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Metal-organic framework nanoparticles for catalytic electrodes in metal-air batteries

A. Ghafari [a,b], B. Akhoundi [c], S. Akbari [a,b,d] *

[a]*NanoSciTec GmbH, Hermann Weinhauser str. 67, Munich, 81867, Germany*
[b] *BioMedEx GmbH, weyringerg 37 Stiege 1, 1040, Vienna, Austria*
[c] *Department of Mechanical Engineering, Sirjan University of Technology, Sirjan, Kerman Province, Iran*
[d] *Green International World Ltd, 128 City Road, London, United Kingdom*

Abstract

Metal-organic frameworks (MOFs) are innovative porous materials with diverse, tunable functionality, high porosity, and surface area, making them promising for use in gas storage, separation, and catalytic applications. Furthermore, their derivatives compensate for MOFs' lack of electronic conductivity and chemical stability, providing a new optimum for precise control of material structure. Many efficient electrocatalysts have been created based on MOFs and their derivates for O2 reduction/evolution processes and CO2 reduction/evolution reactions in metal-air batteries. In this review, we highlight the most recent developments in MOFs and their derivatives in metal-air batteries, as well as explore the structural properties of these materials and their respective modes of action. By thoroughly reviewing the benefits, problems, and prospects of MOFs, we can have a better understanding of the future development of electrocatalysis and energy storage technologies.

Keywords: *Metal-air battery, Metal-organic framework, Reduction/evolution reactions, Zn-air battery, Catalytic electrode.*

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* Corresponding author: S. Akbari. Tel.: +49-151-664-32106 E-mail address: somayeh.akbari@nanoscitec.com

1. Introduction

The world's insatiable demand for energy continues to rise, fueled by population growth, industrialization, and technological innovation. However, reliance on fossil fuels raises serious environmental and geopolitical concerns. This has resulted in a global trend toward cleaner and more sustainable energy sources including solar, wind, and hydroelectric power [1]. However, the intermittent nature of these renewable energy sources needs effective energy storage and conversion technologies to assure a consistent and uninterrupted energy supply [2]. Batteries, as electrochemical energy storage devices, play an important role in this transformation, functioning as key components in electric vehicles, portable devices and grid-scale energy storage [3-5].

Metal-air batteries, a promising type of energy storage technology, have emerged as a viable option for high-energy-density applications [6]. These batteries, which were first envisaged in the nineteenth century, use the abundant oxygen in the air as a cathode reactant, providing a considerable energy density advantage over traditional lithium-ion batteries. This property is due to oxygen's enormous theoretical capacity, which greatly exceeds that of usual cathode materials [7]. Furthermore, metal-air batteries have environmental benefits since they use commonly available and inexpensive components. These batteries work by conducting electrochemical processes. The anode is often made of a metal, such as lithium, zinc, sodium, or aluminum. During discharge, the metal oxidizes, releasing electrons that go through an external circuit to the cathode, where the oxygen in the air is reduced [8]. This electrochemical process produces an electric current, which powers external equipment. During charging, the reverse process happens, replacing the anode with metal and renewing the cathode with oxygen [9, 10].

A wide variety of metal-air batteries have been studied, each with its own distinct properties and potential applications. Lithium-air (Li-air) batteries have the highest theoretical energy density, making them ideal for electric cars [11]. Zinc-air (Zn-air) batteries, highlighted for their safety and affordable cost, are ideal for portable electronics and grid-scale energy storage. Sodium (Na-air) and aluminum-air (Al-air) batteries, which use abundant and sustainable materials, are viable alternatives to lithium [12, 13].

Metal-air batteries have several disadvantages that prevent their widespread utilization. These include short cycle life, slow kinetics, and limited air-electrode efficiency. Metal-organic frameworks (MOFs) can successfully address these difficulties by functioning as efficient catalysts, having a large surface area for gas diffusion, and providing structural stability for enhanced cycling performance [14, 15]. MOFs, a type of crystalline porous material, have received a lot of attention in recent years due to its unique qualities, such as large surface area, variable pore size and functionality, and chemical stability [16, 17]. These characteristics have led to their broad use in a variety of industries, including gas storage, separation, and catalysis. MOFs have enormous promise to improve battery performance and address electrode material issues [18, 19].

This research investigates MOFs' promising role in promoting the development of metal-air batteries, looking at their applications in improving electrode performance and overcoming important limitations. This comprehensive analysis focuses on three major types of metal-air batteries: Li-air batteries, Zn-air batteries, and Na/Al-air batteries. It analyzes the precise functions and mechanisms of MOFs in each type of battery, shedding light on their potential to revolutionize energy storage technology. Through this comprehensive analysis, the paper aims to provide a comprehensive understanding of the potential of MOFs in transforming metal-air batteries into a viable and sustainable energy storage solution.

2. MOFs for Li-air batteries

Lithium-air batteries offer the highest theoretical specific energy (3,458 Wh kg^{-1}) among rechargeable batteries, making them a promising choice for future battery technologies. The predicted specific energy range is 500-900 Wh kg^{-1}, allowing electric vehicles to go more than 550 km. Over the years, extensive research has been conducted to investigate the mechanisms of oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs), as well as to create innovative ways to improve the reaction kinetics and stability of Li-air systems. On the negative electrode side, a considerable amount of Li metal is frequently employed in lab-scale cells, which obscures the negative electrode's reversibility difficulties [20]. Traditional cathode materials often suffer from issues such as poor stability, low conductivity, and insufficient catalytic activity, prompting the exploration of novel materials to enhance their performance [21]. MOFs have garnered attention as a versatile class of materials that could address these challenges [22]. MOFs are crystalline compounds composed of metal ions or clusters coordinated to organic ligands, forming porous structures with high surface areas [23]. Their tunable porosity, adjustable chemical functionality, and structural diversity make MOFs highly suitable for applications in catalysis, including in Li-air batteries as cathode.

