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Covalent Organic Frameworks: Advanced Organic Electrode Materials for Rechargeable Batteries

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Abstract: Covalent organic frameworks (COFs), featuring with structural diversity, framework tunability and functional versatility, have emerged as promising organic electrode materials for rechargeable batteries and garnered tremendous attentions in recent years. The adjustable pore configuration, coupled with the functionalization of frameworks through pre- and post-synthesis strategies, enables a precise customization of COFs, which provides a novel perspective to deepen the understanding of the fundamental problems of organic electrode materials. In this review, we provide a summary on the recent researches of COFs electrode materials for rechargeable batteries including lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), potassium-ion batteries (PIBs), and aqueous zinc batteries (AZBs). Besides, this review will also cover the working principle, advantages and challenges, strategies to improve the electrochemical performance, and the applications of COFs in the rechargeable batteries.

1. Introduction

Energy and environmental issues have been regarded as the major challenges to maintain the sustainable development of human society. With the depletion of fossil fuels and ever-increasing energy demands as well as adverse green-house effect, the efficient utilization of renewable power sources (e.g wind, wave, solar) has become the most significant issue that must be confronted.^[1-4] However, the intermittent characteristic of these renewable energy sources indicates that they cannot be used directly. Such a problem urgently requires scientists to pursue efficient energy-converting devices and reliable energy-storage systems with high specific energy, long lifespan and excellent safety.^[5-7] Among them, the rechargeable secondary batteries have been demonstrated as the most promising candidate for electricity storage and utilization.^[8-11] As one of the most popular batteries, lithium-ion batteries (LIBs) have been found immense success in consumer electronics and electric vehicles, and are under the consideration for energy-storage power stations.^[12-14] However, the commercial LIBs based on transition metal-based inorganic compounds have encountered a bottleneck.^[15-17] The charge storage of inorganic electrode materials is governed by the oxidation-state variation of transition metal centers and achieved a charge balance with the insertion of counter-ions.^[18] Restricted by crystal lattice and structure stability, the size and valence of counter-ions are required to match the crystal structures, which severely limit further improvement of energy density.^[19-21] Clearly, these factors intrinsically weaken the versatility of inorganic materials. For instance, the similar electrode materials, which are successful in LIBs, are not suitable for other alkali ions batteries.^[22-24] Additionally, from the viewpoint of economical and renewable factors of mineral resources, the existing LIBs based on transition metals (e.g., cobalt, nickel and manganese) are difficult to meet the requirement of large-scale energy storage.^[25] Nowadays, various demands have been raised up for the state-of-the-art batteries, not only in the enhancement of cycle-life, fast-charging and safety, but also in the focus of cost, light-weight, pollution-free and environmental benign.^[26,27] Under this background, researchers gradually shift their studies on novel batteries system and electrode materials.^[28-31] Among them, explorations on the possibility of using organic compounds as potential alternatives of current inorganic electrode materials has never been stopped.^[32,33]

Organics have been demonstrated as promising electrode candidates due to their variety, sustainability, relatively low cost, and environmental friendliness.^[34-36] The structural diversity implies that the richness of organic materials will provide abundant options and

room in this field. The molecule engineering means that the electrochemical properties of organic electrodes can be rationally tuned with different functional groups, which exhibits a good designability of organic materials. These important features allow various designable synthetic routes and convenient functionalization. Although organic electrode materials are endowed with many advantages, their development and investigations still encounter several issues.^[37-41] For example, most of organic electrode materials are nonporous bulk solids, which would result in the inefficient utilization of active centers and the slow transportation of electrolyte ions. Importantly, it would impose obstacles in establishing the structure-activity relationships due to the lack of structural and/or chemical precision. As a complicated system issue, the performances of rechargeable batteries are affected by various factors in different scales.^[42-44] Also, the electrochemical behaviors of organic electrodes are not solely determined by active functional groups. To deepen the understanding of the relationship between structure and performance, it is necessary to expand the perspective from molecular design to materials construction.

Fortunately, the diversity of organic materials provides various and novel opportunities to perform the designability at a higher level. Especially, extending molecule materials into two- and three-dimensional (2D and 3D) organic frameworks would offer a viable strategy to approach this goal.^[45] Among them, covalent organic frameworks (COFs) combine the porosity with structural precision, versatility, and tunability, representing an excellent platform to construct the controllable materials for specific performance.^[46] COFs are composed of lightweight elements (e.g C, H, N, O) and recognized by several charming advantages including abundant pores, high surface areas, and low densities.^[47] As an emerging but rapidly developed crystalline porous materials, COFs featured with structural diversity and functional tunability.^[48-50] In recent years, these distinguished features have attracted tremendous attentions in the field of gas storage, separation, catalysis and sensors.^[51-53] It should be noted that increasing interests have also been devoted to the application of COFs in electrochemical energy storage,^[54-56] where COFs are considered to be promising electrode materials due to their unique features including their intrinsic insolubility in electrolyte, abundant pores, ordered open channels for the facilitated ions transportation, and π -conjugated frameworks for the improved charge transportation.^[57-60] Different from traditional organic electrode materials, COFs with robust frameworks that combine crystallinity and high porosity present an excellent platform to allow the material design at a

new horizon. Recently, two-dimensional (2D) materials have attracted tremendous research interests and received plentiful investigations.^[61-63] Many scientists believe that the migration length of both electrons and ions will be effectively shortened in the exfoliated 2D COFs with mono- and few-layer, and the utilization efficiency of redox sites will be dramatically improved.^[54] The well-defined alignment of π building units in the 2D layers enables the growth of COFs on conductive carbon additive (carbon nanotube or graphene) to greatly improve the conductivity.^[64] Therefore, the performances of 2D COF-based electrode materials are undoubtedly very promising.

Although the discussions of electroactive COFs have been mentioned in some comprehensive reviews,^[54,59] a systematic introduction to the superiorities and challenges of COFs as electrode materials is still lacking. Herein, we venture to present a concise review on COFs standing on the points of the perspective and requirements of organic electrode materials. Apart from the crystalline COFs, the investigations on their similar counterparts such as the covalent organic nanosheets and covalent triazine frameworks are also involved. We start this review with a brief introduction of the reaction mechanism of COFs as electrode materials. Then, an overview of the advancements of COFs in LIBs and sodium-ion batteries (SIBs) will be presented. The strategies related to the improvements of electrochemical performance of COFs electrode materials will be summarized. Moreover, the applications of COFs in potassium ion batteries (PIBs), aqueous zinc batteries (AZBs), lithium-sulfur (Li-S) batteries will also be presented as well. Finally, the challenges and the prospective of COF electrode materials will be discussed. By summarizing and identifying the critical issues of COFs for electrode application, we believe that this review will arouse more interests and consideration in this field.

2. Working principles of COFs electrode materials

Figure 1 depicts the discharging and charging process of metal-COFs secondary batteries. The charge storage process of COFs electrode materials is based on the reversible variation of charge state in the electroactive organic groups or moieties.^[35,65] In the light of the charged state of species during the redox reactions, organic electrode materials generally fall into two categories: n-type and p-type organics.^[26] During the reaction process, n-type organics will be reduced to form negatively charged anions, while p-type organics will be oxidized to form positively charged cations. Most of the prevailing COFs electrode materials

can be attributed to the n-type organics. Taking LIBs as an example, accompanied with the reduction of COFs, there will be a concomitant balance of the negative charged species through the movement of cations (Li^+). In the reverse oxidation, through the release of Li^+ ions into the electrolyte to recover the neutral state, a discharge/charge process of COFs is completed. As a representative of n-type electrode materials, carbonyl compounds have attracted substantial investigations during the past decades.^[66] Among them, quinone, carboxylates, anhydrides and imides are considered as four typical organic carbonyl electrode materials and have gotten successful applications in lithium-organic batteries.^[34] In the discharge/charge process, carbonyl compounds will undergo a reversible fracture and reconstruction of $\text{C}=\text{O}$ bonds. The redox mechanism can be viewed as a nucleophilic addition reaction of carbonyl groups, in which the enolization reaction is a central step.^[26]

