

Review article

Incorporation of redox-activity into metal-organic frameworks for enhanced supercapacitors: A review

Kabir O. Otun^{a,b,*}, Azfarizal Mukhtar^a, Sodiq A. Nafiu^c, Ismaila T. Bello^d, Jibril Abdulsalam^e^a Institute of Sustainable Energy, Putrajaya Campus, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Malaysia^b Department of Chemistry and Industrial Chemistry, Kwara State University, Malete, PMB 1530, Ilorin, Nigeria^c Department of Chemistry, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia^d Department of Physics, College of Science, Engineering and Technology, University of South Africa, Johannesburg 1710, South Africa^e School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, WITS, 2050 Johannesburg, South Africa.

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ABSTRACT

Metal-organic frameworks (MOFs) have gained significant research attention in recent times as electrode materials for energy storage devices due to their high porosity, high chemical and structural tunability, and excellent textural properties. However, one of the key drawbacks to the applications of MOFs as electrodes for energy storage is their low electrical conductivity induced by the insulating nature of most organic linkers and the low overlap between conjugated π -orbitals of the linkers and/or the d-orbitals of transition metals which define the structures of MOFs. A variety of approaches that mostly preserve the intriguing properties of MOFs have been established to impart redox activity into MOFs to improve their electrochemical performance such as redox hopping/electron self-exchange between fixed sites, covalent incorporation of redox active mediators, imparting bandlike electronic conductivity, among others. As a result, this review discusses recent advances in the strategies to prepare redox-active MOFs with targeted properties including electrical conductivity, ionic conductivity, stability, and porosity to maximize their potentials in the fabrication of supercapacitor devices with excellent performance. Along with a critical analysis of the reported performances of conductive and redox-active MOFs for supercapacitors, their energy and charge storage mechanisms are discussed. Finally, a brief outlook to the future research directions is outlined for advancing MOF research for electrochemical energy storage applications.

1. Introduction

The hunt for reliable and efficient renewable energy sources has increased globally because of the extensive use of depleting fossil fuels occasioned by population explosion and the growing energy demand [1]. However, for renewable energy resources to be of immense benefit for future generations, the research endeavor in this regard must figure out ways to store and use energy efficiently. Over the past few years, several energy storage and conversion devices have been developed, including batteries, fuel cells, and supercapacitors for use in commercial energy storage and conversion systems [2]. While large quantities of energy can be stored in batteries, charging them is usually time consuming. Conversely, capacitors charge almost immediately but can only hold very little energy. Supercapacitors are likely going to hold the

key for future energy storage when we need to rapidly store and release large amounts of electricity. Supercapacitors combine the best features of batteries and capacitors because they have the capacity to store and release significant amounts of energy. As a result, they are highly sought after in the demand of future electronic devices. Supercapacitors have several key benefits, including reduced susceptibility to temperature, reduced self-discharge with high energy and average power density, and high cyclic stability [3].

Supercapacitors can be divided into three groups based on their storage mechanism as electric double layer capacitors (EDLC), pseudo-capacitors, and hybrid supercapacitors. When an external voltage is provided to the positive and negative electrodes, respectively, the EDLCs store charges electrostatically and function to cause the charge in the electrolyte to produce an electrostatic pull effect [4]. The surface of the

* Corresponding author at: Institute of Sustainable Energy, Putrajaya Campus, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Malaysia.

E-mail address: otun.kabir@uniten.edu.my (K.O. Otun).<https://doi.org/10.1016/j.est.2024.110673>

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positive electrode absorbs anions, and the surface of the negative electrode absorbs cations, thereby creating a significant potential difference that enables charge storage. Carbon materials constitute the EDLCs, and examples include activated carbon, carbon nanotubes, graphene oxides, reduced graphene oxides, mesoporous carbons, among others. Some of the outstanding benefits of carbon materials include their great mechanical qualities, huge specific surface area, good chemical and thermal stability, and exceptional electronic conductivity [5]. For instance, Su et al. prepared activated carbon from biomass which showed high specific capacitance (300 Fg^{-1} at 1 Ag^{-1}), high porosity, and high specific area (up to $3000 \text{ m}^2\text{g}^{-1}$) [6]. However, the electric double-layer energy storage process based on ion adsorption and desorption causes carbon materials to typically exhibit relatively low capacitance, which leads to unsatisfactory energy density residuals for supercapacitors [7]. Conversely, pseudocapacitors can store electrical charges electrochemically since they are made of redox-active materials. Through redox reactions, electrosorption, and intercalation processes, pseudocapacitance function by moving electron charge between the electrode and electrolyte. [8]. The energy density of pseudocapacitor materials is higher than that of EDLC materials, which makes it possible to store energy density both at the surface and in the bulk of the electrode materials. Examples include metal oxides such as nickel oxide, iron oxides, cobalt oxide and conducting polymers. The hybrid supercapacitors combine the properties of both pseudocapacitors and EDLCs. The performance of supercapacitors is largely dependent on the electrode material. As a result, the design and optimization of the performance of electrode materials have emerged as the main areas of study for supercapacitors [9].

In the past thirty years, metal-organic frameworks (MOFs) have caught the attention of researchers all over the world as potential electrode materials for SC due to their intriguing chemistry including high specific surface area, rich redox metal centers, and tailorable porosity [10]. MOFs are a group of crystalline coordinated compounds made up of organic linkers and metal nodes. The organic linker in MOFs provides porosity and conjugated π electron cloud, which typically demonstrate the characteristics of EDLC. Layer-stacked MOFs known as conjugated MOFs are composed of ortho-substituted conjugated building blocks and square-planar links with weak out-of-plane van der Waals interactions and substantial in-plane conjugation. There has been a report on the synthesis of 2D conjugates MOFs with intrinsic charge transfer. The 2D plane's expanded π -conjugation can help towards delocalization of charge carriers in the MOF framework, which is advantageous for high conductivity and mobility [11]. The metal nodes in MOFs provide redox sites, characteristic of pseudocapacitive behavior [12]. The two mechanisms exhibit hybrid capacitance properties when they simultaneously emerge. In energy storage devices such as supercapacitors, the performance of MOFs as electrode material is largely dependent on the choice of metal nodes, nature of organic linkers, surface morphology and design architecture. Both metal nodes and organic ligands can be used as the sources of charge carriers in MOF-based compounds. Through the conjugation in MOFs, both metal centers with unpaired electrons and organic ligands with steady redox activity can guarantee charge delocalization [13].

Despite the progress recorded on the use of MOFs for SCs, the application of MOFs is limited by low conductivity and poor electrochemical stability. Similarly, the lack of redox activity and ease of breaking of coordination bonds under certain operating potentials limit the utility of pristine MOFs in energy storage applications [14,15]. One of the key strategies in this research endeavor is to systematically tune the properties of MOFs to synergize their unique design with electrochemical features that are relevant to boost their electrochemical energy storage applications. By incorporating redox activity into MOFs, the properties of MOFs can be tailored to improved materials with enhanced electrochemical performance. The redox activity in MOFs could emanate from variable metal nodes, organic linkers, and/or guest molecules confined within the framework. Conductivity, which considers

both carrier movement and carrier concentration, can quantify the effectiveness of charge transmission. The two main methods are band-like and hopping transport; the former depends on strong interactions and can create continuous energy bands. For the latter, there are substantial barriers between the networks because of the discretely localized charge carriers [16].

Two methods can be used to introduce redox-active functionality into MOFs. The first step is to apply a predesigned building block approach to produce the redox-active MOFs [17]. Most of the time, coupling functional groups are added to redox-active compounds. The resulting redox-active building blocks can subsequently be linked via a variety of organic processes. Second, a post-synthetic method can be used to introduce redox-active functionality into the MOFs. The functionalized redox-active moieties can then be added to the MOF through side group or main chain post-synthetic modification after MOF platforms are designed in this case by the coupling of relatively simple organic building blocks [18].

There are several published research works that centered on tuning the properties of MOFs and their composite electrodes with a view of improving their electrochemical energy storage performance [19–23]. However, research on exploiting redox activity in MOFs for electrochemical energy storage applications is still in its infancy. Hence, it is critical to summarize important advances in this field to unmask the latest research development in this area. Although a few review articles have been published on redox-active MOFs for electrochemical energy storage [14,15,24–26], there is no comprehensive review yet on incorporating redox-active MOFs for supercapacitors. Therefore, in this review, we summarized extensive research on the use of redox-active MOFs for supercapacitors. The two fundamental charge transfer processes in redox-active MOFs—hopping transport and band transport—are emphasized. The techniques for introducing redox-active sites into metal-organic frameworks (MOFs) are also described. These techniques involve the use of electron-rich or electron-deficient linkers, open redox pairs metal clusters, and redox-active guests. Lastly, the difficulties and future directions for enhancing redox-active MOF performance in supercapacitors are explored.

2. Supercapacitors

Supercapacitor was designed to serve as an improvement over conventional capacitor to allow for greater power density thanks to its high capacitance and low resistance to charge transfer [2]. The difference in the energy density of a supercapacitor compared to the traditional capacitor can be attributed to the difference in their charge storage mechanism. A traditional capacitor typically consists of two conducting plates (electrodes) and an insulator or dielectric that separates the plates. As a result, when one electrode is supplied with a voltage, an electric field forms across the dielectric in which negative charges (electron accumulation) build up at one electrode and positive charges (hole accumulation) at the other. Charge buildup on the corresponding plates thus contributes to the mechanism of storing energy, which eventually hinders direct current. At this point, it is fully charged; the capacitor retains its charge even when it is taken out of the circuit. On the contrary, the capacitor loses its charge while the discharge process takes place. The electrodes of capacitors are often constructed from the same metal thin film, aluminum foil [27].

Conversely, supercapacitors store energy and charge it at the interface of electrode and electrolyte. They use electrode materials that have high surface area and small dielectrics to deliver higher capacitance [28]. The mechanism of storage depends on the type of electrode materials used. For instance, carbon-based electrode materials such as activated carbon, graphene, activated carbon, etc., store energy by EDLC (non-faradaic) while metal oxides contribute to reversible redox reaction (faradaic). Supercapacitors are renowned for their distinctive qualities, including their high-power density, high specific capacitance, outstanding life cycle with high-capacity retention and fast charging

[29]. Compared to capacitors, supercapacitors have a relatively high energy density; but the energy density of supercapacitors is lower compared to batteries as shown in Fig. 1. Nevertheless, modifications of the electrode materials as well as the electrolyte can improve the capacitance and specific energy of a supercapacitor [30].

2.1. Energy storage mechanisms of supercapacitors

Supercapacitors are majorly categorized based on the mechanism of charge storage into electric double layer capacitors (EDLCs), pseudocapacitors and hybrid supercapacitors [32]. The most reported SC is EDLCs which employs highly porous carbonaceous materials as electrodes. Porous carbon electrode materials behave as an electric sponge and adsorbs the ions from the electrolytes and subsequently releases them at discharge [33]. Due to no evidence of charge and ion transfer across the electrode/electrolyte interface, the energy storage mechanism in EDLC is referred to as a non-Faradaic process [34]. On the other hand, pseudocapacitors displays the energy/charge storage mechanism via a reversible Faradaic reaction at the surface of electrode with the most widely used RuO_2 [35] and MnO_2 [36,37] electrode materials. Hybrid SCs majorly fabricated from the EDLC and pseudocapacitor composite materials in order to improve the energy density of EDLCs [38,39].

2.1.1. Electric double later capacitors (EDLCs)

The charge storage mechanism of EDLCs, which are commercially available and technologically advanced devices, is based on the physical adsorption of electrolyte ions onto the surface of extremely porous carbon. Electrode materials such as carbon nanotube, activated carbon, carbon fibers, etc., store energy primarily by this process [27,40]. The electric double layer effect is mainly created by the movement of positive and negative charges in the electrolyte solution on the interface side, which is used to balance the charge imbalance caused by the change of the high-energy conduction band electrons on the electrode surface. In practically all electrochemical energy storage systems, the contact between the electronic and ionic conductors is where the electric double layer effect takes place. Two carbon-based electrode materials, an adequate number of electrolytes, and a separator make up an EDLC. Electrochemical double-layer storage (EDLC) allows charges to be stored electrostatically or non-Faradaically without charge loads being transferred [39]. The absence of charge transfer between the electrode and electrolyte means that non-Faradaic reactions do not result in any changes to composition or chemistry. Because of this, EDLCs have extremely reversible charge storage, enabling them to reach extremely

high cycle stabilities. EDLCs often exhibit consistent performance traits over an extended period of charge-discharge cycles, up to 10^6 cycles in some cases.

