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# A review on development of metal–organic framework-derived bifunctional electrocatalysts for oxygen electrodes in metal–air batteries

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Worldwide demand for oil, coal, and natural gas has increased recently because of odd weather patterns and economies recovering from the pandemic. By using these fuels at an astonishing rate, their reserves are running low with each passing decade. Increased reliance on these sources is contributing significantly to both global warming and power shortage problems. It is vital to highlight and focus on using renewable energy sources for power production and storage. This review aims to discuss one of the cutting-edge technologies, metal–air batteries, which are currently being researched for energy storage applications. A battery that employs an external cathode of ambient air and an anode constructed of pure metal in which an electrolyte can be aqueous or aprotic electrolyte is termed as a metal–air battery (MAB). Due to their reportedly higher energy density, MABs are frequently hailed as the electrochemical energy storage of the future for applications like grid storage or electric car energy storage. The demand of the upcoming energy storage technologies can be satisfied by these MABs. The usage of metal–organic frameworks (MOFs) in metal–air batteries as a bi-functional electrocatalyst has been widely studied in the last decade. Metal ions or arrays bound to organic ligands to create one, two, or three-dimensional structures make up the family of molecules known as MOFs. They are a subclass of coordination polymers; metal nodes and organic linkers form different classes of these porous materials. Because of their modular design, they offer excellent synthetic tunability, enabling precise chemical and structural control that is highly desirable in electrode materials of MABs.

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## 1. Introduction

Increased fuel demand and its consumption is associated with environmental pollution and health issues due to greenhouse gas emission into the atmosphere. Fossil fuels, which are

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limited energy sources and release harmful gases into the atmosphere like carbon dioxide and methane, are a major contributor to global warming and the annual rise in Earth's temperature. Excess global warming is disturbing the whole ecosystem: marine life, wildlife, humans *etc.* The amount of water in the world's oceans and seas is rising owing to melting of glaciers, sea ice and polar ice sheets brought on by warmer temperatures. Extreme financial setbacks might result from extreme weather. In addition to rising house and health insurance costs for customers, food and energy prices are also rising. Factors including declining tourism and industrial profitability, rising energy, food, and water needs, disaster cleanup, and border tensions have an impact on governments and then on our economy.<sup>1–3</sup> This has sparked considerable research into renewable and ecologically suitable energy sources. Effective energy storage systems must be created to put new sustainable energy sources in use efficiently. By offering sustainable power sources and fuel diversity, renewable energy sources improve energy security, lower the possibility of fuel leaks, and decrease the requirement for imported fuels. The nation's natural resources are also protected using these green energy sources. High demand can be reduced *via* energy storage, and any cost savings might be passed on to consumers. Energy storage can assist in meeting peak energy demands in highly populated places, reducing grid load and price increases.<sup>4,5</sup>

Environmental degradation outweighs fossil fuels against renewable energy sources. Systems for storing energy can aid in the switching to renewable energy sources from fossil fuels. Due to the negative environmental effects of greenhouse gases (GHG) created by fossil fuels, electric power generation is altering drastically all over the world. By implementing energy storage systems (ESSs), the unpredictable daily and seasonal variations in electrical energy consumption can be addressed, reducing the additional GHG emissions into the atmosphere. Mechanical, electrochemical, chemical, thermal, and other energy storage methods are all possible. When there is an imbalance between supply and demand, energy storage systems

(ESS) offer a way to increase the effectiveness of electrical systems.<sup>4,6,7</sup> The most extensively used options for dealing with concerns related to oil shortage, upsurging fossil fuel consumption, and global warming are renewable energy sources including hydro power, photovoltaics, and wind turbines. Strongly reliant on weather resources with sporadic and variable characteristics are solar and wind energy. With benefits like quick response time, sustained power delivery, and regional independence, battery energy storage systems have gained widespread acceptance among the possible methods to solve this problem of power shortage.<sup>8</sup>

Nickel-cadmium, lead-acid, sodium-sulfur metal-air, lithium-ion, and other types of energy storage batteries are commonly employed for this purpose since they compared to engines and turbines, exhibit faster charge and discharge characteristics.<sup>9,10</sup> One of the best ways to store energy is using batteries, which come in a variety of shapes and sizes. The primary focus of this review article will be metal-air batteries, which harness the energy of atmospheric oxygen to create power. This has the benefit that the oxygen does not need to be preserved inside the battery, unlike a standard alkaline or Li-ion battery (LIB). The theoretical specific energy of these metal-air batteries is noticeably (3–30 times) greater than that of Li-ion batteries. Because safer aqueous electrolytes are employed, these batteries are also intrinsically safe in that they won't catch on fire or explode while in use. Due to their comparably high energy density, flexible metal-air batteries have attracted a lot of attention lately and may compete with them for use in wearable or roll-up electronic devices. Flexible nonaqueous LIBs, aqueous zinc-ion batteries (ZIBs), and aqueous aluminum-air (ALBs) batteries are a few examples of metal-air batteries that have recently been produced.<sup>11,12</sup>

Researchers are keen to find cleaner energy technologies for storing and converting energy, including the smart grid, due to the effects of global warming and the shifting price of oil. The creation of portable electronics has also been advancing, necessitating the use of power sources with steadily increasing



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energy and power densities. LIBs, which have a higher energy density than more traditional power sources like Ni-MH batteries, are projected to be able to meet these demands. However, electrode materials with a complex chemistry have a restriction on the highest energy density of modern lithium-ion batteries, making them unsuitable for use in actual electric car applications. Metal-air batteries have generated a lot of interest as a potential alternative due to their incredibly high energy density in comparison to traditional rechargeable batteries.<sup>13,14</sup> For Li-air batteries, it is possible to prevent unfavorable reactions and issues with electrolyte deterioration brought on by organic solvents by employing aqueous lithium salt solutions as the electrolytes. Aqueous electrolytes have a small potential window, which restricts their use in Li-based batteries. When employing high concentration hydrate-melt or water-in-salt (WiS) electrolytes, for example, one can get aqueous electrolytes to operate at high voltages by eliminating free water molecules from the electrolyte.<sup>15</sup>

We will also go over the application of MOFs and their derivatives which are being researched as prospective electrode materials because of their vast specific surface areas, numerous modular and programmable topologies, and enormous internal pore volume in metal-air batteries. Due to their tunable pore widths and metal ions with redox activities, huge specific surface areas and enormous internal pore volumes have made MOFs gain a lot of interest recently as electrode materials with high energy capacities.<sup>16,17</sup> An open framework that may be permeable characterizes the structure of MOFs (porous materials). This type of MOF was initially recognized and described by the Yaghi team in 1995.<sup>18</sup> A coordination bond between a key core metal ion and a bolstering organic ligand self-assembles in this organic-inorganic hybrid material. The MOF has significantly changed over time, beginning with its first direct synthesis, and ending with its current broad utilization. When compared to weak bonds like hydrogen bonds and van der Waals bonds, MOFs' coordination bond energy is much larger (usually 60–350 kJ mol<sup>-1</sup>). MOFs are stable, as a result they can create permanent pores.<sup>19</sup>

Furthermore, MOFs' structure, as well as their physical and chemical characteristics, are highly designable. Researchers have developed more than 20 000 MOFs since the MOF was coined; this numerical figure is continually rising. This is due to the fact that these various center-metal ions can combine with a wide range of organic ligands to generate a vast variety of MOF compounds.<sup>20</sup> Zhang *et al.* created the PCN-128W metal-organic framework in 2015 with the use of zirconium salt and chromophoric linker. The emission maximum shifts from 470 to 538 nm, and the hue of PCN-128W reversibly changes from white to yellow. This piezofluorochromic behavior is quite fascinating. Fluorescence spectroscopy was used to track the stepwise fluorescence change, and it showed that consecutive compression gradually shifted the emission maximum. To get profound understanding of the piezofluorochromic process, structural studies are conducted on both the white and yellow phases.<sup>21</sup>

Recently, there has been a lot of interest in rechargeable sodium-air batteries (SABs), which have a high theoretical

specific capacity, a high energy density, a low price, and no bad environmental consequences. Based on the electrolytes utilized in the system, SABs are categorized into two classes: non-aqueous and aqueous/hybrid. The electrochemical performance of non-aqueous SABs is constrained by the insolubility of solid discharge products like Na<sub>2</sub>O and Na<sub>2</sub>O<sub>2</sub>, which impedes long-term operation by fouling the air electrode. The potential of carbon nanostructures produced from MOF as non-noble metal-based oxygen electrocatalysts for metal-air batteries was investigated by Yuqi Wu *et al.* For the first time, hybrid sodium-air batteries (SABs) with N-doped carbon nanotubes (MOF-NCNTs) (OER) have shown improved electrocatalytic activity and stability for the oxygen reduction reaction (ORR) and oxygen evolution process.<sup>22,23</sup>

The sole purpose of this review is to provide the most recent developments in MOF-based materials utilized in MABs. A lot of significant factors that have a major impact on how active water splitting reactions are discussed along with how to construct catalysts. In addition to a summary of the major challenges in the areas of photocatalytic and electrocatalytic water splitting, some information on recent developments in the production of MOF-based catalysts has also been included. Future research objectives are listed, with an emphasis on achieving the required. For identifying and comprehending the factors influencing catalytic activity, MOF functionality and framework correlations are being developed. This paper highlights recent developments in this rapidly growing field and offers some suggestions for constructing extremely effective photo- and electrocatalysts for water splitting/redox reactions that are based on electrode made of MOFs which take place inside MABs.<sup>24,25</sup>

### 1.1. What are metal-air batteries and what is their working mechanism?

In MABs, the metal anode which is composed mainly of Li, Zn, Al, or Na is inserted first. The liquid or solid electrolyte and the air cathode are then added. This is true for mechanically rechargeable MABs, where the electrolyte and metal plate are occasionally replaced after being used up during discharge. The solid-state MAB, which is typically a gel-polymer based on PVA for Zn-air batteries and has an electrolyte in the solid phase. The electrically rechargeable MAB, it utilizes a breathing carbon-based or metallic porous foil cathode and supports the essential bifunctional electrocatalyst *via* a gas diffusion layer (GDL), has an open battery design. Such batteries with aqueous system are ideal for metals like Zn, Fe, Al, Cd, *etc.* Zinc-air batteries have a particularly promising future as an alternative energy storage device. Aluminium air batteries (AIBs) have a substantial energy density greater than ZABs, even though aluminum corrodes more readily than zinc in alkaline conditions. Additional benefits of Zn include its abundance, affordable, environmentally friendly, low equilibrium potential, flat discharge voltage, and long-time span of usability. These batteries' primary advantage is that oxygen reduction reactions can be catalyzed by non-noble metals and have a potential specific energy density of 1084 W h kg<sup>-1</sup>.<sup>26,27</sup>



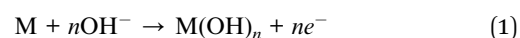
One of the distinguishing features of metal–air batteries is their open cell structure, which uses oxygen gas from the air as the cathode material. Traditional rechargeable batteries have a closed system for their cell arrangement. These batteries come in countless variations based on different metal types, and additional cell components are needed because of their unique reaction kinetics. Based on their electrolytes, these batteries are typically divided into two categories, the first is a cell structure that is impervious to moisture and operates with an aqueous electrolyte. The alternative approach makes use of an electrolyte and aprotic solvents and is water sensitive, but moisture damages this type of system.<sup>28,29</sup> The two main chemical reactions in metal–air batteries are the oxygen evolution reaction (OER) during charging and the oxygen reduction reaction (ORR) during discharging.<sup>30</sup>

The creation of extremely effective bifunctional electrocatalysts that perform with outstanding chemical stability in electrolytes containing oxygen is the main problem in the development of metal–air battery technology. Although precious metals like Pt, Ru, and Ir are known to be efficient electrocatalysts for ORR and OER, their high cost has hindered their widespread accessibility. Recent studies have demonstrated the efficiency and affordability of carbon nanomaterials as platinum alternatives for ORR, including carbon nanotubes, porous carbon, carbon nitride, and N-doped graphene. The surface polarity and electrical properties of nitrogen can be modified by co-doping it with another heteroatom, such as S or P, which increases ORR catalytic activity. However, the OER activity of the bulk of these metal-free catalysts is subpar. The most efficient OER electrocatalysts to date, according to some research, are constructed using transition metal hydroxides and oxides.<sup>31,32</sup>

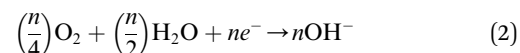
A feasible method for using air as an electrode for batteries has long been desired by the battery industry. Theoretically, air is a material with no cost. If there were no obstacles to enhancing the practical specific energy, specific power, and cycle life of these batteries which commonly comprise earth-abundant components like Zn, Al, Mg, Si, C, Mn, as mentioned before their market price would be far lower.<sup>33</sup> Despite the existence of metal–air batteries for more than a century, their application has been constrained by the performance and stability of the electrodes, electrolyte, and cell design. Recently, aqueous metal–air batteries have undergone significant advancements due to the necessary components that assist the enhancement of long-term

stability and the demonstration of superior electrochemical performance.<sup>34–36</sup>