In fact, COFs electrode materials can be regarded as the redox active sites embedded within porous organic framework. Hence, the incorporation of redox units into the framework is a straightforward strategy to construct COFs electrode materials. Taking the polyarylimide redox unit as an example, its excellent performance of lithium storage can still be maintained in the network of COFs. Feng et al. synthesized a crystalline 2D-PAI@CNT via the polycondensation reaction between tris(4-aminophenyl)amine (TAPA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) in the presence of carbon nanotube (**Figure 2a**).^[67] Based on the reduction of carbonyl group to form lithium enolate, it is believed that the imide units participate in the lithium storage of 2D-PAI@CNT. Besides the prevailing carbonyl compounds, organic electrode materials based on $\text{C}=\text{N}$ bond reactions have also garnered considerable interests.^[68-72] Through the reaction between tetraminophenone and cyclohexanone, Chen and co-workers reported a honeycomb-like nitrogen-rich covalent organic framework (TQBQ-COF) with multiple functional groups as the cathode in SIBs (**Figure 2b**).^[73] Due to the adjacent environment of N and O atoms, there exists a simultaneous coordination of N and O to the Na^+ ions. Hence, for the organics with multiple redox sites, both pyrazine ($\text{C}=\text{N}$) units and carbonyl ($\text{C}=\text{O}$) groups will exhibit revisable redox activity during the electrochemical energy storage, which might shed light on the design of COFs electrode materials in the future.

Apart from the cathode, COFs can also be employed as promising anode materials. Wang and coworkers reported a composite electrode (COF@CNTs) through the controllable growth of imine-based 2D COFs on the exterior of carbon nanotube (CNT) (**Figure 3a**).^[74]

After experiencing the activation process, COF@CNTs anode material displays an ultrahigh lithium storage capacity of 1536 mAh g⁻¹ (correspond to 14-lithium-storage for a COF monomer) (Figure 3b). The underlying reason might be attributed to the efficient utilization of active sites, which include both C=N bonds and C=C bonds in benzene rings (Figure 3c). Different from the common C=O or C=N bonds with limited lithium-ion storage capability, the six lithium ions on per benzene ring supply a much greater specific capacity during the lower voltage range. According to the Raman spectra (Figure 3d), the signal corresponding to the C=N and C=C groups will be weakened, and then almost disappears in the discharge process, while reemerging during the charge process. In the *Fourier Transform Infrared Spectroscopy* (FTIR), there exists a redshift in the peak of C=N stretching modes (from 1618 to 1638 cm⁻¹) during the lithiation process, while recovered in the delithiation process (Figure 3e). The reversible change of aromatic C=C stretching modes in benzene rings (at ~1506 cm⁻¹) can also be observed in the FTIR spectra, which confirm the reversible C=C bonds destruction and restoration during the lithium storage process.

Different from n-type organics, it is anions (such as ClO₄⁻, PF₆⁻, BF₄⁻ and TFSI⁻) that act as the positively charged species in the p-type mechanism. As one of the typical p-type organics, conducting polymers including polyacetylene, polyparaphenylene, polyaniline, polypyrrole, and polythiophene have received widely investigations in the past decades.^[26] Compared with n-type organics, p-type conducting polymers are featured with a relatively higher redox potential and lower specific capacity. Recently, p-type mechanism is also found in the organic framework electrode materials, particularly in the bipolar organics. Bipolar organics refer to this type of materials that can be either reduced to a negatively charged state or oxidized to a positively charged state. This unique mechanism could achieve both p-dopable and n-dopable in the same substance during the different potential ranges. Sakaushi and co-workers have investigated amorphous covalent triazine-based frameworks (ACTF-1) as lithium batteries cathode, in which the charge/discharge processes of triazine ring (C₃N₃) occur in two continuous linear redox reactions and displays a capacity-like bipolar behavior (**Figure 4a**).^[75] In the potential range of 4.5–3.0 V, the anion PF₆⁻ is involved in the p-doping process, while below 3.0 V, the cation Li⁺ participates the n-doping process (Figure 4b,c). Furthermore, Sakaushi et al. reported a type of bipolar porous polymeric frameworks as organic cathodes for sodium-organic batteries.^[76] Through the ionothermal reaction between *p*-dicyanobenzene and ZnCl₂, the as-obtained bipolar porous organic electrode (BPOE)

featured with a 2D honeycomb structure containing benzene rings and triazine rings. The strong aromatic triazine linkages endow covalent triazine frameworks (CTFs) with high chemical stability and high nitrogen content. In most cases, covalent triazine frameworks (CTFs) are related to COFs. However, it should be noted that most of the reported CTFs are amorphous. Although various building units and synthetic methods have been developed, it is still challenging to synthesize high crystalline CTFs. Due to the bipolar character of BPOE, the discharge capacities obtained in p-dopable region (4.1-2.8 V versus Na/Na⁺) and n-dopable region (2.8-1.3 V versus Na/Na⁺) were 55 mAh g⁻¹ and 185 mAh g⁻¹, respectively. The difference between p-doping and n-doping process derived from their distinct energy storage mechanism. In the p-doping/dedoping process, a pseudo-Faraday reaction happened through the movement of ClO₄⁻ on the surface of the BPOE, which featured with a capacitive behaviour and displayed high rate performance. During the n-doping/dedoping process, Faradaic reaction was completed by the insertion/de-insertion of Na⁺ into the BPOE. In the bipolar working principle, the operation in a wide working potential will provide high energy and power density, which is superior to the electrode materials with the only p- or n-dopable property.

3. Strategies to improve the performances of COFs electrode

3.1 Exfoliation to obtain 2D morphology

Compared with the nonporous bulk organic materials, the open and aligned porous channels are very useful and help to facilitate the transportation of electrolyte ions. However, the bulk sample is very difficult to display this advantage from COFs electrode. The closely-packed 2D layers usually result in a restricted penetration of ions into the interior active sites between layers.^[77] The ion migration will experience a lengthy pathway along the open channels to reach the deeply buried active centers. This inevitability results in a lower utilization of active centers, and is especially worse at fast charge/discharge conditions. Due to the strong π - π stacking interactions, an efficient exfoliate strategy is requisite to obtain 2D COFs sheets from the tightly stacked bulk samples, thus improving the ions diffusion and exposing more active sites.^[78]

To address this challenge, Wang and co-workers presented a universal approach to exfoliate COFs into 2D few-layer nanosheets (**Figure 5a**).^[79] As an efficient strategy, a ball-

milling process has been demonstrated to only break the π - π interactions between the layers without causing any damage to the chemical structure. Besides, the thickness of exfoliated COFs is tunable by adjusting the frequency and time of vibration. With the aid of this method, the few-layered DAAQ-TFP-COF (denoted as DAAQ-ECOF), featured with sheet-like morphology, were obtained (Figure 5b). Thanks to the insolubility and the robustness of the framework, the decay caused by dissolution in electrolyte does not exist in DAAQ-TFP-COF and DAAQ-ECOF, thus guaranteeing a stable cycle performance. Due to the buried redox sites inside the channels, the bulk DAAQ-TFP-COF only completes 73% (capacity is 110 mAh g⁻¹) of its theoretical value, whereas the exfoliated sample (DAAQ-ECOF) could achieve 96% (capacity is 145 mAh g⁻¹) of its theoretical value (Figure 5c). At the same current density, the capacity retention of DAAQ-ECOF is always higher than that of DAAQ-TFP-COF and especially prominent in the fast charge/discharge process (Figure 5c). The same phenomenon and the effect can also be found in other COFs electrode materials. The applicability of this strategy and the designable properties of COFs materials were further demonstrated by the performances of two other COFs materials (DABQ-TFP-COF and TEMPO-COF) (Figure 5d-5e). The enhanced rate capability and higher utilization of active sites are closely related to the improved kinetics. In comparison to DAAQ-COF (2.48×10^{-11} cm²s⁻¹), DAAQ-ECOF (6.94×10^{-11} cm²s⁻¹) exhibits a 3-fold increase in lithium-ion diffusion coefficient, indicating a higher ionic conductivity in the exfoliated COF sheet. For the 2D COFs with limited few layers, the migration of both ions and electrons will be facilitated by the shortened diffusion path. More active sites would be exposed and become accessible on the surface or near-surface region, which is beneficial to make full use of the sites and enhance the reaction kinetics. In the few-layered COFs, lithium storage occurs mainly on the surface and/or near-surface of active materials, which seems like a pseudocapacitance behavior. In this event, the reaction kinetics is controlled by the charge transfer instead of the mass transfer, and typically displays a fast discharge/charge characteristics. In comparison, the reaction process is governed by the diffusion of Li⁺ into the bulk COFs, indicating a typical diffusion-controlled insertion mechanism.

