Introduction

Electrical energy storage devices have proven to be key in the transition from conventional fossil fuels because they can efficiently store the electricity generated from renewable sources, helping to mitigate climate change. Lithium-ion batteries (LIBs) are among the most promising electrochemical energy storage devices due to their superior performance compared to other conventional rechargeable batteries, widespread use in portable electronics, and potential for the development of long-range electric vehicles.\(^1\,^2\) However, current state-of-the-art of LIBs presents significant development bottlenecks in terms of efficiency and raw materials availability. For instance, transition metal oxide cathode materials have energy density limitations that are constrained by their specific capacities (e.g., ~140 mAh g\(^{-1}\) for LiCoO\(_2\)). In addition, the large-scale production of these materials is limited by their reduced resources availability and raises serious environmental concerns.\(^3\,^4\) Several critical elements used in LIBs, such as cobalt, would inevitably face supply shortages in the near future\(^5\) and raise some environmental and ethical concerns.\(^6\)

Electroactive organic materials have long been proposed as alternatives to inorganic electrodes due to their tuneable electrochemical properties, high theoretical capacity, resources availability, and environmental friendliness. In particular, redox-active covalent organic frameworks (COFs) have recently emerged as promising electrodes due to their structural versatility, insolubility in electrolyte, and modulable porosity. In this feature article, we review some recent strategies to improve the energy density, power density and cycling stability of COF-based electrodes from the perspective of molecular design and electrode optimisation. Some other aspects such as scalability and recycling are also discussed. Finally, the main challenges to improve their performance and future prospects for COF organic batteries are highlighted.

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can be finely tuned by the judicious selection of electroactive organic building blocks and conjugated linkers.\textsuperscript{26,27}

In recent years, redox-active COFs have emerged as promising organic electrode materials for rechargeable batteries.\textsuperscript{28–33} Compared to conventional organic polymers, COFs offer some advantages mentioned above, such as the abundant availability of raw materials, sustainability, high stability and insolubility in electrolyte. In addition, COFs present ordered porous channels to facilitate ion diffusion and their high surface area allows better accessibility to the multiple redox active sites. On the other hand, the possibility to introduce π-conjugation and improve electronic delocalisation through the framework can help to enhance the electronic conductivity of COFs.\textsuperscript{27} Another important difference with respect to amorphous organic polymers is their ordered crystalline nature which allows their structure and properties to be predicted by computational modelling, being of great interest for molecular (pre)design. Similar to other conventional redox polymers, redox-active COFs can undergo redox processes in a reversible manner, thus being able to be reduced and oxidised during the charge and discharge of the battery. COFs have recently been explored as electrode materials in different metal-ion (including multivalent) batteries\textsuperscript{34} (Li\textsuperscript{+},\textsuperscript{35,36} Na\textsuperscript{+},\textsuperscript{37,38} K\textsuperscript{+},\textsuperscript{39,40} Mg\textsuperscript{2+},\textsuperscript{41} Ca\textsuperscript{2+},\textsuperscript{42} Zn\textsuperscript{2+},\textsuperscript{43} Al\textsuperscript{3+},\textsuperscript{44,45} etc.) and lithium-sulphur (Li-S) batteries.\textsuperscript{46–49} The first reported COF electrodes for each type of battery are shown in Fig. 1. Note that we have also included the first reported covalent triazine frameworks (CTFs), which tend to be much more amorphous.

In this Feature article, we provide an overview of recent design strategies to improve the electrochemical performance of COF electrode materials for metal-ion batteries within the context of the organic batteries field. In particular, we discuss some principles for the molecular design of COF cathodes in LIBs to increase both the energy and power densities. We also highlight the need to optimise the COFs processing, electrode and electrolyte composition from a materials engineering point of view. Some other aspects such as cycling stability, scalability and recyclability are also considered. Finally, the main challenges and future prospects for COF electrode materials for rechargeable batteries are highlighted.