2.1.2. Pseudocapacitors

In contrast to EDLCs, charge storage in PCs is primarily facilitated by a quick and completely reversible electronic transfer process called reversible redox reaction or Faradaic charge transfer [41,42]. The pseudocapacitance of a material can be either intrinsic or extrinsic. In the first instance, a wide range of particle sizes and morphologies show pseudocapacitive behavior in the materials. For nanosized materials, extrinsic pseudocapacitance only manifests under specific circumstances; in contrast, the same material does not exhibit pseudocapacitive behavior in bulk. Electroanalytical tests may be used to differentiate pseudocapacitive materials from battery-type materials in terms of their kinetics. The kinetics of pseudocapacitive are constrained by a surface-related process, whereas battery electrodes' electrochemical response is regulated by diffusion-controlled processes [43]. Underpotential deposition, redox reactions of transition metal oxides, intercalation pseudocapacitance, and reversible electrochemical doping and de-doping in conducting polymers are among the several charge storage processes that may be identified in a pseudocapacitive electrode. Typically, conducting polymers and metal oxides are employed to construct these electrodes.

The specific capacitance of an electrode is increased by faradic processes that coexist with EDL charge storage. An EDLC's capacitance is typically ten to one hundred times lower than that of a pseudocapacitor. However, because a pseudocapacitor uses slower Faradic processes, its power performance is often lower than that of an EDLC. When charge and discharge cycles occur, electrodes with pseudocapacitance are more likely to expand and contract, which can result in limited cycle life and poor mechanical stability.

2.1.3. Hybrid supercapacitors

Electrodes in hybrid supercapacitors (SCs) combine the advantages of pseudocapacitors and EDLCs. Typically, distinct electrode materials such as metal oxides and compounds derived from carbon are respectively used for the positive and negative electrodes. It also uses the characteristics of both Faradic and non-Faradic processes and is composed of electrodes with polarizable (carbon electrodes) and non-polarizable (polymers) qualities. It may be classified into three types: (1) asymmetric, (2) composite, and (3) battery-type. In particular, the power density of asymmetric hybrid solar cells (SCs) with two non-similar electrodes is provided by the carbon-derived material used as the negative electrode and the energy density by metal oxide used as the positive electrode. The goal of this kind of SC is to combine the best features of pseudocapacitors with EDLC. Moreover, carbon and metal oxide composite electrodes are employed in composite hybrid SCs. The metal oxide holds the charge, and the carbon allows the charge carrier to travel through. The composition of the composite components determines the conductivity of this hybrid composite SC. Lithium ion doped graphite is utilized as the negative electrode while graphite is used as the positive electrode in battery type solar cells. Because of its greater kinetics, this structure boosts the energy density by a factor of two to three when compared to EDLC [44–46]. A thorough representation of the operational concepts and in-depth knowledge pertaining to SC categories is shown in Fig. 2.

3. MOFs for supercapacitors

MOFs are highly favored by SC researchers due to their high designability, customizable composition, controllable porosity, and large specific surface area. Additionally, MOFs combine the benefits of organic materials' flexibility and inorganic materials' rigidity, and during the past two decades, they have attracted the attention of several experts in the field from all over the world. Redox sites are provided by

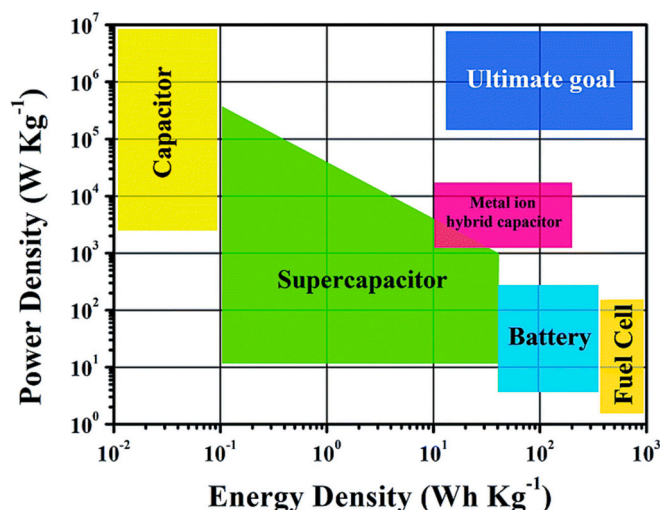


Fig. 1. Ragone plot showing the performance of various energy devices [31].

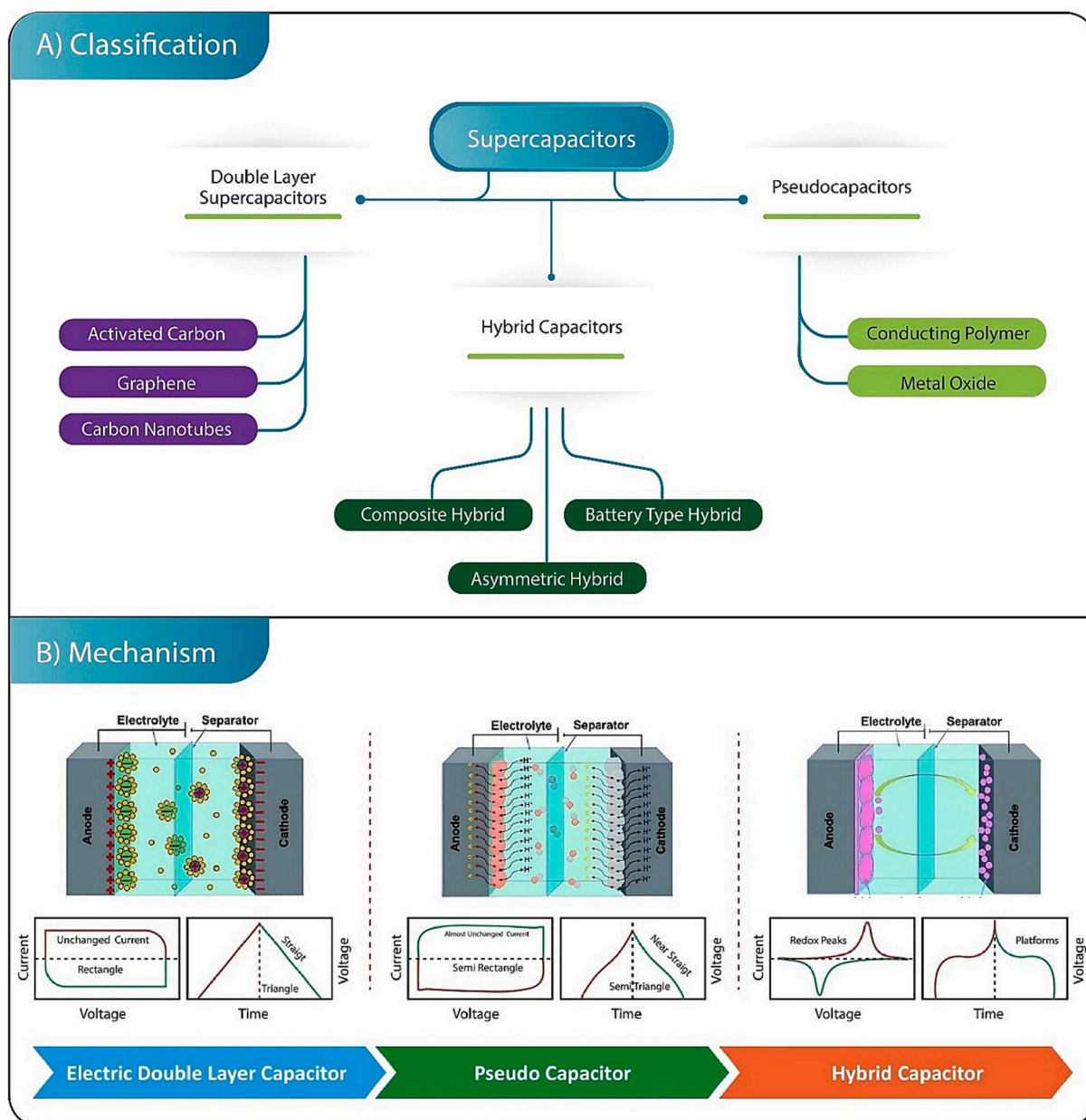


Fig. 2. (a) Classes of supercapacitors (b) Energy storage mechanisms of supercapacitors [47].

the metal in MOFs, which mostly display Faradaic pseudocapacitance characteristics. Porous structure and conjugated electron clouds are provided by the framework in the ligand, which typically exhibit the characteristics of EDLC. The two mechanisms exhibit hybrid capacitance properties when they both operate at the same time [14].

Some significant drawbacks have prevented the adoption of MOFs as electrodes. As an illustration, poor conductivity, particle aggregation, and degradation of electrode materials over the charge discharge cycle [48]. Recent MOF research showed how to overcome the materials' electric conductivity and stability issues. In comparison to their individual components, MOF composites perform better due to their ability to combine adaptability and new physical and chemical properties. The very high electronic conductivity, broad surface area, and huge pore volume of MOF-derived composites make them excellent candidates for charge storage in SCs. Because MOFs have regular morphologies and both metal and carbon sources, they are excellent templates or precursors for the creation of electrode functional nanomaterials. Consequently, a lot of information about their derivatives as supercapacitor

electrodes.

3.1. Pristine MOFs for SCs

The first pristine MOF to be ever employed as electrode material for supercapacitor was Co₈-MOF-5 which demonstrated how the MOFs electrode functions as an electric double layer capacitor and how careful adjustment of the MOFs structure may significantly increase capacitance values [10]. Since then, a variety of different MOFs, including MIL-47, Ni-MOF-71, MIL-100(Fe), bimetallic MOFs, etc have been employed for supercapacitors [25]. Gittins et al. researched the supercapacitor behavior of Cu₃(HHTP)₂ prepared by solvothermal technique, which showed specific capacitance of 114 F/g and areal capacitance of roughly 18 F/cm² at 0.05 A/g. The MOF demonstrated exceptional stability with capacitance retention of 79 % (2.0 A/g) and 86 % (1.0 A/g) after 10,000 cycles. This study was able to demonstrate that the capacitive-type may be produced by MOFs with various architectural configurations and is not limited to layered conducting MOFs, such as Ni₃(HITP)₂ in organic

electrolytes[49]. Because of the Cu(II) redox centers, HKUST-1 were thought to be promising electrodes. Recent studies have previously shown that HKUST-1 materials can be employed as either direct electrodes or as precursors to make SCs electrodes. Table 1 gives the summary of selected pristine MOFs employed in supercapacitor applications.

The insufficient accessibility of the metal nodes responsible for redox activity limits the use of pristine MOFs as pseudocapacitive electrode materials. A bimetallic MOF (i.e., NiCo-BDC MOF) with very thin nanosheets has been used successfully by Ma and co-workers as a promising electrode material for pseudocapacitor applications. Accordingly, the hydrothermally produced bimetallic MOF showed good pseudocapacitive performance in basic aqueous electrolyte (KOH), with specific capacitances of 1945.83 F/g (0.5 A/g) and 1700.40 F/g (1.0 A/g) [63]. The strong metal connection between Ni and Co, which improved the oxidation state of Ni^{2+} and transfer of charges during the redox activity, was attributed to these outstanding results.

In response to the low electrical conductivity of pure MOFs, a conducting MOF, $\text{Ni}_3(\text{HITP})_2$ was first created as the supercapacitor material without the addition of binder or conductive agent. It is composed of two-dimensional layers with stacked conjugation.[61]. Furthermore, in comparison with other carbon-based materials, an improved areal capacitance of 18.9 mF/cm² is demonstrated. Subsequent research revealed that the mechanism underlying high capacitance is linked to a pseudocapacitive reaction at low pH and is dependent on redox activity from the ligand core. The properties of MOFs can be further enhanced by selecting the ideal ligand and metal center. For example, cobalt was coordinated with 2,6-naphthalenedicarboxylic acid (NDC), benzendicarboxylic acid (BDC), and 4,4-biphenyldicarboxylic acid (BPDC) to synthesize three MOFs. As molecules got longer, the discharge capacitance increased from 131.8 to 179.2 F/g [64].

3.2. MOF-derived electrodes for supercapacitors

To address this issue with functional materials that can have more active sites and stabilize at faster rates, MOFs are developing at a critical pace. The breakdown of MOFs into their respective MOF derivatives occurs when they are heated directly in air. Models for tunable porous high surface area materials have found MOFs to be appealing. Their surface can be manipulated to give derivatives that inherit the properties of the pristine MOF. When used as electrodes, these derivatives can result in good conductivity, steady cycling, and good capacitance, among other electrochemical properties. [65].

