Modified Metal–Organic Frameworks for Electrochemical Applications

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Metal–organic frameworks (MOFs) are neo-type porous materials synthesized via organic ligands and metal ions, which have drawn much attention due to their unparalleled advantages such as high specific surface area, large and clear pore structures, and uniformly distributed active sites. In these years, modified MOFs are regarded as kinds of materials with excellent electrochemical properties, that overcome poor conductivity and stability of original MOFs and narrow the gap between the basic science of MOFs and their future applications. At the same time, it also provides an opportunity to elaborate the synergistic effect of the synthesis strategy of modified MOFs on the performance. This review focuses on the synthesis, structure characterization, and electrochemical adhibition of modified MOFs and discusses the challenges and application prospects of modified MOFs in energy storage and conversion.

1. Introduction

The ever-growing energy dilemma and subsequent environmental pollution have stimulated global efforts to develop clean and renewable energy resources.[1] Among the next-generation energy technologies, rechargeable batteries (i.e., lithium-oxygen batteries (Li–O2), sodium-ion batteries (SIBs), and lithium-ion batteries (LIBs)), supercapacitors (SCs), and fuel cells show excellent potential for electrochemical energy storage,[2–6] and water electrolysis is a representative electrochemical energy conversion system. As for rechargeable batteries, the key to realizing high performance lies in electrode materials.[7–12] However, traditional electrode materials, such as graphite, conductive polymers (CPs), and transition metal oxides, have the drawbacks of low capacitance, high cost, and poor stability, which are far from enough to satisfy the requirements of high energy density, high capacity rate, and long cycle life. In comparison with rechargeable batteries, SCs have the advantages of long cycle life, fast charge–discharging capability, and high-power density, but their wide adhesion is impeded by the low-rate capability and inferior energy density. For fuel cells, their overall efficiency is severely hampered via the sluggish oxygen reduction reaction (ORR). Similarly, in the electrochemical energy conversion system of water splitting, the two half reactions (at the anode: oxygen evolution reaction (OER), at the cathode: hydrogen evolution reaction (HER)) require an excess of driving force to overcome resistance such as activation energy barriers from the electrode/electrolyte and solution contact interfaces. Therefore, efficient electrocatalysts are urgently needed to optimize the efficiency of specific applications. To date, the commercial electrocatalysts for ORR, HER, and OER are mainly precious metal-based materials (e.g., Pt-based materials for HER and ORR and Ru/ Ir-based materials for OER). Nonetheless, their expensive cost and inferior durability greatly restrict the widespread practical applications in renewable energy technologies.[13] In view of these limitations, it is urgently needed to develop cost-effective electroactive materials with high activity and long-term durability, being challenges.

Metal–organic frameworks (MOFs), which are known as porous coordination polymers (PCPs), are a class of crystalline porous materials assembled by inorganic nodes (clusters/metal ions) and organic ligands through coordination bonds.[14–20] Up to now, MOFs, as functional materials, have received extensive attention in multiple advanced technology adhibition, such as separation,[21,22] drug delivery,[23–25] sensing,[26,27] gas adsorption,[28,29] catalysis,[30,31] and energy storage.[32–39] As MOFs are constructed by two main components, the structure can be easily adjusted to realize the desired properties for target applications by properly selecting the organic ligands and inorganic nodes.[40–49] Recently, MOF-based materials have been proved to be more competitive than other porous materials as electroactive materials in electrochemical energy storage and conversion due to their high specific surface areas, huge and clear void structures, and uniform

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DOI: 10.1002/sstr.202100200
distribution of active sites. Recently, MOF-based materials have been proved to be more competitive than other porous materials as electroactive materials in electrochemical energy storage and conversion due to their high specific surface areas, huge and clear void structures, and uniform distribution of active sites. According to the reported literature, MOF-based materials are mainly segmented into three grasshoppers, including pristine MOFs, MOF composites (e.g., metal nanoparticles [MNPs]@MOFs, MOFs/conductive substrates), and MOF-derived materials (e.g., metal oxides/nitrides/sulfides/phosphides). Thereinto, although pristine MOFs have attracted considerable interest as electroactive materials, their poor electrical conductivity and insufficient chemical stability severely impede their electrochemical applications. Nevertheless, the structural and compositional features enable MOFs to be versatile hosts, precursors, or sacrificial templates for designing MOF composites and MOF derivatives. What’s more, the synthesis of these materials can be realized easily via combining MOFs with other advanced functional materials (e.g., conductive substrates and MNPs) and converting MOFs/MOF composites into inorganic micro-/nanomaterials by direct annealing or indirect post-treatments. These strategies not only avoid the modified of pristine MOFs, but also introduce the advantages of advanced functional materials into the composites. Meanwhile, the obtained modified MOFs often possess high specific surface area, favorable electrical conductivity, and superior chemical stability, which are conductive to improving the electrochemical process in specific energy technologies. Modified MOF means without destroying itself, its own structure under the condition of the MOF’s skeleton structure does not change, for a series of processing, including but not limited to composite and other functional materials (such as carbon material, MNPs, metal oxides, CPs, etc.), thermal conversion and partial derivatives, etc. The advantages of modified MOF materials add other advantages, such as larger specific surface area, superior chemical stability, and so on.

Under these guidelines, considerable MOF-based electroactive materials have been exploited and summarized in these years. Nevertheless, few reviews concentrated on summarizing the design of highly active MOF-based materials on the premise of preserving MOF structures. In recent years, many articles have introduced the excellent electrochemical performance of modified MOF materials. The modified MOF materials still retain the advantages of the MOF base materials such as high specific surface area, large and clear pore structure, uniform distribution of active sites, as well as good electrical conductivity and excellent chemical stability. These advantages make modified MOF materials have good electrochemical application potential, but there are few reviews in this area. Therefore, a comprehensive review on modified MOFs for electrochemical applications is noteworthy, which will provide insightful guidance and inspiration for the exploitation of modified MOFs and their applications in energy-related technologies. Herein, this review outlines the recent advances of modified MOFs, including their synthesis, structural characterization, and electrochemical applications, putting emphasis on their applications in electrochemical energy storage and conversion.
on the synthetic strategy of modified MOFs and their synergistic effects on their performance. Finally, the outlook and perspective of modified MOFs in energy-related technologies are presented, in the hope that this review will inspire further investigation of modified MOFs toward energy storage and conversion (Scheme 1).

2. Synthesis Methods for Modified MOFs

Over the past decades, several advanced methods have been developed to synthesize modified MOFs. Herein, we will summarize the synthesis strategies of modified MOFs, including the design of MOF composites, thermal transformation, and partial derivatization.

2.1. Synthesis Methods for MOF Composites

The controlled integration of MOFs with functional materials has induced brand new multifunctional composites that show split-new characteristics betony individual components. MOF composites are composed of MOFs and one or more materials with different constituents, including but not limited to different MOFs,[58–60] metal–NPs,[61–63] metal oxides,[64–66] and conductive carbon materials.[67–69] The integration combines the advantages of MOFs and functional materials, such as the structural adaptability and flexibility, high porosity and ordered structure of MOFs, and the unique advantages of the introduced functional materials. It is expected that the obtained MOF composites can exhibit enhanced electrochemical capability.[70]

2.1.1. Carbon-Based Materials@MOFs

Carbon has a variety of allotropes, such as graphite, nanotubes, diamonds, etc. The types of carbon materials are more diverse, like graphene, carbon cloth (CC), carbon nanotubes, and so on.[71,72] Carbon can exist in dimensions from 0D to 3D in various forms (e.g., particles, fibers, foams, fabrics, and composites). Taking graphene and carbon nanotubes as examples, carbon materials are held to be the most valuable structural fillers in MOF composites due to their great tensile strength, superlight weight, and distinguished chemical and thermal stability.[73,74] So far, composites of carbon-based materials and MOFs have been extensively used in many fields.[75–79]

Graphene oxide (GO) is ionic conductive, and its incorporation can improve the ionic conductivity of most MOFs.

