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Metal–organic frameworks for next-generation energy storage devices; a systematic review

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The future of renewable energy and sustainable transportation depends on advanced energy storage technologies. However, the capacity, durability, and safety issues associated with traditional technologies are often problematic. The rapidly developing field of metal–organic frameworks (MOFs) as essential components for the development of new energy storage technologies is investigated in this study. MOFs, which include technologies like batteries, supercapacitors, and fuel cells, provide fascinating platforms for energy storage due to their distinctive structures and configurable porosities. This review describes the underlying engineering, highlights the performance advancements, and examines the difficulties still associated with the application of MOFs. It highlights the value of ongoing study and the potential for MOFs to alter our energy landscape. Overall, this study provides in-depth knowledge of MOFs in terms of energy storage potential and recent developments making them a crucial resource for academics and engineers for providing a foundation with more sustainable energy in the future.

1 Introduction

Energy, in all of its appearances, is the driving force behind all life on earth and the many activities that keep it functioning.[1] For decades, the search for efficient, sustainable, and reliable energy storage devices has been a key focus in the scientific community.[2] The field of energy storage has been a focal point of research in recent years due to the increasing demand for renewable and sustainable energy sources.[3] Metal–organic frameworks (MOFs) are a distinct class of porous materials and in the past few years, have drawn a lot of interest from the scientific community because of their exceptional characteristics and numerous potential applications.[4] These crystalline compounds, which are made up of metal ions or clusters coupled to organic ligands, have outstanding surface areas, a high degree of structural diversity, and adjustable porosity, making them the perfect choice for a variety of applications.[5]

Numerous methods have been discovered for modifying the structural and functional features of MOFs, which have been the target of research.[6] These synthesis techniques, such as solvothermal,[7–9] microwave-assisted,[10–13] mechanochemical,[14–16] and others, have proven essential for synthesizing MOFs with certain properties appropriate for specific uses.[17] Designing MOFs with specific pore sizes, shapes, and functions is made possible by their capacity to modify the metal and organic components, which allows for the fine-tuning of their physical as well as chemical properties.[18] Energy storage is one of the most promising uses of MOFs.[19–21] Researchers have been exploring innovative materials and technologies in response to the global energy crisis and the increasing demand for sustainable and efficient energy storage solutions.[22,23] MOFs have shown tremendous promise in this area due to their unique characteristics.[19,24,25] They have been intensively researched for applications in a variety of energy storage devices such as batteries,[26–28] supercapacitors,[29–31] and fuel cells.[32–34] Their high porosity and surface area allow for fast ion transport and high capacitance, while their structural diversity allows for the integration of active energy storage sites.[35]

Furthermore, MOFs may be used as outstanding electrode materials or as precursors for the production of other sophisticated materials.[36] MOFs, for example, have been utilized to develop carbon-based materials,[37,38] metal oxides,[39,40] and metal sulfides[41,42] with outstanding electrochemical performance.[43] MOF design and synthesis for energy storage applications is a fast-emerging subject, with fresh discoveries and developments constantly extending the possibilities of these interesting materials.[44] The purpose of this paper is to offer a complete understanding of MOF synthesis and their use in energy storage devices. We will investigate the different

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synthesis techniques and their effects on MOF characteristics, investigate the processes through which MOFs contribute to energy storage, and highlight some of the most recent, noteworthy advances in this sector. We hope that this analysis sheds light on the potential of MOFs in tackling the global energy crisis and inspires further research on this intriguing subject. More efficient and stable MOFs for energy storage applications are expected to be produced as synthetic methods increase and our knowledge of the structure–property linkages of MOFs deepens. The present study places particular emphasis on the advancement of energy storage devices generally referred to as 'next-generation' technologies. Considerable attention is devoted to the investigation of emerging technologies and their potential to revolutionize the field of energy storage. This comprehensive analysis involves advanced batteries, supercapacitors, and novel gas storage systems, all of which show promise in shaping the future of this fundamental field.

2 Properties of MOFs

MOFs have a wide range of tunable properties, including structural tuneability, high porosity, very large specific surface area, and superior conductivity as depicted in Fig. 1. They have unique functional materials with these properties that can be employed in a variety of applications.[45] These qualities can be increased even further based on the structure units used in the MOF, rather than the stability that distinguishes it from other porous materials. MOFs can also be utilized to create other materials, such as carbon with a controlled porosity structure, as well as a variety of MOF-based composites with superior properties to the original material.[46] MOFs have gained recognition for their ability to be customized using metal and organic ligands to build the structure that allows them to function efficiently in the applications they were designed for. There are several synthetic methods for altering the framework's chemistry, stability, dimension of particles, and flexibility.[47] To enhance the attributes of MOFs, certain metal vertices and ligands within the framework can be interchanged, modified, or eliminated.[48] MOF rigidity would be especially significant in sustaining structural integrity in some devices where the active element undergoes to volume change. Mechanical properties can also be improved by constructing frameworks with varied metal nodes, incorporating flexible linkers, and altering crystal sizes.[45]

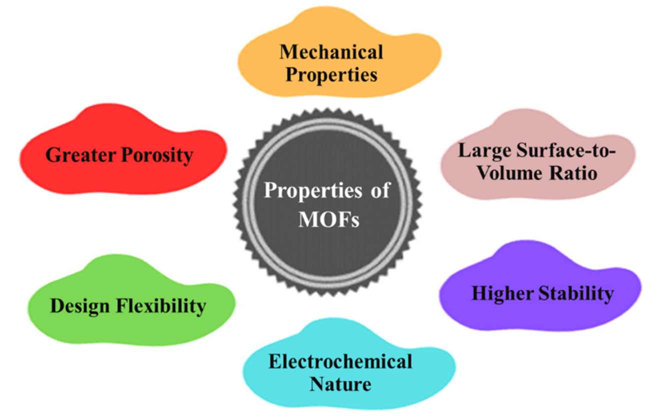


Fig. 1 Distinguishing properties of MOFs.

MOFs provide a large number of uniformly distributed active sites in comparison to conventional materials, and the quick flow of electrolyte ions is facilitated by their distinct pore topologies. Because of this, MOFs are great options for supercapacitor materials.[49] With repeated cycles of charge and discharge, MOF pore structures tend to irreversibly collapse.[50] As a result, the electrode's specific surface area drastically decreases, reducing the electrolyte's conductivity and ion site diffusion. The pore structure and supercapacitor efficiency of MOFs are significantly influenced by their specific surface area (Fig. 2). Many charge storage sites are provided by a large surface area, yet in MOFs where pseudo-capacitance predominates, this may threaten stability.[51] The utilization of porous materials has become more prevalent recently in the area of energy storage due to the advantages associated with abundant reactive sites and enhanced mass transfer.

Ionic and electric conduction play a pivotal role in enhancing the performance of electrochemical devices. These devices often face challenges like large overpotentials due to high internal resistances arising from sluggish ionic motions.[53] These issues lead to diminished power output and performance limitations. The utilization of novel materials for charge transport applications and the advancement of synthetic methods to enhance ionic and electric conductivity in MOFs provide valuable insights for material research as shown in Fig. 3. Scalability and processing capacity are vital considerations in the synthesis of metal–organic frameworks. To enhance scalability, the utilization of more affordable metal resources, such as metal mineral salts, oxides, hydroxides, nitrates, carbonates, along with organic binders, can yield further cost reductions. Moreover, the application of microwave radiation expedites reactions, consequently enhancing scalability.[54]

The capacity of MOFs to preserve their initial long-range organized structure in a certain chemical environment is referred to as stability. The reliability of frameworks is influenced by the strength of coordinate bonds, with increased bond strength leading to greater overall framework strength.[56] To achieve durability in metal–organic frameworks one approach is to create a synthesis method by pairing hard bases with high-valent metal ions, or soft bases with bivalent metallic ions. Additionally, the operational conditions, specifically pH levels, can significantly influence framework solidity.[57] External and internality stability of materials concerned with adsorption media surrounding it and the formation of metal ligand bonds respctively.[58] The various factors involved in the stability of the MOFs are presented in pictorial form in Fig. 4.