3.2.1. MOF-derived carbon materials

As electrode materials for batteries and supercapacitors, carbon materials have received massive attention [66]. The advantages of MOF-derived nanoporous carbon over carbonaceous materials made with conventional precursors include a straightforward synthesis with intrinsic diversity that allows for fine control over textural properties

including porosity, and surface areas [67]. Li et al. synthesized a single-crystalline ordered connected macro-microporous Cu-BTC using polystyrene (PS) as the hard template. When used as an electrode in SCs, the macro-microporous carbon made from Cu-BTC showed exceptional rate performance and cycling stability because of its robust hierarchically porous structure [68]. By pyrolyzing ZIF-8@ZIF-67, Tang et al. created nitrogen-doped carbon (NC) and highly graphitic carbon (GC) [69]. The NC@GC inherited the benefits of NC, including its good electrical conductivity and high N content and surface area. It performed better in terms of capacitance as a result. By thermally treating Co-MOF powders, Xu et al. reported creating P-doped and sheet-like porous carbon (PC-600). At current densities of 1.0 A/g, the electrode attained a higher supercapacitor capacitance of 168 F/g. The PC-600-based electrode preserved around 97 % of its capacitance after 3000 charging/discharging cycles at 20 A/g.

3.2.2. MOF-derived transition metal oxides and hydroxides

Because of their low electronic conductivity, MOFs are not recommended for direct usage as supercapacitor electrode materials. However, by utilizing their unique and designable benefits, they have been widely employed as prospective precursors and templates to synthesize transition metal oxides and hydroxides [70]. Guo et al. employed the simple hydrothermal process, followed by a calcination process, to produce the very stable gully-network Co_3O_4 nanowire arrays. The Co_3O_4 showed remarkable performance as an electrode, with a high specific capacity of 582.8C/g at a current density of 1 A/g, a desirable rate capability at 20 A/g with capacity retention of approximately 84.8 %, and an exceptional cycle performance at 25,000 cycles with 93.1 % retention.

Additionally, bimetallic MOFs outperform mono-metallic MOFs in several ways, including by having a stable crystal structure, rich redox centers, variable oxidation states, and good conductivity, which are attributed to the presence of more redox centers.

3.2.3. Transition metal sulfides and phosphides

Transition metal sulfides (TMSs) have gained recognition as state-of-the-art electrode materials for supercapacitors due to their remarkable properties. Strong electrical conductivity, unique crystal forms, low electronegativity, high specific capacity, and high redox activity are a few of these. [71]. Transition metal sulfur (TMS) compounds outperform transition metal oxides (TMOs) electrochemically because sulfur atoms are substituted for oxygen atoms. The properties and performance of TMSs are greatly influenced by their sizes, surface morphologies, and architectures. The TMS nanostructure improves the usage of active electrode material and electrochemical reaction efficiency. As a result, TMSs have outstanding energy and power densities, and the nanostructures of TMS electrodes have seen significant advancements. Recent research works have looked closely at the usage of binary metal sulfides for supercapacitors [72].

Liu and his colleagues achieved hollow NiCo_2S_4 nanocages by

Table 1
Different pristine MOFs synthesized for supercapacitor applications.

MOF	Electrolyte	Specific capacitance (Fg ⁻¹)	Specific Current (Ag ⁻¹)	Energy density	Cyclic stability	Retention (%)	Ref.
Co-BTC	1 M KOH	427.8	0.5	30.6	3000	–	[50]
Mn-MOF	2 M KOH	211.4	5	66	10,000	92.3	[51]
Ni-MOF	1 M KOH	102.4	1	13.74	5000	49	[52]
V-MOF	1 M Na ₂ SO ₄	520.8	1	6.72	10,000	92.8	[53]
Co-MOF	0.5 M LiOH	179.2	1	31.4	5640	–	[54]
MOF-5	6 M KOH	212	0.05	–	10,000	–	[55]
Zn-MOF	6 M KOH	322	1	70	100,000	–	[56]
ZIF-8	1 M H ₂ SO ₄	251	7.5	10.86	2000	–	[57]
Cd-MOF	6 M KOH	647	4	–	10,000	78	[58]
MOF-74 (Ni)	6 M KOH	925	0.5	–	5000	–	[59]
Cu-MOF	6 M KOH	149	0.5	–	2000	–	[60]
Ni ₃ (HITP) ₂	0.5 M Na ₂ SO ₃	15.69 mA/cm ²	0.1 mA/cm ²	0.0488 mWh/cm ²	10,000	84	[61]
Ni-MOF	3 M KOH	1021	1.4	4.18mWh cm ⁻³	–	–	[62]

hydrolyzing ZIF-67 (a sacrifice template) to produce NiCo-LDHs, and then sulfurizing further. The device delivered 689.5 W/ kg of power density and energy density (41.4 Wh/ kg) [73]. Like this, Liu et al. developed a hollow CoSx@NiCo-LDH core-shell structure using ZIF-67 as a template, and the electrode exhibits excellent capacity retention and high energy density (42.81 Wh/ kg at 800.17 W/ kg). In Guo's research, NiCo₂S₄/NF (NiCo₂S₄ arrays on nickel foam), which had a good energy density of 55.8 Wh/ kg at 695.2 W/ kg, was also made using the same synthetic method.

Guan et al. showed how to create mixed metal sulfide particles that resemble onions using a sequential ion-change method. Direct pyrolysis is a method that can be used to create Co₃O₄ particles with hollow, structured shells. Co₄S₃ particles, which resemble onions, were created by reacting the as-produced Co₃O₄ particles with Na₂S through an anion-exchange method. Finally, a cation-exchange interaction between the Co₄S₃ particles and the Ni²⁺ ions produced the final onion-like NiCo₂S₄ particles. The NiCo₂S₄ electrode, which had the appearance of an onion, had a high specific capacitance of 1016 F/g at 2 A/g, and it continued to have a multi-shelled structure and retain 87 % of its capacitance after 10,000 cycles. The researchers hypothesized that the distinctive shell architecture and sturdy matrix are responsible for these enhanced electrochemical performances.

As a family of electrode materials for SC applications, transition metal phosphides (MPs) with metalloid properties and good electrical conductivity have demonstrated exceptional performances and considerable potential [74]. For reaching high power densities of SCs, transition metal phosphides are kinetically more advantageous for fast electron transport than transition metal-based compounds like oxides, hydroxides, and sulfides. MOFs, which are porous materials with easy tunability, have been seen as attractive candidates as a means of creating MPs with hollow structures. Because of their large surface area and distinctive hollow structure, the MOF-derived CoP microcubes with hollow structures (560 F/g) produced by low-temperature phosphorization at 350 °C performed better as supercapacitors than the solid counterparts (427.6 F/g at 1 A/g). By reducing friction at the interface between the active electrode and the electrolyte ions and by providing a large area for volume deformation during cycling, the hollow shape can help improve electrochemical performance. It has been demonstrated that an ASC device with N-doped graphene as the negative electrode and hollow CoP bacteria (CoP-350 °C) as the positive electrode has a high energy density of 21.4 W h kg⁻¹ at a power density of 373 W/kg and good stability [75]. In another work, the electrical conductivity of MOF-derived phosphides was greatly increased by Elayappan and his teams using a binder-free technique, which involves directly forming MOF nanostructures on the substrate without the use of any binders or additives [76]. Table 2 gives the summary of selected MOF-derived electrode materials employed in supercapacitor applications.

Table 2
Different MOF-derived materials synthesized for supercapacitor applications.

MOF precursor	Derived materials	Electrolyte	Specific capacitance (Fg ⁻¹)	Current density (Ag ⁻¹)	Energy/power density	Cycles/CR (%)	Ref.
Al-MOF	Porous carbon	6 M KOH	272	2	17.49/388.8	10,000/100	[77]
ZIF-8	N-doped carbon	1 M H ₂ SO ₄	244	0.67	—/—	10,000/98.5	[78]
ZIF-67	NC@GC/CNTs	1 M NaCl	140	1	—/—	50/93.5	[79]
Bi-MOF	Bi ₂ O ₃ @C	1 M KOH	1378	0.5	49/807	4000/93	[80]
Co-MOF	CoMoO ₄	3 M KOH	6120	2	321/—	5000/96	[81]
Fe-MOF	rGO/Fe ₂ O ₃	6 M KOH	869.2	1	79.2/405	5000/96.3	[82]
Ni-MOF	NiO	2 M KOH	1863	0.5	38.4/400	5000/82	[83]
Co-MOF	NiCo-LDH/V	6 M KOH	581	1	55.22/375	5600/93.14	[84]
NiCoMOF	NiCo-MDH	3 M KOH	1088	1	66.5/825	18,000/94	[85]
NiZn-MOF	Ni _{2-x} Zn _x (OH) ₂ @C	6 M KOH	1962	5	34.5/624	6000/91.8	[86]
Ce-MOF	CeO ₂ @(Ni, Co) ₃ S ₄	2 M KOH	1319	1	34.2/849.2	10,000/84.8	[87]
Co-MOF	Co ₉ S ₈	1 M KOH	2831	1	—/—	5000/95	[71]
Ni-MOF	Ni ₂ P/C	4 M KOH	1676	1	42.4/764.23	5000/92	[88]
Ni-MOF	MXene-NPO	1 M KOH	639	0.5	72.6/932	10,000/85	[89]
ZIF-67	CoMoSe _x	3 M KOH	286.1	2	45/2222	8000/95.2	[90]
Mo-MOF	Ti ₃ C ₂ T _x @MoS ₂	1 M LiPF ₆	300	0.15	—/—	800/100	[91]

3.3. MOF composite electrodes for supercapacitors

A composite is a substance made up of several components and at least one continuous phase. MOF composites have garnered a lot of attention lately because of their many uses, which include supercapacitors [92,93]. The shape, stability, and physicochemical properties of MOFs can be significantly enhanced by assembling them with the right ingredients [94]. The performance of MOF composites generally hinges on three factors: (1) the metallic ions and structural architecture of MOFs which influences the diffusion and movement of electrolyte ions, (2) The physical and chemical characteristics of hybrid materials containing metal oxides, conductive polymers, metal, and carbon. These extra functions impact conductivity and stability on MOFs and can make up for the low-rate performance and limited cycling stability of pure MOFs. (3) The interfacial effect and electron transport between the two separate components in the MOF hybrids produce a synergistic effect, which is evident in an improved electrochemical performance [94].

3.3.1. MOF/carbon composite electrodes

Pure MOF has a very low conductivity when used directly as a capacitor material, which will result in low-rate capability and slow electron transmission speed. To speed up electron transmission, carbon compounds can be used to assist in generating a conductive matrix [94]. For instance, successfully designed composites of Ni-MOF and carbon nanotubes (Ni-MOF/CNTs). The unique structure of Ni-MOF and the high conductivity of CNT work together to produce composites that have outstanding electrochemical performance on asymmetric SCs. Similarly, Meng et al., prepared a porous Fe₃O₄/carbon composite using a Fe-MOF (Fe-MIL-88B-NH₂) as the electrode material for a supercapacitor, and they were able to achieve a specific capacitance of 139 F/g at 0.5 A/g and a capacitance retention of 83.3 % after 4000 cycles [95]. With a constructed Fe₃O₄/carbon electrode, the specific capacitance may be increased by raising the operating temperature. A high surface area metal-organic xerogel (Fe₃O₄/Fe/carbon hybrid) was demonstrated by Mahmood et al. in a different investigation. This material had a high specific capacitance of 600 F/g at 1 A/g. An NPC that was created hierarchically from Al-MOF gels displayed a high capacitance of 272 F/g at 2 mV/s. With a power density of 388.8 W/kg, an aqueous ASC constructed using these two derived materials as electrode had a high specific energ.5 Wh/kg [77].