![Figure 1. Chemical structure of: a) Cu-MOF, b) GO, and c) pure Cu-MOF paddle-wheel grade-building units. SEM images of d) Cu-MOF, e) GO, f) (GO 2 wt%) Cu-MOF, g) (GO 4 wt%) Cu-MOF, and h, i) (GO 8 wt%) Cu-MOF. Reproduced with permission.[80] Copyright 2013, Wiley-VCH. j) The synthetic illustration of ZnCo-ZIF@GO; k) TEM and l) SEM images of ZnCo-ZIF@GO. Reproduced with permission.[81] Copyright 2020, The Royal Society of Chemistry. m) Preparation course of PANI-ZIF-67-CC; SEM of n) the CC fibers, o) ZIF-67-CC, and p) PANI-ZIF-67-CC. Reproduced with permission.[82] Copyright 2015, American Chemical Society.](image)
Loh’s group combined Cu-MOFs with GO via hydrothermal methods, in which the 3D Cu-MOF was synthesized using paddle-wheel Cu2(COO)4(ted)2 as the secondary building unit (SBU) (Figure 1a–c). The group mixed different mass fractions of GO with Cu-MOF precursors. The morphologies of Cu-MOF, GO, and (GO X wt%, X = 2, 4, or 8) Cu-MOF were demonstrated through scanning electron microscopy (SEM), which revealed that with the increase in GO concentration, the morphology of Cu-MOF changed significantly (Figure 1d–i). Especially, when 8 wt% GO was added to the Cu-MOF precursor, a cubic symmetry distortion displayed on the space group from P4/ncc (No. 130) to P4/mmb (No. 127). Wang’s team grew the bimetal mixed ZnCo-ZIFs (mole ratio of Co to Zn is 4/6) on GO nanosheets via the in situ growth method to obtain ZnCo-ZIFs@GO (Figure 1j). Transmission electron microscopy (TEM) and SEM images demonstrated that ZnCo-ZIF@GO showed well-defined ZIF-67 rhombohedral dodecahedrons and were dispersed on GO nanosheets uniformly, with a medial dimension of about 60 nm (Figure 1k–l).

In addition to combining graphene with MOFs to enhance the composites’ ionic conductivity and thus improve their electrochemical performance, porous electrodes were constructed by pouring MOFs onto a CC with the assistance of CP. Wang and co-workers developed a two-step process to fabricate PANI-ZIF-67-CC electrode, (Figure 1m), in which a slurry containing ZIF-67, conductive super P, polyvinylidene fluoride (PVDF), and NMP was cast on CC to obtain ZIF-67-CC and then interconnected by conductive polyaniline (PANI) via electropolymerization. The fabrication process did not change the MOF structure, and ZIF-67 crystals with a medial dimension of about 300 nm were distributed on the surface of CC fiber uniformly (Figure 1n,o). After electropolymerization of aniline, the ZIF-67 crystal’s external surface displayed evident morphology changes. The formed PANI chains were coated on the surface of ZIF and served as bridges between the isolated MOF crystals (Figure 1p).

### 2.1.2. Metal Oxides@MOFs

Metal oxides have been investigated in electrochemical energy storage and conversion extensively, because of the controllable shape, size, crystallinity, and functionality. Nonetheless, their adhesions are usually impeded via the low superficial areas and high surface energies. To further improve the function of metal oxides, hybridizing them into MOFs with large surface areas and well-organized pores is a promising approach, which not only enhances the surface areas of metal oxides, but also integrates the advantages of both MOFs and metal oxides, so as to comprehensively improve the performance of the composites.

Xu and co-workers synthesized high-alkaline and stable metal oxide@MOF materials (Co3O4@Co-MOF) through a steerable one-pot hydrothermal method using ptcda (perylene-3,4,9,10-tetraarcabonylic dianhydride, C24H8O6) as ligand and Co2+ as the metal nodes under the pH range of 11–13 (Figure 2a). As shown in SEM and TEM graphics, Co3O4@Co-MOF showed a leaf-like (Figure 2b), and Co3O4 nanocrystals with a medial dimension of 50 nm were evenly scattered on each side of Co-MOF (Figure 2c,d). Keggin-type POM is a distinct polymetallic oxygen cluster, in which three or more transition metal/oxygen anions share an oxygen atom, forming a closed 3D structure. Owing to the high polarity of the surface, Keggin-type POM is regarded as a potential multifunctional material. Pang and co-workers successfully introduced a typical Keggin-type POM (i.e., H3PW13O40) to coat with ZIF-67 and then prepared the yolk/shell structure ZIF-67@POM hybrids (Figure 2e). The POM was dispersed on the exterior surface of ZIF-67 evenly. It can be found in SEM images that the primitive ZIF-67 displays a typical dodecahedron shape with a mean dimension of around 500 nm (Figure 2f), while 6-ZIF-67@POM (6 represents the time value in hours of the synthetic process) is irregular dodecahedron and has an average size of about 250 nm (Figure 2g). The inimitable yolk/shell structure of 6-ZIF-67@POM was further proved by TEM (Figure 2h).
2.1.3. Metal nanoparticles@MOFs

MNPs have drawn extensive attention in many fields, because of their special electronic structure and physiochemical features. However, MNPs have a high superficial area to bulk factor, and the excellent exterior energy usually brings about MNPs’ aggregation and fuse, which is adverse to maximizing their activities in specific applications. Assembling MNPs into porous materials (e.g., zeolites, mesoporous carbon, and metal oxides) could significantly suppress the accumulation of MNPs and then stabilize MNPs in a confined space. MOFs, as new porous materials which possess a large superficial area and well-organized pores and cavities, can serve as compatible supports to incorporate with MNPs to maximize their advantages.

Pang et al. successfully loaded Au NPs on ZIF-67 through a bottle-around-ship tactics, obtaining Au@ZIF-67 (Figure 3a). Thereinto, the constraint of ZIF-67 effectively suppressed the aggregation of Au NPs and then induced their uniform distribution. The synergetic effect between Au NPs and porous ZIF-67 in Au@ZIF-67 deeply enhanced their individual advantage and then improved the electrocatalytic activity. Even conducting thermal treatment on Au@ZIF-67, the Au NPs still dispersed homogeneously on the pyrolyzed ZIF-67, as presented in Figure 3b,c.[99] Xu’s group reported a composite (AuNRs@ZIF-8) synthesized via nucleus coalescence or epitaxial growth, in which the highly dispersed gold nanorods were encapsulated inside ZIF-8 with flying colors (Figure 3d).[100] The SEM image exhibited that the surface of the monodispersed ZIF-8 particles is smooth (Figure 3e). The TEM image clearly showed that the synthesized ZIF-8 had a polyhedral morphology with a mean dimension of 230 nm (Figure 3f). With the addition of AuNRs, the particle size range of AuNRs@ZIF-8 increased to about 400 nm, and the shape of the sample became atactic, along with the appearance of distinct dark nanorods, making clear the formation of core–shell nanostructures (Figure 3g). As displayed in the inset of Figure 3h, the medial length of AuNRs’ core was around 160 nm, and the width radius was 36 nm.