One of the primary strategies in utilizing MOF nanoparticles for catalytic electrodes is optimizing their structure to maximize surface area and porosity [24]. This optimization allows for better oxygen diffusion and greater active site exposure, crucial for enhancing catalytic activity [25]. For example, incorporating open metal sites within the MOF structure can significantly improve the catalytic performance by providing more active sites for the ORR and OER [25]. Crucially, comprehending the reaction mechanisms governing ORR and OER on these materials is essential for maximizing their efficiency and effectiveness in various applications [26]. Functionalization of MOFs with specific functional groups, such as amines (NH_2), hydroxyls (OH), and carbonyls (C=O), has also proven effective [27]. These functional groups can enhance the interaction between the MOF and the electrolyte, improving ionic conductivity and catalytic efficiency [27]. Additionally, modifying the organic linkers in MOFs can tailor the electronic properties, further enhancing their catalytic performance [28].

The most researched MOFs are microporous, which limits mass transport capabilities and reduces storage capacity for insoluble discharge products of aprotic metal-air batteries. Wang et al. described a method for partially removing ligands to induce the formation of defects in the mesopores and unsaturated coordination in the mostly microporous Cu-BTC (BTC = 1,3,5-bezenetricarboxylic acid). The mesopores in the Cu-BTC structure were created by including isophthalic acid as a partial ligand. Isophthalic acid differs from BTC by lacking one carboxylic group. This modification resulted in the formation of mesoporous Cu-BTC (MCu-BTC). Co species were added to MCu-BTC to enhance its bifunctional catalytic performance in oxygen reduction and oxygen evolution reactions, resulting in Co/MCu-BTC. The electrochemical analyses demonstrated that the mesopores of MCu-BTC significantly improved the discharging capacity (approximately 7000 mAh g^{-1}) of Co-10/MCu-BTC in an aprotic Li-air battery. This enhancement is attributed to the mesopores, which facilitate the infiltration of electrolytes for efficient mass and charge transfer and also offer additional storage space for the discharge product [29].

Ultrathin 2D MOFs have the potential to increase Li-O2 battery performance by providing high O_2 accessibility, open catalytic active sites, and huge surface areas. To create highly efficient cathode catalysts for aprotic Li-O2 batteries, a simple ultrasonication process was established to synthesis three types of 2D MOFs (2D Co-MOF, Ni-MOF, and Mn-MOF) by Yuan et al. The 2D Mn-MOF cathode achieved a discharge specific capacity of 9464 mAh g^{-1}, which is higher than that of the 2D Co-MOF and Ni-MOF cathodes, owing to the Mn-O framework's intrinsic open active sites. During the cycling test, the 2D Mn-MOF cathode worked steadily for more than 200 cycles at 100 mA g^{-1}, with a reduced discharge capacity of 1000 mAh g^{-1}, which was significantly longer than that of the others. According to additional electrochemical investigation, they discovered that the 2D Mn-MOF outperforms the 2D Ni-MOF and Co-MOF due to improved oxygen reduction and oxygen evolution reaction activity, specifically the efficient oxidation of LiOH and Li_2O_2 [30].

Majidi *et al.* revealed remarkable properties of a conductive metal organic framework (c-MOF) that supports the formation of nanocrystalline Li_2O_2 with amorphous areas. This provided a platform for the continued growth of Li_2O_2 units distant from the framework, allowing for rapid discharge at high current rates. Furthermore, the Li_2O_2 structure functions in tandem with the redox mediator (RM). Because of the conductivity of Li_2O_2's amorphous portions, the RM can act directly on the Li_2O_2 surface rather than the catalyst edges, and then travel to the Li_2O_2 surface via the electrolyte. This direct charge transfer allowed for a modest charge potential of <3.7 V at high current densities (1-2 A g^{-1}) and a long cycle life (100-300 cycles) for big capacity (1000-2000 mAh g^{-1}) [31].

Liu et al. developed a multifunctional quasi-solid-state electrolyte based on a MOF and an ionic liquid (IL) to sustain the cathode while protecting the Li anode in Li-O2 batteries at high temperatures. The electrolyte had low volatility and good wettability with the electrodes, and the combined action of the IL and MOF suppressed lithium dendrite formation by generating a homogenous Li+ flow. At 60 °C, the Li-O2 battery with this electrolyte demonstrated a high discharge capacity and increased cycle life (>1100 h) while maintaining a low overpotential. Furthermore, the Li-O2 battery demonstrated increased electrochemical performance at a higher temperature of 80 °C due to the electrolyte's superior thermal stability. Their findings revealed that the quasi-solid-state electrolyte could be a viable technique for commercializing Li-O2 batteries [32].

In 2022, Xu and colleagues successfully synthesized Cu-tetra(4-carboxyphenyl) porphyrin (Cu-TCPP) nanosheets using the solvothermal process. An efficient Li-CO_2 battery with Cu-TCPP as a catalyst achieved a high discharge capacity of 20393 mAh g^{-1} at 100 mA g^{-1}, a long-life cycle of 123 at 500 mA g^{-1}, and a decreased overpotential of 1.8 V at 2000 mA g^{-1}. According to density functional theory calculations, Cu-TCPP had larger adsorption energy of CO2 and Li_2CO_3 than TCPP, and a considerable number of electrons accumulated near the Cu-N4 active sites. As a result, the porphyrin ligand's outstanding CO_2 capture ability, together with the synergic catalytic activity of the Cu atom in Cu-TCPP, promotes the thermodynamics and kinetics of CO_2 reduction and evolution processes [33].