### Molecular design of redox-active COFs to enhance the electrochemical performance

#### Energy density

Rechargeable batteries are mainly evaluated in terms of energy density, power density, and cycling stability.\textsuperscript{8} The energy density ($E_d$) is directly related to the specific capacity ($Q$) and output voltage ($E$) (Eq. 1), so both parameters should be increased to improve battery performance through molecular design, electrode composition, electrolyte optimisation, etc.\textsuperscript{8,9}

$$E_d = E \times Q$$  \hspace{1cm} (Eq. 1)

Both the theoretical specific capacity and voltage can be tuned by selecting the appropriate electroactive organic building blocks\textsuperscript{26} and by structural design\textsuperscript{23} (see below). However, the practical capacities can be influenced by several factors such as the electrode composition, electronic conductivity, ion diffusion, binder, particle size of the active material, or the electrolyte used. The maximum specific capacities and average discharge voltages reported for some representative COF-based cathodes\textsuperscript{35,36,50–65} for lithium batteries are summarised in Fig. 2.

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**Fig. 1.** An overview of the development of COF-based electrodes (including CTFs) for batteries, including the first reported examples for lithium-ion (LiBs), sodium-ion (SiBs), potassium-ion (PiBs), zinc-ion (ZiBs), magnesium-ion (MiBs), calcium-ion (CiBs), aluminium-ion (AiBs) and lithium-sulphur (Li-S) batteries.

**Fig. 2.** Average discharge voltage and practical specific capacity of some representative COF-based cathode materials for rechargeable lithium batteries. The specific capacity refers to the maximum reported reversible capacity.
Capacity. According to Eq. 1, high specific capacity is required to achieve high energy density. The specific capacity is defined as the electric charge that can be stored in a cell per mass of active material. The theoretical specific capacity \( Q_{\text{theo}} \) of an electrode material can be calculated from the following equation:

\[
Q_{\text{theo}} = \frac{n \times F}{3.6 \times M_w} = 2680.1 \times \frac{n}{M_w} \text{ (mAh g}^{-1})
\]

(Eq. 2)

where \( n \) is the number of electrons transferred per redox reaction, \( F \) is the Faraday constant (C mol\(^{-1}\)) and \( M_w \) is the molecular weight (g mol\(^{-1}\)). Therefore, to increase the specific capacity it is necessary to maximise the number of redox active sites while reducing the molecular weight. An illustrative example of increasing the theoretical capacity by decreasing the molecular weight is the substitution of anthraquinone (AQ) for benzoquinone (BQ) units in \( \beta \)-ketoamine-linked COFs. As both quinone derivatives undergo two-electron reactions, the calculated theoretical capacities are 155 and 221 mAh g\(^{-1}\) for DAAQ-COF and DABQ-COF, respectively (Fig. 3). The theoretical capacity can be further increased to 271 mAh g\(^{-1}\) (PT-COF) by using pyrene-4,5,9,10-tetraone as redox-active moieties, as it involves a 4 e-/Li\(^+\) process. Therefore, the selection of electroactive building blocks taking into account their molecular weight as well as the number of electrons transferred is crucial to increase the charge storage capacity.

Reducing the number or molecular weight of inactive moieties in the framework is also critical to maximise the theoretical capacity of COF electrode materials. An example is the replacement of 1,3,5-triphenylbenzene (Mw = 306 g/mol) by triphenylenamine (Mw = 245 g/mol) in PI-COFs, increasing the theoretical capacity of PI-COF-1 up to 142 mAh g\(^{-1}\) (Fig. 4). Therefore the connection of linear redox-active building blocks by using electroactive linkers/linkages (quinoxalines, tetraphenyl-p-phenylenediamine, triazines, polyanilines, phenanazines, etc.) (Fig. 5) is an efficient strategy to increase the active sites density. Moreover, the geometry and length of the linkers are determinant for the topology and pore size of the frameworks, which can influence the electrolyte diffusion and thus the practical capacity. However, COFs with small pore size can lead to more rigid structures and be more efficient for charge transport, so the pore diameter needs to be optimised. Other factors affecting the practical capacity, such as the electronic conductivity or particle size, are discussed below.

\[ E = \text{cathode potential} - \text{anode potential} \]

(Eq. 3)