3.3.2. MOF/polymer composite electrodes

The class of MOF composites has recently expanded to include MOF/polymer composites. Because of the wide range of potential polymer functions, their light weight, easy processing, and chemical stability, they frequently garner a lot of interest. Furthermore, these composites may be included as devices for a range of uses, such as supercapacitors

[96]. Liu et al. constructed 3D networked MOF particles by employing precast conductive PPy tubes as support for the in-situ development of MOF particles to increase the overall conductivity and efficiency of MOF particles [97]. Another polymer that has been shown to be effective at enhancing SCs' electrochemical properties is polyaniline (PANI). Using a controlled root etch-wrap fabrication technique, Cao and colleagues produced the hollow core-shell heterostructure electrode involving PANI and ZIF-8 MOF. At 5–30 mA/cm², the improved electrode had an ultra-high area capacitance of 4839–3987 mF/cm². Additionally, the cycle stability of the symmetrical flexible SCs produced by PANI/ZnO@ZIF-8-CC was up to 87 % for 10,000 cycles at 5 mA/cm² [98].

The swelling and shrinking of the polymer during charge/discharge cycles can also be partially offset by adding a polymer into the MOF structure. The creation of a hybrid using conducting polymers like PEDOT or PPy provides a remedy for one more MOF drawback. They can only be found as brittle pellets or powders, therefore additional mixing with binders is required to create a supercapacitor electrode.

3.3.3. MOF/metal oxides or hydroxides

MOFs have few uses for electrochemical energy storage because of their weak intrinsic conductivity. Metal oxides are further effective nanomaterials for enhancing the supercapacitor capabilities of original MOFs [70]. Metal hydroxides and oxides are seen as practical alternatives to CPs as pseudocapacitive materials [99]. Their combination with MOFs, however, has not been thoroughly investigated for possible uses as supercapacitor electrodes. Due to the variable valences of the metal ions that can act as redox centers, MOFs themselves exhibit some pseudocapacitance [100]. Therefore, if they are bound with metal oxides and hydroxides, this feature of MOFs can be enhanced.

MOFs have been combined with mixed metal oxides in addition to composite formation with bare metal oxides for supercapacitor applications. Two main hypotheses underlie the production of supercapacitor electrodes using MOFs and binary metal oxides. Such oxides can support a variety of redox processes, to start. They also have excellent electrical conductivity because of improved electron transport among the involved cations [100]. For instance, Duan et al. prepared a composite of MnO₂ and MOF for high-performance electrochemical energy storage which delivered a high capacitance. As a result, an aqueous asymmetric supercapacitor device was constructed, showing a high Coulombic efficiency (>95 %) and maintaining 89.1 % of its initial capacitance at a power density of 650 W/kg. The device also had a high energy density of 51.1 Wh/kg [101].

3.3.4. MOF/Mxenes composite electrode

MXenes feature distinct 2D layer spacing and variable transition metal oxidation activity, which can speed up the ion reaction kinetics and give more intercalation and pseudo capacitance [102]. As a result, MXenes are added to MOFs to establish supercapacitor with good properties. For high-performance supercapacitors, Pang and colleagues designed a 3D porous Ti₃C₂T_x/ZIF-67/CoV₂O₆ via “ion conversion and exchange” [103]. The Ti₃C₂T_x/ZIF-67/CoV₂O₆ electrode showed 285.5 F/g at 1 A/g. The electrode also demonstrated exceptional cycle stability (94.4 % after 4000 GCD cycles at 3 A/g). Similarly, two identical electrodes that have huge voltage windows and release optimal energy density can be combined to form a symmetric supercapacitor. In another study, porous Co–Fe oxide nanorods made from MOF were glued onto separate MXene films [104]. In 1 M LiCl, the Co–Fe oxide/Ti₃C₂T_x composites' ideal volume capacitance was 2467.6 F/cm³. A symmetric supercapacitor constructed from it displayed a specific surface area capacitance of 356.4 mF/cm². The symmetric supercapacitor also demonstrated good cycling performance, with 88.2 % of its capacitance remaining after 10,000 cycles [104].

The carbon-based capacitive negative electrode and the metal-based battery-type positive electrode was used to assemble asymmetric supercapacitors (ASCs). Sun and colleagues used in-situ “top-down” etching to create MXene/NPO [105]. Fast ion/electron migration

between the NPO and MXene surfaces is made possible by the structure. The MXene/NPO electrode produced cycle stability and a high specific capacity (639C g^{−1} at 0.5 A g^{−1}). Then, MXene/NPO//rGO ASCs were constructed utilizing KOH/PVA gel as the electrolyte, MXene/NPO//rGO as the anode, and PPD/rGO as the cathode. The energy density of the resulting electrode was high, coming up at 72.6 Wh/kg at 932 W/kg [105].

The battery-type faradaic electrode and the electrical double-layer electrode are used to design hybrid supercapacitors (HSCs). For the high-performance HSCs, Zhang and colleagues designed a nanorod-like hierarchically porous MOF/MXene/NF-300 composite by annealing Ni-MOFs/MXene/Ni foam at 300 °C [106]. As the annealing temperature increases, it is evident that the hierarchically-porous structure in nanorods is evolving, as depicted in Fig. 3a–i. Following low-temperature annealing, MOF/MXene/NF-150 retains its characteristic hexagonal nanorod morphology, with a length comparable to that of MOF/MXene-NF. TEM examination clarifies that the surface of MOF/MXene/NF-150 gets noticeably wrinkled and that certain pores begin to appear in nanorods. The electrode that had been tuned had an impressive specific capacity. The HSCs were put together using composites as cathodes and activated carbon/NF as anodes, and they had a remarkable capacitive retention rate (with about 118.1 % after 15,000 cycles) and a high energy density of 46.3 Wh/kg at 746.8 W/kg [106].

3.3.5. MOF and other composite materials

Aside from the above-named materials, MOFs can also be used to composite other materials to improve supercapacitor performance. For instance, Ni-MOF@Co(OH)₂ arrays grow vertically were successfully built on NF by Shi et al. [107]. This plan resolves the conductivity and orientation issues, as well as showing how to combine two different 2D materials and completely utilize them to encapsulate improved storage performance. To create a symmetric all-solid-state SCs electrode, Liu and colleagues created a unique multiple-compositing 3D PANI/ZNO/ZIF-8/G/PC material with the maximum areal capacitance recorded for the electrode at 1 mA/cm² was calculated to be 1.378 F/cm². The hybrid electrode showed no discernible change under various twisting angles and maintained 84 % of its capacitive retention even after 100 cycles of bending, according to the results of the bending and twisting tests. This SC device also includes buttons for a calculator and a red LED light [108].

Jafari and colleagues also designed HKUST-1/PANI composites using the same compositing method and used them as the cathode for SCs. The greatest power density of the HKUST-1/PANI//rGO device in the 1.5 V potential window was 7497 W/kg [109]. Table 3 gives the summary of selected MOF-derived composites employed in supercapacitor applications.

4. Conductive MOFs with redox activity

There have been reports recently of the synthesis of several dozen conductive MOFs with electrical conductivities. High electrical conductivities in these MOFs are attained via advantageous spatial and energy overlaps between the orbitals of the ligand and nearby transition metals. If extrinsically conductive frameworks—in which conductivity is produced by guest molecules or chains of conductive polymers contained within the MOF's pores—are also taken into consideration, the number of conductive MOFs can be further enhanced. Although employing MOFs as a sacrificial template or creating composites with them in the manner described above has some benefits, such as high conductivity or high specific capacity, the preparation method for these MOF-derived materials is complicated. Additionally, some non-conductive MOF-derived electrodes may accidentally collapse during charging cycles, which might impair their electrochemical performance and limit their uses [117]. Researchers have realized that the conductivity of MOFs may be controlled by the suitable design of the organic ligands and metal nodes or clusters thanks to their fundamental

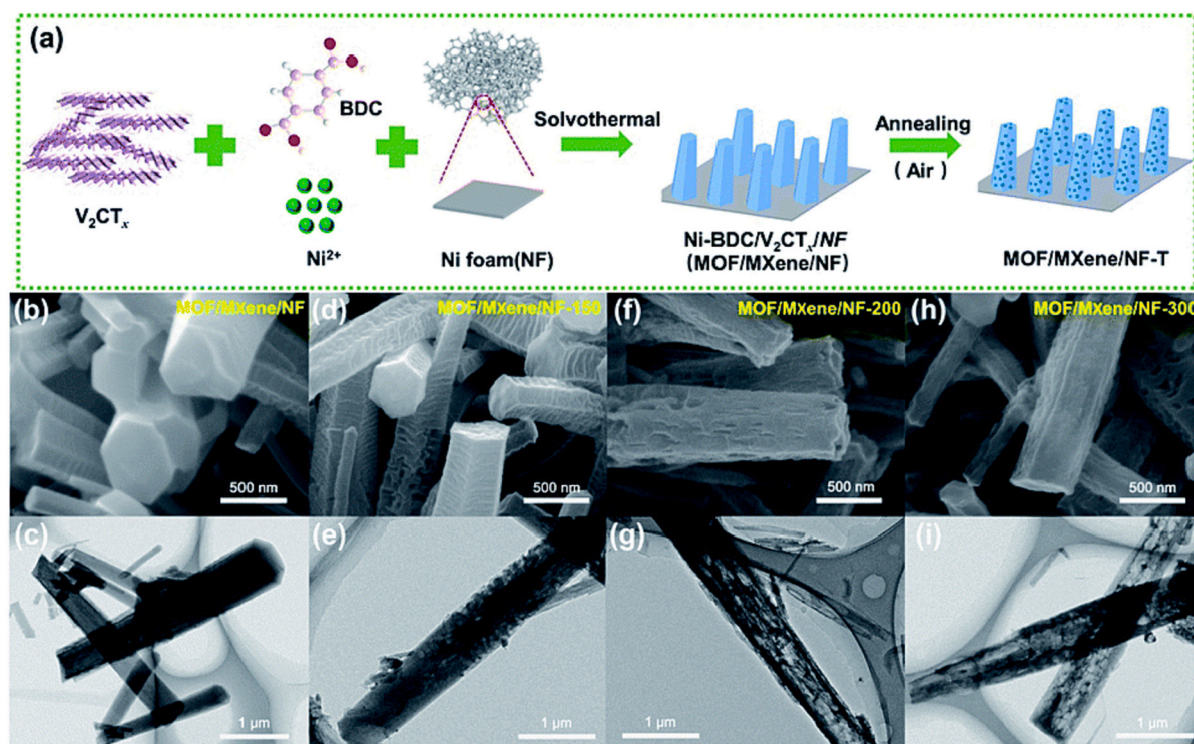


Fig. 3. (a) Illustrations of the preparation of MOF/MXene/NF electrodes. (b) SEM and (c) TEM images of MOF/MXene/NF. (d) SEM and (e) TEM images of MOF/MXene/NF-150. (f) SEM and (g) TEM images of MOF/MXene/NF-200. (h) SEM and (i) TEM images of MOF/MXene/NF-300 [106].

Table 3

Selected MOF-based composites for supercapacitor applications.

hMOF	Electrolyte	Specific capacitance (Fg^{-1})	Specific Current (Ag^{-1})	Energy/Power Density	Cyclic stability	Retention (%)	Ref.
PANI/ZIF-67	1 M KOH	512	1	71.1/504	9000	92.3	[97]
ZIF-8/PANI	1 M H_2SO_4	477	1	21/400	20,000	86	[110]
$CeO_2@ZIF-8$	1 M KOH	132	1	18.3/1	5000	90	[111]
Fe-MOF@Ni(OH) ₂	—	188.75	1	67.1/800	4000	100	[112]
NiCoFe-LDH@ZIF-67	3 M KOH	1202.08	0.5	69.58/750	—	—	[113]
Ni-MOF@Co(OH) ₂	3 M KOH	1448	2	45.7/22400	8000	87.3	[114]
PPy@UiO-66@CT	1 M H_2SO_4	565	0.8 mA cm^{-2}	38.2/37.7	500	90	[115]
UiO-66/rGO	6 M KOH	302	0.15	10.86	—	90.3	[116]

understanding of the electron transport process in MOFs [118]. In metal-organic frameworks (MOFs), charge transport occurs via either a redox-hopping or band-like process that governs electric conductivity. Theoretically and physically, conductivity through the band-like process is well established, while redox conductivity, which is facilitated by the electron hopping mechanism, has proven difficult to demonstrate in experiments. Redox-active MOFs can be divided into two main categories: those that (i) contain redox-active metals or ligands in the framework as it was synthesized, and those that (ii) introduce the redox-active molecules (typically organic species) post-synthetically into redox-inactive frameworks through covalent bonding or guest impregnation [119]. In the first category, the source of the activity is either a metal center (whose geometries are unaffected by redox state changes) or a ligand (which frequently has stable radical states). The second class of redox-active MOFs takes advantage of the strong affinity of MOFs for non-polar and polar guest molecules to infiltrate redox-active species into redox-inactive frameworks. As demonstrated by the integration of redox-active metallocenes into [VO(bdc)], which caused partial framework reduction, redox manipulation of the guest can occasionally cause a change in the electronic characteristics of the framework [25].