3 Sustainability and environmental impact

MOFs can considerably increase the efficacy of energy storage due to their enormous surface area and porosity. This enhances

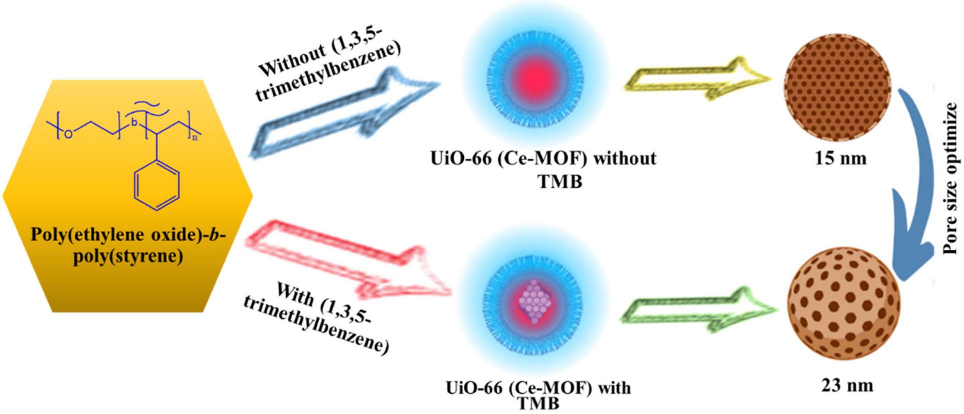


Fig. 2 Porosity of Ce-MOFs optimized using 1,3,5-trimethylbenzene.[52]

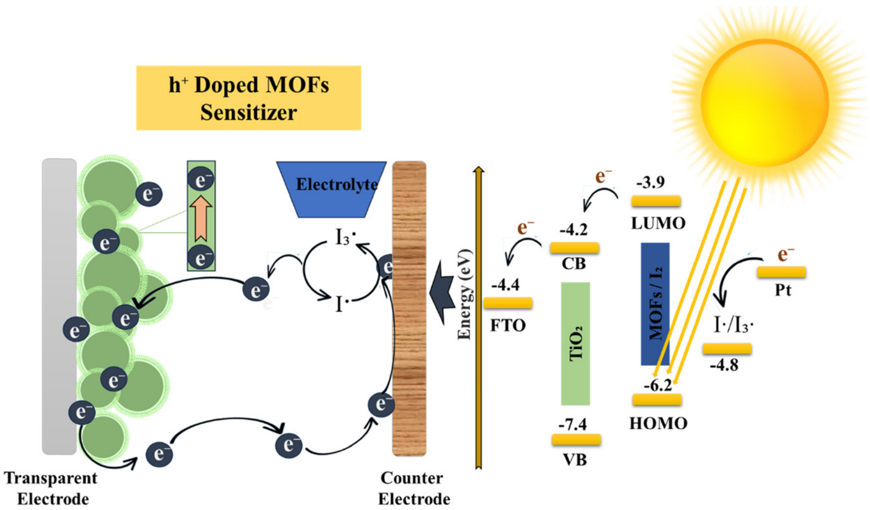


Fig. 3 Electroactive and conductive nature of MOFs.[55]

the absorption and storage of gases such as hydrogen and methane. For applications such as fuel cells and natural gas vehicles, efficient gas storage is essential, and MOFs can improve the energy density and performance.[50] The synthesis and utilization of metal–organic frameworks have the potential to result in a noteworthy reduction in greenhouse gas emissions when contrasted with conventional materials. In the field of natural gas storage, it is worth noting that MOFs have emerged as an exciting opportunity for advancing the development of lightweight and high-capacity storage systems, particularly for vehicles.[60] By exploiting the unique properties of MOFs, it becomes possible to facilitate the development of portable storage systems that possess a remarkable capacity to store natural gas while maintaining a reduced weight profile. This, in turn, has the potential to contribute significantly to the reduction of emissions by encouraging the adoption of cleaner fuels in various transportation applications.[61] MOF fabrication requires energy-intensive procedures, especially in the process of activation and solvent removal. The utilization of this particular material may potentially yield a greater carbon footprint in comparison to conventional materials. The reduction of energy intensity in the synthesis of metal–organic frameworks can be achieved through the utilization of sustainable energy sources and the optimization of manufacturing techniques.[62] Numerous methodologies for the synthesis of MOFs necessitate the utilization of organic solvents, thereby promoting adverse environmental implications. The advancement of solvent-free or environmentally friendly solvent synthesis pathways constitutes a pivotal domain of investigation with the objective of addressing this concern.[63] The utilization of green synthesis methods has been shown to effectively mitigate the environmental impact associated with the production of metal–organic frameworks. By employing these environmentally friendly techniques, the overall carbon footprint and ecological consequences of MOF synthesis can be significantly reduced.[14] The use of certain metal–organic framework precursors necessitates the inclusion of rare or expensive metals, thereby developing doubts regarding the accessibility of

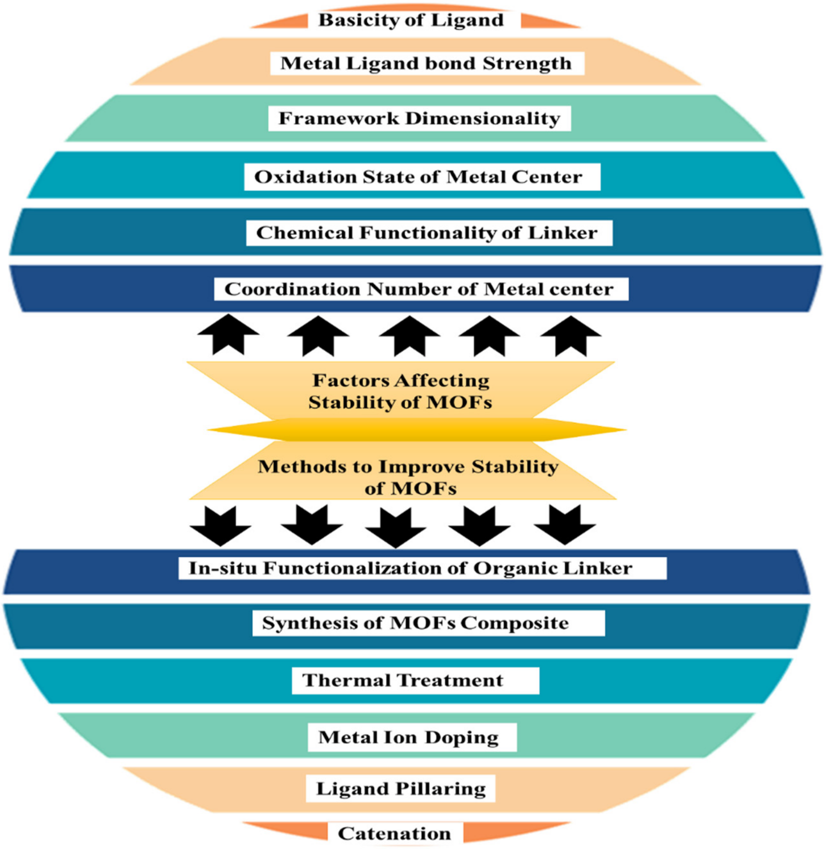


Fig. 4 Factors affecting stability and methods to improve the stability of MOFs.[59]

resources and the sustainability of the environment. In response to this clicking matter, diligent researchers are currently engaged in the investigation of alternative precursors and metal sources. This endeavor involves the exploration of recyclable materials and the utilization of abundant elements such as iron and aluminum.[64]

4 MOFs *vs.* traditional materials: a comparative analysis

4.1 Carbon capture and storage (CCS)

Carbon capture and storage (CCS) stands as a highly beneficial area for the utilization of metal–organic frameworks in the context of energy storage. They have exhibited exceptional promise in the realm of capturing carbon dioxide (CO_2) from industrial flue gases.[65] In contrast to conventional amine-based sorbents, metal–organic frameworks have been found to possess superior selectivity, capacity, and cyclic stability. The aforementioned observation implies that a diminished quantity of MOF materials suffices to achieve an equivalent level of CO_2 capture, thereby resulting in a reduction in material consumption and the associated environmental implications.[66] Due to their high surface area and superior adsorption performance, zeolite (ZSM-5) and a copper metal–organic framework (Cu-MOF) are chosen as adsorbents. The maximum particle size distribution and area for ZSM-5 were in the range of 25–66 m and 1.7–442 m^2 respectively. Whereas for Cu-MOF they were 102–149 m and 1.7–1400 m^2, respectively.[67] The results demonstrate that Zn-MOF works well in the low-pressure system with a higher CO_2 adsorption capability. Under ideal circumstances, the CO_2 adsorption of Zn-MOF was 145.1.[68] In order to create effective CO_2 adsorbents, a combination of Cu-BTC framework with porous carbon materials such as ordered mesoporous non-activated carbon (OMC), ordered mesoporous activated carbon (AC), and nitrogen-containing microporous carbon (NC) was used to form a NC–Cu-BTC composite with the maximum CO_2 capacity, measuring 8.24 and 4.51 mmol g^{-1} under 1 bar at 0 and 25 °C, respectively.[69] The lowest parasitic energy (PE) for postcombustion CO_2 collection has been observed in a nickel isonicotinate-based ultramicroporous MOF. Although a PE of 655 kJ kg^{-1} CO_2 is less than that of Mg-MOF-74, the highest performing material that was previously been reported.[70] In addition to the oxygen stored on the Ce(III)/Ce(IV) centers, the Pd nanoparticles supported on the Ce-MOF also store oxygen in the form of a thin palladium oxide layer at the particle–support interface. At 373 K, the CO oxidation process can cause the release of oxygen from these reservoirs. The Pd/CeMOF exhibits a substantial CO_2 absorption of 3.5 mmol g^{-1} at lower temperatures (273 K).[71]