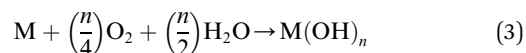
Table 1 compares energy density and open potential circuit of different MABs and showcasing that ALB has the highest value for energy density whereas iron air batteries have lowest. Not only does this iron air battery also has lowest potential value where cadmium air batteries having highest which is 3.10 volts. Batteries use chemical energy to store electrical energy. Because they have a theoretically higher density than lithium-ion batteries, metal–air batteries are being researched. An M-denoted metal anode is oxidized, releasing metal ions ( $M^+$ ), which travel through the electrolyte to the cathode and react with oxygen to form metal oxides as shown in the equations below.<sup>36,38</sup> The metal on the anode oxidizes during discharge to release electrons, and the liberated metal ions mix with the hydroxide ions to form metal hydroxide:



In the next step hydroxide ions are created when oxygen molecules from the atmosphere react with water on the cathode, incoming electrons, and water. Where M could be any metal (for example, Zn, Al, or Mg). The liberated electrons participate in the oxygen reduction reaction at the cathode after travelling through the external circuit (ORR)



The generated hydroxide ions pass *via* the separator from the cathode to the anode to complete the current loop. Combining eqn (1) and (2) results in the following generic reaction:



Zn, Al, and Mg are the only air batteries that can currently be recharged electrically in aqueous electrolyte; nevertheless, metal anodes cannot be transformed from ions to metals in the electrolyte, necessitating manual recharge of metal–air batteries. One of the essential parts of a metal–air battery is the air cathode, and reliable air electrodes guarantee that the battery operates effectively and consistently. An effective air electrode should typically have quick OH-migration, alkaline condition, good electrochemical stability.<sup>39</sup> Oxygen evolution and reduction exhibit considerable electrochemical activity in rechargeable batteries as well as primary metal–air batteries (especially under high potentials). The design of air electrodes is hindered by these contradicting and difficult requirements. According to the literature, the development of air electrodes with improved catalytic activity, longer life, and lower production costs has thus been the main emphasis of metal–air battery research over the past 50 years.<sup>40,41</sup>

We have discussed almost all metal–air batteries in this section but, in this paper, our primary focus will be on the most common ones which are lithium and zinc air batteries.

**Table 1** Various metal–air batteries' energy densities.<sup>37</sup>

Battery type	Open circuit potential (volts)	Energy density (W h L <sup>-1</sup> )	Energy density (W h kg <sup>-1</sup> )
Zn–air	1.68	5960	1045
Li–air	2.96	6102	3458
Fe–air	1.35	1431	763
Mg–air	3.08	12 200	3991
Ca–air	3.10	9960	2980
Al–air	2.71	14 100	4116





## 1.2. Lithium air batteries

If a workable device could be created, the rechargeable LIBs, which has the greatest energy density among any rechargeable battery, might revolutionize energy storage. As a technology for energy storage, LABs have generated interest due to their high energy and power density. By surpassing the energy capabilities of traditional LIBs, these batteries are anticipated to revolutionize both the electrochemical energy storage systems and the automotive sector (for usage in electric and hybrid vehicles). Non-aqueous (aprotic) solvents, aqueous solvents, and hybrid (non-aqueous/aqueous/aqueous) solvents are the basic types of Li-air batteries as shown in Fig. 1 below it basically represents overall configuration of these batteries. Li salts are dissolved in all solid-state electrolytes. The anode and cathode materials in each of the four systems are formed of lithium metal and oxygen gas, respectively. Nevertheless, the type of electrolyte utilized affects how they react. Non-aqueous LIBs have porous cathodes where oxygen is reduced and converted to solid  $\text{Li}_2\text{O}_2$ . As a result, the main constraints limiting the capacity of this battery system are the solid product obstruction and/or passivation of active surfaces at the porous cathode. The configuration of the non-aqueous electrolyte system is similar to that of traditional LIBs.<sup>42,43</sup>

Like standard LIBs, the non-aqueous electrolyte system is configured. Anodes composed of carbon or alloy materials, cathodes constructed of Li metal oxides or phosphates, and electrolytes formed of aprotic solvents in which Li salt is dissolved are all used in conventional batteries. Because oxygen gas acts as the cathode in Li-air batteries, porous carbon

materials and catalyst composites must be considered. Since anodes are the lithium source in these batteries, this metal must be employed as the anode here. The primary difference between the two systems is that Li-air batteries need an open system. Additional parts, including air-dehydration membranes, are needed for an open system.  $\text{Li}_2\text{O}_2$  is a precipitate that forms when  $\text{Li}^+$  ions near the air cathode's surface in Li-air batteries interact with oxide ions.<sup>42,44</sup> Compared to previous rechargeable battery systems like nickel-cadmium or lead-acid, LIBs and LABs batteries offer a higher energy density, which has led to their significant success in the field of portable devices.<sup>45</sup>

Significant research is currently being conducted on them with the goal of storing energy produced by electric vehicles as well as renewable energy sources like solar and wind energy. Due to issues with energy, power, cycle life, cost, and safety, Li-ion batteries are not frequently employed for these later applications.<sup>46,47</sup> For instance, the highest current capacity of insertion-oxide cathodes is  $250 \text{ mA h g}^{-1}$ , and liquid electrolytes currently on the market typically dissolve above 4.3 V. New battery chemistries in addition to the next generation of electrochemical energy storage devices will require Li-ion technology. Due to its high specific gravity, lithium metal is the most promising anode material for high energy density batteries. During battery discharge, a solid product that forms in the porous cathode is strongly related to the multi-phase transport mechanisms that move electrons in the solid materials and dissolved oxygen and lithium ions ( $\text{Li}^+$ ) in the liquid electrolyte. For increasing battery capacity and design, particularly under

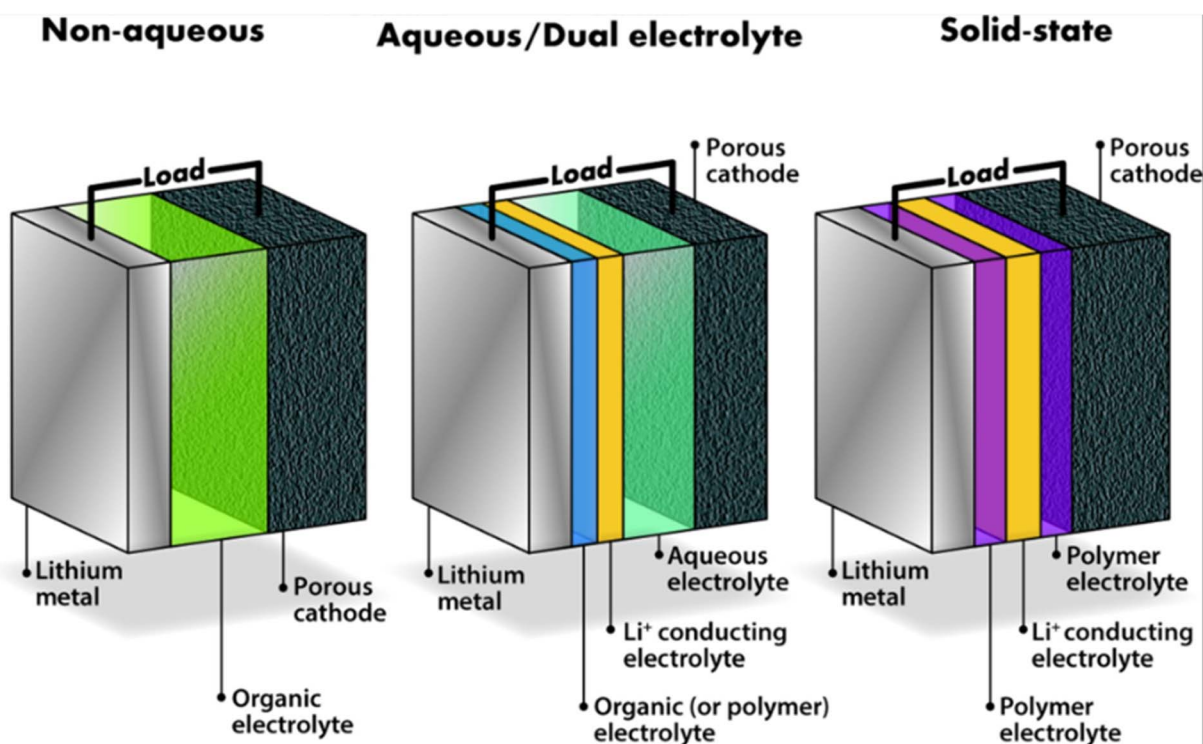


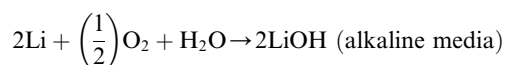
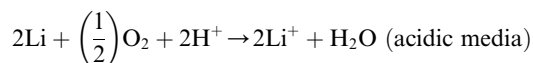
Fig. 1 Schematic cell configurations for the three main types of Li-air battery. Copy with permission from ref. 42. Copyrights 2015, Wiley Online Library.

high-rate situations, one must have a thorough understanding of the physics underlying transport phenomena as well as an accurate assessment of efficient transport attributes.<sup>48,49</sup>

The transport governing equations for porous-average level macroscopic continuum models are presented below. The simplest net reaction envisioned for the aprotic battery is a two-electron process:



The basic processes in an aqueous cathode electrolyte are:



The chemistry of the all-solid-state battery is most likely equivalent to the aprotic electrolyte battery, despite not yet being known. Due to its advantageous energy density and durability, LIBs are the ideal option for energy storage in portable devices. For usage as power sources for electric vehicles and smart grids, batteries must have a long lifespan, a high energy density, continuous safety performance, and a low price.<sup>50</sup> Electrolyte additives have greatly improved in their ability to handle the problems with conventional electrolytes that lead to substandard cycle performance and unwanted gas generation because of advancements in electrode materials. The capacity of the cathode and anode materials, as well as the operating voltage, have a major impact on the energy density of LIBs. Reversible battery operation requires long-term electrode-electrolyte interfacial stability, even if high-energy-density LIBs can be created utilizing high-capacity electrode materials and a high operating voltage. Electrolyte additives' formation of electrochemically resistant interfacial layers and preservation of the interfacial structures of electrodes for high-performance LIBs will be advantageous for high-capacity electrodes to achieve electrochemical reversibility.<sup>51</sup>

Large pore volumes, clearly defined pores, and evenly dispersed catalysts are characteristics of materials generated from MOF that are beneficial for large-scale transportation, redox processes involving oxygen discharged products (*e.g.*, lithium oxide). One such substance, a cage-type graphitic porous carbon-Co<sub>3</sub>O<sub>4</sub> (GPC-Co<sub>3</sub>O<sub>4</sub>) polyhedron made from core-shell MOFs (ZIF-8@ZIF-67), provided low charge potentials and an exceptional cycle life when utilized as a cathode substance for lithium batteries. This was made feasible thanks to the advantages of the graphitic carbon component, which improves conductivity, and the cage-type and mesoporous structures, which can bind to Li<sub>2</sub>O<sub>2</sub>.<sup>52</sup> Graphene/graphene-tube nanocomposites, cobalt-manganese oxide, Co<sub>9</sub>S<sub>8</sub>@carbon porous nanocages, Fe<sub>2</sub>O<sub>3</sub>/carbon, and ZnO/ZnFe<sub>2</sub>O<sub>4</sub>/C nanocages are also listed as cathode materials for LABs.<sup>53</sup>

Li<sub>2</sub>O<sub>2</sub> may cause the carbon components of materials made from MOFs to break down, resulting in low cycle stability. To help in the development of suitable MOF-derived materials for use in real-world LABs, it would be wonderful to have a deeper knowledge of the fundamental chemistry of LABs. Due to their incredibly high theoretical capacities and energy densities, rechargeable LIBs and LABs are one of the most promising power sources for the upcoming generation of electric vehicles. The technology has gone through several revisions over the years, but significant problems still need to be resolved before it can be successfully marketed. A few concerns that need to be resolved include its practicality, round-trip effectiveness, and riding time. The advantages of this type of battery are discussed in this review. The battery's electrolyte and electrode optimization are considered at the system level of design. This study also offers viewpoints on how to achieve the necessary battery performance to satisfy the criteria for commercial feasibility.<sup>54,55</sup>