It should be noted that the yield of few-layered or even single-layered COFs sheets is usually very low, which poses a great challenge to realize their large-scale applications. As one of the most promising method for the large-scale preparation of 2D materials, the intercalation-assisted exfoliation has garnered a high expectation.^[80] However, the all-organic

skeleton of COFs is hard to be well-preserved under the destructive oxidation or reduction conditions. Given that the conventional redox-driven intercalation method will bring an unavoidable damage, Fan et. al. reported a new approach to prepare single-layered and few-layered covalent triazine frameworks (CTF-1) based on acid-base driven intercalation reaction and subsequent oxidation exfoliation.^[81] The electron-donating property of networks is favorable to the acid intercalation. Therefore, the layered CTF-1 allows a reversible intercalation of either oxidizing or non-oxidizing acid.

Most of 2D COFs prepared by condensation reactions usually exhibit a strong aggregation. In comparison, covalent organic nanosheets (CONs) with reduced aggregation tendency and featured with few-layer 2D nanosheet structures.^[82] To a certain extent, CONs can be viewed as the delaminated COFs (the promising COF alternatives). In general, CONs are prepared through exfoliating the bulk COFs. Banerjee and co-workers proposed a strategy to chemically exfoliate anthracene-based COF through [4+2] cycloaddition reactions.^[82] By using maleic anhydride as a functionalizing exfoliation agent, Halder et. al. successfully exfoliated anthracene-based COF into few-layer-thick CONs through this type of chemical exfoliation.^[83] Ogale and coworkers reported a novel CON structure (IISERP-CON1), composed of triazole and phloroglucinol units, via the self-exfoliation of COFs into nanosheets under solvothermal conditions (**Figure 6a**).^[84] At a current density of 100 mA g⁻¹, IISERP-CON1 exhibited an ultrahigh discharge capacity (2060 mAh g⁻¹), but faded rapidly in the 2nd cycle (835 mAh g⁻¹) owing to the formation of SEI layer (Figure 6b). Luckily, the performance soon became stable and maintained a high capacity of 720 mAh g⁻¹ after 100 cycles. The modularization design of frameworks allows a stoichiometric introduction of heteroatoms to regulate the interactions with target species. Besides the common Li-C₆ ring interactions, the introduction of hetero atoms with electron-donating ability into the skeleton is beneficial for the stabilization of positive charge, and thus acquire the enhanced interaction with lithium ions.^[65] In Ogale's studies, besides sp²-N and -OH groups, triazole units are also important active sites (Figure 6c). Based on the stable capacity of 720 mAh g⁻¹, the authors proposed that 16 lithium ions can be stored in each CON unit. According to the computational studies of lithiated structure, it is assumed that the mild Li-framework binding is favorable for the reversible lithium intercalation, which shed light on the design principle of COFs anode materials. Because the electron-rich phloroglucinol nodes are connected by short linkers, the as-obtained framework not only present nanopores with a high density of active centers, but

also bring benefits to make full use of the synergic effect of different functional groups. Furthermore, the flexible nature of triazole units favors the buckling of layers, which is helpful to the generation of π -stacking columns and ensures stable performance (Figure 6d).

3.2 Enhancement through using conductive carbon matrix

The advancement on conventional organic electrodes is often hindered by the following drawbacks: (i) the dissolution in nonaqueous electrolytes; (ii) the limited access to the active sites for the electrolyte ions; and (iii) low conductivity.^[85,86] Introducing the conductive carbon substrates into the organic materials to form composite electrodes would provide the feasibility to simultaneously conquer these barriers. Jiang and co-workers reported a redox-active COFs/carbon composite (DTP-ANDI-COF@CNTs), which was prepared via the *in situ* polycondensation of DTP-ANDI-COF on CNT wires under solvothermal condition (**Figure 7a**).^[87] In the backbone of DTP-ANDI-COF, only naphthalene diimides (NDINA) experienced a reversible two-electron redox reaction. Other components include the triphenylene knots and boronate linkages did not contribute much to the electrochemical activity (Figure 7b). Compared with the NDINA, the utilizing efficiency has been improved significantly when the units were integrated into the crystalline mesoporous frameworks. The insolubility of COFs as well as their robust frameworks endowed the electrodes with a good structural stability. The transportation of electrolyte ions was facilitated by the open and aligned mesoporous channels, thus accelerating the redox reaction. Through the *in situ* polycondensation of DTP-ANDI-COF on conductive CNTs wires, a decreased charge transfer resistance was achieved. Thanks for the conductive CNTs and the porous structure of composite electrode, not only the electron conductivity was enhanced, but also the accessibility of active centers were promoted. In the absence of CNTs, the first discharge capacity of DTP-ANDI-COF only reached 42 mAh g⁻¹, and a decayed capacity during the 50 cycles (Figure 7c) was observed, while the DTP-ANDI-COF@CNTs cathode exhibited stable cycling and delivered a capacity of 67 mAh g⁻¹ (Figure 7e). Increasing the current density to 12C, DTP-ANDI-COF@CNTs delivered a capacity of 58 mAh g⁻¹, corresponding to a high retention of 85% (relative to that of 2.4 C) and displaying a clear contrast with the rate performances of the electrode without CNTs (Figure 7d). As the current rate increased, the charge-discharge behaviors always remained stable and displayed a small voltage polarization (Figure 7e). This means that the electron or ionic transport is rapid enough to respond the fast charge and discharge reaction. Even operated at a high rate, the Coulombic efficiency still retained 100% (Figure 7f) with an average working voltage of 2.4

V, indicating the electrochemical reversibility of electrodes. The remarkably improved performance of COF/carbon composite electrodes is a synergistic effect from the combination of different components, which is a promising strategy for the effective utilization of COFs materials.

Apart from the one-dimensional CNTs, the electrical conductivity of 2D COFs electrodes can be boosted by graphene due to their similar sheet structures. Li and co-workers reported a poly(imide-benzoquinone)/graphene (PIBN-G) through the reaction between tetramino-benzoquinone and pyromellitic dianhydride in the presence of graphene (**Figure 8a**).^[88] Because of their similar 2D features, there exists a charge transfer through the conjugation of π - π stacking, which implies a strong interaction between PIBN and graphene. Facilitated by these merits, fast Li^+ and electron transport were achieved in the rate capability. When operated at the same current rate, the specific capacity of PIBN was always lower than that of PIBN-G. At a current rate of 0.1C, PIBN-G and PIBN deliver a discharge capacity of 271.0 mAh g⁻¹ and 244.8 mAh g⁻¹, reaching 96.8% and 86.1% of their theoretical values, respectively (Figure 8b). It should be noted that both imide and quinone groups were electrochemically active centers (Figure 8g). Both obvious redox couples appeared in the CV curves attributed to the two distinctive lithiation/delithiation steps on the C=O bonds in different groups (Figure 8c). The vibration of C=O bonds in imide groups gradually weakened and then almost diminished in the first lithiation stage (Figure 8d-8e). After fully discharged to 1.5 V, the vibration of C=O bonds in quinone groups diminished at the end of the second lithiation stage. During the delithiation process, the signals of C=O bonds in the imide and quinone groups gradually recovered. The successive lithiation in two steps could also be detected by the ex-situ solid-state ¹³C NMR spectra (Figure 8f).

The preparation of COFs/graphene by the *in situ* compositing method required a strictly-mixed solvent during the polymerization process to form COFs, which might limit its application scope. Huang and coworkers proposed a general tactic to enhance the performance of polyimide (PI)-based COFs (PI-COFs) as cathode materials in LIBs.^[89] Due to its facile and cost-effective features, ball-milling method has been regarded as a promising technology to obtain 2D nanomaterials, which is also suitable to exfoliate PI-COFs into few layers. It was found that the capability of exfoliated PI-COFs (PI-ECOF) could be further enhanced by chemically reduced graphene oxide (rGO) via the ball-milling strategy.