4.2 Hydrogen storage

Metal–organic frameworks have drawn significant attention in the discipline of hydrogen storage for fuel cell applications. The conventional techniques employed for hydrogen storage, namely high-pressure tanks and cryogenic liquefaction, have been subject to investigation due to their inherent safety risks and inappropriate energy efficiency.[72] Metal–organic frameworks present an appealing option as they offer a more energy-efficient and safer alternative for hydrogen storage. This is achieved through their unique ability to facilitate hydrogen storage at reduced pressures and moderate temperatures. By harnessing the remarkable properties of MOFs, the energy industry can potentially overcome the challenges associated with conventional hydrogen storage methods.[73] The data showed that two novel zinc(II)-pyrazolate metal–organic frameworks have very excellent chemical and thermal stability. Most importantly, Zn(1,4-benzenedi(4-pyrazolyl)) demonstrates an excess H_2 uptake of 4.7 wt% at 40 bar and 77 K with a BET surface area of 1710 m^2 g^{-1}.[74] Based on the binuclear $[Sc_2(\mu_2\text{-OH})(O_2CR)_4]$ building block, the metal–organic frameworks NOTT-400 and NOTT-401 were synthesized and characterized; the framework NOTT-401 exhibits a BET surface area of 1514 m^2 g^{-1} and a total H_2 uptake of 4.44 wt% at 77 K and 20 bar.[75] The MOF hydrogen delivery capabilities between 100 bar/77 K and 5 bar/160 K were determined using molecular modeling on a vast and structurally varied collection of 13512 possible MOF structures based on 41 distinct topologies. The greatest volumetric deliverable capacity (compressing hydrogen to 700 bar at ambient temperature) was 57 g L^{-1} of MOF, above the 37 g L^{-1} of tank of the existing method.[76] The usable volumetric H_2 storage capacities of the metal–organic frameworks containing Co, Ni; dobdc4- = 1,4-dioxido-1,3-benzenedicarboxylate, which are known to have open metal cation sites that strongly interact with H_2, were assessed over a range of near-ambient temperatures relevant to on-board storage, with a useable volumetric capacity between 100 and 5 bar of 11.0 g L^{-1} at 25 °C and 23.0 g L^{-1} with a temperature swing between 75 and 25 °C. Ni_2(m-dobdc) was discovered to be the best physisorptive storage material based on adsorption isotherm data.[77] In order to create effective adsorbents for hydrogen gas, trimesic acid, a very electron-deficient and polar molecule, is produced as an organic ligand. This results in nanostructured Zr(IV) metal organic frameworks (MOFs-808) with excellent stability. The improved MOF-808's hydrogen storage capacity at 4 MPa is 7.31 wt% at 77 K, which is near to the maximum hydrogen storage capacity specified.[78]

4.3 Natural gas storage

In the subject of natural gas storage for vehicle applications, it is worth noting that metal–organic frameworks present notable advantages in the form of weight reduction and enhanced volumetric capacity. The utilization of compressed natural gas (CNG) as an alternative fuel source for transportation has been hindered by the weight and volumetric constraints associated with traditional CNG storage systems.[79] These limitations have impeded the widespread adoption of CNG as a viable option for powering vehicles. Metal–organic frameworks, renowned for their exceptional storage capabilities, have the potential to significantly mitigate the carbon footprint associated with compressed natural gas (CNG) vehicles by facilitating the utilization of smaller and lighter storage tanks.[80] MIL-101(Cr) MOF (metal–organic framework) production, characterization, and property assessment for CH_4 adsorption was carried out. The total volumetric absorption of CH_4 on MIL-101(Cr) MOF is reported to be about 30 cm^3 cm^{-3} at 5 bar, 150 cm^3 cm^{-3} at 35 bar, and 215 cm^3 cm^{-3} at 65 bar at 298 K. It has been discovered that MIL-101(Cr) exhibits a high CH_4 delivery or working capacity using LNG-ANG coupling.[81] Five novel zinc-based metal–organic frameworks (MOFs) were synthesized and also have crystal structures and methane adsorption capabilities. All of these MOFs are made up of benzene-1,3,5-triacrylate, or BTAC, and secondary building units (SBUs) of $Zn_4O(CO_2)_6$. With a volumetric working capacity (desorption at 5 pressure) of 203 cm^3 cm^{-3} at 80 bar and 298 K, MOF-905 is one of the best-performing methane storage materials, rivaling the value of HKUST-1 (200 cm^3 cm^{-3}), the industry-standard compound for methane storage in MOFs.[82] For methane storage with a high deliverable capacity, the flexibility and stability of hydroxy-functionalized MIL-53(Al) MOFs were explored. In addition to effective stacking, the location of the hydroxy groups encourages weak hydrogen bonding, which regulates the breathing behavior of these MOFs. In MIL-53(Al)–OH at 65 bar and 298 K (regarding crystallographic density), a promising deliverable capacity of 164 v/v was obtained. This value is near to the record of 197 v/v by Co-BDP.[83] Purified multi-walled carbon nanotubes (MWCNTs) have been added *in situ* during the production of MIL-53-Cu to create a composite MOF material called MIL-53-Cu with MWCNTs. At 298 K and 35 bar, it was shown that the methane sorption capabilities of MIL-53-Cu increased from 8.52 to 13.72 mmol g^{-1}.[84] In a different study, polyvinyl alcohol (PVA) nanofibers were combined with a tantalum(V) metal organic framework (Ta-MOF) nanostructure to create an electro spun porous composite that served as a new CH_4 adsorbent. The greatest methane adsorption may be reached at 24.40 °C and 3.70 bar in 23.60 min, according to the results of response surface methodology (RSM) optimization.[85] A comparison of the MOFs with other conventional materials has been tabulated in Table 1. It is depicted in the table that MOFs have great potential for energy storage as compared to metal oxide, polymer or carbon-based materials.

5 Energy storage applications of MOFs

Metal–organic frameworks, which are made up of metal ions/clusters and organic ligands, have recently emerged as one of the most popular porous crystalline inorganic–organic materials.[96] MOFs have already been used in a variety of applications because of their unique compositional and structural properties. Significant effort has lately been directed toward the fabrication of MOF micro/nanomaterials with

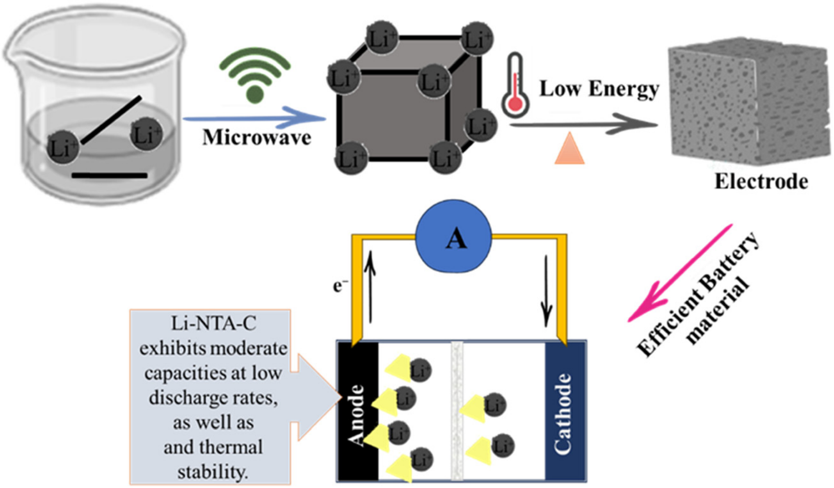
Table 1 Comparison of the MOFs and other conventional materials for energy storage

Material	Porosity	Surface area (m^2 g^{-1})	Conductivity	Charge/discharge rate	Energy density	Cyclability	Environmental impact	Ref.
Metal–organic frameworks (MOFs)	High porosity due to a well-defined structure	Extremely high surface area	Generally low electrical conductivity	Typically slow charge/discharge rates	Moderate energy density	Can suffer from low cyclability due to structural instability	MOF production can have high a environmental impact	86–89
Traditional metal oxides	Limited porosity	Moderate to high	Insulating or semiconducting	Varies depending on material	Moderate to high	Generally good cyclability	Varies depending on material	90 and 91
Conducting polymers	Low porosity	Moderate to low	High electrical conductivity	Fast charge/discharge rates	Moderate to low	Varies depending on material	Moderate environmental impact	92 and 93
Carbon-based materials	Variable porosity based on structure and activation methods	High surface area for activated carbons	Varies from insulating to highly conducting	Moderate to fast charge/discharge rates	Moderate to high energy density	Generally good cyclability	Low environmental impact	94 and 95

adjustable morphologies for improved performance in a variety of applications.[97] Furthermore, due to their customized compositions and porous architectures, MOFs can serve as effective models and precedents in high-temperature operations to build nanostructures with tunable pore topologies, huge specific surface area, great chemical stabilities, and a wide range of functions.[98] To cope with this, as well as environmental concerns, researchers have focused on designing MOFs for clean energy applications such as lithium-based batteries, supercapacitors, and hydrogen production and storage.[99] Greater charge/discharge rates, higher theoretical capacities, and improved electronic stability are all required for energy storage systems to operate at peak output effectiveness and performance.[100] Batteries and supercapacitors are more practical and cost-effective energy storage technologies. The most significant component of development is energy storage, and the uses of renewable sources of energy are essential in our daily life. MOF-based electrodes have huge potential and several benefits, such as a large specific surface area, highly changeable porosities, efficient active sites, and rapid response.[101]