2.1.4. CP@MOFs

CPs, including polyanilines, polythiophenes, and polypyrroles, are kinds of organic materials possessing electronic

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**Figure 3.** a) The synthetic illustration of Au@ZIF-67 and Au@ZIF-67-x; b) SEM and c) TEM images of Au@ZIF-67-500. Reproduced with permission.[99] Copyright 2021, Springer Nature. d) Synthetic diagram of ZIF-8/AuNRs. Representative SEM and TEM images of e,f) ZIF-8 and g,h) AuNRs@ZIF-8. Reproduced with permission.[100] Copyright 2019, The Royal Society of Chemistry.
conductivity.\textsuperscript{[101]} CPs are usually prepared by chemical/electrochemical polymerizations of monomer.\textsuperscript{[102,103]} In view of the unique features of CPs, such as high thermal and chemical stability, high mechanical flexibility, and low density, the combination of CPs and MOFs is expected to produce new materials with high conductivities and activities.

Chen's group first incorporated conductive polypyrrole (PPY) into bimetallic organic framework (Zn/Ni-MOF) via an “oxidant-free additive” to construct SC electrodes (Zn/Ni-MOF@PPY) (Figure 4a).\textsuperscript{[104]} In Zn/Ni-MOF, the terephthalic acid and water molecules were coordinated with central metal Ni/Zn (Figure 4b). During the process of constructing Zn/Ni-MOF@PPY, Zn/Ni-MOF assisted the formation of PPY owing to the characteristics of Lewis acid, while PPY increased the interlamellar spacing of Zn/Ni-MOF and facilitated the charge transfer. What's more, the incorporation of PPY did not alter the flower structure of Zn/Ni-MOF, except that the surface of Zn/Ni-MOF@PPY became rougher (Figure 4c,d).

Duan and co-workers developed a viable one-pot electrodeposition method to design UiO-66/PPY hybrid which was coated on carbon fibers under the presence of dopamine (Figure 4e).\textsuperscript{[105]} The uniform coating of UiO-66/PPY on the carbon fiber was realized, as presented in Figure 4f,g. The PPY coated on the surface of UiO-66 was well served as the conductive link filled into the interparticle of UiO-66.

2.1.5. MOFs@MOFs

In view of the unique structural features of MOFs, covering one MOF on another MOF (namely assembling MOF@MOF composites) is a promising strategy to enhance the conductivity, hierarchical porosity, activity, and stability of MOF composites. This strategy will greatly expand the structural complexity and induce the synergetic effect beyond individual MOFs. For this, core—shell and hollow structures have attracted considerable attention due to the promising properties.\textsuperscript{[106]}

Yamauchi and co-workers designed and prepared core—shell-structured ZIF-8@ZIF-67 using a seed-mediated growth method (Figure 5a).\textsuperscript{[107]} In the core—shell structure, white ZIF-8 crystals with good dispersity and uniform diameter were selected as the seeds. With the addition of Co\textsuperscript{2+} and 2-methylimidazole, bright purple ZIF-67 shells were covered outside ZIF-8 crystals, obtaining the uniformly dispersed ZIF-8@ZIF-67 with rhomboid dodecahedron (Figure 5b–d). The thickness of ZIF-67 shell could be turned as reflected by the color of ZIF-8@ZIF-67. For comparison, the construction of ZIF-67@ZIF-8 was attempted in the

![Figure 4. a) Synthetic diagram of Zn/Ni-MOF@PPY; b) wireframe diagram of Ni-MOF along axis α; and the SEM images of c) Zn/Ni-MOF and d) Zn/Ni-MOF@PPY. Reproduced with permission.\textsuperscript{[104]} Copyright 2017, The Royal Society of Chemistry. e) Instructions for synthesis of UiO-66/PPY; the SEM images of f) carbon fibers and g) UiO-66/PPY-coated carbon fibers. Reproduced with permission.\textsuperscript{[105]} Copyright 2018, American Chemical Society.](image-url)
identical protocol, but no core–shell structures were obtained, likely because of the rapid nucleation reaction of ZIF-8. Oh et al. prepared a leaf-shaped core–shell hybrid MOF (ZIF-L@ZIF-67) using ZIF-L as the seeds (Figure 5e). The growth of ZIF-67 shells on the external surface of ZIF-L did not alter the shape of ZIF-L, except that the thin flats became rougher (Figure 5f,g). Huang et al. chose a simple ultrasonication-assisted stepwise synthesis method to prepare Ni-MOF@Fe-MOF hybrids (Figure 5h). The flexible ultrathin Ni-MOF nanosheets were prepared for the first time, whose morphology and good dispersity enable its further decoration with Fe-MOF nanosheets by the in situ coordination of Fe³⁺ and terephthalic acid (H₂BDC) (Figure 5i,j). The introduction of Fe-MOF NPs on the ultrathin 2D Ni-MOF nanosheets brought about the enhanced activity of Ni-MOF@Fe-MOF toward OER.

2.1.6. Others

Apart from designing MOF composites, thermal transformation, and partial derivative strategy of MOFs as described earlier, many other methods can also be used to enhance the electrochemical performance of MOFs. For example, one can combine MOFs with functional materials different from those mentioned earlier.

Su’s group prepared a heterogeneous MOF, A₂₋₋B-MOF-FeCo₁₋₋₋, through assembling metal, terephthalic acid (A), and 2-aminoterephthalic acid ligands (B) (Figure 6a). The team chose MIL-88B-Fe and benzoic acid ligands with 1D channels and good stability as the matrix and substituted Fe³⁺ in MIL-88B with Co²⁺ to synthesize bimetallic MOFs. The morphology of A₂₋₋B-MOF-FeCo₁₋₋₋ was represented via SEM and TEM, and the uniform rod-like morphology was found (Figure 6b,c).

In addition, MOFs can also be combined with Co(OH)F to improve the electrochemical performance. Luo’s group synthesized Co(OH)F precursors by hydrothermal method, converted Co(OH)F by vapor phase, and generated Co(OH)₂ coating on Co(OH)₂ surface by in situ cathodic electrodeposition (Figure 6d). SEM images of Co(OH)F showed smooth needle-like and brush-like structures. After annealing with imidazole at 300 °C in Ar atmosphere, Co(OH)F was successfully transformed into Co(MOF). The SEM images showed that the nanorods were replaced by smooth nanorods, and the brush-like structure was maintained well (Figure 6e). TEM images further demonstrated the smooth nanorod structure of Co-MOF. SEM (Figure 6f) and TEM (Figure 6g–i) images showed that Co(OH)₂ nanosheets were coated on the appearance of Co-MOF.

