initial capacity was retained when the current density switched between 5 A g⁻¹ and 0.3 A g⁻¹) and cycle stability (>94% capacity retention after 250 cycles).

2.5. Triazine

Covalent triazine frameworks (CTFs) represent a novel class of COFs which are notable for their intrinsic redox properties, making them viable candidates for cathodes in metal-ion batteries. Within these structures, triazine units serve as pivotal nodes. Specifically, the positions 1, 3, and 5 on the triazine rings act as reactive sites engaged in electrochemical interactions, while positions 2, 4, and 6 act as linking sites which are crucial for the structural connection of the framework (**Figure 7a**). The presence of multiple reactive sites within CTFs renders them particularly suitable as cathode materials for batteries using multivalent metal ions, offering enhanced capacity and efficiency prospects.

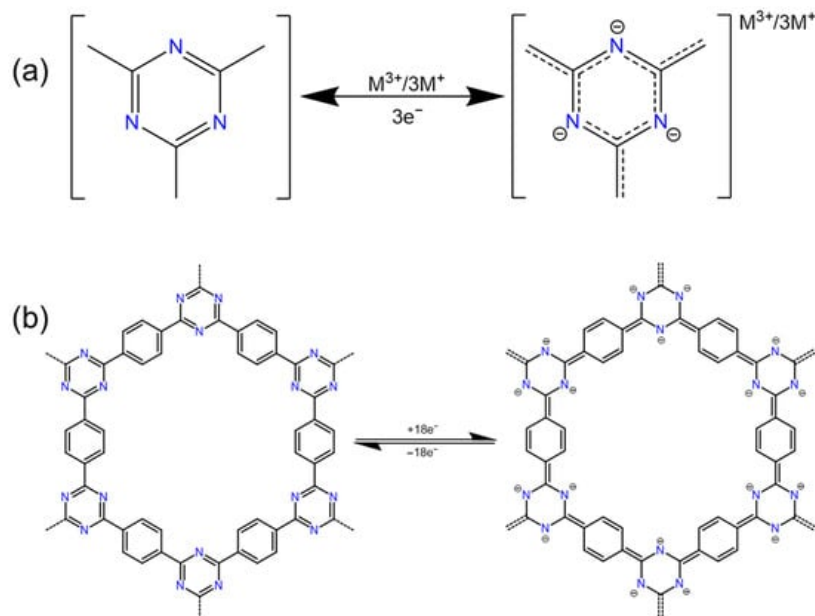


Figure 7. The redox reaction mechanism of (a) triazine and (b) CTF.

Sun et al. crafted a two-dimensional porous honeycomb polymer CTF composed of a benzene ring and triazine ring for rechargeable magnesium-ion batteries (RMBs) [55]. At a high rate of 5 C, a reversible capacity of 72 mAh g^{-1} was achieved, and the capacity decay rate was only 0.0196% after 3000 cycles. Since the triazine ring is the redox active site of this porous COF electrode, each COF ring unit can reversibly bind to up to nine magnesium ions during charge and discharge (Figure 7b). And a triazine-connected triazine framework CTF-TTPQ (poly (triazine-5,7,12,14-tetraaza-6,13-pentabenzquinone)) for aqueous zinc-ion batteries was reported by Wang et al. [54]. CTF-TTPQ exhibits a high energy density ($432.28 \text{ Wh kg}^{-1}$) and excellent cycle stability (>94% capacity retention after 250 cycles at 0.5 A g^{-1}).

The low conductivity, low redox potential, and poor electrochemical stability of CTFs greatly limit their application. It is usually necessary to make the CTF form large enough pores so that the electrolyte can fully infiltrate the inner surface, or introduce extended π conjugation and other similar methods to increase the overall conductivity of the CTF.

Wang et al.'s research used 4,4'-(piperazine-1,4-diyl) dibenzonitrile (CN-A) as the starting material to explore the effect of introducing fluorine atoms to its benzene ring [56]. They used two fluorine-containing monomers: 4,4'-(piperazine-1,4-diyl) bis (3,5-difluorobenzonitrile) (CN-B) and 4,4'-(piperazine-1,4-diyl) bis (2,3,5,6-tetrafluorobenzonitrile) (CN-C), to synthesize CTF-B and CTF-C. These compounds were used as CTF-A counterparts to study the effect of fluorine groups on the pore structure and electrochemical properties of CTFs. It was found that the specific surface area and the first charge capacity of the synthesized CTF increased with the increase in the fluorine doping amount. This indicates that the fluorinated monomer is beneficial to the formation of defects in the CTF framework. In particular, CTF-C exhibits a specific surface area of up to $2515 \text{ m}^2 \text{ g}^{-1}$ and a high specific capacity at a current density of 0.1 A g^{-1} in LIBs. It is worth noting that the incorporation of strong electron-withdrawing groups such as halogen atoms into COF materials is beneficial and can improve the voltage platform, and the high defect content caused by halogens will increase the specific surface area of the formed COF [56]. However, replacing hydrogen atoms with halogens will reduce the theoretical specific capacity because the relative atomic mass of halogen atoms is much larger than that of hydrogen atom.

There is a highly stable three-dimensional π -conjugated covalent triazine core framework (Azo-ctf) that uses triazine as an electron-rich center and is bridged by an azo redox active connector [41]. The Azo-ctf cathode has abundant redox azo sites, elastic and accessible pore networks, and good intramolecular and interfacial electron transfer capabilities. The extended π -conjugated network facilitates the rapid transfer of electrons and ions, and the introduction of electron-withdrawing triazine units in the organic framework can help adjust the electronic structure of the material to optimize the redox potential. In an LIB, the Azo-ctf cathode has an ultra-long cycle life (89.1% capacity retention after 5000 cycles), an extremely low-capacity decay rate per cycle (0.00218%), and an excellent rate capability (84.4%, 1.0 A g^{-1} vs. 0.1 A g^{-1}). It is far superior to many reported organic cathodes. In addition, the design ideas were used to conjugate electron-withdrawing and electron-donating groups to control molecular energy levels and band gaps, and other molecular structures will provide good inspiration for the development of new high-performance organic electrodes.

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