5.1 Lithium-ion-based batteries (LIBs)

Due to their high storage capacity, long lifespan, high energy density, light mass, excellent cycle performance, and environmental friendliness, rechargeable lithium-ion batteries are essential energy storage devices.[102] During the charging process, lithium ions leave the cathode and enter the anode as they move through the electrolyte, storing energy; when the lithium ions return to the cathode, the (LIBs) discharge.[103] The very porous structure of MOFs may result in massive lithium ion accommodation and adequate lithium ion routes. MOFs have a three-dimensional structure that allows metal cations to be accommodated in interstitial space.[100] Significant attention has been paid to the use of metal organic frameworks (MOFs) as innovative and promising electrode materials in lithium-ion batteries (LIBs) as presented in Fig. 5. A straightforward solvothermal approach for the fabrication of Fe-MOF/reduced graphene oxide (RGO) composites. The synthesized Fe-MOF/RGO (5%) composite exhibits outstanding Li storage when utilized as anode materials for LIBs, with a reversible capacity of 1010.3 mA h g^{-1} after 200 cycles and a good rate performance.[104] The metal–organic frameworks (MOFs)



Li-NTA-C exhibits moderate capacities at low discharge rates, as well as and thermal stability.

Fig. 5 The application of MOFs in lithium ion batteries.[108]

NENU-506 and NENU-507, two new isostructural polyoxometalate-based MOFs with diamond topology, were produced hydrothermally. Notably, NENU-507, used as an anode material in lithium-ion batteries, demonstrated a high reversible capacity of 640 mA h g^{-1} after 100 cycles.[105] A foam-like CoO@N,S-codoped carbon hybrid composite was made using an N,S-containing precursor that was first synthesized and described. Within 500 cycles, the specific capacity can maintain a constant value of 809 mA g^{-1} at a current of 1000 mA g^{-1}.[106] A successful method has been developed for producing silica-based anodes for lithium-ion batteries (LIBs) beginning with the precursor zeolitic imidazolate framework-67 (ZIF67)/mesopores silica ($mSiO_2$). The engineered hybrid silica-based electrode (EHSiE), which has a high reversible capacity of 410 mA h g^{-1} at 5 A g^{-1} *vs.* Li/Li^+ in the LP30 electrolyte, has outstanding stability for 1000 cycles.[107] Li-NTA (2-nitro terephthalate) s-block MOFs synthesised using a scalable microwave-assisted method and then converted to carbonaceous material (Li-NTA-C) for electrochemical energy storage (EES) applications as an anode for Li-ion batteries with significant low-rate capacities and cycling stability are shown in Fig. 5.[108]

5.2 Lithium–sulfur batteries (LSBs)

LSBs have gained attention due to their high specific capacity and energy density which are much higher than the commercialized LIBs.[109] Commercialization of LSBs is problematic due to huge gaps between theoretical and real capacity, energy density, and poor cycle stability; nevertheless, the use of plentiful and non-toxic sulfur may reduce battery manufacture costs.[110] LSBs are a form of secondary battery with negative electrode lithium and positive electrode sulfur that has a high specific capacity of 1675 mA h g^{-1} and an energy density of up to 2600 W h kg^{-1}. Because the sulfur element is environmentally favorable, found in abundance on earth, and affordable, LSBs are one of the most important next-generation secondary batteries.[111] When paired with conductive carbon nanotubes (CNTs), the antiferroelectric perovskite dimethyl ammonium zinc formate MOFs serve as a potent molecular filter to reduce polysulfide (PS) migration in lithium–sulfur batteries (LSBs). With a sulfur loading of 5 mg cm^{-2}, the hybrid MOF based electrode provides an initial high specific capacity of 1260 mA h g^{-1} at 0.05 °C and 1007 mA h g^{-1} at 0.1 °C with just 0.07% deterioration after 120 cycles.[112] The rate capability of LSB based on a hierarchically porous TiO_2–S cathode exhibits a considerably improved specific capacity and coulombic efficiency. Due to the Ti–S chemical bonding occurring during the charge/discharge process, the diffusion coefficient of Li-ions significantly increases and is about 17 times greater than that of a fresh TiO_2–S hybrid cathode.[113] By annealing and phosphorizing Ni-ZIF-67 precursor at high temperatures, Ni/Co bimetallic phosphides were enclosed in a nitrogen-doped dual carbon conductive network (NiCoP@NC). With an initial capacity of 1083.4 4 mA h g^{-1} at 0.5 °C and exceptional cycle stability with a capacity degradation rate of just 0.09% per cycle for 300 cycles, the cells demonstrated excellent performance when utilized as a modified separator for LSBs.[114] The iron single-atom (FeSA-CN) catalyst is decorated on the nitrogen-rich, metal organic framework (MOF)-derived carbon nanocage to initiate the surface-mediated reaction of LiPSs. The FeSA-CN/S electrode produced a specific capacity of 1123 mA h g^{-1} at 0.2 °C and showed an exceptional rate performance of 605 mA h g^{-1} at 4.0 °C with an ultralow capacity fading rate of 0.06% each cycle for 500 cycles.[115] A schematic presentation of the lithium sulfur based battery is presented in Fig. 6. The use of nickel-based hexa-iminotriphenylene MOFs, with an ordered microporous and a 2D structure with a large specific surface as a separator, not only increased the overall conductivity but also had a strong absorption capacity for lithium polysulfides. Fig. 6 depicts the $Ni_3(HITP)_2$/PP production process which is used as a separator in lithium sulfur batteries.[116]

5.3 Lithium–air batteries (LABs)

Because of their greater energy density, lithium-ion batteries (LABs) with an oxygen cathode and lithium metal anode show

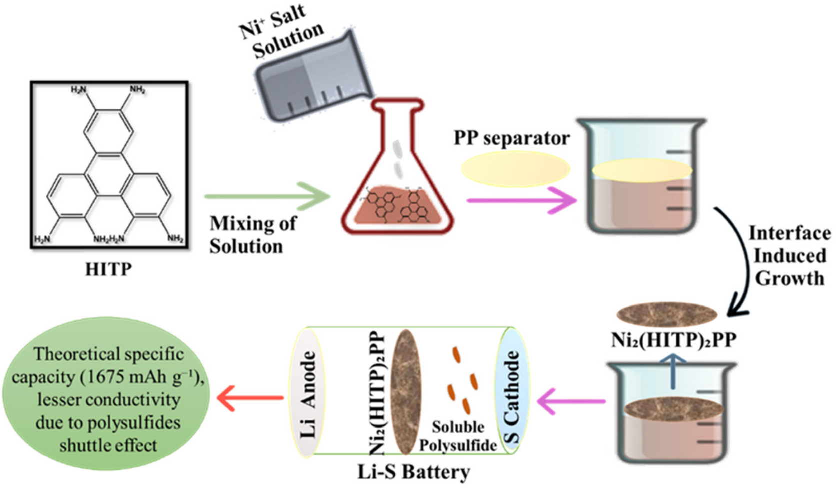


Fig. 6 The application of MOFs in lithium sulfur batteries.[116]

enormous potential as yet another set of advantageous LIB alternatives,[117] as shown in Fig. 7. As an example, Co_3O_4 carbon nanofiber composites made from ZIF-9 by electrospinning and thermal treatment act as LAB cathodes and have exceptional mechanical flexibility, which explains their prospective use in energy storage systems for electronics.[101] According to electrochemical characterizations, mesopores in MCu-BTC increased the discharging capacity (approximately 7000 mA h g^{-1}) of Co-10/MCu-BTC in an aprotic Li–air battery because they allowed for electrolyte infiltration for both mass and charge transfer and gave more space to store the discharge product.[118] Electrospinning and post-thermal processing were used to create a self-standing, binder-free ZIF-9 Co_3O_4/carbon nanofiber composite for use as the cathode in a non-aqueous Li–air battery. Co_3O_4/carbon nanofiber composites have an initial discharge capacity of more than 760 mA h g^{-1}, which is much larger than the initial discharge capacity of pure carbon nanofiber (72 mA h g^{-1}).[119] A conductive metal organic framework (c-MOF) has an exceptional property that encourages the formation of nanocrystalline Li_2O_2 with amorphous areas. For large capacity (1000–2000 mA h g^{-1}), direct charge transfer provides a minimal charge potential of 3.7 V at high current densities (1–2 A g^{-1}) sustained for a long cycle life (100–300 cycles).[120] Additionally, the produced UiO-67-Li@rGO aerogel demonstrates continuous and plentiful O_2 diffusion channels as well as $Li^{+/e}$ transfer channels. The solid-state Li–O_2 battery accomplishes suppression of anode dendrite development, resistance to air-corrosion, and existence of numerous low-impedance wetting interfaces including anode/electrolyte and electrolyte/cathode by making use of the special chemical features of the UiO-67-Li SSEs layer. The solid-state Li–O_2 battery benefits from this clever design by having a low overpotential (0.8 V), improved rate capability, and consistent cycling life of 115 cycles.[121] The synthesis of hollow N-doped porous carbon sphere-structured atomically distributed Co–N–C catalysts has been achieved, as has the design of aggregate fruit electrocatalysts for Li–O_2 batteries. Because of the strong metal-support interactions, this unique structure produces more stable Co SACs as shown in Fig. 7.[122]