Because of the porous framework structure and high surface area, the energy storage of COFs is usually a combination of ion insertion and capacitive behavior. The contributions of capacitance behaviors will be increased when the bulk COFs are exfoliated into nanosheets. Wang et al. synthesized two types of triazine-based CONs with different pore sizes: 2 nm for covalent imine network-1 (CIN-1) and 0.5 nm for Schiff base networks-1 (SNW-1), respectively (**Figure 9a**).^[90] Through mechanical milling, the as-prepared CONs are favorable to ameliorate the surface-control kinetic. To achieve an enhanced lithium storage, the as-exfoliated CONs were further composited with CNTs to improve the ions/electrons diffusion and expose more active sites. Undoubtedly, this sophisticated design displays a significantly improved electrode kinetic. The relationship between peak current and scan rate is efficient to reveal the kinetics behavior of electrode materials. For the pristine electrode, it was governed by the diffusion-controlled reaction process. After conducting 250 cycles, the surface-controlled kinetics played a dominant role. Hence, the capacitance contribution of the cycled electrode was substantially higher than their pristine state. Based on the varied lithium-ion diffusion coefficients obtained from the galvanostatic intermittent titration technique (GITT) measurement, the diffusion coefficients of exfoliated electrodes were much higher than those of bulk materials. As to anode materials with large reversible capacities (1005 mAh g⁻¹ for E-CIN-1 and 920 mAh g⁻¹ for E-SNW-1 after 250 cycles), the lithium storage mechanism was worth exploring. During the lithium storage process, triazine rings and benzene rings were speculated as promising active centers (**Figure 9b**). Other groups include the C=N and -NH- were also considered to provide the contributions to the capacity (**Figure 9b**). For the E-CIN-1/CNT electrode, the peak for C=N groups could not be observed and the signals for triazine ring and piperazine ring (C-N groups) weakened significantly in the lithiation process (**Figure 9c**). Luckily, these signals reappeared during the delithiation, indicating the participation of triazine rings, piperazine rings and C=N groups in lithium ions storage. The similar reversible change of triazine rings and -NH- groups can also be found in E-SNW-1/CNT (**Figure 9e**). The reversible change of bending vibration peaks for benzene rings was also demonstrated. In contrast, only a slight change in these peaks of the C=N and -NH- groups can be observed in the CIN-1/CNT (**Figure 9d**) and SNW-1/CNT (**Figure 9f**), indicating the partial participation of active groups for lithium storage. The efficient utilization of triazine rings and piperazine rings/benzene rings could be attributed to the few-layered lamellar CON structures after exfoliation. Few-layered structures were beneficial for the insertion of more lithium ions and facilitating the thoroughly reaction of functional groups.

3.3 Optimization of preparation procedure

The properties of COFs are closely dependent on the preparation conditions. Therefore, to achieve the desired functionality for specific application, a precise selection of monomers and preparation approach is very significant. Among various preparation methods of COFs materials, condensation reaction is the widely used one, and most of 2D COFs obtained from this method showed strong aggregation.^[91] In order to remedy the above-mentioned defects, Stille cross-coupling reaction was adopted by Park et al to prepare CONs with a weak aggregation tendency, as well as an enhanced colloidal stability in organic solvents.^[92,93] The as-prepared CONs were characterized to display 2D lamellar morphology, which can be regarded as the delaminated COFs. Park and coworkers found that through a precise control of reaction conditions and monomer combination, the as-obtained CONs were adjustable on specific surface area, self-assembled morphology, and molecular planarity.^[91] In their research, three types of network structures were prepared through the Stille cross-coupling reaction with adjustable conditions (**Figure 10a**).^[91] Specifically, the procedure was implemented by the reaction between two monomers in mesitylene solutions under the refluxing or solvothermal conditions. By changing the combination of monomers, a precisely-tuning atomic connectivity in the network was realized, and three CONs with different ring diameters of ~2.8, 3.3, and 4.2 nm were obtained, respectively. Under refluxing or solvothermal condition, the as-obtained samples exhibited variable surface areas, which confirms that the synthetic condition and the choice of backbones have a great impact on the aggregation structures of CONs. The sheet-like CONs structures were comprised of lamellar primary particles. The morphology of these primary particles as well as their self-assembled structures were controlled by the synthetic route, which comes from the nature of the polymerization reaction and interlayer interactions. The card-house-like structure, constructed by a random stacking of 2D lamellar, existed in these samples prepared through the refluxing approach (CON-10 and CON-33) (**Figure 10b,d**). The interpenetrated and fibrous morphology, derived from a random stacking of small particles, was observed in the samples obtained through solvothermal method (CON-16 and CON-34) (**Figure 10c,e**). The transmission electron microscopy (TEM) images of CON-10 and CON-16 showed that the sheet-like CON structures were composed of lamellar primary particles with a thicknesses of less than 7-10 layers (**Figure 10f,g**). The authors believed that the sodium storage mechanism was closely related to the characteristic of frameworks rather than the self-assembled morphology,

implying that CONs with identical networks should have the similar electrochemical behaviors. During the first discharge process, all the CONs displayed an obvious voltage plateaus at 0.5 ± 0.25 V, indicating the SEI formation on the electrode surface caused by the decomposition of electrolyte (Figure 10h). Owing to the high specific surface area, the initial Coulombic efficiencies (CEs) of all CONs were around at a low level (15-40%), but varied with different synthetic conditions (Figure 10i). It is found that the initial CEs for these samples obtained through solvothermal method were higher than those prepared from reflux conditions. This result was strongly correlated to the difference on microstructures, where the CONs prepared from refluxing condition possessed a loosely packed morphology with a larger surface area, while the solvothermally-prepared CONs displayed a relatively dense morphology with smaller surface area. From the measurements of electrochemical impedance spectroscopy (EIS), one can conclude that CONs with rich sulfurous functional moieties would exhibit improved charge-carrier conductivity and ionic transport. The samples with a high density of thiophene moieties (CON-10/16 and CON-31/32) were favorable to achieve low Warburg coefficients (Figure 10j), which enlightens us that a fine selection of synthetic routines and monomers is significant to approach the targeted COFs with the expected performances.

COFs with the preferred alignment is essential for good transport of charged species and high accessibility of active sites. Therefore, how to obtain COFs electrode with a crystalline and oriented arrangement is a challenge. Through the reaction between 2,6-diaminoanthraquinone (DAAQ) and 1,3,5-triformylphloroglucinol (TFP) on Au electrodes, the crystalline and oriented thin films of β -ketoenamine-linked 2D COF (DAAQ-TFP COF) were prepared by Dichtel et al (**Figure 11a**).^[94] Compared with the electrode functionalized with the randomly oriented COF sample, the DAAQ-TFP COF thin films exhibited a much improved accessibility of redox-active anthraquinone moieties, and thus showed a 400% increase in capacitance. This can be explained by a facilitated redox conduction between the layers of anthraquinones and different crystallites in the oriented crystallite of DAAQ-TFP thin films. During the redox conduction process, the cations in the electrolyte need to pass through the COF film to compensate the negatively-charged moieties. For the DAAQ-TFP thin films with the thickness of below 200 nm, this process could be reached in an optimal state. However, in the thicker films, the ions diffusion to the electrode surface would be sluggish. Thus, for the increased quinone accessibility in oriented DAAQ-TFP thin films,

anthraquinone-anthraquinone charge transfer (“self-exchange”) plays an important role. The conductivity through the electron self-exchange processes was favorable to realize in the layered organization of anthraquinone groups. These findings highlight the significance to achieve optimal performance through controlling the morphology of COFs.

Ideally, the ordered packing of 2D layer would induce a 3D architecture with one-dimensional channel. The alignment of cylindrical pores would provide an excellent pathway for ion diffusion. However, the disordered packing usually makes the realistic conditions more complicated. By pressurizing the bulky COF powders into pellets, Vazquez-Molina and co-workers reported a strategy to prepare highly aligned porous 2D COFs with crystallographically-preferred orientation (Figure 11b).^[95] The weak π - π interactions between the COFs layers could allow two neighbouring layers slide easily under mechanical stress, and thus induce an anisotropic packing of the crystallites. With the help of mechanical pressing, five COFs with different functionalities and symmetries displayed similar crystallographic behaviors, implying the applicability of this method. The pellets of COFs impregnated with LiClO₄ exhibit a high room-temperature conductivity (0.26 mS cm⁻¹) and electrochemical stability, which demonstrates the applicability of COFs as solid-state electrolytes in batteries.