Output voltage. Besides capacity, another way to maximise the energy density is to increase the output voltage. The theoretical voltage of a battery can be estimated from the operating potentials of the cathode and anode as shown in Eq. 3. Therefore, in order to achieve a high voltage it is essential to use cathode and anode materials with high and low operating potentials, respectively.
Working potentials of organic electrode materials depend mainly on the molecular structure, which can be finely tuned, for example, by incorporating electron withdrawing or donating groups. In general, n-type organic compounds can store charges at moderate voltage range (<3 V vs Li/Li⁺) whereas p-type organic electrodes exhibit high working potentials (>3 V vs Li/Li⁺). For this reason, p-type compounds are mainly used as cathodes while n-type compounds can also be used as anodes if they have a relatively low potential. In addition, redox kinetics of p-type compounds are usually faster. The redox potentials of representative redox-active groups used in COFs have recently been summarised. In the particular case of COF cathodes for LIBs, the highest voltages have been achieved with TEMPO radical (~3.6 vs Li/Li⁺), phenoxazine (~3.6 vs Li/Li⁺), and dibenzopentalenes-based COFs (~3.9 vs Li/Li⁺) (Fig. 2). However, the capacity of such COFs is rather limited. In contrast, the voltage of COFs with the highest capacity (> 250 mAh g⁻¹), which are based on n-type building blocks, does not exceed 2.5 V vs Li/Li⁺. Therefore, new strategies need to be designed to simultaneously maximise the voltage and specific capacity, as well as to explore new electroactive building blocks for the construction of redox-active COFs with improved electrochemical performance. Remarkably, some p-type organic compounds with high redox potential widely studied in the field of organic batteries, such as phenothiazine, are unexplored for the synthesis of COF-based electrode materials.

**Redox-bipolar COFs.** As mentioned above, the design of COFs with both high specific capacity and high voltage is one of the current challenges to achieve high energy densities. In this sense, the construction of COFs combining n-type and p-type building blocks can be an efficient approach to increase both parameters. This concept was first demonstrated by the synthesis of an imine-linked 2D COF (TP-TA) with Kagome topology based on the condensation reaction between tetraphenyl-p-phenylenediamine (TP) and terephthaldehyde (TA). In this case, the C=N linkages can be reduced acting as n-type moieties, while p-type TP building block can undergo 2 e⁻ oxidation process and combine with two PF₆⁻ from the electrolyte. This bipolar-type COF showed a specific capacity of 207 mAh g⁻¹ (at 200 mA g⁻¹), an average redox voltage of 3.6 V vs Li/Li⁺ and good cycling stability (93% retention after 1500 cycles). Another representative example of this design strategy is a 2D COF (TPPD-CuPor) composed of tetratopic p-type TP and bipolar-type porphyrin building blocks (Fig. 6), which provides a high redox potential and a high number of redox-active centres. Indeed, TPPD-CuPor COF cathode exhibited an average voltage of 2.7 V vs Li/Li⁺ and specific capacity of 142 mAh g⁻¹ at 60 mA g⁻¹, resulting in a calculated energy density of 371 Wh kg⁻¹. In addition, the bipolar redox mechanism was further confirmed by DFT calculations and ex situ XPS.

![Fig. 5. Library of some representative electroactive organic building blocks (theoretical capacities and average discharge voltages), linkers and topologies used for the synthesis of redox-active COF cathodes in LIBs. BQ (benzoquinone), AQ (anthraquinone), PT (pyrene-tetraone), NDI (napththalene diimide), PI (polymide), PH (phenazine), DAPO (phenoxazine), TP (tetr phenyl-p-phenylenediamine), HATP (hexaazatriphenylene).](https://doi.org/10.26434/chemrxiv-2023-4dp12)

![Fig. 6. a) Synthesis of TPPD-CuPor COF. b) Redox reaction of the p-type TP and bipolar-type Cu-TFPP building blocks. Reproduced with permission from ref. 55.](https://doi.org/10.26434/chemrxiv-2023-4dp12)
More recently, Feng and co-workers have reported a redox-bipolar COF based on n-type imides and p-type triazine moieties that was investigated as cathode for rechargeable aluminium batteries achieving a specific capacity of 132 mAh g\(^{-1}\) and excellent cycling stability (97% capacity retention after 4000 cycles).\(^{45}\) We also note that a similar approach has been carried out for the synthesis of an amorphous porous organic polymer based on the polyimide condensation of mellitic acid trianhydride (n-type) and diamino N-methyl phenothiazine (p-type).\(^{74}\) Such dual-redox porous organic polymer was used as electrode in symmetric all-organic batteries displaying a specific capacity of 57 mAh g\(^{-1}\) (2 C) and capacity retention of 57% at high rates (60 C). The design of bipolar-type COFs is still in its infancy and new combinations of building blocks as well as advanced in-situ/ex-situ mechanism studies are still needed to boost the performance of this promising type of COF electrodes.