The capacitances of conductive MOFs are still a long way from the ideal material, holey graphene, despite being equivalent to the majority of porous carbon materials. Using a conductive MOF with high redox-

activity, Feng et al. obtained an improvement in energy storage performance [120]. The ultrasmall hexaaminobenzene (HAB) linker was chosen by the scientists to create square-planar coordination geometry with subnanometre pores (micropores of approximately 0.8 nm) for coordinating metal species (Ni^{2+} and Cu^{2+}). These two 2D honeycomb layered structured Ni-MOFs and Cu-MOFs, aside from their high conductivity ($70 \pm 15 S m^{-1}$ for Ni-HAB and $11 \pm 3 S m^{-1}$), exhibit exceptionally high chemical stability because of the strong orbital interaction between Ni(II)/Cu(II) and HOA ligand (stable in saturated KOH and 1 M HCl), which permits their use in conventional aqueous electrolytes. Ni-HAB and Cu-HAB in 1 M KOH may be made to have gravimetric capacitances of 420 and 215 $F g^{-1}$, respectively. Ni-HAB exhibits a capacitance that is twice as high as the best porous carbon materials, and on par with conductive polymers and transition metal oxides [120]. Based on the components of MOFs, the redox activity could be incorporated into MOFs through the following means: (i) multivalent metal nodes; (ii) redox-active linkers; (iii) charge-transfer frameworks; and (iv) host-guest interactions.

4.1. Redox-active metals

Redox-active metals can exhibit fast redox chemistry on the surface of the electrodes. These reactions can then enhance the charge storage

capacity of supercapacitors [121]. If redox-active metal ions are used to prepare redox-active MOFs, the open metal sites provide a polarized surface in tailored pores to interact with small molecules and ions. For instance, SBUs with partial d-shell transition metal occupation, such as Ni(II/III), Co(II/III), Cu(I/II), etc., can be used in place of redox-inactive Zr-based nodes. As new synthetic breakthroughs for their realization become accessible, the number of redox-active MOFs containing transition metals with stable oxidation state pairings is growing at a rapid pace. Recently, using a polarity-induced solution-phase technique, Nagaraju et al. developed a new class of binder-free dual-layered Ni–Co–Mn-based MOFs (NCM-based MOFs) with three-dimensional (3D)–on–two-dimensional nanoarchitectures for high-performance supercapacitors [122]. Following varying growth durations of 2, 5, and 10 h, the NCM-MOF coated Ni foam samples were gathered, and the corresponding samples were labeled as NCM-based MOF-2, MOF-5, and MOF-10, respectively. As demonstrated by SEM image of Fig. 4d, the Ni foam substrate is completely covered by logically constructed and securely adherent NCM-based MOF nanoarchitectures under sufficient growth conditions (5 h).

When utilized as working electrodes, the corresponding samples significantly affect the redox chemistry and charge storage characteristics. After being developed on nickel foam, the hierarchical NCM-based MOFs show off a battery-type charge storage mechanism with an exceptional cycling durability, good rate capability (61.8% , $811.67\text{ }\mu\text{Ah cm}^{-2}$ at 50 mA cm^{-2}), and outstanding areal capacity ($1311.4\text{ }\mu\text{Ah cm}^{-2}$ at 5 mA cm^{-2}). The enhanced charge storage characteristics are attributed to the combined effects of dual-layered nanostructures' increased accessible active sites, the elevated redox chemistry of multimetallic

guest species, and their synergistic features. The CV and GCD curves in Fig. 5a, b illustrate how the growth time of the NCM-based MOF materials was compared to their electrochemical performance. The battery-type mechanism of the electrode is made clearer by the redox behavior of the NCM-based monolayered MOF-2, dual-layered MOF-5, and truncated MOF-10 nanoarchitecture electrodes. Due to its multidimensional architectures, abundance of nanovoids, and rich redox sites of guest species (Ni, Co, and Mn species), the dual-layered NCM-based MOF-5 electrode showed improved redox chemistry in comparison to the NCM-based monolayered MOF-2 and truncated MOF-10 electrodes. Ni, Co, Mn, O, C, and K were among the elements displayed in the EDX spectrum of Fig. 5g. The KOH electrolyte is responsible for the K peak. Furthermore, the related elemental mapping pictures demonstrate that, even after the cycle test, the NCM-based MOF exhibited strong durability. The dual-layered NCM-based MOF-5 had high electrochemical kinetics and strong conductivity, as demonstrated by the EIS.

4.2. Redox-active ligands

The redox-active ligands in a MOF can increase the efficiency of charge transfer between metal centers because of the electron delocalization within the ligand and/or π – π^* interactions. According to a recent study on a 2D Ni-based MOF, where electron delocalization was shown to be crucial for accessing important intermediates that become energetically prohibitive for similar molecular systems, redox-inactive linkers may eventually increase redox activity [123]. Tetrathiafulvalene (TTF, $\text{C}_6\text{H}_4\text{S}_4$), one of the redox-active linkers, is a potential contender that is occasionally used to create conductive multifunctional

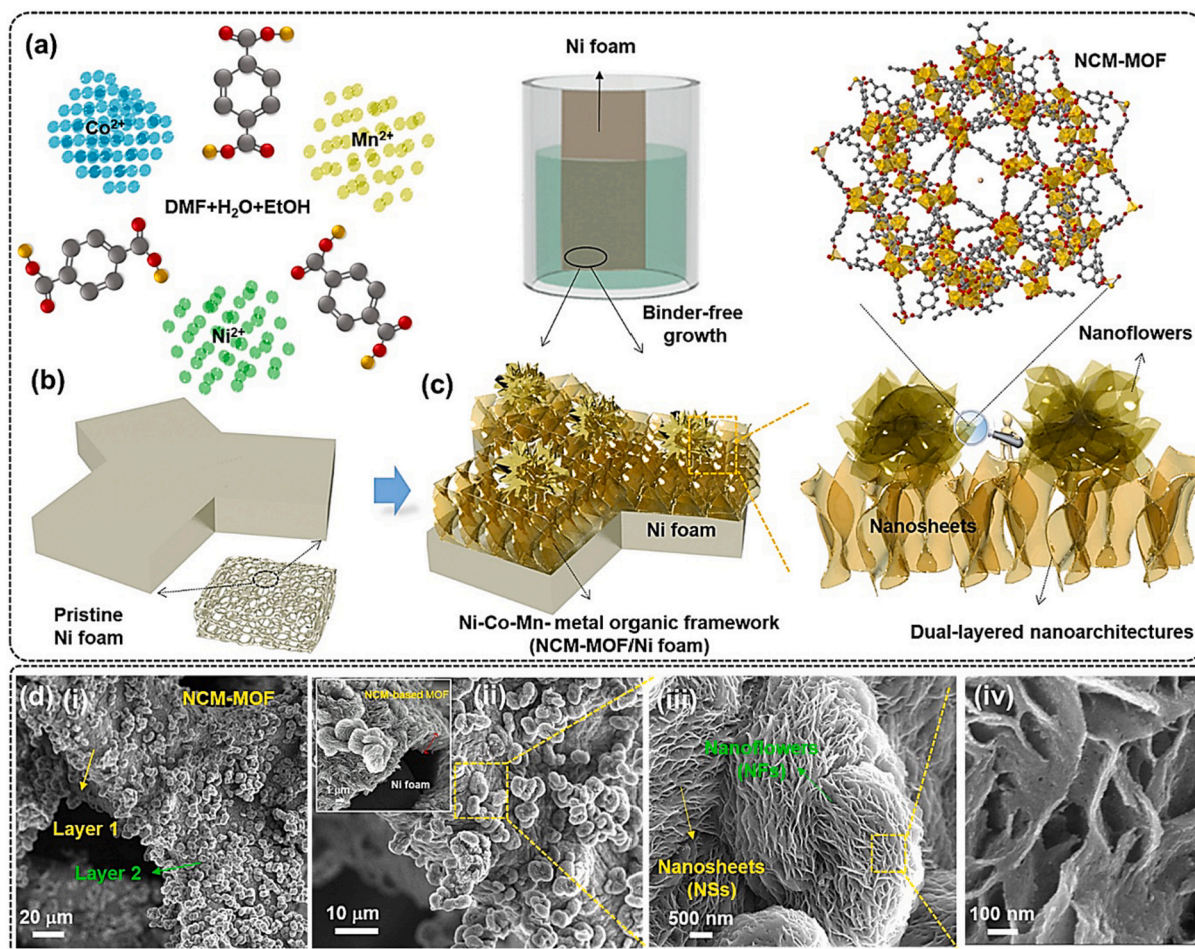


Fig. 4. a–c Synthesis of the dual-layered NCM-based MOF on Ni foam d (i–iv) SEM images of NCM-based MOF-5/Ni foam [122].

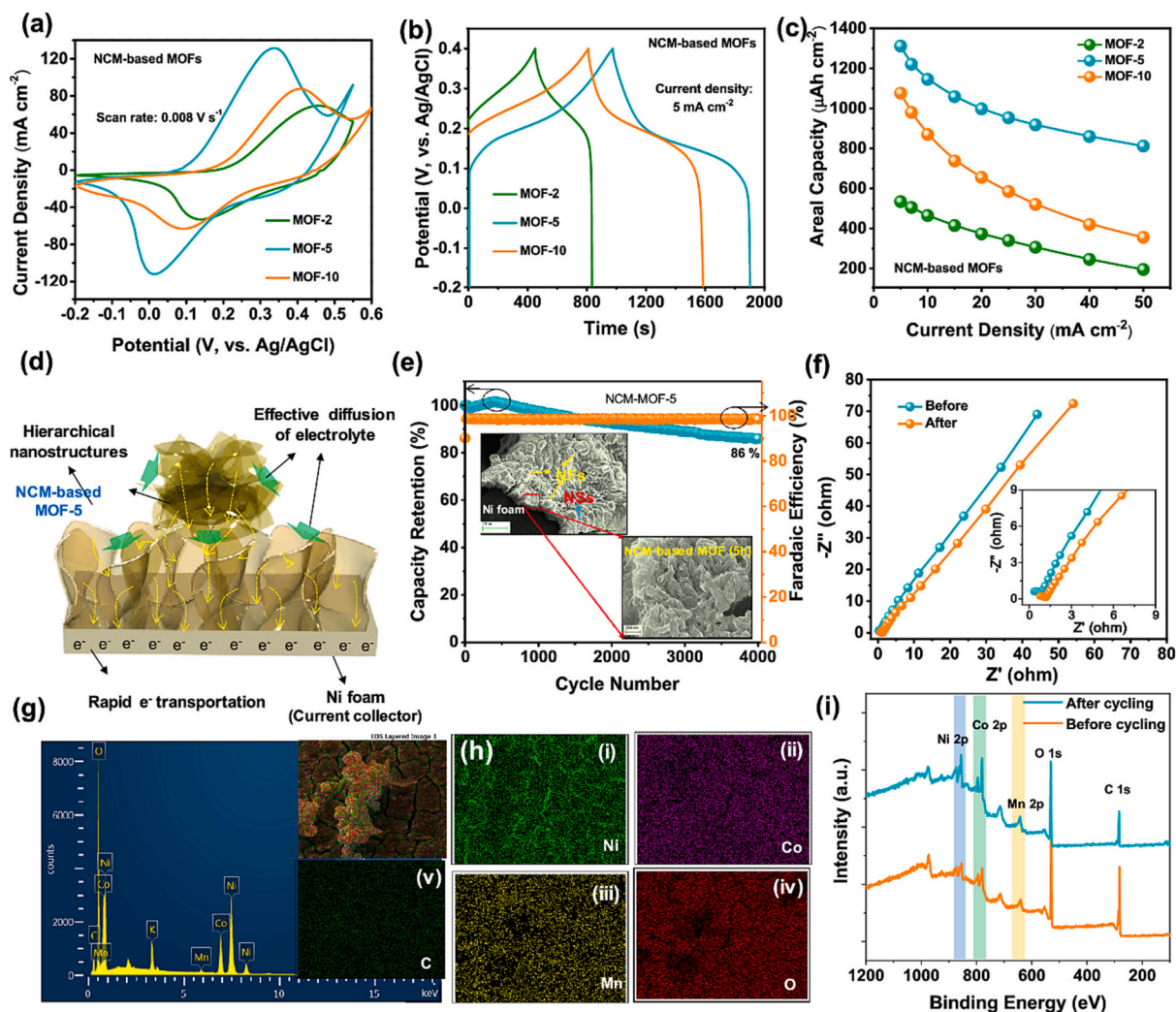


Fig. 5. Comparative a CV curves with scan rate kept at 0.008 V s^{-1} , b GCD curves measured 5 mA cm^{-2} , and c specific capacity values of the NCM-based MOFs. d Scheme showing advantages of the prepared electrodes e Cycling performance of electrodes over 4000 cycles and f EIS plots of the NCM-based MOF-5 electrode before and after cycling. The inset of e shows the FE-SEM images of NCM-based MOF-5 after the cycling test. g EDX spectrum, h elemental mapping images, and i XPS spectra of NCM-based MOF-5 after the cycling test [122].