MOFs contain open metal sites, a large surface area, homogeneous pores, and a tunable chemical environment, which can considerably improve O2 adsorption while also facilitating Li+ transport and product deposition. Furthermore, MOF-based catalysts have a periodic structure and chemical stability that make them excellent for Li-air batteries. While various methods exist for producing MOF nanoparticles, achieving large-scale production with consistent quality and cost-effectiveness remains challenging [34]. Developing scalable synthesis routes is crucial for industrial applications. Lastly, integrating MOF nanoparticles seamlessly into battery architectures while maintaining their catalytic activity and stability requires innovative electrode design [35]. Maximizing the utilization of MOFs within the electrode matrix without compromising structural integrity demands advanced engineering solutions [36]. Looking forward, tailored design approaches that optimize MOF pore structures, functional groups, and metal centers hold promise for enhancing catalytic efficiency and stability [37]. Computational modelling and advanced synthesis techniques will play pivotal roles in achieving these goals. Furthermore, hybridizing MOFs with conductive materials such as carbon nanotubes or polymers can enhance conductivity and stability, offering synergistic benefits for Li-air battery performance [38]

The future of MOF-based catalytic electrodes in Li-air batteries lies in further improving their stability, conductivity, and catalytic efficiency [39]. Developing new MOF structures with enhanced properties, exploring novel functionalization techniques, and creating more effective composites and hybrids will be essential [40]. Additionally, understanding the fundamental electrochemical processes at the atomic and molecular levels will provide insights necessary for designing next-generation MOF-based catalysts [40].

3. MOFs for Zn-air batteries

Primary Zn-air batteries are commercially accessible and commonly utilized in portable applications such as hearing aids and data recorders. Benefiting from proven practical applications, the creation of novel primary and rechargeable Zn-air batteries with higher energy output by lowering discharge/charge overpotentials is more possible than previous metal-air battery systems. Although the interaction between Zn and O_2 is thermodynamically spontaneous, the ORR at the cathode exhibits slow kinetics during battery discharge, necessitating the use of catalysts to expedite the process. On the other hand, efficient OER catalysts are required to achieve a decent charging potential of rechargeable Zn-air batteries. Based on these considerations, the rational design of the air cathode is a critical determinant for producing high-efficiency Zn-air batteries [16]. Figure 1 illustrates the fundamental configuration of the Zn–air battery.

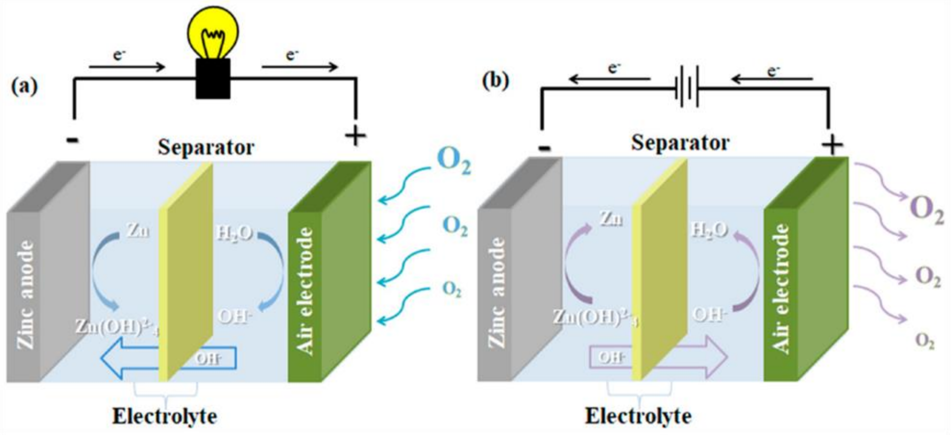

Figure 1. Illustration of Zn-air battery's (a) discharge and (b) charging process. Adapted from Song et al. (2022) [41], under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

Moreover, Zn-air batteries are among the most attractive candidates due to Zn's abundance and low-cost, high-energy density, and great reduction potential. The most major difficulty for primary and rechargeable aqueous Zn-air batteries is the relatively high overpotential caused by the slow kinetics of oxygen reactions on the air cathode. Highly effective oxygen catalysts generated from MOF precursors have shown exceptional ability to facilitate oxygen reactions [16]. Figure 2 shows a classification schematic of MOF-derived for air cathode catalysts in Zn-air batteries.

0 Shinde et al. presented a study where they successfully developed strong and flexible Zn-air batteries using a unique three-dimensional dual-linked hexaiminobenzene metal-organic framework (Mn/Fe-HIB-MOF) as the bifunctional oxygen electrocatalysts and superionic functionalized bio-cellulose electrolytes. The bio-cellulose electrolytes exhibited a high ionic conductivity of 64 mS cm^{-1}. The quintet-shelled hollow spherical MOFs have a well-defined structure consisting of five layers. They also have a hierarchical porous structure, high packing density, with a surface area of 2298 $m^2\ g^{-1}$, and are chemically stable compared to traditional MOFs. The Mn/Fe-HIB-MOF demonstrated excellent bifunctional oxygen electrocatalytic performance, with a half-wave potential of 0.883 V for oxygen reduction and an overpotential of 280 mV at 10 mA cm^{-2} for oxygen evolution processes. These results surpass the performance of commercial Pt/C and RuO_2. Their positive oxygen reactions and surface electrical structures were verified using density functional theory. The Mn/Fe-HIB-MOF cathode exhibited the longest lifetimes ever recorded for rechargeable Zn-air batteries. Specifically, it achieved 1000 hours (with a voltage gap of 0.75 V at a current density of 10 mA

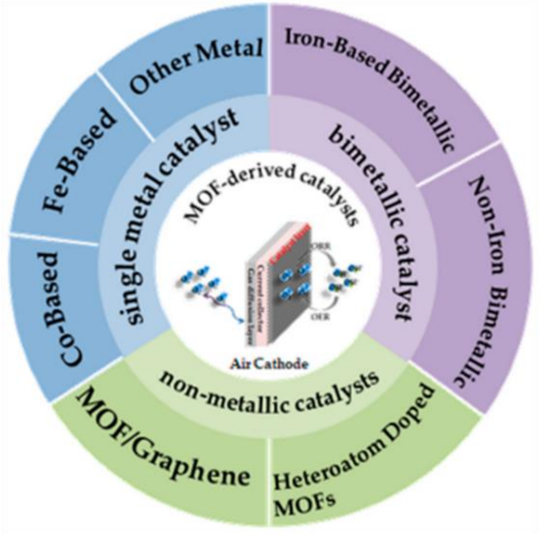

Figure 2. Diagram illustration of the classification of catalysts from MOF-derived for the air cathode in Zn-air batteries. Adapted from Song et al. (2022) [41], under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

cm^{-2}) over 6000 cycles, and 600 hours (with an efficiency of approximately 65.24% at a current density of 25 mA cm^{-2}) over 3600 cycles. Moreover, it demonstrated exceptional flexibility for both liquid and all-solid-state flexible Zn-air batteries [42].