### 1.3. Zinc air batteries

A separator, a catalytic active layer, a gas diffusion layer (GDL), and an air electrode that serves as the cathode make up zinc-air batteries. Oxygen cannot be used as a liquid at atmospheric pressure due to its extremely low solubility; rather, it must be employed as a gas. The catalyst then aids in reducing oxygen to hydroxyl ions in the alkaline electrolyte by using the electrons produced by the oxidation of zinc metal as the anode process. Due to the fact that the catalyst, electrolyte, and oxygen are all in three phases simultaneously, we refer to this process as a "three-phase reaction" (gas).<sup>56</sup> Zinc is oxidized with oxygen from the air in metal-air batteries, such as non-rechargeable zinc-air batteries and zinc-air fuel cells, to generate power (mechanically rechargeable). These batteries are made at quite low prices and have great energy densities. From the comparatively small button cells used in hearing aids to the massive batteries used in grid-scale energy storage, batteries come in a variety of shapes and sizes. Additional battery sizes include those used in mercury-powered film cameras and larger batteries for digital cameras. Interior and exterior of the cell, the porous carbon electrode can absorb atmospheric oxygen.<sup>48,57</sup>

These electrochemical processes taking place in the alkaline solution between the anode and cathode, which constitute the entire discharge process, are explained. How a zinc-air battery works and how each electrode reacts. An electrolyte-saturated porous anode made of zinc particles forms after discharge. To generate zinc hydroxide and release electrons to flow to the cathode, oxygen from the air and the cathode combine to make hydroxyl ions. Water is reintroduced into the electrolyte as the zincate converts to zinc oxide. The water is not used since the hydroxyl and water recycled at the cathode from the anode.<sup>58</sup>

The red circle in Fig. 2 above designates the position of this three-phase interaction. In zinc-air batteries, oxygen absorption is facilitated by this shape. To finish the reaction, hydroxyl ions in the cell go from the zinc anode to the air cathode. Theoretically, the reactions generate 1.65 volts, but in practical cells, this is decreased to 1.35 to 1.4 volts. The oxygen reduction reaction (ORR) requires a significant overpotential in order to



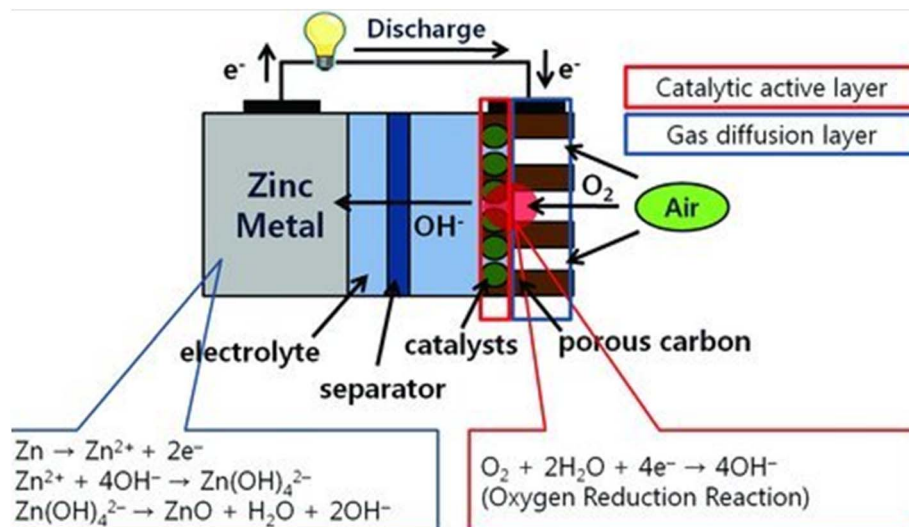


Fig. 2 The zinc–air battery's operating concept and each electrode's reaction. In the air cathode, a three-phase reaction comprising liquid electrolyte, solid catalysts, and gaseous oxygen takes place in the red circle. Copy with permission from ref. 59. Copyrights 2010, Wiley Online Library.

produce hydroxyl ions, as shown by the polarization curve.<sup>60,61</sup> As a result, the actual zinc–air cell's operational voltage and open-circuit potential (OCV) are both substantially lower than 1.65 V. A higher potential is required for charging when the reverse process (the oxygen evolution reaction) is considered (blue line). It is clear from the preceding summary that using the ORR has advantages and disadvantages for zinc–air cells. The positive point enables this cell to have a higher energy density despite the lack of oxygen active material. The subject has already been discussed. The zinc–air cell experiences a considerable potential loss because of the negative point, which affects the cell's power density. As a result, many studies have concentrated on how to create novel catalysts and alter the designs of the air electrodes to lessen the significant over-potential in the cathode reaction.<sup>62</sup>

In a primary zinc–air cell, the zinc anode is not significant since old zinc metal can be spontaneously replenished with new metal through electromechanical charging. To make a zinc–air battery that can be electrically recharged, the electrochemical behavior of the zinc anode must be altered. The creation of a secondary zinc–air battery may be hampered by other issues even if these two primary limitations of zinc–air batteries are ignored.<sup>60,63</sup> In zinc–air batteries, the anode's active component is pure zinc metal, which oxidizes during discharge. Due to this, most of the research has concentrated on making the air electrode rather than the zinc anode. According to the equation  $\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{H}_2$ , zinc corrodes at a slower pace than aluminum does in an alkaline solution, but hydrogen gas is still produced during this corrosion process (hydrogen evolution reaction, or HER). Considering zinc metal's electrochemistry in the alkaline electrolyte as opposed to just its electrochemistry in the gas phase makes more sense. The hydrogen evolution process (HER), which is not intended to take place during discharge, has been identified as the most critical area of study. It is envisioned that to gradually increase capacity of these

batteries zinc metal should be utilized entirely during the process of discharging.<sup>58,64</sup>

Electrolytes regulate the ion transport behavior in ZABs. The most advanced electrolytes for flexible ZABs are hydrogels because of their cohesive flexibility and capacity to transfer ions diffusively like liquids. The local segmental movements of polymer chains, which are responsive to temperature variations, are correlated with the ionic conductivity of hydrogel electrolytes. The hydrogel electrolytes also run the risk of becoming less flexible and conductible at below-freezing temperatures because they are aqueous in nature. Recent studies have used low-molecular vicinal alcohols to generate organ hydrogels that can function at subzero temperatures by replacing some of the water in aqueous hydrogels. However, ORR/OER and the ionic conductivity of gel electrolytes are always degraded (or poisoned) by the addition of organic molecules. But the concentrated alkaline solute utilized in ZABs, enables the use of the solutions' natural capacity to collaborate to lessen the impacts of low temperatures. The introduction of potent alkaline solutions to hydrogel electrolytes can adversely compromise the structural integrity of polymer backbones. The interactions between the terminal groups on these hydrogel electrolytes' polymer backbones, the electrolyte ions, and the water are what keep them from freezing. Although this has not yet been verified, hydrogel electrolyte backbones for ZABs can adjust to low temperatures.<sup>63,65</sup>

Aqueous zinc–air batteries are particularly commendable when working in high-temperature environments due to their inherent safety. However, the possibility of their functioning at high temperatures hasn't been studied very much. Systematically examining the practicability of high-temperature zinc–air batteries is done here. To determine the positive and negative influences of temperature, the impacts on the aqueous electrolyte, zinc anode, and air cathode are separated. Particularly,





parasitic hydrogen evolution process, which is known as the primary bottleneck, intensifies at high temperatures and causes a drop in anode Faraday efficiency. Additionally, zinc–air batteries show that cycling is possible at 80 °C. This research shows how zinc–air batteries may provide energy storage at high temperatures and directs future research into improved batteries toward challenging operating environments. Traditionally, the Zn–air battery's performance-limiting electrode has been the air cathode. They are made by uniformly loading the proper electrocatalysts over porous gas diffusion layers that have been coated with polytetrafluoroethylene (GDLs). Water retention (hydrophilic) and water repulsion (hydrophobic) characteristics in good GDLs are balanced. They have many gas-electrolyte-electrode triple-phase boundaries, a high current density of up to  $>1 \text{ A cm}^{-2}$  and allow  $\text{O}_2$  gas to enter the system quickly. The primary factor accelerating the ORR and OER and, thus, affecting the total battery performance is electrocatalysts placed on GDLs (e.g., power density, energy efficiency and cycle life). You can manually or electrically recharge zinc air batteries. Zn–air batteries that are mechanically rechargeable can be recharged by replacing the anode and electrolyte with fresh ones. They are main rechargeable batteries that merely require ORR electrocatalysts to serve as the cathode.<sup>66,67</sup>

#### 1.4. Other metal–air batteries

Due to incentives to create affordable, ecologically friendly, and reliable rechargeable batteries. When compared to an aluminium or zinc air battery, the iron–air battery emits less energy, but it has the same charge and discharge characteristics and uses an excessive amount of electrode material. The projected operational voltage and capacity of an iron–air battery are lower than those of an aluminium or zinc battery, thus this is accurate. However, compared to zinc–air batteries or aluminium–air batteries, iron–air batteries are less likely to be used as primary batteries because the iron negative electrode's expected capacity and working voltage are lower than those of zinc and aluminium. Iron–air batteries also have an abundance of electrode material. Iron's electrode response is also more difficult in several ways than zinc's, as this article has explained.<sup>68,69</sup> Due to this, commercial iron–air primary batteries are now extremely rare, and almost all of them feature a zinc negative electrode. The electrode reaction of iron in an alkaline electrolyte totally occurs in the solid state without engaging the deposition–dissolution process because the discharge products from iron, such as iron hydroxides and iron oxides, are not highly soluble. Because of this iron feature, a negative electrode's tendency to change form over cycles is bad for primary batteries but good for secondary batteries. This battery system has been perceived as a supplementary battery with more sophisticated technologies as a result.<sup>70</sup>

Although still under development, Mg–air and Al–air batteries are generating a lot of scientific attention. In terms of weight and price per amp hour, aluminium is less expensive than zinc, the fifth most abundant element on earth. Due to its lightness and toughness, aluminium is also well-known as a building and manufacturing material and is frequently used

in industries like automation and construction. Due to the advancement of commercial alloys, metal–air cells may be able to compete with established energy accumulating methods.<sup>71</sup> The main problem is that an oxide coating spontaneously forms on the electrode surface when Al is exposed to air or aqueous solutions. The active dissolving of aluminium is significantly decreased by the presence of this protective oxide coating, which also positively affects the anode's corrosion potential. The amount of extractable energy is significantly decreased by this alteration. Al quickly loses its attraction as a potential component of an energetic anode. Although it still has certain limitations, such as anode corrosion, slow discharge products, a high rate of self-discharge, cell irreversibility, and shelf life, the rechargeable Al–air battery is one of the most promising technologies. By swapping out the current Al electrode, the battery system might be able to provide rapid mechanical recharging if electrochemical recharge is not available.<sup>72</sup>

## 2. MOF as a bifunctional electrocatalyst

A catalytic substance that has two catalytic functions one is catalyzation of cathodic reaction and the other one is anodic reaction and may therefore be referred as a bifunctional catalyst, also known as a dual-function catalyst.<sup>73</sup> Electrocatalysts, a category of catalyst that takes part in electrochemical reactions, speed up the rates of oxidation and reduction in electrochemical cells or MABs. Electrocatalytic materials, which are not consumed during the reaction process, accelerate electrochemical reactions by interacting with reagents to change the reaction pathways and reduce the activation barrier. The majority of conventional single layer electrodes that have been created to date have substantial mass transport resistance and have subpar performance. The design of the double layer electrode also affects the reaction rate, most conventional single layer electrodes created to date have substantial mass transport resistance and have subpar performance. For flow batteries, a double-layer electrode has a backing layer and a catalyst layer. Therefore, by altering the electrocatalysts on the electrode surface, the electrochemical reaction rate can be managed. The OER and the ORR, which are the subjects of our review work, are two separate types of reactions that these bifunctional catalysts catalyze.<sup>74</sup>

The catalysed oxygen evolution and oxygen reduction processes are crucial components of numerous energy conversion and storage systems (OER and ORR, respectively). Over the past ten years, they have evolved into viable choices to meet the market's increasing demand for renewable energy. It is anticipated that developing (bi)functional, inexpensive non-noble metal or metal-free electrocatalysts will boost useable energy density and significantly lower production costs. The amount of surface area and unique pore characteristics of mesoporous materials have a substantial impact on how reactive they are to electrochemical processes. As a result of the fact that the effectiveness of the electrochemical processes occurring at the electrodes during the charging and discharging activities





directly determines how well these storage devices perform generally.<sup>75,76</sup>