3.4 Tuning of the stacking interaction and thickness

A finely-tuning on the stacking interaction is critical in regulating the electrochemical performance. For the 2D COFs, the optimization of stacking thickness has been proven as an efficient strategy to realize a precise control on the reactivity and the stability of radical intermediates. In most cases, organic compounds will experience the formation and transformation of radical intermediates during the redox process.^[96] Featured with high reactivity, the inherent unstable organic radical intermediates with unpaired electrons are preferred to react with other moieties (active parts in the electrolyte or between the radicals) to form inactive compounds. In this situation, an irreversible redox process and capacity loss would be observed. The frustrating unstability of radical intermediates is always a potential hazard to deteriorate the performance, which strictly limits the reversibility and hence hinders the development and application of organic electrode materials. How to avoid the irreversibility and the inactivation of electrode materials is an unavoidable question. Specifically, it is necessary to stabilize the radical intermediates and thus to obtain an improved reversibility of organic electrode materials. To achieve the goal, numerous

investigations have been put forward. With the help of unpaired electron internal-consumption mechanism, an efficient practice is to incorporate the unpaired electrons into the π -conjugated system, where the π - π and p - π conjugation interactions are favorable to delocalize the unpaired electrons. Lu et.al. proposed a strategy to stabilize the α -C radical intermediate through the resonance effect of p - π conjunction and the steric hindrance effect of the rigid geometry.^[96,97] The disappearance of unpaired electrons, triggered by irreversible binding among the intermolecules, would be largely inhibited by electronic resonance effect and steric hindrance effect (**Figure 12a**).^[97] Based on these principles, rigid aromatic rings containing conjugated structure and steric effect are ideal building blocks to control the activity of radical intermediates. But, how to incorporate these modules economically without the risk of the reduction on the energy density, and meanwhile to improve the stability of radical intermediates become very challenging. Lu et al. reported a β -ketoenamine-linked DAAQ-COF via the reaction between 1,3,5-triformylphloroglucinol (TFP) and 2,6-diaminoanthraquinone (DAAQ) (**Figure 12b**).^[97] With the help of mechanical milling, 2D DAAQ-COFs with different stacking thickness were prepared (**Figure 12c**). During the sodiation process, the O K-edge *ex situ* X-ray near-edge absorption spectroscopy (XANES) clearly revealed the transformation from C=O to C-O-Na, which is consistent with the radical intermediate mechanism (**Figure 12d**). The authors demonstrated that the stability of the α -C radical intermediates was strongly correlated with the thickness of COFs. The thinnest sample exhibited excellent stability, while the thick samples displayed a serious decay on the radical signal, implying that there exists a severe quenching of radical intermediates in the closely-stacked COFs (**Figure 12e**). Compared with its small molecule analog TSAQ or even after soaked in electrolyte, α -C radical intermediates in the thinnest sample (4-12 nm) always display a high stability (**Figure 12f,g**), which was further confirmed by the integral peak areas from the simulated ^{23}Na NMR profile. Clearly, the sample with 4-12 nm thickness possessed the higher value compared to any other three samples (**Figure 12h**). This conclusion was also consistent with the percentage of the capacity contributed by the α -C radicals (26%, 19%, 15%, and 13% for 4-12 nm, 50-85 nm, 100-180 nm, and 100-250 nm, respectively). To explain this phenomenon, they have proposed that a weaker stacking interaction environment in 2D COFs would result in a constrained electron self-exchange behavior, which is helpful to obtain high stability and capacity. The closely packed radical intermediates could be released to avoid the self-exchange behavior as the thickness of COFs is reduced. Herein, 2D COFs are taken as an excellent platform to achieve the controllable regulation on the stability of radical

intermediates. These results clearly confirm that reducing the film thickness not only makes more active sites available, but also plays a significant role in the stabilization of radical intermediates, thus obtaining an improved electrochemical performance.

3.5 Improving the conductivity of COFs

Electrical conductivity and ionic conductivity are viewed as two of the crucial parameters in evaluating the electrochemical performance of COFs materials. To improve the low electrical conductivity of COFs electrode, various methods have been developed.^[54] First and foremost, the internal structure of COFs plays a significant role in the electron conductivity, and highly π -conjugated skeleton is essential to obtain a high charge carrier mobility in the 2D flat sheet structures. 2D COFs with an extended planar π -conjugation system are expected to shorten the interlayer distances and allow for efficient electronic interaction between the different sheets. Through the condensation reaction of 2,7-diaminobenzophenanthroline-tetraone (DANT) and 1,3,5-triformylphloroglucinol (Tp) or 1,3,5-triformylbenzene (Tb), naphthalimide-based crystalline COF (Tp-DANT-COF and Tb-DANT-COF) were synthesized and used as LIBs cathode by Zhou and co-workers (Figure 13a).^[98] By replacing the linker Tp with Tb, Tb-DANT-COF has better conjugation than Tp-DANT-COF, leading to a faster kinetic performance. Based on the electrochemical impedance spectroscopy, the charge-transfer resistance (R_{ct}) and the Warburg impedance of Tb-DANT-COF were lower than those of Tp-DANT-COF, which confirms a facilitated charge transfer and Li-ion diffusion in Tb-DANT-COF. This result reveals that the extension of the conjugation in the backbone is a fundamental strategy to improve the intrinsic electrical conductivity of COFs.

Post-modification is another important strategy to tailor the properties of COFs materials.^[99,100] Among various post-modification methods, implanting active guest species (small molecules or polymers) into the porous hosts has been demonstrated as an efficient tactic to enhance the electrical conductivity. For example, tetrathiafulvalene (TTF) is featured with π -electron-donating abilities and exhibits excellent performance in the field of organic conducting materials. Zhang and co-workers reported the synthesis of 2D COF containing the electroactive TTF unit (TTF-COF) (Figure 13b).^[101] On one hand, building TTF units in the framework will facilitate the electronic interactions between TTF units. On the other hand, the

COF constructed with electron donating building blocks can accept electron acceptor dopants. Both points are benefited to increase the conductivity of COFs. The doping of tetrathiafulvalene (TTF)-based COFs with iodine or tetracyanoquinodimethane (TCNQ) could achieve a significant improvement in electrical conductivity.^[102] Dichtel et al. reported a doping method to improve the electrical conductivity by introducing conducting polymers into the pores of COFs.^[103] After 3,4-ethylenedioxythiophene (EDOT) monomers were electropolymerized within the pores of DAAQ-TFP, PEDOT-modified DAAQ-TFP films exhibited an increased conductivity, where the resistance (20 Ω) was at least one order of magnitude lower than that of unmodified DAAQ-TFP (430 Ω). Although this strategy results in some reduced porosity of COFs, the PEDOT-infiltrated COFs displayed significantly improved electrochemical responses comparing to unmodified COFs. Consequently, such a facile doping approach will exhibit an universal applicability if a full consideration of the porosity and electrical conductivity is addressed. Apart from enhancing the conductivity, the introduction of functional electroactive moieties into the pores of COFs through the post-synthesis strategy also presents an excellent opportunity to approach the targeted COFs with specific properties.