Zheng et al. described the rational design and synthesis of bimetallic CoNi-MOF nanosheets/reduced graphene oxide (rGO) hybrid electrocatalyst. CoNi-MOF nanosheets were generated in situ on rGO with surfactant modulation. The newly created CoNi-MOF/rGO hybrids, which are made up of uniformly distributed nanosheets encased by rGO, demonstrated remarkable electrocatalytic activity for OER and ORR. The improved bifunctional catalytic performance was attributed to the synergy between the CoNi-MOF nanosheets and rGO, the abundance of exposed active sites, and the increased electron conductivity. Furthermore, rechargeable Zn-air batteries with CoNi-MOF/rGO-based air electrodes revealed remarkable energy density and cycling stability, indicating tremendous promise for enhanced bifunctional electrocatalysis in electronic devices [43].

Qian et al. pyrolyzed a MOF with Zn, N, and B as a precursor to develop dual-doped and metal-free porous carbon materials that are excellent ORR/OER bifunctional electrocatalysts. Pyrolysis under an H2-containing atmosphere has the potential to significantly increase the surface area of produced carbon compounds. Furthermore, the crystalline MOF precursor ensures that N and B are equally distributed throughout the carbon components. The resulting carbon materials demonstrated high ORR and OER catalytic activity in both half-cell and single-cell battery tests. This study showed for the first time that MOFs might be employed as precursors for producing metal-free ORR/OER bifunctional cathodic electrocatalysts with high potential in rechargeable Zn-air batteries [44].

Chen et al. presented co-based MOF arrays as innovative bifunctional oxygen electrocatalysts. The Co-MOF is formed in situ using a hydrothermal process on a three-dimensional graphite foam (GF). In a 1 m KOH aqueous solution, the resulting Co-MOF/GF displayed an OER overpotential of just ≈ 220 mV at 10 mA cm^{-2}, which was substantially lower than that of Ir/C and previously reported noble metal-free electrocatalysts. The Co-MOF/GF electrocatalyst has a lower potential gap of ≈ 0.75 V compared to Pt/C-Ir/C and other bifunctional oxygen electrocatalysts, despite having an ORR half-wave potential of 0.7 V (against RHE). A rechargeable zinc-air battery with Co-MOF electrocatalyst in an air electrode achieved a maximum power density of 86.2 mW cm^{-2} and improved charge-discharge performance [45].

Zhang et al. utilized a one-pot approach to synthesize a multimetal (Fe, Co, Cu, and Zn) mixed zeolitic imidazolate framework (MM-ZIF) by employing a straightforward in situ redox reaction. Additional pyrolysis of the MM-ZIF material resulted in the formation of FC-C@NC, a carbon polyhedron with a high level of porosity, that was grafted with a large number of carbon nanotubes. Within this structure, extremely small Co nanoparticles were implanted, with some of their lattice positions being replaced by Fe and Cu. The FC-C@NC material developed exhibited a significant surface area, a highly porous structure, a wide distribution of metal active sites, and conductive carbon frameworks. These characteristics led to exceptional ORR activity and long-term stability. The catalyst demonstrated exceptional resistance to methanol crossover, surpassing both the Pt/C catalyst often used in commercial applications and the majority of non-noble-metal catalysts previously documented. The zinc-air battery, based on FC-C@NC, demonstrated remarkable performance with an open-circuit potential of 1.466 V, a specific capacity of 659.5 mAh g^{-1}, and a gravimetric energy density of 784.3 Wh/kg Zn. These results were much better than those achieved with the Pt/C-based cathode [46]. The synthetic approach of FC-C@NC is illustrated in figure 3.

Figure 3. Schematic representation of the synthetic approach for FC-C@NC. Adapted from Zhang et al. (2020) [46], under CC BY 4.0. (https://creativecommons.org/licenses/by/4.0/)

MOFs that possess high surface area and have exceptional thermal and chemical durability are extensively employed in Zn-air batteries. Nevertheless, because most MOFs have limited electrical conductivity, the design of electrocatalysts must be based on their derivatives. Indeed, the inherent benefits of MOFs are not fully harnessed. The primary challenge we face with Zn-air batteries is achieving optimal efficiency in the ORR and OER. To address this, we aim to develop suitable catalysts based on MOFs in our future research.

4. MOFs for Na and Al-air batteries

4.1. Na-air batteries

Because of its low cost, abundant reserves, and relatively high electrode potential, sodium is an excellent anode for air batteries. The energy density of Na-air batteries is 1,683 Wh kg-1, which is determined by the reaction 2Na+ + O2 + 2e- ↔ Na$_2$O [47-49]. The discharging and recharging processes of Na-air batteries are hindered by slow kinetics, specifically in the ORR and OER. These reactions occur at the three-phase interfaces and involve complex multielectron interactions. As a result, the batteries experience significant polarization [47].