The above Fig. 3 illustrates the oxygen reduction reaction's stoichiometries, which vary depending on the medium. To form molecular oxygen in OER, several proton/electron-coupled processes are necessary. Theoretically, a higher energy density might be achieved by using  $4e^-$  ORR rather than  $2e^-$ . The properties of the electrode surface and any extra catalysts affect the complicated ORR path. The various critical steps of the multielectron reactions known as the ORR and the OER involve many reaction intermediates. The oxygen reduction reaction, sometimes referred to as the reduction half reaction, is a chemical process that turns oxygen ( $O_2$ ) into water or hydrogen peroxide. Oxygen consumption reaction.<sup>78</sup> Electrocatalyst activity, affordability, toughness, and stability are crucial for practical application. Exceptional electrical conductivity, superior chemical stability in a range of electrolytes, and a strong catalyst support with a large surface area are also necessary. Metal oxide nanostructures can be regarded as an essential electrocatalytic material because of its very distinctive optical, electrical, and molecular properties, easily functionalize nature, exceptional resistance to alkaline corrosion in an electrochemical environment, and other attributes.<sup>79</sup>

Table 2 above shows that a high Tafel slope corresponds to a large band-gap energy, which results in a high overpotential

since a lot of energy is required to produce activity and *vice versa*. The rate-determining phase of the electrochemical reaction is similarly described by the Tafel slope. The graph representing the relationship between the current produced in an electrochemical cell and the electrode potential of a specific metal is called a Tafel plot, which is frequently logarithmic. OER is a vital phase in energy conversion and storage, particularly in water electrolysis. Presently, the OER process makes extensive use of precious metals and their oxide complexes (Ir, Ru,  $IrO_2$ , and  $RuO_2$ ) as cutting-edge catalysts to lower energy consumption and improve energy conversion efficiency.<sup>81</sup> OER which provides the electrons needed for electrochemical conversion cycles between renewable electricity and chemical fuels, is significantly reliant on these energy storage devices. In a metal-air battery, OER occurs on the cathode, and its activity and stability can be readily assessed. Electrocatalysts are necessary for MAB device charging and discharging as well as for critical electron transport, chemical bond formation, and rupturing.<sup>82</sup>

Electrocatalysts can be used to increase the activity and stability of ORR and OER. Noble metals are effective oxygen evolution catalysts. However, they are unable to be reversible, which is required for all applications involving energy storage because only one sort of reaction is the focus of their high activity. Reversible MABs and other energy storage technologies may be used more widely as a result of the identification of bifunctional

ORR	In acid aqueous system	$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$ ( $4e^-$ ) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ( $2+2e^-$ ) $H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O$
	In alkaline aqueous system	$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$ ( $4e^-$ ) $O_2 + 2e^- + H_2O \rightarrow HO_2^-$ ( $2+2e^-$ ) $HO_2^- + 2e^- + H_2O \rightarrow 3OH^-$
	In an aprotic electrolyte	$O_2 + e^- \rightarrow O_2^-$ $O_2^- + e^- \rightarrow O_2^{2-}$
OER	In acid aqueous system	$2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$
	In alkaline aqueous system	$4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^-$
	In an aprotic electrolyte	$O_2^{2-} \rightarrow O_2\uparrow + 2e^-$

Fig. 3 Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) equations in various electrolytes. Copyrights 2019 from ref. 77.

Table 2 Performance evaluation of the oxygen evolution process (OER) using different transition metal hydroxides and oxides<sup>80</sup>

Materials	Electrolyte	Over potential for 10 mA cm <sup>-2</sup> V <sup>-1</sup>	Tafel slope mV <sup>-1</sup> dec <sup>-1</sup>
RuO <sub>2</sub>	1 M KOH	0.3	42
MnCo-G	KOH	0.33	48
CoP	1 M KOH	0.36	66
CoMoO <sub>4</sub>	1 M KOH	0.31	56
NiFe LDH	1 M KOH	0.33	41
CoFe LDH	0.1 M KOH	0.36	49
Co <sub>3</sub> S <sub>4</sub> @MoS <sub>2</sub>	1 M KOH	0.33	56
CuCo <sub>2</sub> O <sub>4</sub> /N-rGO	1 M KOH	0.36	64



catalysts active in ORR and OER. There is a constantly expanding interest in the creation of high-performance stable catalysts because these combinations and structures serve as the foundation for hybrid compositions, spinels, non-noble (mixed) transition metal oxides, and oxides of carbon.<sup>81,83</sup>

In OER, several proton/electron-coupled reactions are required to produce molecular oxygen. To enhance efficiency for practical applications, a full reduction is used. Furthermore, the slowness of OER and ORR reactions is well recognized. For OER and ORR to be beneficial for energy storage devices like MABs, where OER occurs, it is imperative to keep in mind that oxygen molecules must renew when charging. A full water splitting process that utilizes a ground-based, dual-purpose electrocatalyst as both a cathode and anode. The development of inexpensive, effective, stable, and bifunctional electrocatalysts has attracted a lot of scientific interest, as have air battery-based energy storage technologies.<sup>84</sup> The oxygen reduction reaction is a crucial electrochemical process for generating energy in fuel cells (ORR). Recently, this reaction has been enhanced by several study teams employing size-selected clusters. Fuel cells and metal-air batteries both rely on the ORR. Although Pt-based nanoparticles exhibit excellent ORR activities, their high cost and limited shelf life preclude them from being widely used.<sup>85,86</sup>

The most difficult holdback of these advancements is the slow kinetics of electrochemical half-reactions like the (ORR) and (OER), which lowers the overall output efficiency throughout the process. Noble metal-based catalysts are frequently used to overcome these issues (such as Pt/C catalysts for ORR and Ru/Ir-based catalysts for OER), but their poor methanol tolerance, high cost, and low stability severely limit their future potential. The primary goal is to create a bifunctional catalyst with high catalytic activity and low-cost characteristics for the two distinct processes. A single active site catalyst is often unable to provide strong bifunctional catalytic activity because ORR and OER use distinct routes. The hybrid or composite of Co<sub>2</sub>P/CoP is thus expected to demonstrate the enhanced bifunctional ORR/OER activity. CoP and Co<sub>2</sub>P can coexist thanks to an improved three-dimensional self-supported electrocatalyst made of nitrogen-doped carbon nanotubes (NCNT), which works by phosphorylating molecules at low temperatures first. The resulting three-dimensional carbon network structure also enables rapid charge transfer. Additionally, the active sites of the carbon foam (CF) are greatly increased by hollow structural architecture.<sup>87</sup> With only low overpotentials of 133 and 289 mV respectively, CoP/Co<sub>2</sub>P/NCNT@CF displayed outstanding catalytic activity for the oxygen evolution reaction and hydrogen evolution reaction in alkaline media. The developed catalysts also have exceptional long-term stability; they continue to have significant catalytic activity even after 20 hours of continuous operation.<sup>88</sup>

## 2.1. MOF types and derivatives

A special class of hybrid porous crystalline materials was developed in the 1990s by fusing organic linkers with inorganic metal centers. This novel family of porous materials, sometimes referred to as porous inorganic-organic hybrid materials

(PCPs), is most frequently referred to as metal-organic frameworks (MOFs). For decades, scientists have worked to incorporate various metal centers and valuable organic molecules into porous materials to change their physical and chemical properties. Due to their adaptability in terms of their chemistries and structural makeup MOFs have captivated the interest of scientists, engineers, and technologists ever since their discovery.<sup>89</sup> The development of synthesis techniques has been the focus of countless studies and research publications since it directly affects how MOFs crystallize, which determines their characteristics and functional performance. MOFs can have multiple topologies for their frameworks, pore patterns, and sizes by selecting various metal centers and organic linkers. By chemically functionalizing linkers and subsequently applying modifications, their chemical characteristics can be altered.<sup>90,91</sup>

One of the most common ligands utilized is the substance 1,4-benzenedicarboxylic acid, often known as “struts” or “linkers” (BDC). Metals are often thought of as electron donors, whereas ligands are thought of as Lewis bases and acids. Among other things, ligands are classified according to their charge, size (bulk), kind of coordinating atom or atoms, quantity of electrons supplied to the metal, cone angle and other characteristics (denticity or hapticity), where cone angle is a measure of ligand magnitude.<sup>92</sup> There are numerous alternate ranking systems for ligands and metal ions; one of them places emphasis on the “hardness” of the ligand. Metal ions prefer certain ligands over others when binding. Strong-field ligands bind metal ions in accordance with the Aufbau principle, while weak-field ligands bind complexes in accordance with Hund’s rule. In the process of joining with the ligands, the metal creates new HOMO and LUMO structures that specify the properties and reactivity of the final complex as well as the configuration of the metal’s five d-orbitals (which may be filled, or partially filled with electrons).<sup>93,94</sup>

Many different processes can be used to produce carbon materials, including physical or chemical carbonization from carbon, direct carbonization from organic precursors, the use of zeolites and mesoporous silica as template materials, high temperature solvothermal and hydrothermal processes, electrical arc techniques, and chemical vapor decomposition (CVD) procedures. Direct carbonization of organic precursors is the most popular technique for creating nano-porous carbons (NPCs) due to its adaptability and simplicity. These NPC materials do, however, have several shortcomings, including limited surface areas, disorganized patterns, and unequal sizes, which will significantly restrict their applications.<sup>95</sup>

Researchers studying fuel cells and metal-air batteries have recently become interested in non-noble metal oxygen reduction reaction (ORR) catalysts made by carbonizing metal-organic framework (MOF) due to their distinct inherent advantages, such as high catalytic activity, low cost, simple synthesis, and good adaptability. In contrast to the typical high-active noble metal investigations, this study carefully investigates recent advancements on non-noble metal ORR catalysts produced by various MOFs carbonization in diverse metal centers, including Fe, Co, Cu, Ni, Mn, and Mo. The topologically structured zeolite-like MOF (ZIF) and the Materials of Institute



Lavoisier (MIL) with a significant specific surface area are two examples of the innovative MOFs with distinctive properties that have been created ( $5900 \text{ m}^2 \text{ g}^{-1}$ ).<sup>96</sup> MOFs have advanced to the point that they are now active areas of research in many areas. The enormous surface area, plentiful active centers, and adaptable structure of MOFs have made them the subject of intense research in recent years. However, it cannot be effectively used in water electrolysis due to its low conductivity and inaccessible active sites. Lei Y., *et al.*<sup>97</sup> developed a self-supporting electrocatalyst by growing a MOF derivative on the surface of iron foam (IF) using a self-template partial transformation approach. The production of several catalysts with various morphologies was also accomplished by varying the Ni concentration and reaction duration. The resulting NiFe-LDH@Fe-MOF/IF-2 exhibits excellent oxygen evolution reaction (OER) activity in an alkaline electrolyte with the required overpotentials of 183, 237, and 257 mV because of its distinct hierarchical structure, large active area, and abundant active sites, strong combination of highly active amorphous NiFe-LDH and Fe-MOF, high conductivity, and stability of the MOFs array *in situ*. Using a straightforward ultrasonic process, bimetal-organic framework nanosheets wrapped around polypyrrole nanotubes (NiCo-MOF@PNTs) were effectively produced. PNTs may effectively prevent the aggregation of NiCo-MOF nanosheets and boost the electronic conductivity of NiCo-MOF in NiCo-MOF@PNTs nanocomposites. The unique structural architecture of NiCo-MOF@PNTs enables their improved electrochemical performance. The assembled NiCo-MOF@PNTs/AC asymmetric supercapacitor, which displays a high energy density of  $41.2 \text{ W h kg}^{-1}$  at a power density of  $375 \text{ W kg}^{-1}$ , and the excellent cycling stability with a capacitance retention of 79.1% after 10 000 cycles, demonstrates the potential of the NiCo-MOF@PNTs nanocomposites as supercapacitor electrode materials.<sup>98</sup>

Scientists have learned that carbon compounds produced from metal-organic frameworks (MOFs) can overcome these limitations as research has progressed. Carbon materials made from MOFs include high porosity (up to 90%), an incredible amount of surface area (nearly  $10\,000 \text{ m}^2 \text{ g}^{-1}$ ), tunable pore widths, excellent cycle lifetime, and other advantages. The efficiency of different applications has been the subject of numerous significant studies in the past. For instance, MOFs are suitable for energy-related electrocatalysts depending on the choice of coordination metal due to their high surface areas and atomic metal sites. The electrocatalytic processes of oxygen reduction, carbon dioxide reduction, and water splitting have all extensively used MOFs HER and OER as shown also on Fig. 4.