It is noteworthy that the interactions between the porous hosts and the guest species will influence the performance of COFs, which is especially significant in the improvement of ionic conductivity. Interestingly, the well-defined components and structures of COFs present an excellent platform to explore the relationship between host material and electrochemical behavior. The potentials of COFs-based lithium-ion conductors in solid-state batteries were demonstrated by many publications.^[104-106] The ordered one-dimensional channels provide a facilitated pathway of ions transportation. However, the straightforward way to introduce salts into the bare channels of COFs might not be the best choice. Therefore, Jiang et al. proposed a solid-state polyelectrolyte COF (Figure 13c).^[107] The designability of COFs allow the integration of oligo(ethylene oxide) chains within the 1D channels, thus benefiting the dissociation of ionic bonds of lithium salts and presenting a lithium ion conduction pathway. In contrast to these bare pore walls, the ion conductivity was enhanced significantly in the poly(ethylene oxide) modified polyelectrolyte COFs (more than three orders of magnitude). Proton exchange membrane fuel cells (PEMFC) has attracting enormous interests due to the environmental friendliness and highly efficient energy conversion efficiency.^[108] As a potential alternative to Nafion membrane, crystalline porous materials received a lot of

attentions as proton-conducting materials. Montoro et. al. reported the potential applications of COFs as solid electrolyte membranes in fuel cells (Figure 13d).^[108] Through the Schiff reaction between 1,3,5-tris(4-aminophenyl)benzene and 1,3,5-benzenetricarbaldehyde, a series of imine-based COFs with different guest molecules trapped in the cavities were synthesized and exhibited a high ionic conductivity. It is found that the introduction of water and guest ion pairs (LiCl, acetic acid) into the porous structure is important in the proton conduction. The proton conductivity is closely related to the hydration of materials, where there exists an enhancement of conductivity with increasing wetting time. The intrinsic low ionic conductivity is viewed as an obstacle to improve the kinetic performance of COFs electrodes. These investigations undoubtedly provide valuable explorations on the improvement of ion conduction in COFs materials. In the future, the details of ion migration path and activation energies of ion diffusion are also indispensable to reveal the ion conduction process.

4. Applications in other advanced batteries

Considering the sustainability and the limited availability of lithium mineral sources, enormous efforts have been paid on the alternative battery systems. Herein, the advancements of COF materials in potassium-ion batteries, aqueous zinc batteries and Li-S batteries will be highlighted.

4.1 Potassium-ion batteries

As one of the alternative battery technologies to LIBs, PIBs have drawn a lot of attentions due to the abundance and low cost of potassium resources.^[109,110] The standard potential of K^+/K (-2.92 V vs SHE) is close to the Li^+/Li (-3.04 V vs SHE), indicating a higher energy and voltage of batteries than the Na counterpart.^[111,112] In comparison with other alkali metal ions, the weaker Lewis acidity will endow the K^+ with a larger transfer number and higher mobility, which provides a fast kinetics for PIBs.^[113] Considering the challenges for inorganic electrode materials to accommodate with the large sized K-ions (1.38 Å), switching to the organic electrode materials is a good option.^[114-117] Previous studies have shown that there exists a strong cation- π interaction between the alkali metal cation (Li^+ , Na^+ , K^+) and 2D carbon materials.^[118-120] It is found that strong $\pi-K^+$ interaction offers great opportunities for π -conjugated 2D COFs in the potassium storage.^[22] Therefore, Wang et al.

proposed a COF-10@CNT as anode materials for PIBs, where a boronic ester based covalent organic framework (COF-10) was *in situ* grown on the exterior surface of CNTs (**Figure 14a,b**).^[121] Benefiting from its hierarchical pore structure of COF-10, a sufficient void space was presented to relieve the volume expansion/contraction during potassiation/depotassiation, resulting in a stable performance (Figure 14b). The discharge/charge curves almost overlapped even after 100, 200, 300, 400 and 500 cycles, indicating the stability of electrode structure and excellent reversible electrochemical behaviors (Figure 14c). Benefiting from the enhanced π - π stacking in the few layered COF-10@CNT, more active sites were exposed and the diffusion distance of ion and electron would be shortened, leading to an improved kinetics of K^+ . At the current density of 25 and 5000 mA g⁻¹, the capacities of COF-10@CNT could reach 330 and 68 mAh g⁻¹, which were higher than those of COF-10 (203 and 12 mAh g⁻¹), respectively (Figure 14d). According to the C1s X-ray photoelectron spectroscopy (XPS) peak of the COF-10@CNT (**Figure 15a,b**), the peaks appeared at 293.1/295.8 eV were attributed to the interaction between K^+ and π electrons of the aromatic rings. Due to the interactions between K^+ and sp² carbon from the benzene ring of COF-10, the I_D/I_G value is increased during potassiation, while decreased in the depotassiation process (Figure 15c). Therefore, based on the characterization of structural evolution, the potassium storage mechanism of COF-10 could be attributed to the π -cation effect (Figure 15d). Driving by the interaction between cation ions and the π electron clouds of aromatic rings, this mechanism might shed light on the potentials of π -conjugated 2D COF materials.

4.2 Aqueous zinc batteries

Low cost, long cycle life, excellent safety and high specific energy are considered as the critical requirements of rechargeable batteries for large-scale energy storage. To response the growing demand of electricity consumption, aqueous rechargeable batteries hold particular attentions for its inherent safety and cost-effective.^[122,123] Beyond LIBs, multivalent ion batteries (Zn^{2+} , Mg^{2+} , Al^{3+}) have garnered particularly interests because of their superior volumetric capacities.^[124-126] Hence, multivalent ion batteries coupled with aqueous electrolyte are highly attractive for large-scale electricity storage applications.^[127,128] As a typical example, aqueous zinc batteries (AZBs) have attracted considerable attentions in terms of low cost and good safety.^[129-131] The superiorities of using aqueous electrolyte were embodied on the safety and cost-effective in both zinc salts and solvents. The advantages of

using zinc metal anode include its high-capacity (820 mAh g^{-1}), low redox potential (-0.76 V vs SHE), high abundance, and low-cost.^[127] Moreover, unlike the current LIBs which must be prepared under stringent atmospheric assembly conditions, AZBs will be cost-effective in the manufacturing process. These merits are just suitable for AZBs to be used in large-scale energy storage. However, the issues that hinder the advancement of AZBs are also obvious. The size of Zn^{2+} ($0.74 \text{ \AA}$) is comparable to that of Li^+ ($0.76 \text{ \AA}$), which will cause a higher activation barrier for divalent cations during ion migration.^[132] From the viewpoint of electrolyte solvation and ionic association, the strong solvation of Zn^{2+} will impose an impediment for the interfacial charge transfer.^[133,134] Nowadays, most of the investigations of AZBs focus on the transition-metal-based cathode materials.^[135,136] Owing to the strong ionic interactions and particular requirements of ion migration pathways, a stringent demand on inorganic host structures is indispensable. However, the continuous development of multivalent metal-ion batteries strongly encourages scientists switching to organic electrode materials. Organic electrode materials is capable to accommodate various ions, regardless of monovalent or multivalent ions, and metal ions or non-metal ions. Based on the character of large space and soft lattice, organic electrode materials present an elastic matrix for reversible intercalation of Zn^{2+} and facile ionic diffusion, which seems a pre-prepared nature for multivalent metal-ion batteries.

Recently, some organic molecular materials have been investigated in AZBs.^[137,138] Assembled by the intermolecular van der Waals forces, organic materials imposed a modest Coulombic repulsion for the Zn^{2+} migration. To ensure a facilitated entry of Zn^{2+} , molecular reorientation is permitted in the soft lattice structure under the electrochemical environment, which is a critical mechanism to accommodate various ions.^[138] To fill the gap of polymeric materials, hydroquinone-linked β -ketoenamine COF (HqTp) is employed as a cathode to accommodate the electrophilic Zn^{2+} ions for the first time (**Figure 16a**).^[139] The crystalline honey-comb porous structure presents a migration pathway for Zn^{2+} ions. Featured with a high content of $\text{C}=\text{O}$ moieties and a broad interlayer distance ($3.4 \text{ \AA}$), the hexagonal 2D lattice affords a comfort active area between the layers that host numerous Zn^{2+} . Density-Functional Tight-Binding (DFTB) calculations proposed the possible interlayer interactions of Zn^{2+} ions with nucleophilic centers of COF (**Figure 16b**). The distance of $\text{C}=\text{O}\cdots\text{Zn}$ ($2\text{--}2.3 \text{ \AA}$) and $\text{Zn}\cdots\text{N-H}$ ($\sim 2.0 \text{ \AA}$) was coincide with the possibility of intermolecular interactions. The changes of $\text{C}=\text{O}$ stretching peaks in the FT-IR spectra demonstrate the interaction of active

groups with Zn^{2+} ions (Figure 16c). After charging up to 1.8 V, the hydroquinones were electrochemically oxidized into quinones and appeared as a new stretching vibrational peak formed at 1603 cm^{-1} . When discharged to 0.2 V, the signals of C=O group cannot be detected in the FT-IR spectra. Owing to the porous nature of COFs, HqTp was featured with a charge-discharge profile without voltage plateau. At a current density of 125.0 mA g^{-1} , the HqTp cathode delivered a high capacity of 276.0 mAh g^{-1} (Figure 16d). Enriched with active centers in the backbone, the zinc storage of COFs was achieved by virtue of the reversible interaction between Zn^{2+} ions and functional groups in the adjacent layers (Figure 16e). Even cycled at a current rate of 3750.0 mA g^{-1} , HqTp electrode still exhibited a 95% retention of its initial capacity (85.0 mAh g^{-1}) after 1000 cycles (Figure 16f). It should be noted that the Coulombic efficiency was still maintained at 98% after 1000 cycles, implying the highly reversible characteristics of the HqTp COF. This study not only reveals the advantages of COFs acting as a multifunctional platform on the zinc storage, but also enriches the knowledge about the interaction between zinc ion and COFs materials.