**Power density.** The power density \(P_d\) is another important parameter to evaluate rechargeable batteries and is directly related to the charge-discharge ability of organic electrodes at different rates\(^{8}\). Materials with high power density transfer large amount of energy in a short time. The power density depends on the output voltage \(E\) and rate capability \(I\) as follows:

\[
P_d = E \times I \quad \text{ (Eq.4)}
\]

Therefore, the rate capability must be increased by improving both ion and electron transport during the charge/discharge processes. The rate capability depends on both intrinsic (molecular design of the framework) and extrinsic (electrolyte, processing of active material, conductive additives, etc.) factors that need to be optimised to improve the electronic and ionic conductivities. Here we will focus on how to improve intrinsic electronic and ionic conductivities from a molecular design point of view (Fig. 7). Extrinsic factors (beyond molecular design) to increase the rate capability will be discussed in the next section.

Like most organic compounds, 2D COFs typically exhibit low intrinsic electronic conductivity although some strategies have recently been identified to improve the electronic transport in these materials.\(^{27}\) For example, conjugated planar building blocks are likely to exhibit a better \(\pi\)-orbital overlap between the layers which can facilitate the out-of-plane conductivity. On the other hand, the choice of conjugated linkages, such as vinylene or pyrazine, is critical to ensure efficient electron delocalisation throughout the framework, thereby increasing the in-plane conductivity. Band structure calculations are also a useful tool to predict important information about the charge transport through different directions and to extract structure-property relationships for the design of conductive COFs. One of the highest conductivities \((10^{3}-3 \text{ S cm}^{-1})\) among neutral (non-doped) COFs has very recently been reported for a fully conjugated vinylene-linked COF (TFPPy-ICTO-COF).\(^{53}\) This COF has been used as cathode in LIBs, providing excellent rate capability without the addition of conductive additives (e.g., carbon nanotubes, graphene, etc.). Another conjugated 2D COF (BQ1-COF)\(^{57}\) showed a relatively high intrinsic conductivity \((10^{6} \text{ S cm}^{-1})\) for a neutral COF, which together with the efficient Li\(^{+}\) diffusion was responsible for the excellent rate performance when used as cathode in lithium batteries. The incorporation of heteroatoms or electron-withdrawing groups in COFs is another effective approach to reduce their band gap and increase the conductivity. For example, the introduction of fluorine atoms into a covalent triazine framework (FCTF) significantly narrowed its band gap (from 2.35 to 1.45 eV), resulting in a superior conductivity and rate capability.\(^{75}\) In addition, thiazole-linked COFs have also proved to exhibit high out-of-plane conductivity because of the efficient \(p\)-orbital overlap of the azo groups across the layers,\(^{76}\) resulting in a superior rate performance compared to other similar COFs when used as electrodes in LIBs.

In addition to the electronic conductivity, rate performance can be enhanced by significantly improving the ionic conductivity through chemical design.\(^{77}\) The simplest approach to modulating the ionic conductivity is to modify the size and arrangement of the pores, as this can facilitate ion diffusion. In general, COFs with small pores may present diffusion problems at high rates, especially for those metal ions and counterions with large ionic radius. For example, HATN-AQ-COF\(^{53}\) (pore size = 3.8 nm) shows a higher active sites utilisation efficiency (63%) at high current density (10 C) than that of BQ1-COF\(^{57}\) (pore size = 1.4 m, active site utilisation of 22% at 10 C) when explored as cathode materials for Li-ion batteries. This reveals that the design of mesoporous COFs (pore size = 2-5 nm) with well-defined channels may be key to improving ion diffusion. The design of hierarchical COFs with the presence of both meso- and micropores has also proven to be efficient for simultaneous ion and electron transport.\(^{86}\) The interlayer distance can also be modulated to improve the ionic conductivity. In general, COFs present stacked layers that often hinder the ion transport during electrochemical processes, so larger interlayer distances can favour better ion diffusion, higher utilisation of the redox-active sites, and higher rate performance. This approach was explored in a redox-active piperazine-terephthaldehyde COF based on nonplanar linkages exhibiting a chair-shaped conformation, resulting in a large interlayer distance of 6.2 Å.\(^{78}\) This interlayer distance facilitated ion transport, improving the electrochemical performance even at high rates (207 mAh g\(^{-1}\) at 5 C) when used as anode in LIBs. However, this strategy is in contrast to a better interlayer overlap which is favourable for a high out-of-plane electronic conductivity. Other strategies to increase the ionic conductivity in COFs are based on the preparation of cationic frameworks,\(^{79}\) the incorporation of sulfonate groups,\(^{80}\) or post-functionalisation of the channels by anchoring, for example, oligo(ethylene oxide) moieties.\(^{81,82}\) However, these strategies significantly reduce the specific capacity and are therefore more focused on solid electrolytes applications.
Fig. 7. Summary of some molecular design strategies to improve electronic and ionic conductivities in COFs.