Wu et al. first used MOF-derived N-doped carbon nanotubes (MOF-NCNTs) as electrocatalysts for hybrid Na-air batteries, which showed higher electrocatalytic activity and stability for ORR and OER than commercial Pt/C [18]. MOF-NCNTs battery had the lowest voltage gap of 0.30 V at 0.1 mA cm-2 compared to other evaluated catalysts such as commercial Pt/C (0.50 V), RuO$_2$ (0.50 V), Co-CNTs (0.67 V), NCNTs (0.77 V), MWNTs (0.90 V), and carbon paper (1.18 V). The battery achieved an average discharge plateau of 2.81 V and a round-trip efficiency of 87% after 35 cycles at a current density of 0.1 mA cm-2. The exceptional electrocatalytic activity is mostly due to the synergistic effect of N dopants and confined Co nanoparticles in CNTs, the hollow structure of NCNTs, and the strong porous cage structure. The N dopants and restricted Co nanoparticles in the CNTs increase catalytic active sites and facilitate electron transport for the ORR and OER. The hollow framework structure of NCNTs provides structural defect sites for O2 adsorption while simultaneously improving mass transfer and electronic conductivity, resulting in increased catalytic activity. The strong and permeable cage construction enhances the stability of the catalysts. The NCNT, generated from MOFs, is a cost-effective and highly efficient bifunctional oxygen electrocatalyst. It has great potential for practical use in hybrid Na-air batteries and other MABs [18].

Zhu et al. reported a remarkable Co–N–C nano-framework consisting of well-distributed Co nanoparticles on N-doped defective carbon [50]. This nano-framework was developed from a ZnCo bimetal organic framework (bi-MOF). The evaporation of zinc leads to a high specific surface area, which enhances the ability of oxygen to be adsorbed and desorbed, hence increasing the accessibility of catalytic sites. The plentiful Co–N–C species serve as robust bridging bridges between Co nanoparticles and carbon materials, promoting interfacial electron transport. Co–N–C-0.5, with a molar ratio of 0.5 of Zn in the original ZIF-67, demonstrates a small overpotential gap of 0.94 V. This is attributed to the presence of several active sites, such as N-doped defective carbon and the CoNx/Co composite, as well as rapid interfacial electron transport. In addition, a hybrid Na-air battery utilizing the Co-N-C-0.5 material exhibits a minimal voltage difference of 0.31 V and a substantial round-trip efficiency of 90.0% while operating at a current density of 0.1 mA cm^{-2}. Significantly, the hybrid Na-air battery exhibits exceptional cyclability for both charging and discharging owing to its inherently stable structure. The outcomes of this study validate that Co–N–C materials, obtained from a bi-MOF, can serve as viable substitutes for expensive Pt/C catalysts in MABs, namely for ORR and OER activities [50].

Rechargeable solid-state Na-air batteries are being investigated as advanced electrochemical storage systems with great energy density for the future [51, 52]. Nevertheless, the battery's rate performance and cycle life are significantly impacted by the restricted triple-phase boundaries and sluggish kinetics between the cathode and electrolyte. The cathode material in the battery enables the oxygen reduction and evolution reactions, which are responsible for determining the capacity and rechargeability of these MABs [53, 54].

Sun et al. developed a new type of catalyst called Co0.6@N–C, which is a two-dimensional porous material [55]. This catalyst has a high catalytic activity and is derived from a cobalt/zinc bimetallic zeolite-like imidazole skeleton structure known as Co0.6Zn0.4-ZIF-L. The Co0.6@N–C catalyst, which is two-dimensional, offers a greater number of active sites/channels for oxygen adsorption and desorption. Additionally, it facilitates faster electron transfer at the interface between the electrolyte and catalyst. This clever arrangement enhances the performance of the solid-state Na–air battery, resulting in an impressive capacity of 11,150 mAh g^{-1} and excellent cycling stability in air [55].

Because of the inadequate thermal stability, low efficiency of the active site, and poor conductivity at the interface of directly carbonized MOFs, there is a growing trend in research to control the active sites by modifying the MOFs to satisfy the requirements of practical applications. In addition, the many categories of MOFs enable the creation of a wide range of nanocomposites produced from MOFs. Undoubtedly, MOFs possess significant potential in Na-air batteries as the optimal material for synthesizing carbon nanocomposites [47].

4.2. Al-air batteries

Zaromb was the first to suggest using high energy density aluminum metal anodes in aluminum/oxygen systems in 1962 [56]. With a potential energy density of 8,000 Wh kg^{-1}, Al-air batteries are highly valuable for use in electric vehicle and submarine power supply applications. An appealing option for electric vehicles is the Al-air batteries system, which is a superior electrochemical storage system with a high energy density [57].

Li et al. discovered that a MOF with copper at its center, known as Cu–MOF, may be used as a self-sacrificing precursor to alter the structure of

Ketjenblack (KB) carbon [58]. This process results in the formation of crystalline Cu/Cu_2O nanoparticles and noncrystalline CuN_xC_y species when the material is subjected to calcination. The catalytic activity for the ORR of this modified KB carbon was greatly enhanced, likely due to the combined influence of crystalline Cu/Cu_2O nanoparticles and noncrystalline CuN_xC_y species. This hybrid catalyst demonstrated a half-wave potential (0.82 V vs reversible hydrogen electrode) that was similar to that of the commercial 20 wt % Pt/C. Additionally, it displayed higher limiting-current density and durability compared to the commercial catalyst. The exceptional performance was also validated through the utilization in homemade Al-air batteries, resulting in a very consistent voltage of 1.53 V at a current density of 40 mA cm^{-2} [58].

Liu and colleagues employed a hydrothermal-calcination method to synthesize a new type of carbon nanocages embedded with hollow $ZnO/ZnCo_2O_4$ nanoparticles, supported by reduced graphene oxide (rGO) [59]. The precursor used was a composite of zeolitic imidazolate framework (ZIF-67), graphene oxide, and zinc nitrate. The $ZnO/ZnCo_2O_4/C@rGO$ hybrid has exceptional electrocatalytic efficiency for the oxygen reduction reaction in alkaline environments. It also exhibits superior stability and methanol tolerance compared to the commercially available Pt/C catalyst. In addition, they created innovative and uncomplicated Al-air coin cells using hybrid materials as cathode catalysts under regular air settings to further examine their catalytic effectiveness. The coin cell featuring the $ZnO/ZnCo_2O_4/C@rGO$ cathode catalyst exhibits a greater open circuit voltage and discharge voltage, as well as a slower potential drop compared to the cell with the $ZnO/ZnCo_2O_4/C$ cathode catalyst. This confirms that the presence of rGO enhances both the electrocatalytic activity and stability of the catalyst system. The exceptional electrocatalytic performance of the $ZnO/ZnCo_2O_4/C@rGO$ hybrid can be attributed to the notable conductivity and large specific surface area facilitated by rGO, the increased availability of catalytic active sites due to the distinctive porous hollow nanocage structure, and the synergistic covalent bonding between rGO sheets and $ZnO/ZnCo_2O_4/C$ nanocages [59].