Since electrode materials are an essential part of lithium-ion batteries, they have been the subject of in-depth research. Due to their high porosity and controlled structural characteristics, MOFs make the greatest choices for electrode materials in lithium-ion batteries.<sup>100,101</sup>

## 2.2. MOF composites

Large-surface MOFs make good structural hosts since they can hold a lot of functional guests. Because pure MOFs have

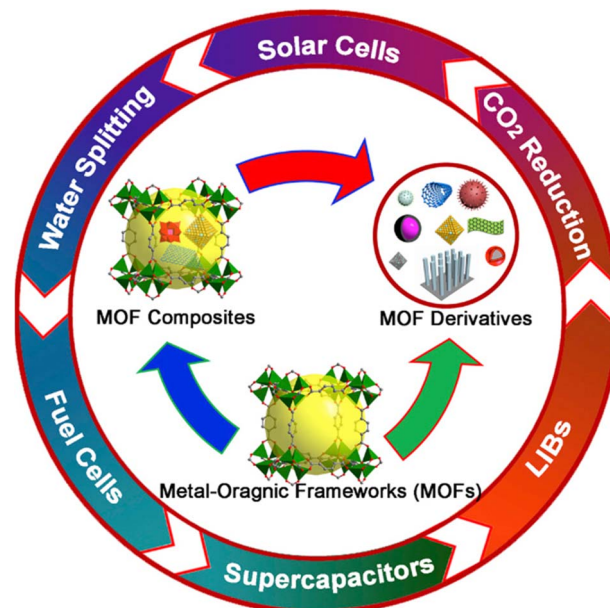


Fig. 4 Showing use of MOFs derivatives and composites in different electrochemical cells and processes. Copy with permission from ref. 99. Copyrights 2017, ScienceDirect.

limitations. For addressing their shortcomings, MOF composites have been researched and created. Since most MOFs composites just not only maintain the porous architectures of MOF precursor but also display superior electrical conductivity brought on by the carbon component, they have a greater probability of success as electrode materials. Overall, the development of materials linked to MOFs, such as MOF composites, and electrode materials made from MOFs, has been an intriguing cross-disciplinary area where opportunities and challenges coexist. There are countless opportunities for the discovery of potential electrode materials for various battery systems when electroactive sites are included in the designable MOF components. Ion transportation and electrolyte penetration are straightforward processes since MOFs are naturally porous.<sup>102</sup> The usage of MOFs in electrochemical processes as well as the expansion of the use of novel advanced materials are both supported by these composites. These composites can improve the intrinsic properties and functionality of MOFs, and these qualities and functioning of MOFs can be improved by 0D materials, which have a tiny size and high surface energy. 0D MOF composites can be created in a variety of methods, but most of them include employing MOFs as carriers for already-formed NPs or as carriers by themselves that use templates to create NPs on their surfaces.<sup>103,104</sup>

Metal oxides created from MOFs have proven to be acceptable candidates for the construction of efficient and well-established cathode catalysts, which are necessary to deal with the slow redox reactions in Li-air batteries. Since electrochemical processes on the cathode are the basis for evaluating Li-O<sub>2</sub> battery performance, high energy density nanostructured enhanced cathode materials have been produced. A new, self-standing catalytic framework was created utilizing thermal



annealing following the 3D printing of a cobalt-based metal-organic framework (Co-MOF). Because the insulating  $\text{Li}_2\text{O}_2$  particles are enclosed within carefully regulated holes and incorporate Co-based electrocatalysts, the unique structure successfully deposits insulating  $\text{Li}_2\text{O}_2$  particles during charging and then expedites their breakdown. Due to its exceptional conductivity and crucial mechanical stability, the carbon framework itself is a superb conducting matrix. By transforming a porous matrix into a self-standing catalytic structure, specific energy with a high energy density of up to  $798 \text{ Wh kg}^{-1}$  cell can be significantly increased.<sup>105</sup>

The scheme in Fig. 5 shows the shape size and types of different MOFs dimension-wise. 0D MOF composites which are also discussed later in the review can be synthesized utilizing the one-pot approach, and by following this simple and effective process, it is possible to improve catalytic performances while also lowering the cost of large-scale production.<sup>107,108</sup>

### 3. MOF/1 dimension

As illustrated on the Scheme in Fig. 5 above, materials with MOFs surrounding them, the term "MOF/1D materials" refers to MOFs with one dimensional nanobelt materials generated on carbon fabric as well as MOFs with one dimensional material on their outer surface. Utilizing polymerization in place, MOFs and 1D nanobelt oxidation can be chemically coupled *in situ*. The self-template technique allows for the construction of 1D composites from 1D components. In order to initiate the synthesis of MOFs without surface modification, it can also be employed as a template to dissolve metal ions in solvents. In addition to being beneficial for generating MOFs like ZIF-8 powder, the spontaneous phase segregation approach is also suitable to a wide range of supported semiconductor 1D material applications. These substances are tiny and have a high surface energy.<sup>109</sup>

Due to its persistent porosity, high surface chemistry, and adjustable pore sizes, MOFs have drawn a lot of interest in the fields of catalysis, gas adsorption, separation, and storage over the past 20 years. The creation of new MOF applications in fields including electrical catalysis, bio-imaging, drug transport, and better features as compared to pure MOFs is facilitated by the addition of functional species or matrix materials to MOFs. This results from interactions between the MOF structures and the functional species or matrix. Even though the creation, chemical alteration, and potential applications of MOFs have all been covered previously, there is growing interest in the creation and use of their composites. In order to close this gap, the creation, characteristics, and applications of MOF composites are discussed in this work. Processing methods, maximizing composite qualities, and potential applications have all been discussed as prospects and problems in upcoming sections.<sup>110</sup>

CNTs@Mn-MOF was created using an effective hydro-thermal method, which may be able to compensate for the drawbacks of traditional Mn-based electrode materials. The method also shows how 2D materials can be encased in MOFs to form MOF/2D materials as well as how MOFs can be grown on 2D nanosheet materials. MOFs are frequently combined with 2D nanosheet materials, including graphene oxide, using solvothermal techniques (GO). In the case of MOF/3D composites, which contain cellular structures with a cubic and core-shell design. Layer-by-layer (LBL) assembly is a versatile sequential technique that permits precise control of the MOF shell thickness. It can be used to create three-dimensional composites like three-dimensional core-shell composites.<sup>111</sup>

#### 3.1. MOF/nanorod composites

MNPs (metal nanoparticles) are frequently utilized in electronics, energy conversion, storage, electrochemistry, and catalytic applications because of their wide variety of forms, sizes, crystallinity, and practicality. The development of various nanostructured electrode materials using MOFs, either directly

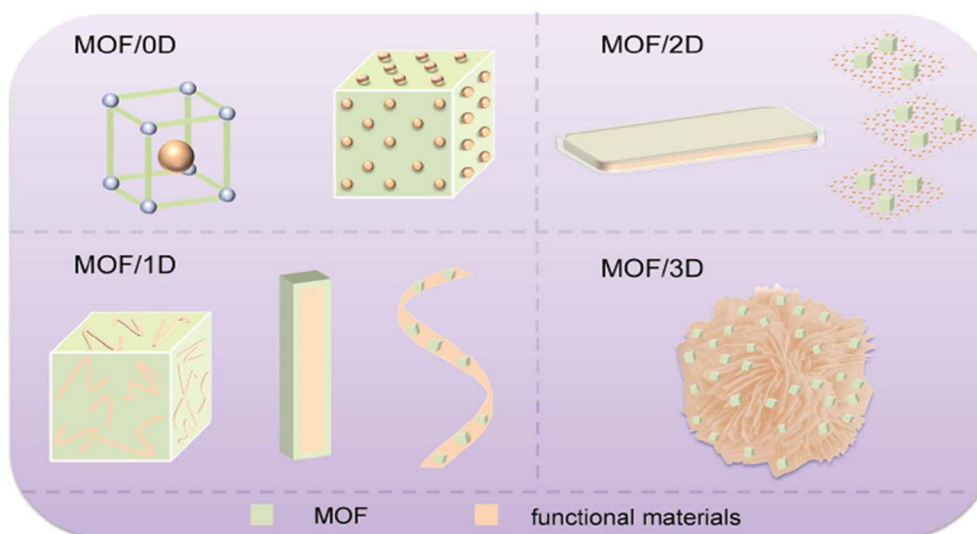


Fig. 5 MOF/composite materials, such as MOF/0D, MOF/1D, MOF/2D, and MOF/3D, are illustrated schematically. Copyrights 2019 from ref. 106.





or as in composite form, are a promising technique to improve the electrochemical characteristics for practical usage.<sup>112</sup>

Combining MNPs and MOFs results in MNP@MOF composites, which have better capabilities and unique functionalities. It has also been attempted to homogenize MOFs and metal oxides into core-shell nanostructures, especially those having semiconductor and magnetic characteristics. Metal oxide NPs and MOF can be combined using a variety of techniques, including the synthetic yolk-shell method, the liquid phase epitaxy method, and the gas phase in titration approach.<sup>113,114</sup> Co oxides were enclosed in an appropriate hollow nanostructure, as illustrated in Fig. 6a, according to Zeng *et al.*<sup>106</sup> This resulted in a distinctive yolk-shell nanostructure that hasn't received much research but will successfully address the previous building challenges. Particularly, the porous outer layer of the nanostructure can prevent nearby Co oxide NPs from accumulating in the hollow nanostructure and protect the contained catalyst from unfavorable environmental conditions without obstructing the movement of the reactants and products. A microenvironment for the oxidation of SO<sub>4</sub> can be created in the nanoreactor's interior chamber, which also serves to protect exposed catalytic sites and make them accessible to reactants.<sup>115,116</sup>

Zeng *et al.* described a one-pot solvothermal method to make yolk-shell Co<sub>3</sub>O<sub>4</sub>@MOF hollow-centered nanostructures. The octahedral MOF-5 shell served as a link between the structure and the catalytically active Co<sub>3</sub>O<sub>4</sub> core. They mainly showed how

useful they might be as a nanoreactor for SR-AOPs. A gas phase method was also used to mix ZnO with a MOF. Fig. 5d shows the high-resolution transmission electron microscopy image of the tiny ZnO NPs on the surface of ZIF-8 (HRTEM). Co<sub>3</sub>O<sub>4</sub>@MOF is one metal-oxide-NP@MOF core-shell nanocomposites that has so far garnered attention. Here, we demonstrate one of the earliest instances of iron oxide particles being successfully integrated into porous MOFs. MOFs feature a lot of active sites and a lot of surface area, which have led to extensive research on them for organic and electrochemical catalytic processes. Research is increasingly pointing to the utilization of "meta-NP@MOF" systems in the fields of catalytic activity and gas storage, where the incorporation of metal NPs into MOFs could be particularly beneficial.<sup>117,118</sup>

### 3.2. MOF/core-shell composites

It was possible to make core-shell composites *via* solvothermal Fe<sub>3</sub>O<sub>4</sub> synthesis. Cai *et al.*<sup>120</sup> presented a general technique for the rational design and synthesis of novel magnetic core-and-shell porous core-shell structures. A few Fe<sub>3</sub>O<sub>4</sub>@MOF core-shell composites with distinctive MOF shells were created using an LBL controlled process. Solvothermal techniques were used to create Fe<sub>3</sub>O<sub>4</sub> nanospheres. Fe<sub>3</sub>O<sub>4</sub>@HKUST-1 number 153 core-shell nanospheres with a similar structure were created. An LBL assembly procedure was used to produce magnetized Fe<sub>3</sub>O<sub>4</sub>@MIL-100 core-shell composites.<sup>119</sup> By using LBL assembly, we were able to create core-shell Fe<sub>3</sub>O<sub>4</sub>@MOF