MOFs materials [124]. TTF functions well as an electron donor because of its conjugated core, which is rich in sulfur. TTF has two readily accessible reversible oxidation states that are the radical cation (TTF^+) and the dication (TTF^{2+}). Therefore, ligand-containing TTF derivatives have been employed to produce redox-switchable MOFs in addition to redox-active frameworks. Tan et al. employed the bipyridinium ligand 1,1'-[1,4-phenylene-bis(methylene)]bis(4,4'-bipyridinium) dichloride to add Lewis acidic sites to a Zn-based MOF that was used to collect ammonia over water in addition to redox-active sites [125]. In a different work, [1,10-bis(4-carboxylatobenzyl)-4,40-bipyridinium] dichloride, a viologen-containing ligand, was combined with Co(II) to produce the redox-active Co-MOF-1.

One common characteristic of ligands in these kinds of systems is their ability to give fresh reactivity to nearby metal complexes by regulating the protons and electrons lost or gained. This allows the framework to take on various resonance configurations, which in turn produces new ligand characteristics. Redox-active ligands are included into MOFs to add redox activity to the system. Redox cycling can provide difficulties because the shift in redox state might break metal-ligand coordination interactions. For example, greater Coulombic repulsion between nearby redox-active entities may affect the structural properties, or a change in the oxidation state of a ligand or metal may affect the coordination geometry of the metal node [24].

4.3. Guest-host interaction

One of the most often used techniques to promote redox activity in MOFs is the addition of a redox-active guest to a framework (Fig. 6) [126]. For host-guest MOF systems to be constructed and their properties realized, controlled host-guest interactions are essential. [126,127]. With MOFs based systems, novel features like electron/energy transfer, redox reaction, or other processes because of host-guest synergy may arise, which can considerably induce emergent properties different from those of the individual hosts or guests. Additionally, the components and structures of host MOFs can be tuned to alter the mode and intensity of host-guest interactions, which could aid in the regulation and optimization of the system's characteristics and functions [26].

Allendorf et al. showed that TCNQ (7,7,8,8-tetracyanoquinodimethane) infiltration into a Cu-based MOF, HKUST-1 results in a significant increase in conductivity from 108 to 0.07 S cm^{-1} . According to the theory, charge conduits formed all throughout the structure because of TCNQ binding to Cu_2 paddlewheel nodes and partial charge transfer between the framework and the visitors. Additionally, the charge transport characteristics of MOFs could be directly modified by using guest inclusion [128].

Another example is the electrically conductive composite NiCB@NU-1000 that was created by encasing nickel(IV) bis(dicarbollide) (NiCB) in

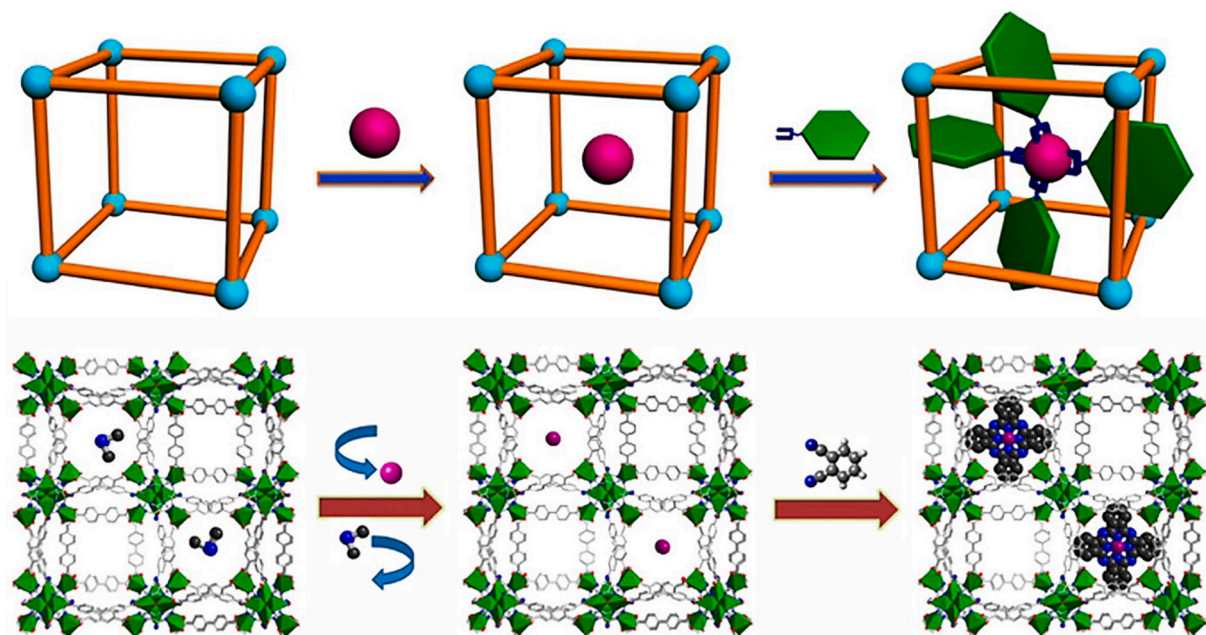


Fig. 6. Schematic representations showing a host-guest interaction in MPC@MOF [126].

mesoporous NU-1000, according to Kung et al. [129]. The composite had a conductivity of 2.7×10^{-7} S/cm because of D-A interaction between the pyrene motifs on the framework and NiCB. NiCB guests were only found in microporous channels, which allowed other guests to be incorporated into the mesoporous channels. SXRD confirmed that NU-1000 has two different types of channels (microporous triangular channels and mesoporous hexagonal channels). To create the composite Mn-AIM-NiCB@NU-1000, manganese oxide was further loaded into NiCB@NU-1000 using atomic layer deposition. The capacitance of the composite is greater than that of Mn-AIM-NU-1000 in 10 folds and can reach a maximum value of 276F/g MnO_2 . With this development, conductive MOFs can now be used in electrochemical applications

[129].

5. Charge transport mechanism in MOFs

In MOFs, the band transport or hopping transport mechanisms can be used to characterize the charge transport mechanism [130]. Redox hopping is the main charge transfer mechanism in MOFs. It involves the movement of counter-balancing ions together with the transportation of electrons because of self-exchange reactions between redox centers. The energy and spatial overlap between the orbitals govern charge transfer in MOFs [18]. In MOFs, there are two processes for charge transfer: through-bond charge transport and through-space charge transport

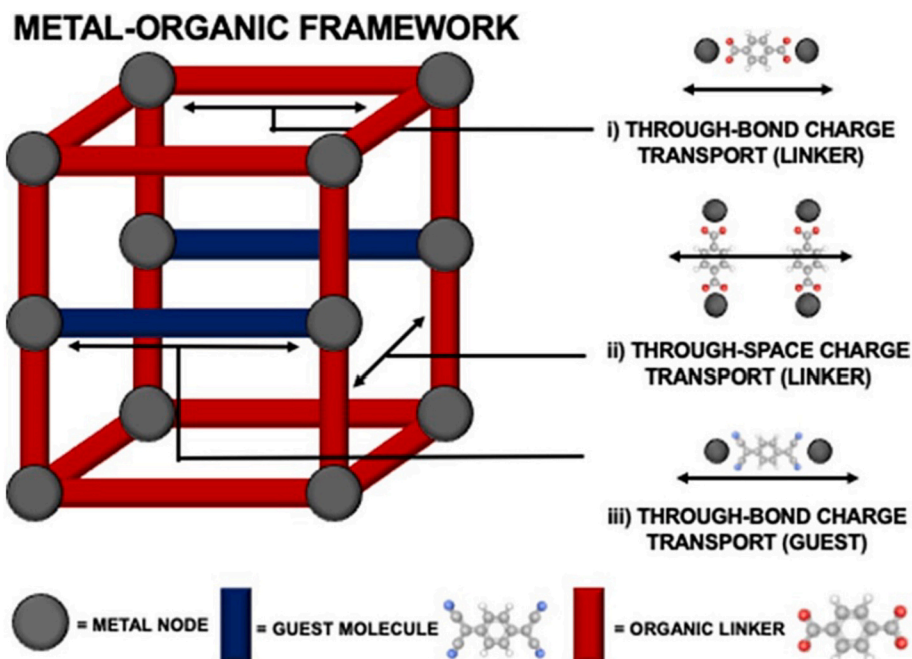


Fig. 7. The modes of charge transport in MOFs featuring (i) through-bond charge transport via the organic linker of the MOF, (ii) through-space charge transport via the organic linker of the MOF, and (iii) through-bond charge transport via an organic guest molecule [131].

[131]. The modes of transfer in MOFs is depicted in Fig. 7.

5.1. Through-bond pathway

Charge transport over continuous valence bands in conductive MOFs is essential for through-bond conduction, which is dependent on both the orbital symmetry and the energy level matching between the metal node and the organic ligand [131]. Only the influence of the linker on the node's orientation and binding atoms are taken into consideration in this situation; its capacity to delocalize charge is unimportant. Three-dimensional through-bond charge transport has also been recorded; however the most common examples only transfer charge in one dimension. Because charge must flow through the orbitals of the coordinating and metal atoms, this kind of conductivity is more likely to be promoted using softer binding atoms that are energetically similar to the metal node. It has been observed that MOFs made of bis(1*H*-1,2,3-triazolo[4,5-*b*,4',5'-*i*]dibenzo-1,4dioxin) (BTDD), 2,5-disulfhydrylbenzene-1,4-dicarboxylic acid (DSBDC), or (1,2,3-triazolate)₂ exhibit this kind of behavior. [132,133]. The most common MOFs based on benzene and triphenylene are those that exhibit this kind of charge transport [133].

5.2. Through-space pathway

In this case, conductivity is strongly correlated with the proximity of the sheets to one another since excessive spacing between sheets reduces charge transport efficiency and wave function overlap [134]. It is challenging to distinguish between through-plane and through-space paths in 2D systems because both rely on significant π conjugation. Both charge transfer types are frequently observed with varying degrees of involvement. Although the exact contribution of through-space charge transport can be challenging to ascertain, DFT calculations have indicated in recent publications that this process may be the primary transport channel in certain MOFs. Tetrathiafulvalene (TTF)-based MOFs, M₂(TTFTB) have revealed this process. Use Zn₂(TTFTB) as an illustration. The TTF motif generated robust one-dimensional helical columns that were strongly stacked, with an SS distance of only 3.7 between adjacent TTF molecules. In this instance, Zn₂(TTFTB) had a notable intrinsic mobility of 0.2 cm²/V. So, by adjusting the “ π ” stacking patterns, the electrical conductivity can be efficiently adjusted [134].

5.3. Redox hopping

The aforementioned techniques of charge transport are inhibited by

stronger ionic bonding in MOFs that lack a good energy overlap between organic linkers and metal nodes. In the MOF, electrons can hop through local minima states similarly to the through-space pathway, as opposed to charge being delocalized throughout. [135]. MOFs in electrochemical applications are well recognized to function by an electron hopping process between fixed sites, also known as redox-active linkers, where charge transport is understood to involve the diffusion of electrons through the material [18]. It should be noted that because the charge transport in these MOFs depends on the redox reaction of the repeating units within the framework, if the redox reaction is not reversible in some electrolytes, the redox hopping may not be stable during electrochemical operations; in this case, the charge transport may stop working even though the framework is still structurally sound. In certain instances, the MOF thin film's redox hopping is insufficiently efficient, which severely restricts the electrocatalytic process's total reaction rate and impairs the ensuing electrochemical performance. To harness the full potential of these materials, charge transport to the redox catalysts within the MOF has to be ensured [136].