2.2. Thermal Transformation

MOFs are characterized by the large specific surface areas, high porosity, and tunable functionality. However, in the specific applications, the performances of MOFs are restricted due to the limited active sites. To this end, rational thermal transformation was applied on MOFs on the premise of preserving MOF structures, which could remove the solvent/water molecules or partial ligands and bring about more exposed active sites. As a result, controlled calcination strategies are performed on MOFs, and the end-products with more active sites and high porosity are promising materials for facilitating the electrochemical process.
Pang et al. assembled straw-bundle-like quasi-Ce-MOF composites via a rational two-step method (Figure 7a). In this process, straw-bundle Ce-MOF precursor was prepared via one-step precipitation, and Ce-MOF was directly heated in nitrogen atmosphere at 350°C for 1 h. Partial pyrolysis of Ce-MOF was achieved and the quasi-MOF material (Ce-MOF-350) was formed through the calcining process. As shown in Figure 7b,c, Ce-MOF-350 maintained the morphology of Ce-MOF without agglomeration or cracking. With the guidance of this strategy, Pang’s team also synthesized a series of quasi-ZIF-67 via calcining ZIF-67 under low temperature (Figure 7d). In the pristine ZIF-67, two facets of (002) and (011) were presented, while only (002) can be observed in quasi-ZIF-67-350 (Figure 7e–h), indicating the formation of more exposed metal sites, which could be ascribed to the loss of sectional ligands during the process of calcine.

2.3. Partially Derivative Strategy

MOF derivatives refer to hybrid materials where MOFs, as precursors/templates, are transformed into metal compounds (or metals) and other materials through simple annealing and other processes. In this part, it is introduced that only part of MOFs is transformed by simple annealing and other strategies, while the remaining part still keeps the structure of MOF material unchanged.

Wang and co-workers first designed coordinately unsaturated metal sites (CUMSs) in ZIF-67 via dielectric barrier discharge (DBD) plasma-etching method (Figure 8a). As shown in Figure 8b–e, the dodecahedral ZIF-67 possesses smooth surface. After the treatment of DBD plasma etching, CUMSs-ZIF-67 maintains the morphology of ZIF-67, except that its surface became rougher and draped. Recently, Yu’s group found that carbon—nitrogen vacancies (VCN) can be achieved by N₂ plasma bombardment, where ionized nitrogen plasma can break the Fe—CN—Ni units in the Ni—Fe Prussian blue analogue (PBA), creating an unconventional carbon—nitrogen vacancy (VCN) (Figure 8f). In the process of creating VCN, NiMoO₄ nanorods were used as templates to construct 1D K₂NiFe(CN)₆ PBAs. After N₂ plasma bombardment, PBA-60 displayed a rod-like structure with jagged edges and was composed of a number of interconnected cubes (Figure 8g).

In addition to the above partially derivative methods, the electrochemical properties of MOFs can also be improved by partial phosphating. Yin and co-workers proposed steerable fractional phosphorylation tactics for generating CoP species in Co-based MOFs. The end-product CoP/Co-MOF/CF was synthesized via sequential process, involving the hydrothermal deposition of Co(OH)F, transformation of Co(OH)F to Co-MOF, and partial phosphorylation of Co-MOF (Figure 8h). As shown in SEM images, CoP/Co-MOF maintains the microstructure of nanorods, whereas the surface was rougher than that of Co-MOF (Figure 8i).

To improve the capacitance, Wei and co-workers synthesized a sequence of layered structural Zn-doped Ni-MOF with diverse dosages of ZnCl (i.e., MOF-0, MOF-1, MOF-2, MOF-3) (Figure 9a). As presented in SEM and energy-dispersive X-ray (EDX) spectroscopy, with the addition of Zn²⁺ ions, the flower-like microspheres were prepared, and the dimension of microspheres grew with the increase in Zn²⁺ ions (Figure 9b–i).

On the basis of zinc doping, Chen’s group reported a method to partially replace Ni²⁺ in Ni-MOF with Co²⁺ or Zn²⁺ to improve the conductivity of MOFs (Figure 9j). Both Co/Ni-MOF and Zn/Ni-MOF retained the original crystal topology of Ni-MOF. It can be clearly observed by SEM images that the flower-like structure of Co/Ni-MOF and Zn/Ni-MOF consists of many nanosheets with relatively smooth surfaces (Figure 9k–l).

2.4. Summary

Several advanced synthetic strategies of modified MOFs in recent years, including MOF composites, thermal transformation, and partial derivatization, were comprehensively introduced earlier.
Figure 7. a) Synthetic illustration of bundle Ce-MOF. SEM images of b) Ce-MOF and c) Ce-MOF-350. Reproduced with permission.[112] Copyright 2020, American Chemical Society. d) Synthetic illustration of quasi-ZIF-67; aberration-corrected TEM images of e,f) ZIF-67 and g, h) quasi-ZIF-67-350. Reproduced with permission.[113] Copyright 2020, American Chemical Society.

Figure 8. a) Synthetic illustration of CUMSs-ZIF-67; SEM images of b) ZIF-67 and c) CUMSs-ZIF-67; TEM images of d) ZIF-67 and e) CUMSs-ZIF-67. Reproduced with permission.[114] Copyright 2017, Elsevier. f) Schematic illustration of VCN-mediated Ni-Fe PBA. g) TEM image of PBA-60. Reproduced with permission.[115] Copyright 2019, Springer Nature. h) Synthetic scheme of CoP/Co-MOF/CF. i) SEM image of CoP/Co-MOF/CF. Reproduced with permission.[116] Copyright 2019, Wiley-VCH.
These methods improve the electrochemical performance of MOF materials by increasing the exposure of active sites, while keeping the structure of MOFs unchanged.

3. Applications

In recent decades, modified MOFs have been extensively used in electrochemical fields such as batteries, SCs, and electrocatalysis, due to their high specific surface areas, large and clear pore structures, and uniformly distributed active sites.\[87–90, 119–121\] In this section, electrochemical application of modified MOFs is discussed with emphasis on: 1) how to enhance the performance of modified MOFs by designing their morphologies and structures rationally and 2) the advantages of modified MOFs in specific electrochemical applications compared with other materials.\[83,118,122–130\]

3.1. Modified MOFs for Electrochemical Energy Storage

In past decades, environmental pollution and resource shortages are becoming increasingly serious. In energy storage and conversion systems, SCs with high power density and batteries with high energy density are potential candidates.\[131–136\] In this part, we will introduce the performance of modified MOF materials, which were as electrode materials for batteries and SCs.\[137–147\]

3.1.1. Batteries

Batteries, including Li–O\(_2\) batteries, lithium-ion batteries (LIBs),\[148,149\] and lithium–sulfur batteries (LSBs),\[127,150\] are investigated in portable electronic devices as a result of their environmental protection, high energy density, and long cycle life. MOFs are identified as potential candidate materials for electrode because of their flexible structure, low cost, and strong redox activity. In this section, we will introduce the excellent properties of modified MOF materials used as battery electrodes.