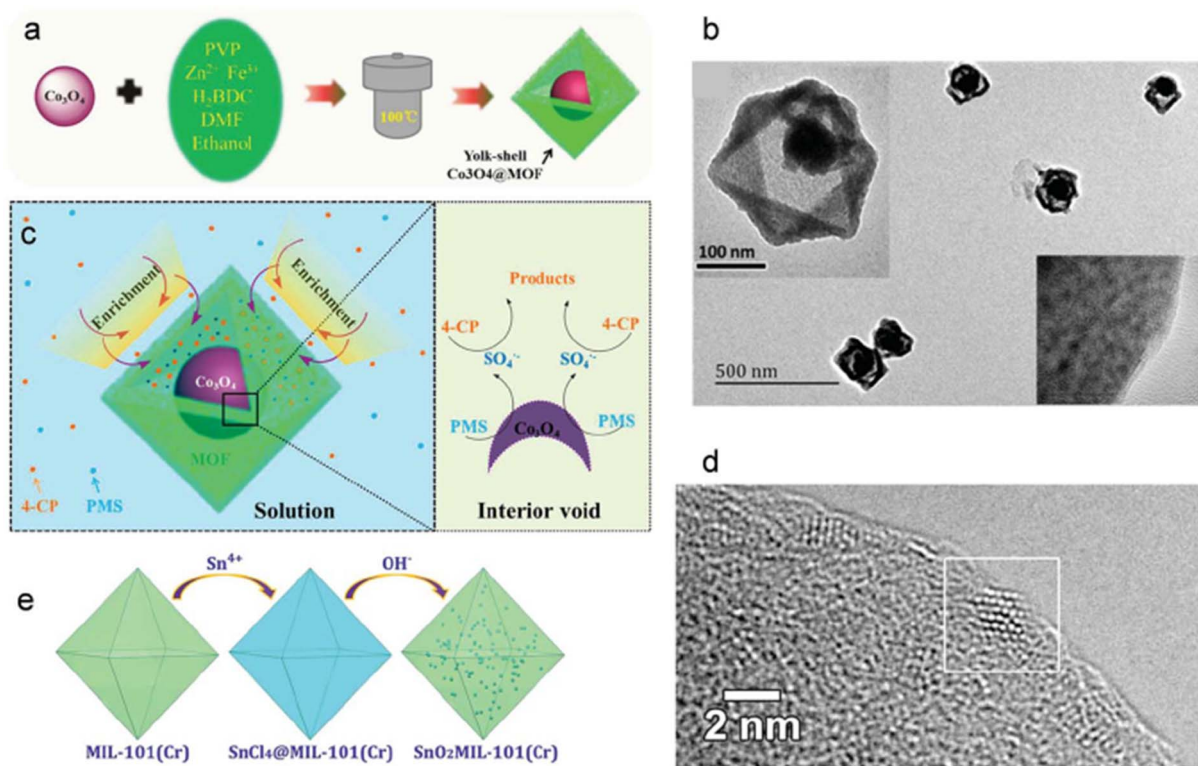


Fig. 6 (a) The method of creating nanocomposites with yolk-shell (b) TEM pictures, of yolk-shell (c) potential process for 4-CP to degrade in the yoke-shell nanoreactor (d) on the surface of ZIF-8 tiny ZnO NPs are visible in the HRTEM image. (e) An illustration of the SnO<sub>2</sub>@MIL-101(Cr). Copyrights 2019 from ref. 106.

microspheres. Additionally, the  $\text{Fe}_3\text{O}_4$  particles were measured using HKUST-1.<sup>120</sup> Iterative circular growth is used to build PS@MOF core-shell microspheres with a potential shell thickness for the LBL construction process.<sup>121</sup> In order to create hollow PS@MOF microspheres, the polystyrene cores from the prefabricated PS@MOF core-shell composites were successfully removed using DMF.<sup>122</sup>

## 4. MOFs application in energy storage systems

The remarkable performance of MOF composites, which are made of two intriguing materials, and their electrochemical applications include catalysis, sensors, supercapacitors, batteries, and other electrochemical devices. MOFs emphasize each MOF's unique properties and encourage the development of electrochemical applications because they are adaptable and constructed of unusual materials. Despite the fact that 3D functional materials made with MOFs have hardly ever been explored or mentioned, they offer a variety of applications in electrochemistry with dimensions ranging from 0 to 2. Based on the various application types and dimensions, this section analyses and deconstructs MOF composites.<sup>123</sup>

### 4.1. MOF composites for catalysis

Over the past few years, there has been a sharp and unpredictable rise in the global demand for and consumption of energy. Burning non-renewable fossil fuels like coal and oil accounts for the majority of global energy use, dramatically increasing atmospheric  $\text{CO}_2$  emissions as well as creating other severe environmental issues. Significant efforts are being undertaken to address the problem of energy scarcity on a global scale. One such attempt is the search for clean, renewable energy sources to replace petroleum-based fuels. Despite their high cost, Pt catalysts are frequently used in electrochemistry. As a result, from an economic and environmental perspective, non-Pt catalysts such MOF composites are gaining popularity. The oxygen evolution process (OER) and hydrogen evolution reaction are both electro catalyzed regularly using MOF composites (HER), and oxygen reduction reaction (ORR).<sup>124</sup>

Hydrogen-based fuel cells, another form of electrolytic cell, also experience ORR at the cathode. The two-electron transfer reaction is an example of a catalytic intermediate that is widely used (HER). The two-step reaction, which needs energy in acidic environments, depends on H. The second stage produces  $\text{H}_2$  by either mixing two  $\text{H}^+$  or  $\text{H}^*$  with a proton. Thus, the overpotential of the HER is decreased by active electrocatalysts such MOF composites. The electrochemical oxidation of water results in the generation of oxygen, or OER. Two water molecules can be oxidized in acidic or neutral electrolytes to yield four protons and one oxygen molecule.<sup>124</sup>

Fig. 7 represents synthesis of bifunctional electrocatalysts. Fig. 7a shows use of various materials drop cast on a glassy carbon electrode, 10 mM  $\text{Fe}(\text{CN})_6^{3/4}$  cyclic voltammograms in 1 M KCl were obtained. Cu-MOF in the following

concentrations: (GO 8 wt%), (GO 6 wt%), (GO 4 wt%), (GO 2 wt%), (GO 5%), Cu-MOF, and (GO 6 wt%) bare glassy carbon electrode.

In contrast, OH can oxidize in basic electrolytes to create  $\text{H}_2\text{O}$  and  $\text{O}_2$ . Due to their exceptional electrocatalytic efficiency and stability, MOF composite electrocatalysts have lately seen an increase in OER activity. A great lot of interest has also been generated by electrocatalysts in ORR for technologies like metal-air batteries and fuel cells. Additionally, the nano-CuS concentrations affected the ORR's  $E_{\text{onset}}$  (onset potential). As the amount of nano-CuS was increased, its porosity shrank, and its electrical conductivity was more than 109 times greater than that of bare Cu-MOF.<sup>125</sup> These values were all exceeded by the  $E_{\text{onset}}$  values of nano-CuS and bare Cu-BTC. However, when superabundant nano-CuS was introduced to or stacked on top of CuS (56 weight percent) @ Cu-BTC. These results demonstrated a substantial relationship between the materials' porosity and electrical conductivity and the ORR electrocatalytic performance of composite electrocatalysts.<sup>126,127</sup>

When compared to pure nano-CuS and bare MOF, the electrocatalytic performance of the nano-CuS@Cu-BTC composite dramatically enhanced in terms of starting voltage, the number of electrons transported, and the density of the kinetic current. These outcomes are the result of interactions between nano-CuS, which increases electrical conductivity, and CuBTC, which improves porosity. He and his colleagues also developed Co/MIL-101(Cr), which was used as a bi-functional electrocatalyst by employing an oxidative or reductive method following the impregnation.<sup>128</sup> They found that the surface's shifting  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{III}}$  composition significantly affected the electrocatalyst's OER and ORR activities. However, neither the BET's surface area nor the overall amount of Co on it had any impact on how well it performed. As the catalyst's OER activity increased. More  $\text{O}_2$  will also be preferentially absorbed as the amount of  $\text{Co}^{\text{II}}$  on the electrocatalyst surface increases, and in a basic electrolyte, electrons will be transferred to oxygen to produce hydro-oxide.<sup>129,130</sup>

### 4.2. MOF composites for batteries

Batteries, which are a proven commercial technology, have a much wider range of applications than supercapacitors and fuel cells. Batteries, which are autonomous devices that transform chemical energy into electricity, may power a variety of items. In these metal-air batteries MOFs are incorporated and that is what will be discussed in this section starting with use of MOFs in LIB.

**4.2.1 Lithium-ion batteries.** Because of their excellent environmental behavior, high energy density, low weight, and extended cycle life, LIBs are widely employed in power grids, portable electrical devices, hybrid and all-electric cars, and other applications. They specifically profit from this as a means of storing energy. Owing to their significant energy density. The lower cycle performance of LIBs is brought on by the weak electrical conductivity of MOFs. Due to the shortcomings of MOFs, LIBs have attracted interest as a potential MOF composite substitute.<sup>131</sup>



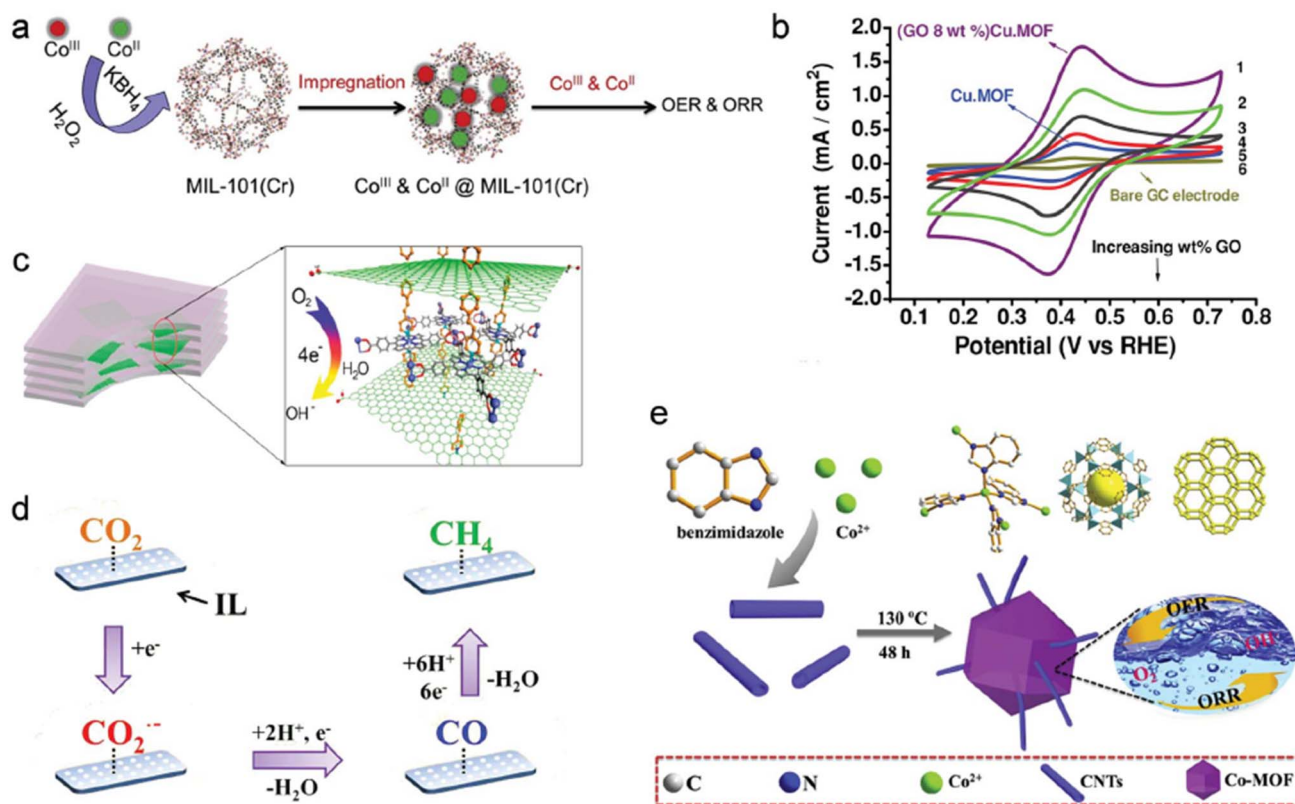


Fig. 7 (a) An example of the bifunctional electrocatalyst's design and preparation. (b) The catalysts' electrochemical activity, sorption surface areas, and surface areas. (c) An enlarged view of the layers inside the  $(\text{G-dye-FeP})_n$  MOF's framework and graphene sheets (d) an electrochemical procedure on the Zn-MOF/CP cathode in ionic liquids that might convert  $\text{CO}_2$  to  $\text{CH}_4$  (e) Co-MOF@CNTs catalyst synthesis. Copyrights 2019 from ref. 106.