In addition, Johnson et al. also reported the UiO/PIZOF topology (Zr (dcphOH-NDI)) by using redox-active dcphOH-NDI as a linker [130]. Hydroxyl groups were included on the dcphOH-NDI linker to facilitate transport of proton through the material (Fig. 8). Diffusion-limited charge transfer was found within the films, which is consistent with the electron-hopping paradigm shared by many MOF-based thin films. Lastly, it was discovered that the MOF thin films performed well in aqueous solutions, enhancing their potential utility in electrocatalytic applications [137].

5.4. Guest-promotion

One distinctive feature of the guest-promoted pathway is its potential applicability to all MOFs [128]. By artificially introducing guest species, which provide electrically conductive channels, MOFs' inherent porosity is exploited. The sizes of the guest species that have been published vary greatly, and the MOF conductivity is increased by iodine/polyiodides, organic/organometallic species, and conductive polymers. Although this approach is quite versatile, it is evident that adding guest species will result in a trade-off where porosity and accessible surface area are reduced [125]. MOFs with pores too tiny to successfully integrate guest molecules also present problems. There is no one optimal way to increase MOF conductivity because there are so many different MOF architectures and charge transport techniques available. Nonetheless, several factors, including the chelating moiety's chemical characteristics and the function of counterion transport,

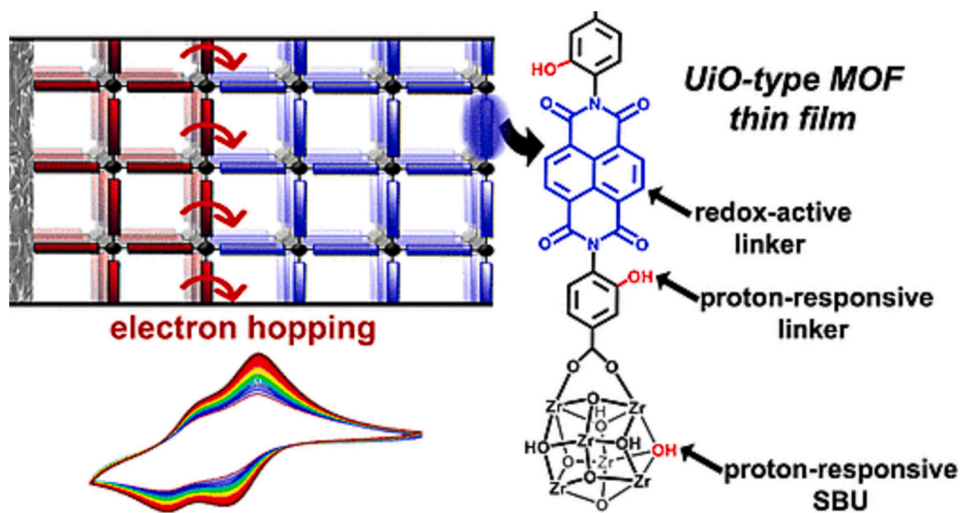


Fig. 8. Development of UiO-type thin film electrocatalysts with redox-active linker via redox hopping [137].

provide broadly applicable foundations for fundamental research. Conversely, because of the degradation of the functionalized MOF framework in aqueous conditions, voltametric responses for ferrocene oxidation declined quickly. With so many possible MOF topologies, and so many possibilities for linker design and metal ion selection, it could seem unnecessary to add guest molecules as an extra element of synthetic design. Nonetheless, the examples demonstrate that this is a fruitful new field in MOF chemistry that is giving rise to unexpected emergent properties.

6. Redox-active MOFs for supercapacitors

Since most MOFs lack electrical conductivity, their use in electrochemical applications, and the fabrication of electronic devices lags significantly behind those of the applications [138]. Although it is a difficult process to “activate” the electrical conductivity of MOFs, several methods have been suggested to do so: One method is the creation of “ π ” stacking moieties derived from charge transport pathways in three-dimensional (3D) MOFs; another is the construction of 2D MOFs with effective interlayer charge transport characteristics, a third is the introduction of conductive oligomeric strains into the one-dimensional (1D) channels of 3D MOFs [117]. The last involves creating long-range donor-acceptor charge transport by adding guest molecules to the framework, using functionalized linkers in the framework for improved charge delocalization.

The redox-active MOFs have redox-active metal ions, which can undergo reversible redox reactions. The reversible redox reactions of the metal ions allow for the storage and release of charge, making them ideal materials for storage applications [139,140]. Both EDLCs and pseudocapacitors based on conductive MOFs have so far been shown to perform exceptionally well. Conductive MOFs are an excellent substrate for studying the charge/discharge mechanism in supercapacitors because of their controllable pore characteristics, specified crystallinity, and concentrated pore size sharing. The pristine configuration of MOFs is predominantly of metal ions such as copper, iron, zinc, nickel, etc.,

and organic ligands such as BTC, PTA, DHTA, etc. In many energy storage devices, including batteries, supercapacitors, and hybrid supercapacitors, MOFs have been wholly applied as electrode materials [141]. Redox-active MOFs have been used as electrode materials in supercapacitors and demonstrated high specific capacitance and excellent cycling stability. One of the most commonly used redox-active MOFs is Cu(BTC) (BTC = benzene-1,3,5-tricarboxylate), which has copper centers that can undergo reversible redox reactions with high capacities [142,143].

With a high conductivity of 1.0 S m^{-1} , Cu-DBC, a novel conjugated Cu-catecholate based conductive MOF that combined the advancement of EDLCs and pseudocapacitors, was reported by Liu et al. (Fig. 9(a) and (b)). The EDLC accounted for 62 % of the total, while the remaining 38 % came from pseudocapacitance, as illustrated in Fig. 9(c) and (d) [144]. The Cu-DBC electrodes exhibit a remarkable cycling performance and an extremely high gravimetric capacitance of 479 F/g at 0.2 A/g (Fig. 9e). Their research showed that the conductive MOFs' abundance of redox-active centers, electrical conductivity, and large specific surface area can open up new possibilities for the practical realization of the application in energy storage devices.

In the same vein, Wang et al. (2022) reported a redox-active MOF of nickel manganese sulfide (Ni/Mn-S) nanoparticles obtained from Ni/Mn-MOF-74 for electrode fabrication of supercapacitors. The NiMn-S electrode exhibits a high specific capacitance of 2510.15 Fg^{-1} at 1 Ag^{-1} and excellent cyclic stability performance of 84.5 % retention after 5000 cycles [145]. According to a study conducted by Wu et al. in 2023, a bimetallic CoFe-MOF-74 grown on nickel foam was synthesized and used as an electrode material for supercapacitors. The converted bamboo-shoot-like $\alpha\text{-Co(OH)}_2/\text{CoFe}_2\text{O}_4$ nanorods obtained showed improved electrochemical properties with high area capacitance $3941.14 \text{ mFcm}^{-2}$ at 2 mAcm^{-2} . The supercapacitor electrodes also displayed excellent cycling stability, good rate capability, and low resistance. The study concluded that the redox-active MOF is a promising electrode material for high-performance supercapacitors [146].

Iqbal et al., 2023, investigated the application of hybrid

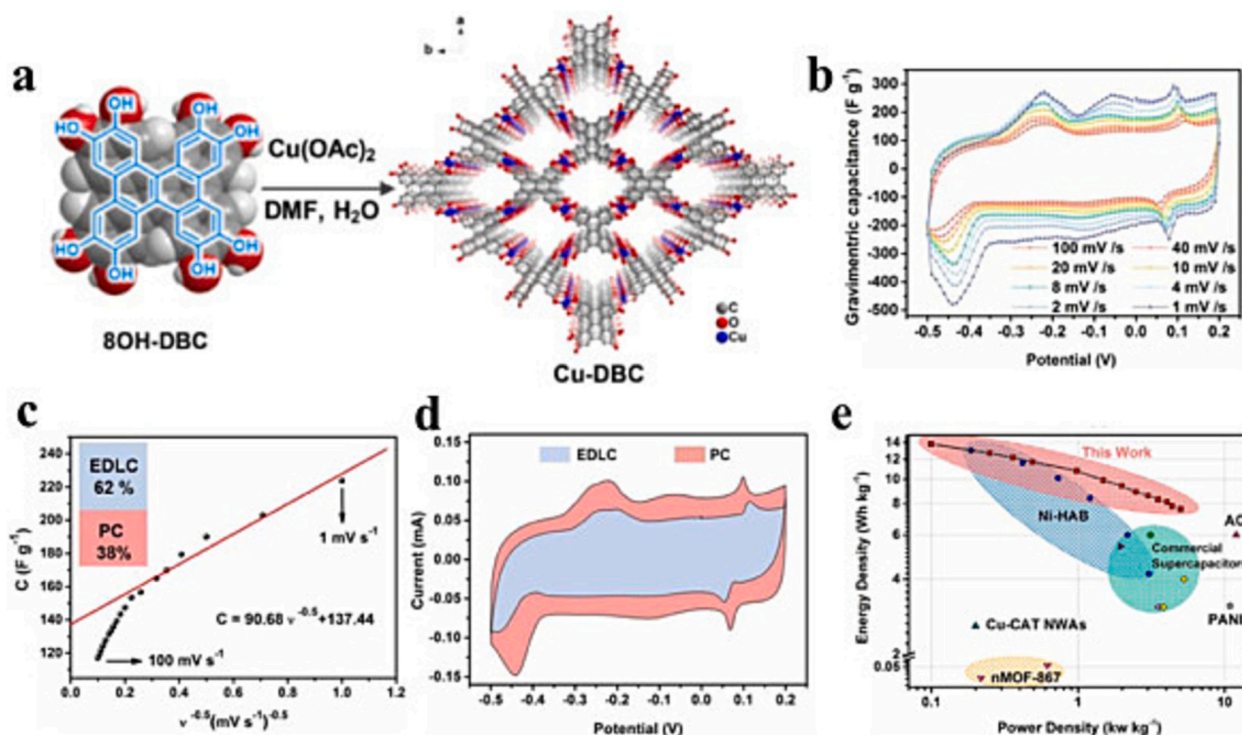


Fig. 9. Preparation of Cu-DBC and its crystal structure. (b) CV curves of Cu-DBC at different scan rates. (c) Plot of specific capacitance versus reciprocal of square root of scan rate. (d) Capacitive contribution of Cu-DBC at 10 mV s^{-1} . (e) Comparison of energy and power density with other materials in the literature [144].

supercapacitor devices using MOF-199 composites as redox-active materials. The MOF-199 composites were synthesized with graphene and polyaniline to enhance the electrochemical properties of copper-based MOFs in energy storage applications. The improved specific capacity recorded for copper-based MOF was 88 Cg^{-1} and the specific capacity of MOF-199 composites with graphene and polyaniline were enhanced to 475 Cg^{-1} and 766 Cg^{-1} , respectively, in three-electrode systems. The maximum energy and power densities of 64 Whkg^{-1} and 7200 Wkg^{-1} were, respectively, revealed from the fabricated hybrid supercapacitor of MOF-199//PANI/AC structure, with 92 % capacity retention after 1000 cycles [141].

In the same vein, the porosity of redox-active MOFs architectures is highly appropriate for accommodating electrolyte ions in electrochemical processes, suggesting their potential electrode materials for high-performance batteries. The redox-active sites in the MOFs structures were incorporated into metal junctions, ligands, and both for the novel electrochemical process of batteries [147]. MOFs have rarely been examined in another rapidly emerging sector, electrical energy-storage materials or battery electrode materials because prior studies revealed that most MOFs are insulators. Because it allows for a faster ionic diffusion rate in these solid-state electrode materials, the main characteristic of MOFs, porosity, is appealing for battery electrode materials despite their low electrical conductivity [148].

Due to the obvious exceptional ability of MOFs to accommodate different metal ions through their nanoscale pores, MOFs have a lot of potential as competitive anode materials. MOFs have low lithiation potentials that are typically $<0.5 \text{ V}$ (Referenced using $\text{V-Li}^+/\text{Li}$), which makes them suitable as anode materials. This is due to the chemical and structural stability of MOFs [147]. Among the two approaches (conversion and ion-intercalation schemes) employed in the Li-ion storage processes, the ion-intercalation scheme has been adopted for all MOF-based anode materials in which the MOFs were embedded with the alkali metal ions. This is due to the decomposition of anode materials and reduction reactions associated with the storage of Li or Na ions in the conversion scheme [147]. The benefit of the intercalated MOFs (iMOF) is a very tiny volume increase of 0.33 % under the lithiated state, which inhibits lithiation-induced disintegration of MOF and results in 96 % capacity retention after 100 cycles. The lithiation locations were typically between the two oxygen atoms of the carboxylate groups and the nitrogen atoms on the ligands, respectively, for carboxylate-linked MOFs and imidazole-linked MOFs [149–152]. The cations were reduced to an extraordinary M(I) oxidation state in the case of Prussian blue analogs (PBAs), and the super-reduced scaffolds were stabilized by the strong coordination bond linkage of cyanide groups [153]. Although the iMOFs demonstrated outstanding cycle stability and rate performance, it is important to highlight that the advantage of iMOFs is the relatively minimal volume expansion following lithiation, which may not be relevant for larger mobile metal ions.