**Electrode and electrolyte optimisation**

**Influence of the electrolyte and binder on the electrochemical performance.** The choice of electrolyte and binder has a direct impact on the practical capacity and stability of the electrode, as it can affect the solubility and efficiency of active sites utilisation. For example, optimising the nature and concentration of the electrolyte can lead to significant improvements in capacity and cycling stability. Very recently, we have reported the first comprehensive study of the influence of the electrolyte and binder on the performance of the anthraquinone-based DAAQ-TFP-COF. Our results showed that the worst performance was obtained when LiPF₆ in carbonate solvents was the electrolyte, due to the higher solubility of the active material and undesired side reactions. On the contrary, the best capacity retention was obtained when using LiFTSI as electrolyte in ether-based solvents (Fig. 8). The electrochemical performance was further improved by substituting PVdF for PTFE as the binder, resulting in practical capacities close to the theoretical one and high capacity retention (99% after 100 cycles). One of the main reasons for the improved performance when using PTFE as a binder is its porous structure, which can lead to better ion diffusion and accessibility to the active sites. Therefore, in addition to the proper design and processing of the active material, the selection of the appropriate electrolyte and binder is critical to achieve optimal performances in COF-based batteries.

**Hybridisation with conductive additives.** As discussed above, the rate capability depends on the electronic conductivity of organic electrodes. However, most organic compounds are insulators ($\sigma < 10^{-9} \text{ S cm}^{-1}$) and their low intrinsic electronic conductivity limits the performance of batteries based solely on organic active materials. For this reason, electroactive organic compounds are usually mixed with large amounts (typically from 30 to 70% in weight) of conductive additives (e.g., carbon black), significantly reducing the specific capacity and energy density of the organic electrode. It is therefore necessary to subtract capacity contributions from carbon black and other conductive additives to determine the real specific capacity of the active material as well as calculating the energy density taking into account the mass of the whole electrode.

In the specific case of COF cathodes for LIBs, the amount of carbon black can vary from 10 to 70% in weight, depending on the intrinsic conductivity of the COF. In addition, a commonly used strategy to increase the electronic conductivity is the hybridisation of COFs with carbon nanotubes (CNTs), reduced graphene oxide, or conductive polymers. The COF/CNT composites are usually synthesised by in situ polymerisation, where COF layers are grown on the CNT surface (Fig. 9). In general, such COF/CNT composites result in higher utilisation of active sites, high rate performance, and can help to improve cycling stability. For example, the preparation of PT-COF/CNTs composite cathodes for LIBs can increase the active site utilisation from 71% (PT-COF) to 98% (PT-COF composite with 50 wt % of CNTs). However, the PT-COF/CNTs composite shows a lower overall specific capacity (109 mAh g⁻¹) than that of PT-COF (128 mAh g⁻¹) when considering the mass of the active material and all conductive additives. This proves that the addition of too many inactive conductive additives can significantly reduce the energy density. It is also worth noting that most COF composites still require a large amount of extra conductive additives such as carbon black to achieve a satisfactory performance. Thus, improving the intrinsic conductivity of COFs and developing new strategies to minimise the amount of conductive additives in the electrode remain the main challenges for the design of high performance COF electrodes.

**Fig. 8.** DAAQ-TFP-COF electrode performance with PVdF as a binder at 150 mA g⁻¹ (1C) in four different electrolytes: 1 M LiTFSI in DOL/DME (1:1, vol%) (red), 1 M LiTFSI in TEGDME (green), 1 M LiPF₆ in EC/DEC (1:1, vol%) (blue), and 1 M LiClO₄ in GBL (yellow). Reproduced with permission from ref. 84.