From Table 3 it can be estimated that the composites made with Fe-MOF and RGO (5%) materials had the highest initial coulombic efficiency. This is because the coating of the Fe-RGO MOF is thick enough to prevent direct contact between the electrode and electrolyte. The battery's performance was improved by combining  $\text{SnO}_2$ 's high specific capacity with MIL-101(Cr), which acts as a protective shell for electrochemical stability. Liu and coworkers developed 2D Fe-MOF/RGO composites for reversible  $\text{Li}^+$  storage.<sup>132</sup>

A 3D core-shell composite of  $\text{Fe}_3\text{O}_4 @ \text{MOF}$  for usage as anode materials in LIBs has been demonstrated by Feng *et al.*<sup>133</sup>  $\text{Fe}_3\text{O}_4 @ \text{MOF}$  displayed exceptional reversible capacity with

a high discharge capacity of  $1001.5 \text{ mA h g}^{-1}$  and a high charge capacity of  $993.7 \text{ mA h g}^{-1}$  in the 100th cycle. These results were significantly higher than the comparable capacities for pure  $\text{Fe}_3\text{O}_4$  of  $696 \text{ mA h g}^{-1}$  and  $993.7 \text{ mA h g}^{-1}$ . After 70 cycles, the current density increased from  $0.1$  to  $2 \text{ A g}^{-1}$ , and the reversible capacity reached  $429 \text{ mA h g}^{-1}$ . Since the HKUST-1 buffer layer reduces the volume expansion of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4 @ \text{MOF}$  displays better discharging-charging behaviors than pure  $\text{Fe}_3\text{O}_4$  during all cycles.<sup>133</sup> Building transition-metal oxides as the cathode elements of potential Li- $\text{O}_2$  batteries is now more practical. Transition metal carbides (TMCs) have recently attracted a great deal of interest due to their outstanding surface

Table 3 Various composites of MOFs for batteries including Li-S and LIBs batteries<sup>106</sup>

MOF composite	Functional materials	MOF	Battery type	Current density/ $\text{C}^a$	Cycle number
Fe-MOF/RGO	RGO	Fe-MOF	LIBs	0.3	200
$\text{Fe}_3\text{O}_4 @ \text{MOF}$	$\text{Fe}_2\text{O}_3$	HKUST-1	LIBs	0.06	100
$\text{S} @ \text{MOF-525 (Cu)}$	S	MOF525 (Cu)	Li-S	0.5	200
$\text{SnO}_2 @ \text{MIL101 (Cr)}$	$\text{SnO}_2$	MIL-101 (Cr)	LIBs	0.1	100
$\text{S} @ \text{S-ZIF-8} @ \text{CNTs}$	CNTs, S	ZIF-8	Li-S	0.1	100
$\text{MOF-5} @ \text{CNTs}$	CNTs	MOF-5	Li-S	0.5	50
$\text{S} @ \text{HKUST-1/CNT}$	CNT	HKUST-1	Li-S	2	40

<sup>a</sup>  $1\text{C} = 1675 \text{ mA g}^{-1}$



physicochemical properties, unique thermal and electrical conduction properties, and other features. Molybdenum carbides have garnered a lot of interest because of their outstanding d-band electronic structures and good electrical conductivity. By utilizing MoC catalysts, Pt-based ORR electrocatalyst activity and durability were dramatically improved. Particularly, heteroatom-doped CNTs doped with metals and nitrogen displayed improved catalytic activity, making them effective MoC<sub>x</sub> conductive materials.<sup>134</sup>

#### 4.3. Use of MOFs in supercapacitors

Flexible energy storage devices are needed to meet the power requirements of new flexible and wearable technology. Due to their superior energy storage properties, such as high-power density and long cycle life, electrochemical capacitors (also known as supercapacitors or ultracapacitors) and metal-ion batteries (such as lithium-ion batteries, sodium-ion batteries, *etc.*) have attracted a lot of attention recently. Metal-ion batteries' lack of flexibility is a significant barrier to their use in wearable technology. They cannot be used in safe on-body device applications because of their low power density and flammability caused by organic electrolytes. However, since aqueous electrolytes can be used to create supercapacitors, they are a safer option for wearable applications. The notable characteristics of MOFs, such as their substantial surface area, three-dimensional porous architecture, permeability to foreign substances, structural adaptability, *etc.*, make them innovative possibilities as electrode materials.<sup>135</sup>

Even while pure MOFs have poor intrinsic conductivity, this can be improved by creating composites with other electronically conducting materials. Due to their high energy and power densities, MOF-based electrodes hold great promise for flexible and wearable supercapacitors. In order to create flexible supercapacitors, new advancements in the field of MOF-based composite electrodes are the main focus of this paper. Due to their considerable tunability, which includes beneficial porosity features, tunable chemical compositions, programmable crystal structures, and a variety of geometric morphologies, metal-organic frameworks (MOFs) have received a lot of attention for supercapacitor applications.<sup>136</sup>

#### 4.4. Use of MOFs in hydrogen fuel cells

The use of MOF-based technologies can hasten hydrogen's integration into the energy mix since MOFs are very adaptable and provide a highly selective medium for hydrogen impurities. MOFs can purify hydrogen by eliminating byproducts like methane, nitrogen, carbon dioxide, and carbon monoxide from mixtures of hydrogen. MOFs, for instance, can enable the production of low cost, low carbon, blue hydrogen by removing CO<sub>2</sub> from current steam reforming processes. The development of cutting-edge solutions that solve significant technological issues in the hydrogen value chain is made possible by the breakthrough adsorbents known as MOFs.<sup>137</sup>

Independent of source, MOF-based hydrogen purification can also produce the ultra-pure hydrogen supply needed by fuel cell vehicles for final usage. High volumetric and gravimetric

capacity hydrogen storage solutions are being developed thanks to the combination of near-infinite pore chemistries and record-breaking porosities. A game-changer for hydrogen transportation, large volumes of hydrogen may now be securely stored and delivered at far lower pressures, improving the range of cars running on H<sub>2</sub>. In order to unlock the hydrogen economy and facilitate the switch to cleaner energy sources, MOFs are a crucial component.<sup>138</sup>

## 5. Limitations and challenges faced by MOFs and metal–air batteries

Due to a lack of lithium supply and security concerns, the development of LIBs devices with high weight-to-energy and volume-to-energy ratios has been delayed. Other types of metal-ion batteries are of great interest (MIBs). In recent years, interest in sodium-ion batteries (SIBs) as prospective replacements has increased due to their electrochemical mechanism and inherent sodium enrichment. Potassium-ion batteries (PIBs) have also drawn more attention as a viable new generation of energy storage technologies because of their global availability and strong potassium-ion transport properties. ZABs on the other hand due to their non-toxic metallic zinc, naturally available, high ionic conductivity in the safer aqueous electrolyte, and other characteristics, zinc-ion batteries (ZIBs) are among all metal-ion batteries regarded as the most desirable option. But still there are a lot of pros and cons related to these batteries and MOFs. By combining MOF with other beneficial materials, MOF composites, the electrochemical performance of MIBs can be greatly enhanced.<sup>139</sup>

### 5.1. Challenges faced by MOFs

Batteries and supercapacitors have profited from recent developments in the study of energy storage devices based on MOF and its composites, (particularly when various functional materials are linked such as carbonaceous materials). The two most significant aspects of MOF composites are their shape and electrochemistry. Due to their outstanding capacity, super-normal cycling stability, high conductivity, strong mechanical property, fantastic rate property, and spectacular electronic features, MOF composites have been proven to be promising materials for EES applications. Because of the beneficial interactions between MOF and functional materials, EES devices have much better electrochemical characteristics than traditional EES devices. But in the actual world, there are still certain challenges.<sup>140</sup>

Some of the major difficulties and problems in MOFs are listed below:

- During charging and discharging, MOF may irrevocably break down or change into an amorphous phase. Aqueous, acidic, and alkaline conditions can all lead to MOF disintegration and framework collapse. It has seriously impeded its widespread use in EES devices.
- Since the significant charge transfer resistance that results from many MOF's low conductivity is detrimental to rate capacity and cycle stability, it is challenging to overcome this





problem. This imposes various limitations on the development and use of MOF composites.

- Although MOF/MOF composite electrode materials offer useful features, it is not apparent how exactly these structural changes impact the electrochemical process. Understanding their workings is essential to creating high-quality, inexpensive, and easily made electrode materials.

- One of the major deterrents is cost hindering the widespread use of MOF/MOF composite electrodes. Large-scale manufacture has become much more difficult due to the employment of pricy ligands and labor-intensive fabric cationic processes.

- A lot of MOFs have low tap density and poor electrical conductivity, which may limit their applicability.

Despite the difficulties and problems listed above, MOF composites can be improved in terms of their electrochemical properties by addressing these difficulties and problems.<sup>141</sup>

## 5.2. Challenges faced by MA batteries

Since the battery's active metal reacts with oxygen drawn from the environment rather than having to be stored there, MA batteries' primary advantage is that their volume and weight are decreased. Furthermore, theoretical specific energies that are significantly higher than those measured for cutting-edge lithium-ion batteries are attainable. It is yet unclear how the stronger environmental interactions of the MA batteries compare to those of closed batteries.<sup>142</sup> The following are some of the main issues with the MA battery system that require significant attention and continue to exist:

**5.2.1 Unstable anodes.** Metal anodes' lifespan is drastically shortened in aqueous solutions due to how unstable they are. But metals like Al, Zn, and Mg can be partially compatible with the aqueous electrolyte by coating their surfaces with a layer of passivating oxide or hydroxide. Many metals, including Li, Na and K, are used with non-aqueous electrolytes despite being highly reactive with them since they are frequently used with aqueous electrolytes, raising serious safety concerns. Using an alloy consisting of these metals as the anode to control corrosion is a typical remedy for this issue. According to some accounts, rechargeable batteries use MOF as a barrier to preserve the anode's stability.<sup>143</sup>

**5.2.2 Catalyst design for air cathodes.** Compared to the values theoretically predicted for the MA batteries, the energy density has been drastically decreased. The air-cathode materials' instability is what leads to low cycle stability. This is primarily due to the inefficiency of the cathode design, the bifunctional electrocatalyst, and the air catalyst. The ORR's slow reaction kinetics must be overcome, hence more potent air catalysts must be developed.<sup>144,145</sup> Additionally, it is believed that developing an appropriate air cathode will enhance the triple-phase boundary and enhance battery performance. The efficiency of MA batteries is being increased by researchers working hard to create efficient air-cathodes and bifunctional electrocatalysts. However, the MA batteries' energy efficiency is still only predicted to reach 65%, which is still cause for concern. MOFs have only ever been utilized in Zn-air batteries

as catalysts. The following sections provide numerous examples of this type.<sup>146</sup>

**5.2.3 Corrosion.** Metal-air batteries face challenges with the metal anode, air cathode, and electrolyte while having a high energy density. The most notable of them is dendrite growth, which causes the metal anode to corrode. When excess metal ions build up on the anode surface and are not quickly absorbed, dendrites form. These dendrites have the potential to shorten two electrodes and result in catastrophic failures over time. Fig. 8 shows us the effects of dendrite development, passivation, and corrosion at a metal anode. During experiments in the lab. Li-air batteries offer a high open-circuit voltage and energy density, but corrosion causes them to degrade quickly.<sup>147</sup>

**5.2.3.1 Passivation layer.** An electrode that was passivated could not be discharged further because an insulating coating on its surface prevented the discharge product from migrating. LiOH, ZnO, and Al<sub>2</sub>O<sub>3</sub> served as the corresponding systems' passivation layers in MABs. A non-conductive layer will be generated on the metal surface from soluble species that were produced at the air cathode. This layer, which is non-conductive, raises the cell's internal electrical resistance and inhibits metal breakdown. The most effective way to prevent the production of passivation layers is to employ porous electrodes.<sup>149</sup>

**5.2.3.2 Dendrite formation and deformation.** While the metal electrode cycles in an alkaline electrolyte, the metal anode releases metal ions during discharge and the metal ions re-deposit on the anode during charging. The metal electrode will afterwards progressively change form and develop irregular thicknesses on its surface. When the irregular shape builds into dendrites during numerous charge and discharge cycles, the battery system becomes unstable or swift route. To reduce dendritic development and deformation, many methods have been tried. Using non-reaction additives in the zinc electrode or electrolyte, for instance, and covering the zinc metal alloying lithium with sodium, Mg, Al has been demonstrated to successfully suppress the growth Li's dendritic.

In conclusion, dendritic structures form in ZABs, LABs, and FABs, passivation layers appear in these materials, and corrosion can occur in any of these materials. Several strategies are needed to resolve these issues.<sup>150</sup>

- Despite having higher ionic radii, sodium has a lower diffusion rate and a greater volume variance, which reduces rate capability and cycling stability. For any battery system, it is essential to find suitable electrode materials with the necessary electrochemical (redox and catalytic activities), physical (electrical and ionic conductivities), and structural and chemical innovations.