5.4 Sodium-ion batteries (SIBs)

SIBs have vast applications in the development of electric vehicles and consumer electronics due to their low cost and globally high demand. The sodium ion battery in which MOF is being used as an electrode is presented in Fig. 8. SIBs are gaining importance as they can be used even at room temperature without any problem.[123] Moreover, sodium is very abundant with low extraction costs, which is advantageous over LIBs and in this way, SIBs are promising alternatives to LIBs.[124] SIBs are characterized by the movement of sodium ions, whereas LIBs involve the migration of lithium ions. However, it is important to note that despite this distinction, the fundamental components and overall structure of SIBs closely resemble those of LIBs.[125] Porosity must be introduced into materials to increase the better cycle life of SIBs. Through an easy and practical process called ion exchange, a new calcium metal organic framework has been successfully synthesized. Calcium terephthalate ($C_8H_4CaO_4$) as-prepared displays a sufficient voltage plateau at 0.5 V for sodium-ion storage and offers a specific capacity of 235.2 mA h g^{-1} at a current density of 0.2 A g^{-1}.[126] Ni-doped Co/CoO/N-doped carbon (NC) hybrids were synthesized employing bimetallic Ni-Co-ZIF as the initial precursor. The Ni-doped Co/CoO/NC hybrid demonstrated a good rate performance when used as an anode material for sodium-ion batteries, with a high discharge capacity of 218 mA h g^{-1} at a high current density of 500 mA g^{-1}, and good cycling stability, as a high discharge capacity of 218.7 mA h g^{-1} can be retained after 100 cycles at 500 mA g^{-1}, corresponding to a high capacity retention of 87.5%.[127] By enclosing nanosized amorphous red P in a nitrogen-doped microporous carbon matrix (referred to as P@N-MPC) generated from zeolitic imidazolate framework-8 (ZIF-8). The P@N-MPC composite exhibits an increased rate capacity (450 mA h g^{-1} at 1 A g^{-1} after 1000 cycles with a very low capacity fading rate of 0.02% per cycle) when used as an anode for NIBs and a high reversible specific capacity of 600 mA h g^{-1} at 0.15 A g^{-1}.[128] The resultant Bi–Sb alloy nanoparticles synthesized from MOF-836 have homogeneous particle sizes of 30 nm, and the amount of Sb in MOF-836 was adjusted to accurately determine their composition. The

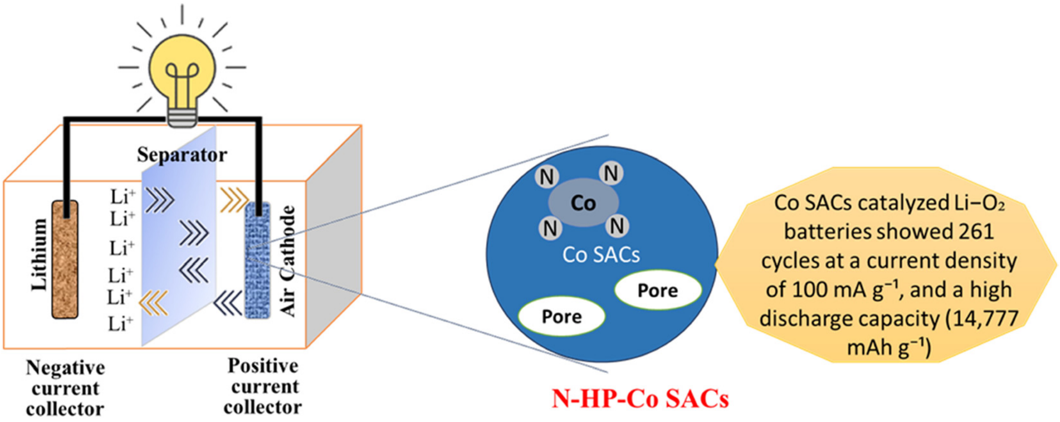
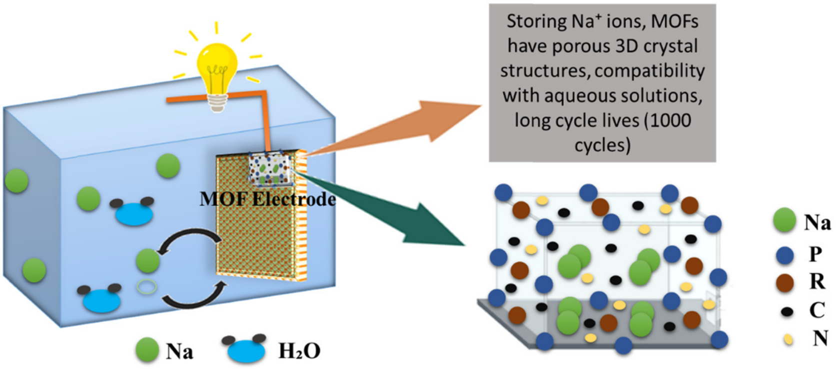


Fig. 7 The application of MOFs in lithium air batteries.[122]



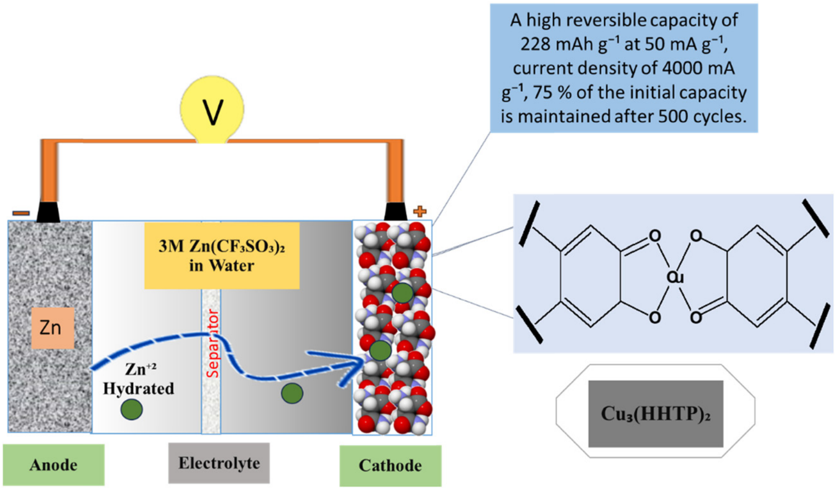
Storing Na$^+$ ions, MOFs have porous 3D crystal structures, compatibility with aqueous solutions, long cycle lives (1000 cycles)

Fig. 8 The application of MOFs in sodium ion batteries.[130]

nanosized MOF-836 alloys showed remarkable cycling performance, a capacity retention of 180.9 mA h g^{-1} at 1 A g^{-1} over 1000 cycles with a capacity loss of just 0.055% each cycle, and a specific capacity of 259.8 mA h g^{-1} at 200 mA g^{-1} after 500 cycles.[129] Metal–organic frameworks (MOFs) were synthesized and utilized as an electrode for an aqueous sodium-ion rechargeable battery (ASIB). MOFs are crystal structure of metal hexacyanometallate (NaP[R(CN$_6$)]), whereas, P and R are transition metals as shown in Fig. 8.[130]

5.5 Zinc-based batteries (ZIBs)

Zn-based batteries have shown a higher probability for use in future energy storage devices for handheld electronic devices due to sufficient Zn sources, low cost, high safety, and excellent aqueous electrolyte compatibility.[131] There is also great interest in ZIBs like for LIBs because of the low redox potential of Zn metal and chemical stability is developed (Fig. 9). Aqueous electrolytes provide an adaptable option for ZIBs due to their minimal toxicity and mild impact on the surrounding system.[132] The important feature of ZIBs is the manufacturing of cathode materials with suitable capacity and stability.[133] For example, V-MOF-derived V_2O_3/C and V_2O_5/C are used as intercalation cathodes for aqueous zin-ion batteries. The V-MOFs have distinctive channels, suitable pore size distribution, improved conductivity, and electrochemical performance. Zn/a-V_2O_5@C showed a rate performance that was maintained at 72.8 mA h g^{-1} with a current density of 200 A g^{-1} with a 2000 cycling performance at 40.0 A g^{-1}.[134] A typical V-MOF (MIL-47) product is successfully created using a single hydrothermal process, and its one-dimensional, layered nanorod-like structure is examined. The aqueous MOF-Zn battery, which has a high initial specific capacity of 320 mA h g^{-1} at 0.1 A g^{-1} and a good rate capability and cycling performance, uses the V-MOF product as the cathode material.[135] MnO/C@rGO composites are created using an *in situ* process that combines a one-step solvothermal approach developed from MOFs by calcinating at 570 °C. It can sustain a discharge capacity of 170.6 mA h g^{-1} after 300 cycles at 500 mA g^{-1} when used as a cathode for AZIBs, according to subsequent evaluation. Importantly, it still yields a reversible capacity of up to 110.1 mA h g^{-1} even when the current density reaches up to 2.0 A g^{-1}.[136] ZnVO-800 is a brand-new cathode material made of a $V_2O_3/V_3O_5/Zn_2VO_4$@NC composite with a hierarchical structure and heterojunction that was created by self-sacrificing the zeolitic imidazolate framework-8 (abbreviated ZIF-8). Particularly, for aqueous zinc ion batteries at an initial discharge of 0.5 A g^{-1}, the activated



A high reversible capacity of 228 mAh g^{-1} at 50 mA g^{-1}, current density of 4000 mA g^{-1}, 75 % of the initial capacity is maintained after 500 cycles.