**Fig. 9.** Representative example of COF/CNT composite synthesis via in situ growth. Reproduced with permission from ref. 89.
**Exfoliation of COFs into few-layer nanosheets.** High exposure of the active sites and fast ion diffusion are key to achieve high specific capacity and high rate capability. In general, reducing particle size or increasing the specific surface area of organic materials are effective ways to improve the practical capacity. Most bulk COFs present strong π-π interactions between layers, which prevent ions from reaching the buried active sites and makes them inaccessible, limiting the practical capacity. Exfoliation of 2D COFs into few layer nanosheets is a successful strategy to increase the number of accessible redox sites and assist ion diffusion, increasing the performance of COF-based batteries (Fig. 10). In general, there are several strategies for the preparation of COF nanosheets, from top-down methods based on different types of exfoliation (including mechanical and chemical exfoliation) to bottom-up approaches based on the preparation of well-ordered nanostructures. In the particular case of COF nanosheets for batteries, different exfoliation techniques have been employed for their preparation: mechanical (ball milling, ultrasound-assisted exfoliation, grinding, etc.), chemical exfoliation (using external agents such as maleic anhydride, MnO₂, acids, thiol-ene reactions, etc.) and self-exfoliation. Regarding bottom-up approaches, an example is the in-situ growth of graphene-supported COF nanosheets that are uniformly dispersed on carbon layers. The relationship between thickness and practical capacity was systematically investigated using a redox-active COF (DAAQ-COF) as anode in sodium batteries. In this case, three different exfoliation techniques were used to obtain different thicknesses: grinding (100-250 nm), ball milling (100-180 nm) and ultrasound-assisted exfoliation in methanesulfonic acid (4-12 nm). The thinnest (4-12 nm) and thickest (100-250 nm) samples showed capacities of 500 and 182 mAh g⁻¹ (at 50 mA g⁻¹), respectively. The resistance of the electrode also decreased from 428 Ω to 146 Ω after exfoliation. This study demonstrates that reducing the COF thickness can be an efficient strategy to improve the practical capacity and rate capability. However, the preparation of COF nanosheets still presents some challenges that need to be addressed. First, the thicknesses of the nanosheets are always obtained in a wide size range so precise thickness control remains challenging and can be problematic for reproducibility. On the other hand, the yields obtained for the preparation of nanosheets are usually relatively low and some exfoliation procedures can affect the crystallinity of the material.

**Fig. 10.** Schematic representation of the sluggish diffusion in bulk COFs and fast diffusion in exfoliated COF nanosheets.

**Other parameters**

**Cycling stability.** Stability is one of the most important parameters for evaluating organic electrodes in batteries. In general, organic compounds may present solubility problems in electrolyte (especially small molecules) leading to possible undesired side reactions, self-discharge issues and poor cycling stability. Other factors leading to low stability can be the instability of intermediates or volume change. Polymerisation is one of the main strategies to avoid solubility problems, along with salification and electrolyte optimisation (see above). When evaluating the stability of organic electrodes, we can take as a reference the capacity retention of some inorganic electrodes such as LiCoO₂ or LiMn₂O₄ which exceeds 80% after more than 1000 cycles. Some COF-based electrodes show a similar or even higher capacity retention after 1000 cycles, especially those based on β-ketoenamine, (cyano)vinylene, phenazine, imide and piperazine linkages (Fig. 11), as they lead to the most stable frameworks. Normally COFs based on more reversible reactions such as boronate ester or imine condensations result in poorer stability. The strategy of pre-orientation, based on an initial reversible reaction followed by irreversible locking of the labile bond, can lead to very crystalline and highly stable COFs. Such a strategy has recently been explored to synthesise a thiazole-linked COF that was used as a cathode in lithium-sulphur batteries. We also note that in some cases COFs are hybridised with insoluble conductive substrates such as CNTs, which can help to improve the stability. As mentioned above, the electrolyte optimisation is also crucial to improve the cycling stability of COFs, as it may affect the dissolution or lead to side reactions.