Except for the typical “rocking chair” principle, dual-ion mechanism has also been found to be applicable in the aqueous zinc batteries. The working principle of dual-ion batteries (DIBs) is based on the reversible acceptance/release of cations and anions into/out the anode and cathode, respectively.^[137,140-142] High operating voltage is a noteworthy feature of DIBs, which is also urgently required for aqueous zinc batteries. To obtain high energy density batteries, the integration of large-capacity AZBs and high-voltage DIBs into one device will be a promising strategy. Interestingly, organic materials can provide an excellent platform to achieve these goals.^[143,144] In most cases, the anion-interaction voltage in organic compounds is just located in a secure operating range and below the electrolysis voltage of water. In 2018, Niu and co-workers developed aqueous Zn/polyaniline batteries with Zn^{2+} insertion/extraction and dual-ion hybrid mechanism.^[145] During the charge process, CF_3SO_3^- bonded with the positively charged nitrogen atoms (C-N^+) in the oxidized polyaniline. In discharge state, it is Zn^{2+} cations that interact with reduced polyaniline. With the aid of this supercapacitor-like hybrid mechanism, the batteries are endowed with a higher operating voltage, long-cycle stability and high-rate capability. In the future, it is anticipated that the enhanced performance of COFs in the aqueous Zn-batteries will be realized through the combination of Zn^{2+} insertion/extraction kinetics and dual-ion mechanisms.

4.3 Lithium-sulfur (Li-S) batteries

Li-S batteries have garnered increasing attentions in recent years due to its high theoretical capacity (1672 mAh g^{-1}) and specific energy density (2600 Wh kg^{-1}).^[146] Unluckily, prior to the practical application of Li-S batteries, several drawbacks need to be conquered.^[147] The polysulfide dissolution is considered as one of the obstacles on the development of Li-S batteries. To response this challenge, various methods have been employed.^[148] Among them, embedding polysulfide within the porous framework is demonstrated as an efficient strategy to improve the cycling stability of Li-S batteries.^[149] As an emerging porous materials, the structures and components of COFs could be controlled precisely through the ingenious design of building blocks to achieve the desired functionality. The ordered packing of 2D planar sheets in the COFs presented abundant nanopores for sulfur impregnation, the variable functionality provides active units to absorb lithium polysulfides.^[150] Therefore, COFs has been employed as host material for sulfur storage in Li-S batteries. The lithiophilicity and sulfiphilicity are considered as two main chemical interactions to stabilize lithium polysulfides. With the aid of lithiophilic interaction between nitrogen atoms and lithium ions, triazine-based framework and porphyrin-based COFs have been employed as a suitable trapping matrix to improve the stability of Li-S batteries.^[151,152] For the boronate ester based COFs, Tang and co-workers found that the positively polarized boron atoms and negatively polarized oxygen atoms could achieve a simultaneous adsorption of polysulfide anions and lithium ions, thus inhibiting the shuttle effect (**Figure 17a**).^[153] To gain insight into the synergetic entrapping ability of lithiophilic and sulfiphilic interactions, Wang et.al. proposed a TB-COF containing triazine and boroxine units through the self-condensation of 4-cyanophenylboronic acid (**Figure 17b**).^[154] In the TB-COF, the lithiophilic and sulfiphilic interactions were performed by triazine and boroxine units, respectively. In conclusion, through a rational design of building block and adjusting the porous environment, there is a wide research space left to optimize the desired functionality of COFs as host matrix in Li-S batteries.

5. Conclusion and perspective

In this review, the recent progress of COFs electrode materials in rechargeable batteries (lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), potassium ion batteries (PIBs), aqueous zinc batteries (AZBs), lithium-sulfur (Li-S) batteries), including their merits, reaction mechanism and strategies to enhance their performance have been summarized. Currently, the

development of COFs electrode materials is still in infancy stage. Besides the above-mentioned discussion on the merits of COFs electrode materials, there are still many challenges in this field required to be addressed.

From the perspective of molecular design and atom economy, organic compounds containing multiple active sites with low molecular weight hold the potential to become high capacity electrodes. In consideration of their structure configuration and synthetic facilitation, bringing inactive building blocks into the COFs framework might be a possible solution. However, the introduction of inactive groups would increase the molecular weight and thus reduce the overall energy densities. Therefore, the structures of COFs should be much slimmer with the reduced non-essential components.

High electronic and ionic conductivity are considered as key factors in affecting the rate capability of electrode materials. Unfortunately, the low electrical conductivity is a real bottleneck for the applications of COFs in electrochemical energy storage. Fundamentally, π -conjugated skeleton is considered as the essential design principle of highly conducting COFs materials. Then, crystalline structures with strong interactions between layers also play a significant role in the electron conductivity. An extended π -conjugation system would shorten the interlayer distances and allows an efficient electronic interaction between layers. The reason that the highly porous COFs generally exhibit poor electrical conductivity is also related to the limited or poor overlap between the conjugated orbitals between adjacent layers. The strong electronic coupling between the π -orbitals is expected to provide an efficient pathway for motion of charge carriers. To optimize the electron transport in 2D COFs, a maximum overlap of vertical p orbitals between adjacent layers is necessary. The electronic conduction of COFs is highly sensitive to the interlayer distance and stacking ordering. The stacking mode of segments should create a facilitated pathway for charge carrier to transport from one sheet to another. Hence, more attentions should be paid on the optimal π -stacking motifs and interlayer space.

For the bulk materials in a pellet or film state, the charge carrier mobility will be influenced by various factors, such as the defects, grain boundaries, and random orientation of grains. The conduction of electrons is carried out through the electronic coupling between adjacent layers along the vertical pathways. The electronic conduction across grain boundaries will encounter with a high energy barrier. Therefore, the conductivity will be weakened by the structural defects derived from poor crystallinity. The control of orientation

of individual grains is significant in obtaining a good electronic conductivity. However, to achieve this goal remains tremendous challenge. Besides, the electronic conductivity is also sensitive to the existing states of the samples. Single crystals, pellets, and films will exhibit different charge transport behaviors. During the preparation of electrodes, the grinding process might damage the anisotropic packing of the crystallites. Consequently, the reasonable size and morphology control of the COFs materials still require strong effort in optimization. In the future, how to keep the numerous advantages of COFs as many as possible during the preparation of electrodes is challenging and needs more exploration.

The diffraction peaks of COFs often vanish in most studies after the cycling process. The as-obtained amorphous morphology makes it more challenging to characterize these components, identify the structure evolution during operation, and master an understanding of the reaction mechanism. As a matter of fact, structure collapse is usually the main cause in the failure of electrode. Therefore, it is necessary to confirm whether the COFs still preserve their crystallinity when the organic building blocks are oxidized/reduced to a certain extent during the charge/discharge process. In other words, whether the robust frameworks still maintain after prolonged cycling.

As an integrated framework, the underlying mechanism that local redox events spread to an overall transformation is a fundamental issue, and still remains unclear. Actually, this has been becoming an enormous challenge for organic electrode materials that involve a complex multi-process coupling. To answer this question, theoretical calculations and simulations would be helpful to gain insight into the charge transport (electronic or ionic conduction) and mass transport (ions transportation).

As advanced electrode materials for rechargeable batteries, COFs not only provide tremendous opportunities on designing novel structure, but also enrich the energy storage mechanisms. The atomic-scale-controllable components and frameworks allow a practical method to optimize the electrochemical behaviors of COFs electrodes, which also set up a platform to tailor their structures. It is reasonable to believe that taking the full advantages of the designability of COFs will deepen the understanding of the relationship between structure and property, which can speed up the research process on the exploration of advanced electrode materials for energy storage and conversion.