One of the main benefits of MOFs is their highly customizable and organized channel, which enables the material composition and structure to be tailored and tuned to meet the specific needs of the Al-air battery system. Hence, there is a need to create cost-effective and highly efficient catalysts based on MOFs. However, it remains difficult to attain practical uses for such catalysts [47].

5. Conclusion

The energy crisis is growing increasingly urgent. Metal-air batteries, a type of electrochemical energy conversion and storage device with abundant resources and a low cost, have been extensively researched in recent years. However, its large-scale applicability is still constrained by the slow kinetics of ORR and OER in the air cathode during discharge and charge processes. The development of effective oxygen electrocatalysts is critical for improving the performance and endurance of metal-air batteries. This paper examined the research development of transition metal and metal-free electrocatalysts produced from MOFs. The original MOFs can be utilized as electrocatalysts for oxygen redox reactions; However, their low conductivity impedes electron transmission in the system. Furthermore, the original MOFs are unstable due to their porous crystal structure, which is prone to collapse in acidic or alkaline conditions. However, the unique structural properties of MOFs make them the most promising electrocatalyst precursor: metal ions are linked and separated by organic ligands, and various metal cations can be introduced by selecting organic ligands, resulting in more active sites for the catalyst. MOF derivatives often preserve the morphology of their progenitors and have a high porosity structure, resulting in an abundance of active surfaces for oxygen electrocatalytic reactions. MOF-derived are regarded as one of the most attractive alternatives for replacing platinum-based catalysts due to their inexpensive cost, abundant resources, and variable catalytic activity. Further research into functional MOFs and MOF-derived catalysts could offer more effective solutions to the problems. More exciting scientific results to address the problems of metal-air batteries are predicted in the near future.

6. Reference

1. N. Abas, A. Kalair, N. Khan, Review of fossil fuels and future energy technologies, Futures, 31-49, 69 (2015).
2. A. Ghasemi Yeklangi, A. Ghafari, F. Asgari Sima, S. Akbari, Advancing lithium-ion battery manufacturing: novel technologies and emerging trends, Journal of Applied Electrochemistry, (2024).
3. M.D. Leonard, E.E. Michaelides, D.N. Michaelides, Energy storage needs for the substitution of fossil fuel power plants with renewables, Renewable Energy, 951-962, 145 (2020).
4. A. Kalair, N. Abas, M.S. Saleem, A.R. Kalair, N. Khan, Role of energy storage systems in energy transition from fossil fuels to renewables, Energy Storage, e135, 3 (2021).
5. A. Ghafari, B. Dashtipour, M. Sam, A.G. Yeklangi, S. Akbari, Covalent organic frameworks as novel materials for overcoming key obstacles in lithium metal battery development, The Canadian Journal of Chemical Engineering, 1-19, (2024).
6. Q. Liu, Z. Pan, E. Wang, L. An, G. Sun, Aqueous metal-air batteries: Fundamentals and applications, Energy Storage Materials, 478-505, 27 (2020).
7. A.G. Olabi, E.T. Sayed, T. Wilberforce, A. Jamal, A.H. Alami, K. Elsaid, S.M.A. Rahman, S.K. Shah, M.A. Abdelkareem, Metal-Air Batteries—A Review, Energies, 7373, 14 (2021).
8. J. Li, K. Zhang, B. Wang, H. Peng, Light-Assisted Metal–Air Batteries: Progress, Challenges, and Perspectives, Angewandte Chemie International Edition, e202213026, 61 (2022).
9. Y. Chen, J. Xu, P. He, Y. Qiao, S. Guo, H. Yang, H. Zhou, Metal-air batteries: progress and perspective, Science Bulletin, 2449-2486, 67 (2022).
10. A. Liu, X. Liang, X. Ren, W. Guan, T. Ma, Recent Progress in MXene-Based Materials for Metal-Sulfur and Metal-Air Batteries: Potential High-Performance Electrodes, Electrochemical Energy Reviews, 112-144, 5 (2022).
11. L. Yaqoob, T. Noor, N. Iqbal, An overview of metal-air batteries, current progress, and future perspectives, Journal of Energy Storage, 106075, 56 (2022).
12. T. Li, M. Huang, X. Bai, Y.-X. Wang, Metal–air batteries: A review on current status and future applications, Progress in Natural Science: Materials International, 151-171, 33 (2023).
13. C. Wang, Y. Yu, J. Niu, Y. Liu, D. Bridges, X. Liu, J. Pooran, Y. Zhang, A. Hu, Recent Progress of Metal–Air Batteries—A Mini Review, Applied Sciences, 2787, 9 (2019).
14. Y. Wang, D.F. Ruiz Diaz, K.S. Chen, Z. Wang, X.C. Adroher, Materials, technological status, and fundamentals of PEM fuel cells – A review, Materials Today, 178-203, 32 (2020).
15. A. Muthurasu, B. Dahal, T. Mukhiya, K. Chhetri, H.Y. Kim, Fabrication of Nonmetal-Modulated Dual Metal–Organic Platform for Overall Water Splitting and Rechargeable Zinc–Air Batteries, ACS Applied Materials & Interfaces, 41704-41717, 12 (2020).
16. Y. Zhong, X. Xu, W. Wang, Z. Shao, Recent Advances in Metal-Organic Framework Derivatives as Oxygen Catalysts for Zinc-Air Batteries, Batteries & Supercaps, 272-289, 2 (2019).
17. A. Ghafari, A.G. Yeklangi, F.A. Sima, S. Akbari, Industrial-scale synthesis and application of covalent organic frameworks in lithium battery technology, Journal of Applied Electrochemistry, 215-243, 54 (2024).
18. Y. Wu, X. Qiu, F. Liang, Q. Zhang, A. Koo, Y. Dai, Y. Lei, X. Sun, A metal-organic framework-derived bifunctional catalyst for hybrid sodium-air batteries, Applied Catalysis B: Environmental, 407-414, 241 (2019).
19. Z. Meng, N. Chen, S. Cai, R. Wang, J. Wu, H. Tang, Recent advances of hierarchically porous bifunctional oxygen electrocatalysts derived from metal–organic frameworks for Zn–air batteries, Materials Chemistry Frontiers, 2649-2667, 5 (2021).
20. Z. Liang, W. Wang, Y.-C. Lu, The path toward practical Li-air batteries, Joule, 2458-2473, 6 (2022).
21. C. Yuan, X. Yang, P. Zeng, J. Mao, K. Dai, L. Zhang, X. Sun, Recent progress of functional separators with catalytic effects for high-performance lithium-sulfur batteries, Nano Energy, 105928, 84 (2021).
22. L. Jiao, J.Y.R. Seow, W.S. Skinner, Z.U. Wang, H.-L. Jiang, Metal–organic frameworks: Structures and functional applications, Materials Today, 43-68, 27 (2019).
23. M. Eddaoudi, H. Li, O. Yaghi, Highly porous and stable metal− organic frameworks: structure design and sorption properties, Journal of the American Chemical Society, 1391-1397, 122 (2000).
24. K. Shen, X. Chen, J. Chen, Y. Li, Development of MOF-derived carbon-based nanomaterials for efficient catalysis, Acs Catalysis, 5887-5903, 6 (2016).