**Fig. 11.** Some typical linkages employed for the synthesis of COFs used as electrodes in metal-ion batteries.

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Scalability. Although large-scale applications of organic electrodes for metal-ion batteries are still a long way off, the possibility of scalability and production using simple low-cost methods needs to be evaluated. Some organic electrodes have already been scaled up at relatively low cost using high mass loading and pouch cells. Most COFs are synthesised using solvothermal conditions (typically between 120-150 °C), acid catalysts and high boiling point organic solvents such as mesitylene, 1,4-dioxane, or N,N-dimethylacetamide. More sustainable and environmentally friendly syntheses have already been proposed by replacing organic solvents with water, or using supercritical CO₂ or solvent-free methods. Microwave-assisted synthesis of COFs has also been extensively explored to considerably reduce reaction times. Recent studies have reported scalable methods to obtain COF nanosheets on a gram scale in a short time and mild conditions. Although most of the COFs used as electrodes in batteries have been obtained via solvothermal reactions, alternative, greener and cost- and time-efficient syntheses should be considered towards large-scale applications in the long term. As for most organic electrodes, the cost of such materials is too difficult to estimate until large-scale commercial scale-up is feasible.

Degradation and recyclability. In addition to scalability, another important aspect to take into account in the near future is the end-of-life and recyclability of organic electrodes for the development of sustainable and greener batteries in a circular economy. In this direction, some naturally occurring and biodegradable organic electrode materials have been reported. A more recent example is based on metal-free polypeptide-based batteries, in which redox-active groups such as violagens and nitroxide radicals were incorporated along polypeptide backbones to be used as anode and cathode materials, respectively. The most important feature of such polypeptide-based battery is its high stability during battery operation and on-demand degradation in acidic conditions. The recycling of some organic electrodes has also been recently proposed by using a simple extraction method without decomposition of the material and with high yields. As for COFs, although the biodegradability of some of them has been studied for other applications, future studies on the degradation and recycling of COF electrodes should be systematically carried out.

Conclusions and outlook

The emergence of redox-active covalent organic frameworks as promising electrodes for rechargeable metal-ion batteries has revitalised the field of organic batteries in recent years. Some of their advantages over conventional electroactive organic polymers are the presence of ordered channels to improve ion diffusion and their crystalline nature, which allows their structures to be modelled and some of their properties to be predicted. In this Feature article we have discussed some of the recent strategies to improve their electrochemical performance (energy density, power density, cycling stability) either by molecular design or by electrode optimisation.

In terms of energy density, some COFs based on n-type moieties have already demonstrated higher specific capacities than those of conventional inorganic cathodes, while high voltages can be achieved by incorporating specific p-type units into the framework. However, the design of COFs with both high capacity and high potential remains a major challenge to give rise to superior energy density. In this sense, redox-bipolar COFs have emerged as promising systems as they allow the combination of electroactive p- and n-type building blocks that can lead to high potential and high capacity at the same time.

Regarding power density, as for most organic compounds, low electronic conductivity is the main problem in achieving high rate capabilities. To overcome this issue, some strategies at the molecular design level can help to construct π-conjugated frameworks incorporating heteroatoms to improve the in-plane and out-of-plane electron transport. However, the intrinsic conductivities of COFs remain relatively low and large amounts of conductive additives are still required, reducing the energy density of the battery. At the same time, ionic conductivity needs to be optimised, for example, by modulating the porosity to facilitate ion diffusion. Therefore, a proper balance between the two conductivities is critical to maximise the rate performance. In addition, in-situ/ex-situ techniques combined with molecular dynamic simulations can provide important insights into the ion transport and charge storage mechanisms in COFs.

Electrode optimisation is also key to improve the electrochemical performance of COF electrodes. For example, the proper choice of electrolyte and binder can significantly increase the practical capacity, whereas the preparation of COF composites with conductive carbon substrates can help to enhance the rate capability. However, the energy density can be reduced if the amount of conductive additives is excessive. The exfoliation of bulk COFs into nanosheets is another approach to increase the accessibility of active sites. However, there is still a need for more straightforward synthetic approaches with improved yield and thickness control towards large-scale applications. Systematic studies for each of these strategies will be useful in order to optimise the composition and processing of COF electrodes.

Cycling stability is one of the key parameters for evaluating COF-based electrodes. Although the stability of COFs has been significantly improved in recent years, some design strategies can lead to new, much more robust linkages. The evaluation of capacity retention after several (>1000) cycles as well as post-mortem analysis of COF electrodes can contribute to a better understanding of the stability of these materials. Although there is still a long way to go, the scalability, cost and recycling of these materials should be considered in the near future for further applications.

The remarkable progress in the design of new redox-active COFs and their use in numerous types of rechargeable batteries (including multivalent) has demonstrated the great potential of these porous polymers as organic electrodes. We expect that this Feature article will stimulate the design of new redox-active COFs and electrode optimisation in the coming years.
Notes and references

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