Wu’s group prepared a composite membrane MOF/PAN by electrostatic spinning which uses polyacrylonitrile (PAN) and MOF materials as raw materials and demonstrated that Co-SIM-1/PAN can be used to improve the efficiency of lithium-ion batteries.\[151\] Co-SIM-1 belongs to ZIF materials and possesses an average particle size of 0.76 \(\mu\)m (Figure 10a). The SEM image shows that the electrospun PAN fiber is relatively smooth (Figure 10b), while the 10% Co-SIM-1/PNA composite fiber is much rougher. The MOF loaded with PAN has two states: one is wrapped around PAN to increase the diameter of fiber and the other is embedded in the fibers (Figure 10c). The cross section of 10% Co-SIM-1/PNA film shows that Co-SIM-1 is embedded in the film (Figure 10d). After the addition of MOF material, lithium-ion transference number (\(t_{Li^+}\)) of the composite increases because MOF can adsorb more electrolytes in the surfaces and pores and fix the anions by the unsaturated metal sites at the same time (Figure 10e). After using four different separators to package NCM811||separator||Li batteries, the cycles and rate performances demonstrated that NCM811||separator||Li battery packaged with 10% Co-SIM-1/PNA has higher capacity than any other separators (Figure 10f). The discharge capacity of batteries assembled by 10% Co-SIM-1/PNA decreases during the process of cycling (Figure 10g). Meanwhile, the battery has distinguished cyclic stability after 250 cycles (Figure 10h).
Except for the Li-ion battery, Li–S battery is also a potential rechargeable energy conversion and storage system due to its high theoretical specific capacity and richness of sulfur on the earth. However, the adhesion of Li–S batteries is hindered via the shuttle effect, which is generated at the cathode, usually bringing about the leakage of active material and decrease of cycle life. For the sake of resolving the problem, Pang et al. proposed tactics to introduce sulfur-friendly metal ions (Cu²⁺) into Al-MOF (i.e., (Al)MIL-53), thus constructing bimetallic MOF (i.e., Al/Cu-MOF) as the host material for sulfur in Li–S batteries (Figure 11a). The distinct reduction peaks on cyclic voltammetry (CV) curves are related to the conversion of S₈ to polysulfides (Figure 11b). The comparison of galvanostatic charge/discharge (GCD) curves among S-Super P, Al-MOF-S, and Al/Cu-MOF-S electrodes indicated that the specific capacity of Al/Cu-MOF-S is higher than that of Al-MOF-S (Figure 11c,d). Further, the high performance of Al/Cu-MOF-S in Li–S battery was confirmed by the high rate performance and small charge-transfer resistance (Figure 11e–g). The incorporation of Cu²⁺ demonstrated that chemical fixation is a favorable means for the adsorption of polysulfide in Li–S batteries.

MOF materials with excellent oxygen accessibility and abundant open metal sites are expected to strengthen the efficiency of Li–O₂ batteries.

Compared with Co-MOF-74 and Mn-MOF-74, the bimetallic MnCo-MOF-74 exhibits higher efficiency and reversibility in charge–discharge cycles. This is mainly due to the porous structure of MOFs and the complementary contributions of Co– and Mn–metal clusters. The microstructure of M-MOF-74 was characterized by SEM, and it was found that the samples of M-MOF-74 were hexagonal crystals, which grew straight in one orientation and the bimetallic MnCo-MOF-74 had the same nanorod structure with the single-metal Co-MOF-74 and Mn-MOF-74 (Figure 12a–c). The curves of charge and discharge of MnCo-MOF-74 at 200 mA g⁻¹ show that the charge and discharge capacity of MnCo-MOF-74 is 11 150 mA h g⁻¹, which is much higher than that of Mn-MOF-74, Co-MOF-74, and mixture-MOF-74 (Figure 12d). As shown in Figure 12e, compared with other electrodes, MnCo-MOF-74 maintained the minimum charging terminal voltage and the maximum discharge terminal voltage indicating that OER and ORR dynamics were improved. In the cycle test, MnCo-MOF-74 provided the termination discharge capacity of 1000 mA h g⁻¹ for 44 times at the rate of 200 mA g⁻¹ stably, which was significantly longer than Co-MOF-74 and Mn-MOF-74 whose cycle index was 22 and 18 times severally (Figure 12f–g). The performance of bimetal MnCo-MOF-74 is better than that of single-metal Co-MOF-74 and Mn-MOF-74. This is due to the synergism of Co– and Mn–metal clusters. MnCo-MOF-74 improves the
conformation of ORR discharge products, which are hastily resolved in OER discharge. This synergistic effect improves the efficiency and reversibility of Li–O₂ cathode. The feasibility of regulating catalytic activity by multifunctional MOFs is thus proved.

3.1.2. SCs

SCs, which are known as electric double-layer SCs, are electrochemical components that store energy through polarized electrolytes. They have high power density and can be used for regenerative braking, short-term energy collection, and burst power supply,[131–134,154] where carbon is usually used. However, SCs have low physical energy density and charge storage. In the past several years, modified MOFs have revealed outstanding advantages and potential in this field because of their outstanding conductivity, high surface specific area, and uniform pore size distribution.[135]

Chen's group combined conductive polypyrrole (PPY) with a bimetallic organic framework to fabricate a high-property electrode (Zn/Ni-MOF@PPY).[104] A coin-type hybrid SC (HSC) was assembled with Zn/Ni-MOF@PPY as the anode, while CNTs-COOH was the cathode. The 2D layered structure of Zn/Ni-MOFs furnishes adequate space for transferring OH⁻/C₃O₂. The PPY chains raise the spacing between Zn/Ni-MOFs layers and also offer a charge transport channel (Figure 13a). The HSC is evaluated at various potential windows, and the results indicate that potential windows can attain 1.4 V without significant polarization (Figure 13b). The shape of CV curves was maintained even at high scan rates, revealing that the system had small resistance and excellent rate performance (Figure 13c). The low internal resistance of HSC was confirmed.

Figure 11. a) Synthetic scheme of Al/Cu-MOF-S; b) CV curves of Al/Cu-MOF-S electrode; the GCD of c) Al-MOF-S and d)Al/Cu-MOF-S-S at 0.1 C; e) comparison of specific capacities of Al-MOF and Cu-MOF with different Cu²⁺ contents; f) rate performances and coulombic efficiencies of Al-MOF-S and Al/Cu-MOF-S-S; and g) Nyquist plots of Al-MOF-S and Al/Cu-MOF-S-S electrodes. Reproduced with permission.[152] Copyright 2021, Wiley-VCH.
Figure 12. SEM images of: a) Mn-MOF-74, b) Co-MOF-74, c) MnCo-MOF-74; d) constant current full discharge and charge–discharge characteristics of KB, Mn-MOF-74, Co-MOF-74, mixture-MOF, and MnCo-MOF-74; e) terminal voltage and cycle number of electrode; f) discharge capacity and g) charge capacity cycle index of the electrodes. Reproduced with permission.[153] Copyright 2018, American Chemical Society.

Figure 13. a) Energy storage mechanism of coin-type hybrid SCs; b,c) CV curves of the HSC; d) charge–discharge curves of Zn/Ni-MOF@PPY; e) Ragone diagram of HSC devices in comparison with reported HSCs. Reproduced with permission.[104] Copyright 2017, The Royal Society of Chemistry. f) CV curves for CFs@UIO-66/PPY; g) constant current charge–discharge curves of CFs@UIO-66/PPY; h) CFs@UIO-66/PPY measures the cycle stability at 100 mV s⁻¹. Reproduced with permission.[105] Copyright 2018, American Chemical Society.
by low IR drops displayed in the charge–discharge curves (Figure 13d). In addition, the Ragone graphic of the HSC illustrated the relation between power density and energy density (Figure 13e) when the power density reached 699 W kg\(^{-1}\); the great potential of the designed hybrid SC is further demonstrated.

Duan’s group designed CFs@UiO-66/PPY composites to assemble all-solid-state fiber SCs. When the scanning rates increased from 5 to 100 mV, the length capacitance of CFs@UiO-66/PPY decreased from 15 to 8 mF cm\(^{-1}\) (Figure 13f) and the weight capacitance was reduced from 90 to 50 g F\(^{-1}\).\(^{[105]}\) The charge–discharge curves at diverse current densities ranging from 50 to 400 \(\mu\)A cm\(^{-1}\) presented the capacitive behavior of CFs@UIO-66/PPY (Figure 13g). At the same time, the CFs@UiO-66/PPY fiber electrode also showed stabilized cycling performance after 1000 cycles (Figure 13h).