25. C. Vogt, B.M. Weckhuysen, The concept of active site in heterogeneous catalysis, Nature Reviews Chemistry, 89-111, 6 (2022).
26. Y. Zhao, D.P. Adiyeri Saseendran, C. Huang, C.A. Triana, W.R. Marks, H. Chen, H. Zhao, G.R. Patzke, Oxygen evolution/reduction reaction catalysts: from in situ monitoring and reaction mechanisms to rational design, Chemical Reviews, 6257-6358, 123 (2023).
27. Y. Zhao, H. Wu, T.J. Emge, Q. Gong, N. Nijem, Y.J. Chabal, L. Kong, D.C. Langreth, H. Liu, H. Zeng, Enhancing gas adsorption and separation capacity through ligand functionalization of microporous metal–organic framework structures, Chemistry–A European Journal, 5101-5109, 17 (2011).
28. Y. Shen, T. Pan, L. Wang, Z. Ren, W. Zhang, F. Huo, Programmable logic in metal–organic frameworks for catalysis, Advanced Materials, 2007442, 33 (2021).
29. H. Wang, F. Yin, N. Liu, H. Yu, T. Fan, B. Chen, Engineering Mesopores and Unsaturated Coordination in Metal–Organic Frameworks for Enhanced Oxygen Reduction and Oxygen Evolution Activity and Li–Air Battery Capacity, ACS Sustainable Chemistry & Engineering, 4509-4519, 9 (2021).
30. M. Yuan, R. Wang, W. Fu, L. Lin, Z. Sun, X. Long, S. Zhang, C. Nan, G. Sun, H. Li, S. Ma, Ultrathin Two-Dimensional Metal–Organic Framework Nanosheets with the Inherent Open Active Sites as Electrocatalysts in Aprotic Li–O2 Batteries, ACS Applied Materials & Interfaces, 11403-11413, 11 (2019).
31. L. Majidi, A. Ahmadiparidari, N. Shan, S. Kumar Singh, C. Zhang, Z. Huang, S. Rastegar, K. Kumar, Z. Hemmat, A.T. Ngo *et al*, Nanostructured Conductive Metal Organic Frameworks for Sustainable Low Charge Overpotentials in Li–Air Batteries, Small, 2102902, 18 (2022).
32. H. Liu, L. Zhao, Y. Xing, J. Lai, L. Li, F. Wu, N. Chen, R. Chen, Enhancing the Long Cycle Performance of Li–O2 Batteries at High Temperatures Using Metal–Organic Framework-Based Electrolytes, ACS Applied Energy Materials, 7185-7191, 5 (2022).
33. Y. Xu, H. Gong, H. Ren, X. Fan, P. Li, T. Zhang, K. Chang, T. Wang, J. He, Highly Efficient Cu-Porphyrin-Based Metal–Organic Framework Nanosheet as Cathode for High-Rate Li-CO2 Battery, Small, 2203917, 18 (2022).
34. Q. Zhang, S. Yan, X. Yan, Y. Lv, Recent advances in metal-organic frameworks: Synthesis, application and toxicity, Science of The Total Environment, 165944, (2023).
35. M.Z.A. Mahmud, A Concise Review of Nanoparticles Utilized Energy Storage and Conservation, Journal of Nanomaterials, 5432099, 2023 (2023).
36. Q. Ma, T. Zhang, B. Wang, Shaping of metal-organic frameworks, a critical step toward industrial applications, Matter, 1070-1091, 5 (2022).
37. D. Li, A. Yadav, H. Zhou, K. Roy, P. Thanasekaran, C. Lee, Advances and Applications of Metal-Organic Frameworks (MOFs) in Emerging Technologies: A Comprehensive Review, Global Challenges, 2300244, 8 (2024).
38. H. Demir, H. Daglar, H.C. Gulbalkan, G.O. Aksu, S. Keskin, Recent advances in computational modeling of MOFs: From molecular simulations to machine learning, Coordination Chemistry Reviews, 215112, 484 (2023).
39. N. Javed, T. Noor, N. Iqbal, S.R. Naqvi, A review on development of metal–organic framework-derived bifunctional electrocatalysts for oxygen electrodes in metal–air batteries, RSC advances, 1137-1161, 13 (2023).
40. J. Annamalai, P. Murugan, D. Ganapathy, D. Nallaswamy, R. Atchudan, S. Arya, A. Khosla, S. Barathi, A.K. Sundramoorthy, Synthesis of various dimensional metal organic frameworks (MOFs) and their hybrid composites for emerging applications–a review, Chemosphere, 134184, 298 (2022).
41. D. Song, C. Hu, Z. Gao, B. Yang, Q. Li, X. Zhan, X. Tong, J. Tian: **Metal–Organic Frameworks (MOFs) Derived Materials Used in Zn–Air Battery**. In: *Materials.* vol. 15; 2022.
42. S.S. Shinde, C.H. Lee, J.-Y. Jung, N.K. Wagh, S.-H. Kim, D.-H. Kim, C. Lin, S.U. Lee, J.-H. Lee, Unveiling dual-linkage 3D hexaiminobenzene metal–organic frameworks towards long-lasting advanced reversible Zn–air batteries, Energy & Environmental Science, 727-738, 12 (2019).
43. X. Zheng, Y. Cao, D. Liu, M. Cai, J. Ding, X. Liu, J. Wang, W. Hu, C. Zhong, Bimetallic Metal–Organic-Framework/Reduced Graphene Oxide Composites as Bifunctional Electrocatalysts for Rechargeable Zn–Air Batteries, ACS Applied Materials & Interfaces, 15662-15669, 11 (2019).
44. Y. Qian, Z. Hu, X. Ge, S. Yang, Y. Peng, Z. Kang, Z. Liu, J.Y. Lee, D. Zhao, A metal-free ORR/OER bifunctional electrocatalyst derived from metal-organic frameworks for rechargeable Zn-Air batteries, Carbon, 641-650, 111 (2017).