- Nickel has the potential to be an OER catalyst, however it is challenging to use in bifunctional catalysts because of its limitations. Due to the conversion of Ni<sup>3+</sup> to Ni<sup>2+</sup> and the formation of NiO impurities during high temperature heat treatment, which is frequently utilized in the production of catalysts, nickel ions have a tendency to migrate inside crystal structures, catalysts lose some of their capacity to carry out two tasks at once as a result of the limited reversibility of this structural change. Iron



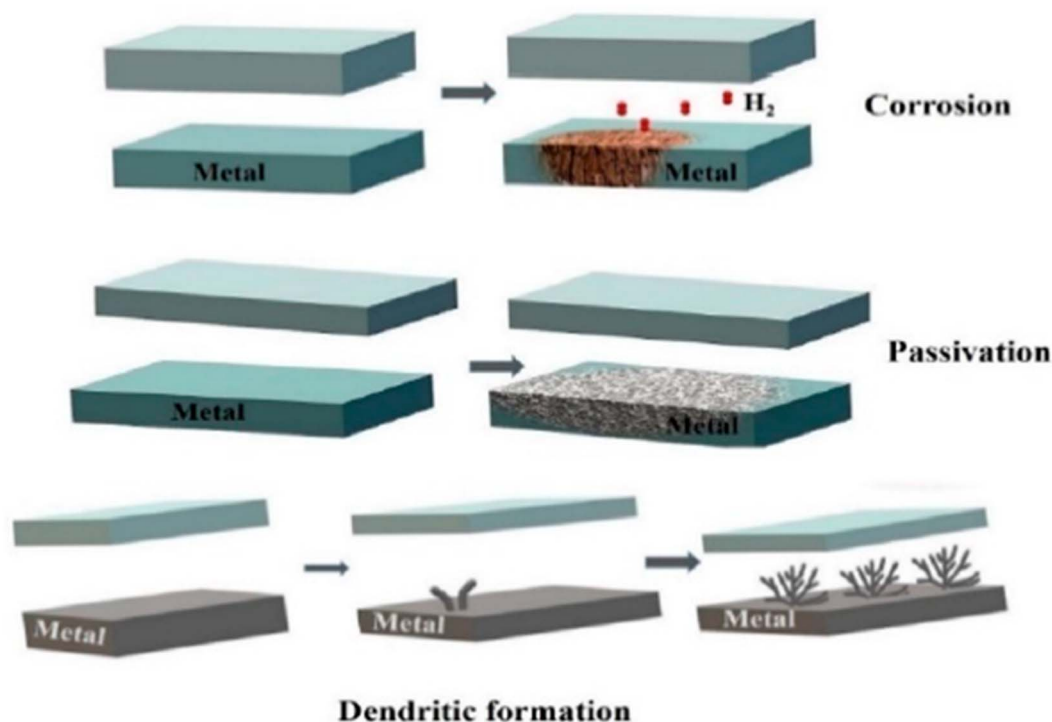


Fig. 8 Processes of dendrite development, passivation, and corrosion at a metal anode. Copy from ref. 148, Copyrights 2019.

addition in the nickel oxide structure is one approach to these stability issues. Nickel-iron batteries have a lower energy density and specific power, or, to put it another way, are less efficient. The cells charge up slowly and discharge it gradually (cannot supply sudden large power spikes). This means that in order to attain the output of a “normal” lead-acid based power system, more batteries and solar panels would be required. As a result of their high hydrogen production, daily gas is necessary to provide the desired performance. Because hydrogen gas is explosive, proper ventilation is crucial. Ni-Fe batteries may endure such treatments without being harmed, although their performance will undoubtedly suffer. Weekly inspections and top-offs are recommended for Ni-Fe batteries. Additionally, the electrolyte solution must occasionally be entirely replenished, which is a nasty and labor-intensive process.<sup>151</sup>

- Last but not the least air electrode's extremely low efficiency is a serious problem for the iron/air and zinc/air batteries and is also susceptible to damage during charge at practical current densities. The stability of the air catalyst in the cathode and the conductivity of the electrolyte continue to pose problems. Researchers from all over the world are delving into these and other problems to realize the full potential of metal-air batteries.<sup>152</sup>

## 6. Conclusion and future perspectives

For energy-related technologies like MABs, research into MOF and COF applications has rapidly increased in recent years. One or more of the benefits that account for this is the potential of the

elements and structures that support electrocatalytic activities to functionalize with semiconducting substrates like graphene, carbon nanotubes, and MXenes.<sup>153</sup> The loaded metal nanoparticles accumulate as the temperature rises during pyrolysis because the carbon catalyst is unable to produce balanced nanostructures. Co<sub>3</sub>O<sub>4</sub> nanosheets were assembled into 2D micro-assemblies using vacancy engineering methods by Hou *et al.*<sup>154</sup> By altering the annealing temperature, changes were made to the oxygen and metal ion vacancy contents. It was discovered that the components' synergistic effects improved the Li-O<sub>2</sub> battery's electrochemical performance. The annealing temperature raises the amount of oxygen vacancies in Co<sub>3</sub>O<sub>4</sub> from 200 °C to 400 °C, with the biggest flaws appearing at 300 °C. By generating the active sites that speed up ORR during the discharge process, these faults also create railroads for O<sub>2</sub> to travel across 2D micro-assembled Co<sub>3</sub>O<sub>4</sub> nanosheets, increasing cycle stability.

Despite the challenges faced by MOF composites, the following strategies have been devised to overcome them and improve their electrochemical properties:

- Low molecular weight functional materials and several redox active sites can function to a great extent when the right proportions of organic ligands, metallic ions, and ions are used.

- By fabricating MOF membranes using certain treatment techniques, such as pressing and phase change, it is possible to overcome their inherent sensitivity and processability restriction without endowing them with primitive characteristics. These restrictions can also be removed by carefully choosing organic ligands and metallic ions.

- Creating enhanced MOF composites by mixing MOF with novel conductive additives is one way to solve this issue.



Composite materials embody the benefits of each component while also offsetting some of the drawbacks of the single component. A solution to this issue is also indicated by the development of conductive MOF, even though the materials are still in their infancy.<sup>70</sup>

- Field measurement, theoretical computation, and simulation must be used to conduct a thorough investigation into the electrochemical mechanism. Additionally, sophisticated characterization tools are crucial.

- The reduced rate capacity, high overpotential, and poor cycle stability of today's MOF and COF catalysts are mostly due to low OER activity, whether it be in ZAB systems or Li-air batteries. In order to give MOFs and COFs distinct ORR and OER performance for the advancement of this type of material in the future, a "structure-oriented" strategy will be developed.<sup>155</sup>

- Since so many of the tens of thousands of created MOFs and COFs are unstable in organic or aqueous electrolytes, it is challenging to understand the electrochemical process and they cannot be scaled for use in MABs. Therefore, the entire efficiency of electrochemical devices is determined by the stable design of this type of air cathode. Designing water-stable MOF and COF materials begins with the production of "water-in-salt" electrolytes.<sup>156</sup>

- It is frequently possible to use a variety of metal ions, carboxylate linkers containing azoles, and hydrophobic ligands to boost structural stability. Because of their remarkable conductivity, catalysts must be utilized as electrochemical components. Unfortunately, MOFs and COFs cannot be used in electrochemical devices like MABs because of their weak conductivity and confined ability to degrade the discharge products. An efficient strategy for raising MAB performance is to carefully develop.<sup>157</sup> In MOF and COF materials, there is better intrinsic conductivity as well as bifunctional ORR and OER capabilities. Conjugated organic linkers, conductive carbon materials/substrates such as graphene, carbon nanotubes, and foam nickel, as well as the development of p-type doping systems are further techniques to somewhat increase the conductivity of the framework materials.<sup>158</sup>

- Using 3D-printed MOFs to create framework cathodes offers a creative, alternative way to increase the specific energy used in Li-O<sub>2</sub> batteries. Metal dust was applied to porous carbon to create an oxygen electrode for LABs. However, throughout the reversible liquid-gas-solid cycles, nanoparticles are susceptible to losing their bond. This problem was addressed by an electrocatalyst constructed from a carbon matrix with stereoscopic Ru nanoparticles dispersed throughout (Ru-MOF). Still after finding solution there is still risk.<sup>159</sup> With current densities of 500 mA g<sup>-1</sup> and potentials of 0.2/0.7 V, a Ru/carbon electrocatalyst design achieved sustained charge-discharge cycling capability with 800 cycles over 107 days at ambient temperature. It opens up a new opportunity for the oxygen electrode of lithium-oxygen batteries (LOBs).<sup>160</sup>

- A nickel oxide-based catalyst that was created on graphene oxide by pyrolysis to produce metal oxide nanoparticles was examined and tested for redox reactions by Liu *et al.*<sup>175</sup> When the metal oxide was coupled directly to the graphene oxide,

further advantages included improved conductivity for the ORR and metal active sites are dispersed uniformly across the graphene sheets. The performance of the OER activity outperformed that of other cobalt and platinum-based catalysts and Ni<sup>2+</sup> was found to be the essential component in both the ORR and the OER. The conductivity was enhanced by graphene oxide, but the Ni-oxide catalyst's ORR activity was only marginal.

- It is necessary to enhance the creation and analysis of creative two-dimensional MOFs. One of the best materials for enabling intercalation may be a two-dimensional MOF. Superior cycle stability and better electrochemical properties can be found in two-dimensional MOFs with appropriately interacting metal clusters and connectors.<sup>161</sup> Additionally, by combining two-dimensional MOF with additional two-dimensional functional materials, novel heterogeneous structures with intriguing properties can be created (such MXene).<sup>162,163</sup>

- A method for catalyst regeneration has been developed that separates monovalent metal ions with a selected cation and a thermally regenerating metal-organic framework (MOF). Crosslinked MOF-808 with functionalized poly(*N*-isopropylacrylamide-*co*-acryloylamidobenzo-18-crown-6) (pNCE/MOF-808) preferentially adsorbs Na<sup>+</sup> and K<sup>+</sup> while leaving Li<sup>+</sup> behind. The size-match effect, ion dehydration effect, and stability constant of the cation-benzo-18-crown-6 complex are responsible for this. It exhibits a high capacity for adsorption of 1.04 mmol g<sup>-1</sup> and excellent selectivity up to 29.4 for Na<sup>+</sup>/Li<sup>+</sup> and 34.4 for K<sup>+</sup>/Li<sup>+</sup> in the mixed solution including 0.5 M LiCl, 0.5 M NaCl, and 0.5 M KCl. Furthermore, at low temperatures (like 45 °C) in water, pNCE/MOF-808 with adsorbed Na<sup>+</sup> and K<sup>+</sup> ions could be effectively regenerated. Additionally, adding functional groups to MOFs enhances their adsorption properties and allows for the selective binding of desired ions. Due to the high binding of the added thiol, Li *et al.* produced a thiol-functionalized MIL-68 with Hg<sup>2+</sup> selectivity. The addition of functional groups to MOFs also improves their adsorption abilities and permits the selective binding of selected ions. However, the bulk of ion adsorbent regeneration reported up to this point has required concentrated salt solution, acid/base, or, which invariably results in secondary pollution, making it essential to identify an environmentally friendly regeneration method.<sup>164</sup>

## 6.1. Conclusion

The construction of MOF depends solely on the type of organic linker used. Each MOF formulation can store more metal ions by utilizing organic linkers for MIBs that contain a lot of redox active sites. The advantage of MOF that may successfully restrict the polysulfide's functional organic ligands is that they can prevent the shuttle effect of sol trisulfide on LSBs. Making hybrid matrix films for LOBs requires the appropriate organic connectors. These layers prevent deposits from accumulating in the battery as a result of carbon dioxide and water entering. Adsorbent MOFs are given the ability to regenerate under stimuli by the addition of stimuli-responsive components. Because the physical surroundings, such as temperature, can be



altered to modify how the material operates, electrical or magnetic conditions, stimuli-responsive MOFs have come under increased scrutiny. Due to their ease of use, components that respond to light and temperature are frequently utilized.<sup>165,166</sup>

The fabrication of a conductive MOF and its electrochemical characteristics are enhanced by the use of suitable organic connections for SCs. In conclusion, by using functional components to further improve the electrochemical behavior of virgin MOF, MOF composites have a significant impact on the field of EES. Research on MOF composites has recently evolved swiftly, despite certain persistent difficulties, and the development of innovative functional materials. The research presented in this review provides a solid platform for future study and is crucial for comprehending how MOF composites are being employed as potential energy storage materials.<sup>167,168</sup> The electrochemical reaction for air cathodes consists of numerous electron transfer processes and the formation of a few transitional products. The development of MOF and COF catalysts in general may become more complicated because the actual catalytic centre and catalysis may be obscured and the disparity between catalytic activity and catalyst specifications may grow. These methods may enable the precise computational synthesis of MOF and COF catalysts.<sup>169</sup>

A number of developments have been made and were investigated here for the MOF and COF materials use as fundamental applications in MABs, especially as a cathode catalyst.<sup>153,170</sup> According to past study, the development of new MABs devices that fully leverage the structural and compositional properties of MOF and COF materials would improve the market prospects for future energy. For instance, recent developments in catalysts for N<sub>2</sub> electroreduction processes have made it possible to develop a unique class of Zn–N<sub>2</sub> aqueous batteries.<sup>171,172</sup> Though there is currently little knowledge about it, nitrogen reduction reaction (NRR) of MOF materials is highly anticipated in future. If MABs are selected as the intended applications, in order to indicate catalyst's useful performance, considerable battery research is also required. On the basis of similar working theories, it can be said that MOF materials could be potential candidates for usage in more MABs, such as sodium–air batteries, aluminum–air batteries, magnesium–air batteries, supercapacitors *etc.* The COF and MOF derivatives created for ZAB systems and Li–air batteries, however, have been included into the batteries on several occasions, particularly as cathode catalysts. Using pure MOFs and COFs directly in MABs, on the other hand, has received much less attention.<sup>173,174</sup>

## Conflicts of interest

The authors declare no known competing conflict of interests.

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