### 3.2. Modified MOFs for Electrocatalysis

**ORR, OER, and HER**\([21,136,148]\) are three essential reactions in the technologies of energy storage and conversion. To improve energy conversion efficiency, high-efficiency electrocatalysts are urgently needed to reduce the overpotential of these reactions.\([69]\) Modified MOFs as promising candidates have been widely investigated in HER, OER, and ORR.

#### 3.2.1. OER & HER & ORR Electrocatalyst

ORR, OER, and HER are three crucial reactions in the evolution of green and sustainable energy systems. ORR is the cathode reaction occurring in hydrogen fuel cells and metal–air cells, OER is the reverse process of ORR, and HER is a typical reaction of double-electron transfer reaction. Drawn on the advantages of both original MOF materials and typical electrocatalytic materials, modified MOFs have exhibited unique structures and low overpotentials, which make it the most ideal materials with the greatest potential in the field of electrocatalysis.

Pang’s group reported a high-efficiency ZIF-67@POM electrocatalyst with yolk/shell structure (Figure 14a).\(^{[94]}\) The distinctive yolk/shell structure and the synergistic effect of structures and components endow ZIF-67@POM with high activity for OER. As shown in Figure 14b, ZIF-67@POM exhibits a lower onset potential and a fast increase in current density, and its Tafel slope (58 mV dec\(^{-1}\)) is among the smallest of all the hybrids (Figure 14c). Therefore, these results are even comparable with those of commercial RuO\(_2\). In addition to improving activity, the yolk/shell structure also heightens the long-term durability of ZIF-67@POM and its activity slightly decreases after 1000 CV cycle (Figure 14d). In addition, Au NPs loaded with ZIF-67 (i.e., Au@ZIF-67) were also constructed by Pang et al. and the composite showed improved OER activity compared with ZIF-67.\(^{[99]}\) Furthermore, taking Au@ZIF-67 as a precursor, thermal treatments were carried out under different temperatures, and a series of Au@ZIF-67-T (T denotes the temperature) were obtained. Among them, Au@ZIF-67-500 achieves remarkable OER performance with smaller Tafel slope, lower overpotential, and lower charge transfer resistance (\(R_{ct}\)) (Figure 14e–h). The improved OER catalytic activity is attributed to Au NP loading, porous frameworks, and induced Co reduction thermally.

Besides OER, modified MOFs are expected to present excellent electrocatalytic performance for HER. Recently, Yin’s group exploited staged phosphating tactics to coat CoP species on top of Co-based MOF (Co-MOF) outer coatings. (Figure 15a,b). The obtained CoP/Co-MOF exhibits remarkable HER activity with
an overpotential of 49 mV (@10 mA cm\(^{-2}\)) in neutral media (PBS, pH = 7.0) (Figure 15c). Furthermore, the high efficiency of CoP/Co-MOF was demonstrated by a smaller Tafel slope (Figure 15d), lower \(R_{ct}\) (Figure 15e), and larger double-layer capacitance (\(C_{dl}\)) (Figure 15f). The long-term stabilization of CoP/Co-MOF was presented via repeated CV cycles

Figure 16. TEM images of a) MOF(Fe) and b) e-MnO\(_2\)/MOF(Fe) (inset: HRTEM image of e-MnO\(_2\)); c) SEM image of e-MnO\(_2\)/MOF(Fe); d) ORR activity of e-MnO\(_2\)/MOF(Fe) with various e-MnO\(_2\) loadings with O\(_2\) in 0.1 M KOH saturated at 1600 rpm; e) CV curves of e-MnO\(_2\)/MOF(Fe) composites at 50 mV s\(^{-1}\) in 0.1 M KOH solution saturated with N\(_2\) or O\(_2\); f) ORR activity of specimens in O\(_2\)-saturated 0.1 M KOH solution (a: MOF(Fe), b: e-MnO\(_2\), c: e-MnO\(_2\) + MOF(Fe), d: e-MnO\(_2\)/MOF(Fe), e: 20% Pt/C). Reproduced with permission.\(^{[162]}\) Copyright 2015, The Royal Society of Chemistry.
The excellent HER property of CoP/Co-MOF was put down to the distinct porous structure of Co-MOF and efficient synergy between CoP and Co-MOF, which not only furnished with more active sites, but also facilitated the release of generated gas.

Yin’s group designed and synthesized $\varepsilon$-MnO$_2$/MOF(Fe) carrier via combining $\varepsilon$-MnO$_2$ with MOF(Fe) carrier.$^{[162]}$ The pristine MOF(Fe) presented a particle microstructure with a mean dimension of about 400–500 nm (Figure 16a). After introducing $\varepsilon$-MnO$_2$, the morphology of MOF(Fe) remained intact, and new protruding nanorods emerged with one anchoring on the MOF(Fe) substrate firmly (Figure 16b,c). Using $\varepsilon$-MnO$_2$/MOF(Fe) as ORR catalyst in alkaline electrolyte, the protruding nanorods, high specific surface area, and ample micropores synergistically facilitated the diffusion of oxygen and its close contact with $\varepsilon$-MnO$_2$ in the ORR process, which demonstrates that ORR activity and stability is better than those of $\varepsilon$-MnO$_2$ and $\varepsilon$-MnO$_2$ + MOF(Fe). Specifically speaking, $\varepsilon$-MnO$_2$/MOF(Fe) with Mn content of 9.57% displayed the best ORR performance, as proved by CV curves and ORR polarization curves (Figure 16d–f).

3.2.2. Multifunctional Electrocatalyst

HER, OER, and ORR are fundamental half reactions in many energy technologies, for example, electrocatalytic water splitting, fuel cells, and metal–air batteries. Given the good performance of modified MOFs in HER/OER/ORR, it is greatly expected that they can be used as bifunctional/trifunctional electrocatalysts, which will not only simplify the material preparation process and reduce costs, but also promote energy conversion and device integration.

Wang’s group synthesized the bimetallic ZnCo-ZIF@GO (Figure 17a) via the in situ growth method, which shows good ORR and OER electrocatalytic activity in alkaline solution.$^{[81]}$ The property of ZnCo-ZIF@GO in ORR and OER was evaluated in 0.1 and 1.0 m KOH severally. The half-wave potential of ZnCo-ZIF@GO was found to be 0.76 V, which is more positive than that of ZnCo-ZIF (0.57 V) and GO (0.71 V) (Figure 17b). The time–current test was used to study its electrochemical stability. After 30 000 s, the initial value of ZnCo-ZIF@GO catalyst was found to decrease slightly, while that of ZnCo-ZIF catalyst decreased significantly, which indicates that the electrochemical stability of ZnCo-ZIF@GO was better. The interaction of ZnCo-ZIF and graphene oxide flakes can improve the durability of the material (Figure 17c). In addition to good ORR properties, LSV curves of ZnCo-ZIF@GO, ZnCo-ZIF, and GO at 90% IR compensation show that the potential ($E_{10}$) required by ZnCo-ZIF@GO is only 1.66 V to reach the current density of 10 mA cm$^{-2}$, which is lower than the potential required for ZnCo-ZIF and GO (Figure 17d). Meanwhile, ZnCo-ZIF@GO also shows excellent OER performance with lower overpotential (at 10 mA cm$^{-2}$) of 430 mV and smaller Tafel slope of 83 mV dec$^{-1}$ (Figure 17e).