45. G. Chen, J. Zhang, F. Wang, L. Wang, Z. Liao, E. Zschech, K. Müllen, X. Feng, Cobalt-Based Metal-Organic Framework Nanoarrays as Bifunctional Oxygen Electrocatalysts for Rechargeable Zn-Air Batteries, Chemistry - A European Journal, 18413-18418, 24 (2018).
46. K. Zhang, Y. Zhang, Q. Zhang, Z. Liang, L. Gu, W. Guo, B. Zhu, S. Guo, R. Zou, Metal-organic framework-derived Fe/Cu-substituted Co nanoparticles embedded in CNTs-grafted carbon polyhedron for Zn-air batteries, Carbon Energy, 283-293, 2 (2020).
47. Y. Xu, H. Xue, X. Li, X. Fan, P. Li, T. Zhang, K. Chang, T. Wang, J. He, Application of metal-organic frameworks, covalent organic frameworks and their derivates for the metal-air batteries, Nano Research Energy, e9120052, 2 (2023).
48. F. Cheng, J. Chen, Metal–air batteries: from oxygen reduction electrochemistry to cathode catalysts, Chemical Society Reviews, 2172-2192, 41 (2012).
49. C.-X. Zu, H. Li, Thermodynamic analysis on energy densities of batteries, Energy & Environmental Science, 2614-2624, 4 (2011).
50. J. Zhu, T. Qu, F. Su, Y. Wu, Y. Kang, K. Chen, Y. Yao, W. Ma, B. Yang, Y. Dai *et al*, Highly dispersed Co nanoparticles decorated on a N-doped defective carbon nano-framework for a hybrid Na–air battery, Dalton Transactions, 1811-1821, 49 (2020).
51. Q. Sun, L. Dai, T. Luo, L. Wang, F. Liang, S. Liu, Recent advances in solid-state metal–air batteries, Carbon Energy, e276, 5 (2023).
52. T. Wang, T. Yang, D. Luo, M. Fowler, A. Yu, Z. Chen, High-Energy-Density Solid-State Metal–Air Batteries: Progress, Challenges, and Perspectives, Small, 2309306, 20 (2024).
53. Q. Ma, F. Tietz, Solid-State Electrolyte Materials for Sodium Batteries: Towards Practical Applications, ChemElectroChem, 2693-2713, 7 (2020).
54. Y. Tian, Y. Sun, D.C. Hannah, Y. Xiao, H. Liu, K.W. Chapman, S.-H. Bo, G. Ceder, Reactivity-Guided Interface Design in Na Metal Solid-State Batteries, Joule, 1037-1050, 3 (2019).
55. Q. Sun, G. Zhu, L. Dai, W. Meng, L. Wang, S. Liu, High-Efficiency Two-Dimensional Catalysts Derived from CoxZny-ZIF-L MOFs for Solid-State Na–Air Battery, ACS Sustainable Chemistry & Engineering, 11625-11634, 11 (2023).
56. S. Zaromb, The Use and Behavior of Aluminum Anodes in Alkaline Primary Batteries, Journal of The Electrochemical Society, 1125, 109 (1962).
57. R. Mori, Recent Developments for Aluminum–Air Batteries, Electrochemical Energy Reviews, 344-369, 3 (2020).
58. J. Li, N. Zhou, J. Song, L. Fu, J. Yan, Y. Tang, H. Wang, Cu–MOF-Derived Cu/Cu2O Nanoparticles and CuN x C y Species to Boost Oxygen Reduction Activity of Ketjenblack Carbon in Al–Air Battery, ACS sustainable chemistry & engineering, 413-421, 6 (2018).
59. Y. Liu, H. Jiang, J. Hao, Y. Liu, H. Shen, W. Li, J. Li, Metal–Organic Framework-Derived Reduced Graphene Oxide-Supported ZnO/ZnCo2O4/C Hollow Nanocages as Cathode Catalysts for Aluminum–O2 Batteries, ACS Applied Materials & Interfaces, 31841-31852, 9 (2017).