Fig. 9 The application of MOFs in zinc ion batteries.[139]

electrode's reversible capacity can reach up to 314.0 mA h g^{-1}.[137] Through the use of a metal–organic framework template, a novel and highly reversible Mn-based cathode material with a porous framework and N-doping (MnO*x*@N-C) is synthesized. It shows superior performance to most reported ZIB cathode materials, exhibiting a high capacity of 305 mA h g^{-1} after 600 cycles at 500 mA g^{-1}, and maintaining a feasible capacity of 100 mA h g^{-1} at a relatively high rate of 2000 mA g^{-1} with long-term cycling of up to 1600 cycles.[138] The cathode material for aqueous rechargeable zinc ion batteries using $Cu_3(HHTP)_2$ was a two-dimensional (2D) conductive metal–organic framework (MOF) that also offers high diffusion rates, low interfacial resistance and allows the $Cu_3(HHTP)_2$ cathode to use the intercalation pseudo-capacitance process as shown in Fig. 9.[139]

5.6 Potassium-ion batteries (KIBs)

KIBs have shown their advantages of high energy and power density at low cost since 2004.[140] Moreover, potassium is one of the most common elements on the planet, accounting for about 2.1–2.4% of the earth's crust. It is important to use those cathode materials which can manage overweight sized K ions because generous sized K ions may cause KIBs to fail.[141] For the extended cycle life anode of PIBs, new ultrathin carbon film@ carbon nanorods@Bi MOFs nanoparticle materials were created. The MOF-based anodes demonstrate a remarkable capacity of 425 mA h g^{-1} at 100 mA g^{-1} and a capacity degradation of 0.038% per cycle over 600 cycles because to their distinctive structure. The capacity degradation is as low as 0.036% per cycle over 700 cycles, even at a greater current density of 1000 mA g^{-1}.[142] Investigations were conducted on a metal organic framework-5 (MOF-5) based high-temperature PIB with extremely high stability. The PIBs have initial discharge specific capacities of 1183 and 210 mA h g^{-1} at a current density of 200 mA g^{-1}, respectively, at a fixed working temperature of 62.5 °C, and have a specific capacity of 160 mA h g^{-1} with a low decay of 0.15% per cycle over 150 cycles.[143] By electrospinning a Zn-based zeolitic imidazolate framework (ZIF-8), ultrafine ZnSe nanocrystals were effectively incorporated into a new N-doped porous carbon nanofiber, which was then thermally processed to provide an improved anode material for KIBs. With a reversible capacity of 270 mA h g^{-1} at 0.5 A g^{-1} and a high-rate capacity of 139 mA h g^{-1} at 2.0 A g^{-1}, the 1D porous nanostructured electrodes demonstrated outstanding long-term cycling stability for 1000 cycles when evaluated as anodes for KIBs.[144] An anode material for PIBs made of a cobalt(II) terephthalate-based multilayer MOF with a high reversible capacity of 188 mA h g^{-1} after 600 extended cycles at 1 A g^{-1}, the extraordinary potassium storage performance of L-$Co_2(OH)_2$BDC is shown, highlighting the significant advantages of MOFs as better potassium storage anodes.[145]

5.7 Magnesium-ion batteries (MIBs)

Due to their greater stability, divalent character, and high melting point, MIBs will be used frequently in the future as electrical energy storage devices. MIB abundance is 104 times greater than lithium and the movement of solid-state transport into an inorganic cathode material is slow which results in a poor reversible capacity and less production of power.[146] To reduce these difficulties, the cathode material must be mesoporous and nanostructured. Enormous efforts have been made recently to develop the cathode materials for MIBs. Bimetallic metal–organic frameworks were effectively constructed for cubic spinel $MgMn_2O_4$ cathode materials using this technique. $MgMn_2O_4$ progressively undergoes a self-activation effect during cycling, which is essential for enhancing the kinetics of Mg^{2+} ions in the host spinel structure. The $MgMn_2O_4$ cathode is given an evident platform at 2 V *vs.* Mg/Mg^{2+} in complete cells as a result of this activation, which offers fresh perspectives for creating high-performance Mg-ion battery cathode materials.[147] Due to its low price, high volumetric energy density, and minimal danger of dendrite development, magnesium batteries are attractive contenders for post-lithium energy storage systems. A Metal–organic framework (MOF) structure called UiO-66 that has been impregnated with magnesium bis[(trifluoromethyl)sulfonyl]imide in 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, an ionic liquid. At room temperature, it is possible to reach a comparably high conductivity of 5.7 10^{-5} S cm^{-1}.[148] Through the use of a sulfurization technique based on MOF, we can create an *in situ* carbon-encapsulated cuprous sulfide (Cu_2S@C) composite and evaluate its electrochemical performance as a displacement reaction cathode for hybrid Mg^{2+}/Li^{+} batteries. The Cu_2S@C composite exhibits 399.2 mA h g^{-1} discharge capacity and the capacity is maintained at roughly 150 mA h g^{-1} at 0.05 °C after 50 cycles in the nucleophilic hybrid electrolyte thanks to the intrinsic property of Cu_2S, the well-defined hybrid porous structure, and the carbon encapsulation derived from MOFs.[149] The benefits of magnesium batteries include a high volumetric energy density, and dendrite-free plating and stripping of magnesium anodes. The Mg–S discharge capacity reaches a maximum of 600 mA h g^{-1} during the first cycle and remains stable for at least 200 cycles at 400 mA h g^{-1}.[150]

5.8 Aluminum air batteries (AABs)

Aluminum air batteries appeared as useful energy storage devices with an energy density of 8100 W h k $g^{-}$and a discharge capacity of 2980 mA h g^{-1}. The electrical energy is produced in AABs when aluminum (Al) reacts with oxygen at the anode, while the reduction of oxygen occurs at the cathode.[151] AABs are more capable than LIBs because the emission of electrons in AABs is three times greater than in LIBs. The drawbacks of AABs are self-corrosion and slowed electrochemical reactions due to the by-products formation.[100] Fe_2O_3@-rGO, $CoFe_2O_4$@-rGO, and Co_3O_4@-rGO are used as electrocatalysts in AABs[152] as shown in Fig. 10. $CoFe_2O_4$@-rGO showed a stable discharge cycle with a good columbic efficiency of 99.6%. Therefore, MOFs and their composites play a vital role in the development of aluminum–air batteries.[153] A new, high-performance Co_3O_4@MWCNTs polyhedron composite cathode was studied in a rechargeable aluminum-ion battery (RAIB) system. MOFs can deliver an initial discharge capacity of approximately 266.3 mA h g^{-1} thanks to the well-defined morphology of

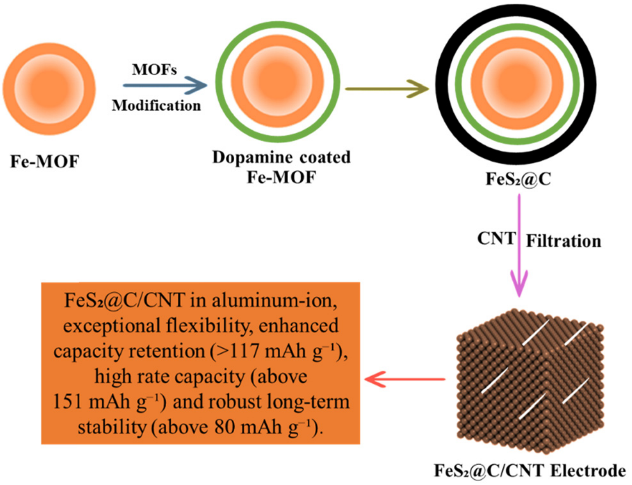


Fig. 10 The application of MOFs in aluminum air batteries.[157]