Figure 17. a) SEM image of ZnCo-ZIF; b) ORR polarization curves of ZnCo-ZIF@GO, ZnCo-ZIF, and GO at O$_2$ saturation 0.1 M KOH (1600 rpm); c) current–time curves of ZnCo-ZIF and ZnCo-ZIF@GO for ORR; d) OER polarization curves of ZnCo-ZIF@GO, ZnCo-ZIF, and GO at 90% IR compensation; e) overpotential values of ZnCo-ZIF, GO, and ZnCo-ZIF@GO (at 10 mA cm$^{-2}$). Reproduced with permission.$^{[81]}$ Copyright 2020, The Royal Society of Chemistry. SEM images of f) (GO 8 wt%) Cu-MOF and g) (GO 20 wt%) Cu-MOF; h) cyclic voltammograms of 10 mM Fe(CN)$_6^{3/-4}$ in 1.0 M KCl with diverse samples loaded on the glass carbon electrode; i) N$_2$ adsorption isotherms of diverse samples at 77 K; j) cyclic voltammograms of the catalysts dropped on GC in 0.5 M H$_2$SO$_4$; k) HER polarization curves, l) Tafel plots derived from the HER polarization curves; m) OER polarization curves; n) comparison of ORR performance of different catalysts. Reproduced with permission.$^{[80]}$ Copyright 2013, Wiley-VCH.
Table 1. Application of modified MOFs.

| Materials                  | Preparation strategies                      | Reaction conditions                      | Applications                  | Performance                          | Ref. |
|----------------------------|--------------------------------------------|------------------------------------------|------------------------------|--------------------------------------|------|
| Cu-MOF@GO                  | Carbon-based materials@MOFs                | Hydrothermal reaction                    | HER OER ORR                  | \( \eta_{\text{HER,10 mA cm}^{-2}} = -0.209 \text{ V in 0.5 M H}_2\text{SO}_4 \) Tafel slop: 84 mV dec\(^{-1}\) OER: \( \eta_{2 \text{mA cm}^{-2}} = 1.34 \text{ V in 0.5 M H}_2\text{SO}_4 \) Tafel slop: 65 mV dec\(^{-1}\) | [80] |
| ZnCo-ZIF@GO                | Carbon-based materials@MOFs                | In situ growth                            | OER ORR                     | \( \eta_{10 \text{mA cm}^{-2}} = 760 \text{ mV in 0.1 M KOH } \) Tafel slop: 83 mV dec\(^{-1}\) | [81] |
| PANI-ZIF-67-CC             | Carbon-based materials@MOFs                | Electropolymization of aniline            | SCs                          | Specific capacity: 371 F g\(^{-1}\) at 10 mV s\(^{-1}\) Capacity retention: over 80% after 2000 cycles at 0.1 mA cm\(^{-2}\) | [82] |
| CoO\(_2\)@Co-MOF           | Metal oxides@MOFs                          | High alkalinity                           | SCs                          | Specific capacity: 1020 F g\(^{-1}\) at 0.5 A g\(^{-1}\) Capacity retention: 3.3% decay after 5000 cycles at 5 A g\(^{-1}\) | [93] |
| 6-ZIF-67@POM               | Metal oxides@MOFs                          | One-pot mechanochemical synthesis        | OER                          | \( \eta_{10 \text{mA cm}^{-2}} = 287 \text{ mV in 1.0 M KOH } \) Tafel slop: 58 mV dec\(^{-1}\) | [94] |
| \( c \)-MnO\(_2\)/MOF(Fe)  | Metal oxides@MOFs                          | Autoclave at 180°C for 3 days            | ORR                         | \( \eta_{10 \text{mA cm}^{-2}} = 840 \text{ mV in 0.1 M KOH } \) Tafel slop: 58 mV dec\(^{-1}\) | [162]|
| Au@ZIF-67-500              | MNPs@MOFs                                  | Calcinated at 500°C                      | ORR                         | \( \eta_{10 \text{mA cm}^{-2}} = 367 \text{ mV in 1.0 M KOH } \) Tafel slop: 87 mV dec\(^{-1}\) | [99] |
| AuNRs@ZIF-8                | MNPs@MOFs                                  | At room temperature for 6 h              | OER                          | \( \eta_{10 \text{mA cm}^{-2}} = 287 \text{ mV in 1.0 M KOH } \) | [100]|
| Zn/Co-MOF@PPY              | CP@MOFs                                    | Stir vacuum drying in air at 80°C         | SCs                          | Specific capacity: 202.2 mA h g\(^{-1}\) at 1 A g\(^{-1}\) Cycling stability: 94.4% after 3000 cycles at 10 A g\(^{-1}\) Specific capacitances: 10 mF cm\(^{-2}\) at 5 mV s\(^{-1}\) Cycling stability: 89% after 10000 cycles at 200 µA cm\(^{-1}\) | [104]|
| CFs@U/O-66/PPY             | CP@MOFs                                    | One-pot electrodeposition method         | SCs                          | Specific capacitances: 270 F g\(^{-1}\) at 2 A g\(^{-1}\) Cycling stability: almost 100% after 10000 cycles at 5 A g\(^{-1}\) | [107]|
| ZIF-8@ZIF-67               | MOFs@MOFs                                  | At 100°C for 12 h                        | SCs                          | Specific capacitances: 1620 F g\(^{-1}\) at 0.25 A g\(^{-1}\), 854 F g\(^{-1}\) at 10 A g\(^{-1}\) Cycling stability: 91% after 1000 cycles at 2 A g\(^{-1}\) | [117]|
| Ni-MOF@Fe-MOF              | MOFs@MOFs                                  | At room temperature for 24 h             | ORR                         | \( \eta_{22 \text{mA cm}^{-2}} = 386 \text{ mV in 0.1 M KOH } \) Tafel slop: 48.7 mV dec\(^{-1}\) | [108]|
| quasi-ZIF-67-350           | Thermal transformation                      | Calcinated at 350°C                     | OER                          | \( \eta_{10 \text{mA cm}^{-2}} = 286 \text{ mV in 1.0 M KOH } \) Tafel slop: 84 mV dec\(^{-1}\) | [113]|
| CUMSSs-ZIF-67              | Partial derivative strategy                | Radiation at room temperature and pressure | OER                          | \( \eta_{10 \text{mA cm}^{-2}} = 410 \text{ mV in 0.5 M KBi } \) Tafel slop: 185.1 mV dec\(^{-1}\) | [114]|
| PBA-60                    | Partial derivative strategy                | Ultrasonic for 2 h                      | OER                          | \( \eta_{10 \text{mA cm}^{-2}} = 283 \text{ mV in 1.0 M KOH } \) Tafel slop: 54 mV dec\(^{-1}\) | [115]|
| CoP/Co-MOF/CF             | Partial derivative strategy               | Hydrothermal deposition Phosphorization | HER                          | \( \eta_{10 \text{mA cm}^{-2}} = 49 \text{ mV in 1.0 M KOH } \) Tafel slop: 63 mV dec\(^{-1}\) | [116]|
| Zn-doped Ni-MOF           | Partial derivative strategy                | Autoclave at 100°C for 8 h              | SCs                          | Specific capacitances: 236.1 F g\(^{-1}\) at 1 A g\(^{-1}\), 195.6 F g\(^{-1}\) at 10 A g\(^{-1}\) Cycling stability: 82.8% after 3000 cycles at 10 A g\(^{-1}\) | [118]|
| CoNi-MOF                  | Partial derivative strategy               | Autoclave at 120°C for 16 h             | SCs                          | Specific capacitances: 202.2 mA h g\(^{-1}\) at 1 A g\(^{-1}\), 1620 F g\(^{-1}\) at 10 A g\(^{-1}\) | [119]|