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Figure 1. Schematic representation of the working process of metal-COFs batteries.

Figure 2. (a) Diagram for the synthesis of 2D-PAI@CNT. (b) The synthesis, chemical structure and Na storage mechanism of TQBQ-COF. Panel (a) reproduced with permission.[67] Copyright 2019, WILEY-VCH. Panel (b) reproduced with permission.[73] Copyright 2020, Nature Publishing Group.

Figure 3. (a) Preparation of COF. (b) Capacity contribution of COF (based on the mass of COF) in COF@CNTs at 100 mA g⁻¹. (c) Schematic depicting the stepwise lithium-storage mechanism of COF anode. (d) Raman spectra of COF@CNTs during lithiation (discharge) and delithiation (charge) process. (e) FTIR characterizations of COF@CNTs during lithiation and delithiation process.[74] Reproduced with permission. Copyright 2018, Nature Publishing Group.

Figure 4. (a) Schematic representation of the energy storage mechanism of ACTF-1. (b) Open-circuit voltage (OCV) curves from initial OCV (3 V vs. Li/Li⁺) to the n-doping region (1.5 V vs. Li/Li⁺). (c) OCV curves from initial OCV (3 V vs. Li/Li⁺) to the p-doping region (4.7 V vs. Li/Li⁺). Reproduced with permission.[75] Copyright 2012, WILEY-VCH.

Figure 5. (a) Schematic representation for the exfoliation of 2D COFs. (b) Structures of DAAQ-TFP-COF, DABQ-TFP-COF and TEMPO-COF. (c) Rate performance. (d) Discharge profiles at 20 mA g^{-1} . (e) Capacities of pristine and exfoliated COFs at 20 mA g^{-1} . Reproduced with permission.[79] Copyright 2017, American Chemical Society.

Figure 6. (a) Structure of IISERP-CON1. (b) Discharge–charge curves at a current density of 100 mA g^{-1} . (c) The interaction of lithium with phloroglucinol and triazole moieties. (d) The Li occupying the interlamellar spaces in the CON. Li-magenta; C-gray; N-blue; O-red; H-white. Reproduced with permission.[84] Copyright 2017, WILEY-VCH.

Figure 7. (a) Chemical structure of DTP-ANDI-COF. (b) Redox mechanism of naphthalene diimide unit. (c) Cycling performance of DTP-ANDI-COF (red circle) and COF-5 (black triangle) at 200 mA g^{-1} . (d) Capacity retention of DTP-ANDI-COF at different rates. (e) Discharge/charge profiles of DTP-ANDI-COF@CNTs. (f) Rate performance of DTP-ANDI-COF@CNTs. Reproduced with permission.[87] Copyright 2015, Nature Publishing Group.

Figure 8. (a) Schematic representation of PIBN and PIBN-G. (b) Rate capability of PIBN-G and PIBN. (c) CV curves at 0.5 mV s⁻¹. (d) Discharge/charge profile at 0.1 C. (e) In-situ FTIR spectra. (f) Ex-situ solid-state ¹³C NMR spectra. (g) Proposed lithium-storage mechanism. Reproduced with permission.[88] Copyright 2018, WILEY-VCH.

Figure 9. (a) Structure of CIN-1 and SNW-1. (b) Schematic depicting the lithium-storage mechanism in CIN-1 monomer (upper) and SNW-1 monomer (down). Ex situ FTIR spectra of the c) E-CIN-1/CNT, d) CIN-1/CNT, e) E-SNW-1/CNT, and f) SNW-1/CNT anodes during the first lithiation and delithiation process. Reproduced with permission.[90] Copyright 2018, WILEY-VCH.

Figure 10. (a) Synthesis routine and structures of CONs along with precursor monomers. SEM images of (b) CON-10, (c) CON-16, (d) CON-33, and (e) CON-34. TEM images of (f) CON-10, (g) CON-16. (h) Charge-discharge profiles of CON-10. (i) Coulombic efficiency of the first charge/discharge for various CONs. (j) Warburg coefficients for CONs. Reproduced with permission.[91] Copyright 2018, American Chemical Society.

Figure 11. (a) Schematic illustration of the structure and solvothermal growth of the DAAQ-TFP COF on Au electrodes. (b) Schematic representation of the mechanically shaped COF. Panel (a) reproduced with permission.[94] Copyright 2015, American Chemical Society. Panel (b) reproduced with permission.[95] Copyright 2016, American Chemical Society.

Figure 12. (a) Redox and deactivation mechanism of the radical intermediates. (b) Structure of DAAQ-COF. (c) Schematic representation of the layer-by-layer stacking in 2D-COF with different thickness. (d) Ex situ O X-ray absorption near-edge structure (XANES) spectra of the electrodes derived from the 4-12 nm thick sample. Electron paramagnetic resonance (EPR) spectra of the (e) COF electrodes and (f) TSAQ sample discharged to 0.30 V before and after 30 cycles at a current density of 100 mA g⁻¹. (g) EPR spectra of 4-12 nm thick sample in electrolyte after different times. (h) ²³Na NMR spectra of the electrodes discharged to 0.05 V. Reproduced with permission.[97] Copyright 2019, American Chemical Society.

Figure 13. (a) Synthesis of Tp-DANT-COF and Tb-DANT-COF. (b) Structural representation of Li⁺@TPB-DMTP-COF and Li⁺@TPB-BMTP-COF with oligo(ethylene oxide) chains on pore walls to form a polyelectrolyte interface. (c) Schematic representation of the synthesis of TTF-COF. (d) Schematic representation of the synthesis and structure of RT-COF-1, RT-COF-1Ac, RT-COF-1AcB, and LiCl@RT-COF-1 materials. Panel (a) reproduced with permission.[98] Copyright 2016, Royal Society of Chemistry. Panel (b) reproduced with permission.[101] Copyright 2018, American Chemical Society. Panel (c) reproduced with permission.[107] Copyright 2014, WILEY-VCH. Panel (d) reproduced with permission.[108] Copyright 2017, American Chemical Society.

Figure 14. (a) Synthesis route of COF-10. (b) Schematic illustration of COF-10@CNT. (c) Charge/discharge curves of COF-10@CNT. (d) Rate performance of COF-10@CNT and COF-10. Reproduced with permission.[121] Copyright 2019, American Chemical Society.

Figure 15. Structural evolution characterizations of COF-10@CNT anodes. XPS results of C 1s: (a) after potassiation, (b) after depotassiation. (c) The change of I_D/I_G in Raman spectra. (d) Schematic of potassium storage mechanism. Reproduced with permission.[121] Copyright 2019, American Chemical Society.

Figure 16. (a) Schematic illustration of HqTp and redox mechanism. (b) The DFTB model of interlayer interaction of Zn^{2+} cations with the adjacent layers of HqTp. (c) FT-IR of pristine; charged and discharged cathodes. (d) Charge/discharge curves of Zn/HqTp battery. (e) Schematic representation of the aqueous Zn/HqTp battery. (f) Cycle performance at a current density of 3750 mA g^{-1} . Reproduced with permission.[139] Copyright 2019, Royal Society of Chemistry.

Figure 17. (a) Schematic illustration of the synthesis and structure of N and B doped COF. (b) Schematic illustration for the lithiophilic and sulfiphilic interactions between TB-COF and lithium PSs. Panel (a) reproduced with permission.[153] Copyright 2016, WILEY-VCH. Panel (b) reproduced with permission.[154] Copyright 2018, Elsevier.

Covalent organic frameworks (COFs) have been demonstrated to be promising electrode materials in rechargeable batteries due to their structural versatility and functional tunability. Aiming to attract more research interests in this field, the working mechanisms, strategies for enhancing the electrochemical performance and challenges of COFs electrode materials for rechargeable batteries (LIBs, SIBs, PIBs and AZBs) are presented.

Keyword: Covalent organic frameworks, rechargeable batteries, lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), potassium ion batteries (PIBs), aqueous zinc batteries (AZBs)

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Covalent Organic Frameworks: Advanced Organic Electrode Materials for Rechargeable Batteries