MOF-derived Co_3O_4 driver reversible specific capacity near 125 mA h g^{-1} at 100 mA g^{-1} over 150 cycles.[154] The Co-MOF exhibited a superior reversible rate capacity (86 mA h g^{-1} at 5.0 A g^{-1}) and remarkable cycling performance (125 mA h g^{-1} after 1000 cycles at 2.0 A g^{-1}).[155] Co_3O_4, Fe_2O_3 and $CoFe_2O_4$ modified with rGO were proposed as affordable metal–oxide cathodes for AIBs. The Co_3O_4@rGO outperformed the most recent state-of-the-art cathode material described in the scientific literature in terms of both capacity and longevity. $CoFe_2O_4$@rGO also demonstrates sensible electrochemical capabilities and an incredibly steady charge/discharge process with a superb coulombic efficiency of 99.6%.[152] More crucially, ZIF-67 nanocrystals may be used as precursors for the quick and easy carbonization/tellurization process that yields $CoTe_2$ nanoparticles@nitrogen-doped porous carbon polyhedral composites ($CoTe_2$@N-PC). Even at high discharge cut-off voltages (voltage window: 0.5–2.3 V), $CoTe_2$@N-PC can generate an extremely high reversible initial capacity of 635.8 mA h g^{-1} at a current density of 200 mA g^{-1}.[156] The acidic treatment of Fe-MOF resulted in yolk–shell hollow Fe-MOF spheres with many active sites to promote electrolyte penetration. The dopamine was coated and calcined to increase the electrode's electron conductivity and regulate volume expansion during cycling. The yolk–shell MOF-derived FeS_2@C was produced after sulfurization as shown in Fig. 10.[157]

5.9 Electrode materials

Due to the presence of abundant metallic and organic redox sites within crystallographic porous materials, alongside their distinct pores and extensive surface area, these materials prove valuable for electrode applications. The investigation of cyclic voltammetry reveals insights through the correlation between peak currents and scan rates, elucidating the electrochemical storage processes.[158] Notably, in 2006 and 2007, both MOF-177 and MIL-53 demonstrated effective utilization as cathode and anode materials in LIBs. For instance, CuTNCQ, which is conductive and redox-active, was formed on carbon nanofibers. This material served as a cathode for SIBs, showcasing a remarkable capacity of 252 mA h g^{-1} at 0.1C. Additionally, it exhibited exceptional redox flexibility across 1200 cycles spanning from 2.5 to 4.1 V. This underscores the advancements in utilizing these materials for enhancing energy storage systems.[159] $M_3V_2(PO_4)_3$ (M indicates Li or Na) acts as an excellent cathode that has sparked attention on both lithium and sodium ion batteries in recent years. For example, $Li_3V_2(PO_4)_3$ (LVP) has a substantial mean voltage (4.0 V) with a particular conductance of 197 mA h g, along with a low ion mobility and strong thermal stability.[134]

5.10 Supercapacitors (SCs)

Supercapacitors as an electrochemical capacitor which is an efficient energy storage device between traditional capacitors and secondary batteries. Supercapacitors are associated with various advantages due to the high power density of traditional capacitors and the high energy density of secondary batteries.[160] These properties indicate efficient rate performances, high safety performances, a long cycle life, and environment-friendly nature. Recently supercapacitors were used in various fields which include power supplies, the automobile industry, and industrial sectors.[161] There are two types of energy storage in supercapacitors, one is through the use of an electrical double layer to reach capacitance storage and the second is through Faraday's capacitor energy storage which used a reversible redox reaction on an electrode surface. As energy storage occurs at the surface of the electrode, porous electrodes with a suitable surface area are necessary.[111] Using a simple chemical oxidation method, an electrode of composite material Ni-MOF@PPy was manufactured from a Ni-based metal–organic framework (Ni-MOF) doped with poly-pyrrole (PPy) to enhance its electron-transport property. The composite material had a specific capacitance of 1815.4 F g^{-1} at a current density of 1 A g^{-1}.[162] Pristine Fe-MOF has been used as an electrode material in supercapacitors due to their unique structures. In comparison with batteries which are associated with high energy density, supercapacitors are efficient electrical energy storage devices with a high power density.[163] Liu *et al.* (2022) effectively manufactured the Zn-BTC by collecting zinc acetate and Na_3BTC in a single process. Calcinating this precursor resulted in efficient porous carbon (BTCC) manufactured with a rich pore structure. The generated BTCC has a high SSA (1464 m^2 g^{-1}) and an appropriate pore size of 3.9 nm. The densely porous structures of BTCC provide a remarkable supercapacitor performance, including a high 310 F g^{-1} at 10 mV s^{-1}, a charging time of only 0.9 s, and excellent cycle stability.[164]

5.11 Hydrogen evolution reaction (HER)

Hydrogen, being a sustainable energy storage medium with the highest gravimetric energy density, has received much interest as a potential replacement for fossil fuels. Water electrolysis can easily produce high-purity hydrogen, but the best Pt-based electrocatalysts utilized in this method are expensive and scarce in platinum.[165] $CoSe_2$–$NiSe_2$/NPFC demonstrated outstanding catalytic activity during the HER in both acidic and alkaline solutions, requiring only 57 and 86mV overpotentials to reach a current density of 10 mA cm^{-2}, respectively.[166] Exorbitant costs and a paucity of resources have limited the broad deployment of the HER. As a result, significant efforts are being directed toward developing metal-based materials as highly efficient electrocatalysts, such as transition metal oxides, nitrides, oxides, selenides, phosphides, and so on, which are expected to replace noble platinum-based electrocatalysts in large-scale applications due to their low cost, intrinsic catalytic properties, and stability.[167] He *et al.* (2022), demonstrated a freestanding HER catalytic molecular organic framework (MOF) (CS@CNC NAs/CC). CS@CNC NAs/CC revealed exceptional HER performance with an overpotential value of 84 mV within 10 mA cm^{-2}, which was roughly the same as the efficacy exhibited by the platinum electrodes (35 mV). The CS@CNC NAs/CC metal electrode additionally showed greater structural stability, with an elevated potential of 84 mV maintained for 72 hours.[101]

6 Stability of metal–organic frameworks for advanced energy storage and conversion

MOFs have become very promising materials for enhanced energy conversion and storage because of their large surface areas, adjustable designs, and remarkable porosity. On the other hand, their actual use depends on the crucial factor of stability. The stability of MOFs for energy storage and conversion is represented in Table 2. It is clear from Table 2, that MOFs of the different metals have great potential for use as either different types of batteries or as supercapacitors. They have unique stability in energy storage devices on the basis of the cyclic stability, cycles and specific capacity. In 2019, Zhao and colleagues successfully synthesized a metal–organic framework material based on anthraquinone and subsequently explored its potential in energy storage applications. This synthesized material demonstrated a remarkable specific capacity of 240 mA h g^{-1} after undergoing 300 cycles. The documented specific capacity establishes this material as a promising candidate for use in next-generation battery technologies.[168]

6.1 Disadvantages of MOFs for energy storage

Recently, there has been a lot of interest in metal–organic frameworks (MOFs) as possible materials for energy storage applications, especially in the fields of gas storage, hydrogen storage, and battery technologies. They do, however, have a number of disadvantages and challenges that must be resolved in order to put them into implementation. In the area of energy storage, it is imperative to critically evaluate the drawbacks associated with metal–organic frameworks (MOFs).[199]

Limited stability. Numerous metal–organic frameworks (MOFs) exhibit a notable vulnerability to moisture and undergo degradation when exposed to water, thereby imposing restrictions on their persistent reliability and stability within achievable energy storage applications.[200]

Synthesis complexity. The synthesis of metal–organic frameworks (MOFs) is a complex procedure, often requiring careful attention to specifics in terms of the conditions and precursors employed.[201] This sophisticated nature of MOF synthesis poses significant challenges when attempting to enhance fabrication for industrial purposes. The complicated composition of MOFs can give rise to diverse expressions in their properties, thereby placing an obvious effect on their overall performance.[202]

Low volumetric energy density. MOFs frequently exhibit comparably lowered volumetric energy densities, thereby requiring enhanced storage volumes in order to accommodate equivalent energy storage capacities compared to alternative substances, such as conventional metal hydrides.[203]

Kinetic limitations. Some MOFs may have slower kinetics when it comes to the adsorption or desorption of gases, which may be a major disadvantage in applications where rapid energy absorption or release is essential.[204]

Chemical compatibility. MOFs have demonstrated remarkable potential in the field of energy storage. However, it is important to acknowledge that their compatibility with certain chemicals and gases may impose limitations on their applicability in specific energy storage scenarios.[20]

Cost and scalability. The cost associated with the fabrication of MOFs is a notable concern, particularly when considering their potential utilization in energy storage applications of practical significance. Moreover, the process of upscaling the synthesis of MOFs for such purposes presents a set of significant difficulties. The commercial viability of a product can be inhibited by the presence of high production costs.[20]

Cycling stability. MOFs have been observed to exhibit a drawback in terms of their cycling stability, wherein they experience degradation over successive charge–discharge cycles within energy storage systems. This particular limitation hinders their practical applicability in batteries and supercapacitors.[111]

Tuning challenges. MOFs with tailored properties suitable for targeted energy storage applications present an immense difficulty, as careful manipulation of both their structural and chemical attributes is required.[205]

7 Commercialization and industrial adoption

Metal–organic frameworks have emerged as a subject of considerable interest and evaluation within the scientific community in recent years due to their immense potential in a multitude of energy storage applications, most notably batteries and supercapacitors. The current state of research in metal–organic frameworks for energy storage primarily resides within the realm of experimental and developmental stages. However, it is worth noting that significant progress, collaborative efforts, and pilot initiatives have emerged, indicating the potential for MOF-based energy storage to transition into a commercially viable solution in the near future.[206]