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Loh and co-workers found that composite materials of GO and MOFs (Figure 17f–g) showed outstanding catalytic properties in ORR, OER, and HER.\cite{86} According to the CV curves, the incorporation of GO increased the electroactive surface area of the composites and then efficiently enhanced its charge transfer kinetics (Figure 17h–i). In addition, as evidenced by the N\(_2\) adsorption isotherms in Figure 17i, the addition of GO also increased the specific surface area of the composites. The trifunctional activity of GO-incorporated Cu-MOF composite in HER, OER, and ORR was estimated in acidic media, as shown in Figure 17k–n. The smaller the overpotentials, the greater the current and the better the stability of the composite materials, which are as a result of the untouchable porous structure, enhanced charge transfer capacity, and the cooperative effects between GO and Cu-MOF.

### 3.3. Summary

The increasing demand for renewable and clean energy has prompted the world to seek efficient energy technologies, which is expected to be both economically sustainable and environmentally friendly. HER is a significant kinetic process for production of hydrogen, which has the potential to replace fossil fuels. In the same way, efficient ORR and OER are essential for renewable energy platforms, especially for rechargeable batteries and fuel cells. Currently, the main task is to develop a practical, economic, and feasible electrocatalyst with enhanced performance and high stability. The excellent performances of MOFs as a reaction catalyst have been introduced hereinafter. It can be used not only as a certain reaction catalyst, but also as a catalyst for many reactions at the same time through some designs, so as to achieve the effect of high efficiency and cleaning (Table 1).

### 4. Conclusion and Outlook

In conclusion, this article reviews an overview of the recent development of modified MOFs on the rational design and their corresponding electrochemical applications in batteries, SCs, and electrocatalysis. The electrochemical properties and applications of MOFs are reviewed from the prospects of composites, functional materials, heat treatment, and partial derivation. In recent decades, the applications of MOFs as electrode materials in energy fields, for example, batteries and SCs, have become a flash topic in material science. Literature has introduced how to enhance the electrochemical performance of MOFs via combining MOFs with functional materials like carbon base, MNPs, metal oxides or CPs, or heat treatment or partial derivatives of MOFs materials, so as to solve the social problems of environmental pollution and resource shortage. Generally speaking, by combining the advantages of functional materials with the disadvantages of MOF materials, MOF composites obtain new physical and chemical performance and ameliorate properties that cannot be achieved by single components. In addition, heat treatment of MOF materials usually improves the electrochemical activity while retaining the porosity to achieve mass transfer. In the case of incomplete decomposition of the skeleton, modification of MOFs can reveal catalytic accelerate electron transfer and active metal sites, thus ameliorating the electrochemical function of the materials. The partial derivation of MOF materials is usually achieved by changing the electrochemical function of the materials to achieve better electrochemical performance.

MOF materials can also ameliorate the electrochemical capability of materials without derivatives or changing their structure, which have already been applied to the electrodes of batteries and SCs and been used as catalysts for HER, OER, and ORR. Improving the electrochemical performance of materials based on nonderivative MOFs remains in its initial phase and many challenges remain to be solved. The future researches are as follows. 1) MOF materials can be combined with MNPs, metal oxides, carbon-based materials, CPs, and other functional materials so as to obtain modified MOFs that will have a broad application in the future. 2) Alternative methods for large-scale syntheses of chemically and thermally stable porous MOFs are...
urgently needed. 3) The properties of functional materials with MOFs are of great importance to the construction of composite structures and the properties of composite materials. 4) Further research is needed to be done in combining more multifunctional materials with MOFs. 5) Exposure to active sites helps to enhance the electrochemical capability of MOF materials, but how to increase it while not changing the structures of MOF materials remains a challenge. 6) After some processing, MOF materials can be used as electrode material to raise the electrochemical properties, but the electrochemical stability of the material is poor. Repeated charge and discharge cycles can lead to the destruction of the structure and the decrease in electrochemical stabilities. Therefore, exploration and evolution of new electrode materials with high-capacity function is still a topic worth thinking about. 7) After certain treatments, MOF materials can be used as a high-performance catalyst in ORR, HER, or OER. However, to efficiently use MOF materials, more researches are needed to be done before MOFs can be used as multifunctional catalysts for all the three reactions. 8) In SCs, the poor conductivity of MOF materials leads to low specific capacitance, low power density, and poor cycle stability problems. Therefore, it is imperative to raise the conductivity of MOF materials. 9) The most attractive aspects of MOF materials are their high porosity and high specific appearance area, which can promote electrolyte penetration, reduce volume conversion, and improve the forthputting of active materials in batteries. Nonetheless, in practical adhibition, due to the high porosity of the electrode material and low volume energy density and coulombic efficiency, adjusting the porosity of the MOFs electrode is of great significance to optimize the volume energy density, coulombic efficiency, and rate capacity. 10) It is a feasible method to combine micro-/nano-MOFs with special morphology with conductive materials such as functional carriers, including graphene and metal foams. Such carriers can quicken electron carriage, promote electrolyte diffusion, and enhance the durability and reliability of MOF materials. 11) The stability and conductivity of MOF electrode materials could also be enhanced through functional modification, which is to graft desired groups/atoms onto organic linkers metal or ions/clusters. Through researchers’ efforts, some new electronically conductive MOFs have been produced, which will greatly promote the direct use of MOFs as electrochemical electrodes.

In recent decades, MOF materials, as a kind of star-based materials, have shown great momentum of growth in electrochemistry despite various challenges. However, as for the practical applications of non-derived MOF materials, such as being used in batteries, ultracapacitors, or as the catalysts in OER, HER, and ORR, there remains a long way to go.

Acknowledgements

K.C. and X.L.W. contributed equally to this work. This work was supported by the National Natural Science Foundation of China (NSFC-U1904215), the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), Natural Science Foundation of Jiangsu Province (BK20200044), Program for Young Changjiang Scholars of the Ministry of Education (Q2018270), Guangdong-Hong Kong-Macao Joint Laboratory (grant no. 2019B121205001), the Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX20_2805), and Excellent doctoral dissertation of Yangzhou university. X-ray absorption spectroscopy (XAS) measurements were performed at the SXRMB beamline of Canadian Light Source, which is supported by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council (NSERC), the National Research Council (NRC), the Canadian Institutes of Health Research (CIHR), the Government of Saskatchewan, and the University of Saskatchewan. The authors thank Drs. Mosenh Shakouri and Yongfeng Hu for technical support. The authors also thank Supercomputing Centres, the National Supercomputing Center in Shenzhen, and the National Supercomputing Center in Guangzhou for providing computational resources.

Conflict of Interest

The authors declare no conflict of interest.

Keywords
electrocatalysis, electrochemical energy storage, modified metal—organic frameworks

Received: November 9, 2021
Revised: January 12, 2022
Published online: February 10, 2022

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