Table 2 Stability parameters of MOF-based synthetic materials

Materials	Applications	Specific capacity (mA h g^{-1})	Cyclic stability (%)	Cycles	Ref.
Anthraquinone	LIBs	240	—	300	168
Ni-MOF coating MoS_2	Supercapacitors	1590.24	87.97	20 000	169
Co/Zn bimetallic oxides	Electrochemical	25.9	71.43	2000	170
Hybrid metal oxides ($NiO/NiCo_2O_4$)	LIBs	732.0	92.5	3000	171
NiZnCoP and S-α-Fe_2O_3	Energy storage	902	88.6	3000	172
Nickel pyrophosphate	Energy storage	1517	58	3000	173
Vanadium(V-MOFs, MIL-47)	Zinc ion batteries	101.8	81.5	300	174
Graphite carbon nitride	Supercapacitors	495	—	5000	175
MWCNTs@Ni(TA)	Energy storage	115	81.6	5000	176
HCSN	Energy storage	720	82.1	10 000	177
Co-MOF nanocrystals	LIBs	1301	—	2000	178
Hexagonal Ni	Energy storage	977.04	92.34	5000	179
Porous carbon	Supercapacitors	323	97.9	20 000	180
MCo_2O_4 (M = Mn and Zn)	LIBs	1289	95–5	20 000	181
ZnS	Energy storage	160	92.9	1000	182
2D carbon	LIBs	553	100	1000	183
$CuCo_2O_4$	Supercapacitors	701	93.6	6000	184
Co_3O_4/Fe_2O_3	Energy storage	312	89.4	10 000	185
CoHCF	Na ion batteries	97.8	94	5000	186
NiCo–P	Energy storage	894	80.4	10 000	187
CC@$CoMoO_4$ $Co(OH)^2$	Supercapacitors	2028	94.5	5000	188
Mn-BDC	Supercapacitors	1590	82	3000	189
Co-MOF/NF	Supercapacitors	13.6	69.7	2000	190
CoS_2	Supercapacitors	146	89	5000	191
$NiCo_2O_4$	Supercapacitors	208.8	100	6000	192
Zn–Co–O@CC	Supercapacitors	1750	94	5000	193
Fe-MIL-88B	LIBs	744.5	~80	400	100
NiO/C@CNF	Supercapacitors	742	—	5000	98
ppy-S-in-PCN-224	LSBs	440	91.3	1000	194
Zn MOF	Supercapacitors	310	89.4	10 000	164
ZIF-67-ppy	Supercapacitors	597.6	95.5	10 000	159
MIL-47	Supercapacitors	572	—	1000	134
Ni-MOF-ppy	Supercapacitors	1815.4	90.2	3000	162
MIL-53 Fe	LIBs	93	87	—	166
c-MOF $Ni_3(HITP)_2$	Supercapacitors	111	89	10 000	29
Cu-MOF/G	Supercapacitors	482	95	1000	195
PET derived- MILL-53	ZIC	391	92.2	10 000	196
MOF-199- PANI	Supercapacitors	766	92	1000	197
UPJS-15	LSBs	235	—	100	198

7.1 Recent developments and partnerships

The widespread use of MOFs in the realm of energy storage devices has garnered substantial momentum, owing to a number of noteworthy advancements and collaborative efforts. The esteemed scholars from Northwestern University have engaged in a fruitful collaboration with A123 Systems, a distinguished purveyor of energy storage solutions, in order to embark upon the development of an electrode material for lithium-ion batteries that is based on metal–organic frameworks.[207] The researchers successfully engineered a carbon composite material derived from metal–organic frameworks, which exhibited remarkable electrochemical characteristics, notably in terms of its substantial capacity and extended cycle life. The aforementioned collaboration serves as a testament to the profound interest exhibited by well-established corporations in leveraging the potential of metal–organic framework technology for the purpose of energy storage.[208]

7.2 PNNL's research on MOF-derived electrodes

The diligent and industrious Pacific Northwest National Laboratory (PNNL) has been deeply engaged in the pursuit of knowledge and understanding regarding the subject matter of MOF-derived materials, with a particular focus on their potential applications in the domain of energy storage. An investigation of metal–organic framework derived carbon materials as potential anode materials for lithium-ion batteries has been undertaken. The research conducted by Pacific Northwest National Laboratory (PNNL) is primarily centered around enhancing the energy density and stability of these materials, thereby advancing the feasibility of metal–organic frameworks (MOFs) for integration into commercial battery systems.[209]

7.3 Collaboration between MOF technologies and EnergyNest

In a collaborative effort, MOF Technologies, a distinguished enterprise focusing on the advancement and commercialization of metal–organic frameworks, has joined forces with EnergyNest, a prominent provider of cutting-edge energy storage technologies. The primary objective of this partnership is to delve into the potential applications of MOFs in the discipline of thermal energy storage. The primary objective of their collaborative effort is to advance the field of thermal storage by devising economically viable and highly efficient solutions through the utilization of MOFs.[210]

8 Future directions and research opportunities

This analysis seeks to delve deeper into the present condition of energy storage utilizing metal–organic frameworks. By doing so, we will endeavor to identify research directions that have promise, while also shedding light on areas that require further investigation. This will enable us to address prevailing challenges and unlock novel applications in this field.

8.1 Promising research directions

MOF synthesis and tailoring. The research should concentrate on establishing scalable and cost-effective MOF synthesis techniques. To tune MOF characteristics for particular energy storage applications, novel techniques such as post-synthetic modification and defect engineering may be investigated. Rational design approaches, led by computer modeling, may help in the development of customized MOFs with improved characteristics.[211,212]

Stability enhancement. One of the most difficult difficulties in MOF-based energy storage is maintaining stability under demanding working environments. MOFs with increased stability should be developed *via* research, particularly in the presence of moisture, high temperatures, and chemical reactions. Techniques for encapsulation and protective coatings may also be researched.[213,214]

Electrode design for batteries and supercapacitors. Advancing battery and supercapacitor technology requires optimizing MOF-based electrode materials. To improve electrical conductivity and charge–discharge rates, researchers should investigate the integration of MOFs with other conductive materials or develop composite structures. This might include creating MOF-based composite electrodes with specific porosity and composition.[215,216]

***In situ* characterization.** *In situ* characterisation methods that have advanced may give useful insights into the electrochemical behavior of MOF-based energy storage materials. Researchers may use *in situ* investigations to better understand the structural changes, redox reactions, and ion dynamics that occur inside MOFs during energy storage operations. This information may be used to guide the development of new materials and technology.[217]

8.2 Challenges and research needs

Scalability and cost-effectiveness. While MOFs have outstanding characteristics, synthesizing them on a big scale remains a difficulty. To make MOFs practicable for energy storage applications, research is required to develop cost-effective and scalable production procedures. In this context, collaboration between materials scientists and engineers is critical.[218]

Safety concerns. MOFs may be dangerous in some energy storage applications, particularly when exposed to high temperatures or chemically reactive conditions. More investigation is needed to create safe handling and storage practices for MOF-based energy storage materials and devices.[219]

Long-term stability. It is critical to ensure the long-term stability of MOFs in real-world applications. Researchers should undertake thorough durability testing and evaluate the effects of cycling, temperature changes, and pollutant exposure on MOF performance.[220,221]

Integration and system-level research. It is a difficult challenge to integrate MOF-based energy storage materials into practical devices and systems. The development of entire energy storage systems, including design concerns, scalability, and compatibility with current technologies, should be the focus of research.[222]

9 Conclusions

Finally, in the context of sustainable energy storage, this study has offered an in-depth review of the rapidly developing discipline of metal–organic frameworks (MOFs). MOFs as a game-changing material for next-generation energy storage systems, owing to their unique features, including as tunability, large surface area, and various metal–organic combinations. The hybrid systems, which integrate MOFs with other materials such as polymers, graphene, or nanoparticles, are an emerging idea. These combinations may improve MOF performance while also addressing stability difficulties. The possibilities of developing functional MOF structures with advanced characteristics such as redox-active sites, charge transport channels, or catalytic centers for improved energy storage and conversion is also a major concern of future study. These applications of MOFs provide opportunities for inventive approaches to energy storage and conversion, in addition to showing promise for tackling the current pressing issues of environmental impact and energy sustainability. But it's important to recognize the hurdles that need to be removed in order to turn these promising ideas into actualities. Furthermore, multidisciplinary cooperation between materials scientists, chemists, engineers, and policymakers is necessary for the integration of MOFs into practical energy systems. The possibilities for MOFs in sustainable energy storage are still very exciting and enormous as we go towards the future. To fully use MOF materials, researchers and industry stakeholders need to keep funding the investigation of new materials, synthesis techniques, and applications. When combined with persistent work, MOFs have the potential to significantly contribute to the worldwide shift toward sustainable, effective, and clean energy storage technologies.

Conflicts of interest

There are no conflicts to declare.

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