Furthermore, structurally robust MOFs are undoubtedly advantageous for improving cyclic behavior [147]. The MOFs possess redox-active metal nodes, organic linkers, and both metal nodes and organic linkers will be discussed in the following subsections.

6.1. MOFs possessing redox-active metal nodes

Redox-active metal nodes in MOFs refer to metal ions that can undergo reversible oxidation and reduction reactions, leading to changes in their oxidation state. These metal nodes can act as redox-active centers, catalyzing various chemical reactions. The ability of these MOFs to undergo reversible redox reactions has significant implications for applications in energy storage, energy conversion as well as in other areas such as sensing and catalysis [142,154,155]. The redox properties of these metal nodes are attributed to their electronic structure and coordination environments. Recently, there has been a growing interest in MOFs possessing redox-active metal nodes, which have shown promise for energy storage and conversion applications [154]. The most used

redox-active metal nodes in MOFs are transition metals such as manganese, iron, nickel, copper, cerium, titanium, cobalt, chromium, and vanadium, which have d-orbitals that can participate in electron transfer reactions. These metals are often coordinated by nitrogen-containing ligands, such as pyridine, imidazole, and triazole, which can act as electron donors or acceptors [142]. Due to the typical oxidation states +2, +3, +4, +6, and +7 found in manganese that cut across all the oxidation states -3 and +7, $\text{Mn(II)} [3d^5]$ is the most common oxidation state in the recently reported Mn-based MOFs [156]. The synthesis of a layered Mn(II)-based MOF and its evaluation as a supercapacitive electrode material was first reported in 2017 by Wang et al. [157]. A simple solution approach was employed to prepare the layered Mn-based MOF [$\text{Mn(2,3,5,6-tetrafluoroterephthalic acid, 4,4'-bpy} = 4,4'\text{-bipyridine)}$] and their electrochemical performance showed specific capacitance of 1098 Fg^{-1} and 1178 Fg^{-1} in two different electrolyte media of 1 M KOH and LiOH, respectively, at 1 Ag^{-1} current density. Excellent cycling capacity and improved rate capability were observed with 92.6 % and 94.6 % capacity retention in 1 M KOH and 1 M LiOH after 2000 cycles, respectively.

In 2020, Shinde et al. also employed a simple hydrothermal technique to prepare layered Mn-based MOFs for direct use in supercapacitor electrodes. An excellent performance evaluation was recorded with high specific capacitance and improved power and energy performance with cyclic stability for its hybrid supercapacitors. The hybrid supercapacitor fabricated exhibits a specific capacitance of 211.3 Fg^{-1} with energy and power densities of 66 Whkg^{-1} and 441 Wkg^{-1} , respectively, and 81.8 % retention capacitance over 10,000 cycles [158]. Synthesis of MOF-derived MnO/C nanocomposite using Mn-based analog of MIL-100 frameworks has been reported for high-performance supercapacitor devices. The nanocomposite electrode exhibits specific capacitance of 421 Fg^{-1} at 0.5 Ag^{-1} current density with 94 % cyclic stability after 5000 cycles. They inferred that the MnO nanoparticle in nanocomposite displayed nanocage structure properties with analogous super-tetrahedron units that might be obtained from the precursor of Mn-MIL-100 frameworks [159].

Ashourdan et al. successfully prepared a nanocomposite of glucose, high-quality graphene, and nickel cobalt manganese MOFs (G-HQG@NiCoMn-MOF) as a novel electrode material for efficient supercapacitor applications. The G-HQG@NiCoMn-MOF electrode displayed an excellent performance as an appropriate working electrode material with a specific capacity of 1263.6 Cg^{-1} at 1 Ag^{-1} and a capacity retention of 89.2 % after 5000 cycles at 7 Ag^{-1} , in supercapacitors. Its asymmetric supercapacitor ($\text{G-HQG@NiCoMn-MOF//AC}$) also has an improved 69.9 Whkg^{-1} specific energy at a specific power of 1217.9 Wkg^{-1} , with an efficient rate capability by retaining 74.1 % of its initial capacitance at 10 Ag^{-1} and excellent cycle life by retaining 85.2 % of its initial capacitance at 7 Ag^{-1} after 5000 cycles [160]. A facile hydrothermal approach was employed by Seo et al. to synthesize a bimetallic Co/Mn-based MOF for supercapacitor application. A high specific capacity of 1176.59 Fg^{-1} was shown by the as-prepared bimetallic Co/Mn-MOF electrode at 3 mAcm^{-2} current density with excellent cyclic stability at 5000 cycles. The fabricated hybrid supercapacitor Co/Mn-MOF//AC displayed specific energy and power densities of 57.2 Whkg^{-1} and 2000 Wkg^{-1} with 93.5 % capacity retention over 5000 cycles [161]. Nickel is another transition metal that has been extensively reported to promote the redox activity in MOFs, especially in energy storage device applications. This can be attributed to the recurrent oxidation state of Ni (+2) as well as the occurrence of various oxidation states presented in other compounds such as Ni^0 , Ni^+ , and Ni^{3+} [162].

In 2019, Wang et al. reported a cobalt-doped Ni-MOF synthesized through a simple hydrothermal process with flower-like hierarchical microspheres. Its electrochemical behavior exhibited a specific capacity of 1300 Fg^{-1} at 1 Ag^{-1} with a great performance rate of 1021 Fg^{-1} at 10 Ag^{-1} current density. A high retention capability of 71 % of the initial capacitance was recorded for $\text{Co}_2\text{-Ni-MOF}$ after 3000 cycles. Excellent power density of 375 Wkg^{-1} and energy density of 25.92 Whkg^{-1} was

obtained for Co₂-Ni-MOF-based hybrid supercapacitors. The remarkable electrochemical performance of the electrode was attributed to the incorporation of Cobalt in Co₂-Ni-MOF electrode materials [163]. In the same vein, Otun et al., 2022, successfully prepared double-linker MOF-derived NiO and NiO/Ni composite electrodes involving various calcination processes (400 °C, 500 °C, and 600 °C) for energy storage applications. The highest supercapacitive performance was recorded for the NiO/Ni electrode composites obtained at 400 °C, with a specific capacitance of 104.6 mAg⁻¹ at 1 Ag⁻¹ current density and a capacity retention of 90 % after 1000 cycles in 3 M KOH electrolyte. They concluded that the calcination processes influence the morphology and electrochemical properties of the electrodes with pseudocapacitive behavior from electrochemical kinetic analysis [164]. Binder free Zn-functionalized Ni-MOF was grown on Nickel foam and employed as an efficient electrode material for electrochemical applications. The electrode's supercapacitive performance was tested in 3 M KOH electrolyte solution and displayed an excellent specific capacitance of 391 Fg⁻¹ at 1 Ag⁻¹ and preserved 70 % of its original capacitance at 10 Ag⁻¹ current density. With a high cyclic stability of 85 % after 5000 cycles, the electrode also exhibited maximum specific energy and power densities of 12 Wh/ kg and 2000 Wkg⁻¹ respectively [165].

6.2. MOFs possessing redox-active organic linkers

A new class of MOFs that incorporates redox-active organic linkers has recently emerged with additional functionality to the material. Redox-active organic linkers contain redox-active groups such as nitro, amino, or thiol, which can undergo reversible redox reactions [166]. The incorporation of such linkers into MOFs can provide an additional level of functionality to the material, leading to improved properties and potential applications. Redox-active MOFs have shown unique properties such as redox activity, charge storage, and electrocatalytic activity, making them promising materials for various applications [167]. A wide variety of opportunities to encourage redox activity in such materials are made possible by the flexible nature of organic linkers that can be exploited in the development of multidimensional metal-organic frameworks. Historically, the incorporation of electroactive organic moieties during framework synthesis has promoted the synthesis of redox-active MOFs with active ligands [168]. The introduction of redox-active ligands, however, provides new possibilities for the growth of multifunctional frameworks through emerging post-synthetic techniques. Moreover, studies have shown that redox-inactive linkers may ultimately increase redox activity in a 2D Ni-based hybrid framework, where electron delocalization is critical for retrieving key intermediates that become physically prohibitive for similar molecular systems [169].

One of the most significant advantages of redox-active MOFs is their ability to store and release electrons, making them potential candidates for energy storage applications. For instance, the incorporation of redox-active organic linkers into MOFs has been shown to improve their electrochemical properties, such as capacitance, power density, and cycle stability. These properties make redox-active MOFs attractive materials for applications in supercapacitors and batteries [167,170]. In this section, we describe the recent advancement of MOFs possessing redox-active organic linkers for their successful applications in energy storage and conversion devices. Among the organic linkers that have been employed for the growth of MOFs involving redox-active organic linkers are Naphthalenediimide (NDI), Triphenylamine (TPA), Quinoid–aromatic transition, and Tetrathiafulvalene (TTF). The various structural topologies, porosities, and functionalities of Naphthalenediimide-based MOFs have endowed them with multifunctional applications such as catalysts, photochromism, gas storage and separation, sensors, energy storage and conversion, and electrochromism [171]. The redox-active NDI-MOFs have been proven to be potential electrodes for improved performances of supercapacitors and lithium-ion battery devices. Due to their high surface area and redox-active NDI cores, NDI-MOFs have been utilized as promising electrode

materials in the field of energy storage and conversion [172–175]. A 3D Zr-based MOF containing redox-active NDI ligand (Zr-NDI-scu-MOF) was reported by Mallick et al. and subsequently used as supercapacitor electrodes. To develop a rigid Zr-NDI-BPy-scu-MOF, the pristine Zr-NDI MOF was functionalized by 2,2-bipyridine-5,5-dicarboxylic acid through a post-synthetic approach. The electrochemical performances of the two Zr-MOF electrodes showed pseudo-capacitance behavior with improved capacitance, rate performance and excellent cycling performances in a three-electrode system. Also, the Zr-NDI-BPy-scu-MOF modified electrode displayed EDLC properties with excellent cycling and structural stability in a two-electrode system. They concluded that the high-performance electrodes can be attributed to the large surface area and redox-active linkers and that a new approach for the preparation of MOFs can be used in energy storage applications [173].

A series of MOFs were designed and synthesized, as described by Mallick et al. by integrating a redox core into the organic linker [25]. The combination of porosity and redox core inclusion, which modify its double-layer and pseudocapacitance, respectively, reveals an improved performance. It was also demonstrated that the capacitive performance can be enhanced by employing organic pillars for post-synthesis structural rigidification. There are no appreciable differences in the PXRD or crystal morphology between the XRD and SEM characterizations conducted before and after the 10,000 cycles of the charge/discharge operation. Notably, in an aqueous medium with a voltage window of 0.0–1.0 V, an areal capacitance of 5.48 mF cm⁻² was obtained, which is higher than most of the reported values produced in far more expensive organic electrolytes for MOF materials. The typical CVs recorded at various scan rates are displayed of the symmetrical device in Fig. 10a. Even at high scan rates, the quasi-rectangular mirror-symmetric shape of the CVs indicates the device's highly reversible charge/discharge response. Fig. 10b displays the triangular symmetric GCD curves, which demonstrate a high coulombic efficiency. Based on the CV curves, the cell capacitance was computed, and at 10 mV/ s, the device can deliver 5.7 F g⁻¹.

Now, the triphenylamine-type polycarboxylic ligands are garnering a lot of attention as a representative organic linker, because they may be utilized to develop MOFs with large porosities that function exceptionally well for gas storage and separation, optical-electrical fields, and energy storage applications [176,177]. For instance, Xia et al. reported the synthesis and characterization of 3D triphenylamine-based bifunctional Tb^{III}-MOF and successfully applied it in luminescence sensing and supercapacitor applications. They observed that Tb^{III}-MOF displays bright green luminescence with ⁵D₄ lifetime of 864.09 μs and could be employed as an excellent fluorescent sensor for Fe³⁺ ultrasensitive detection. Furthermore, electrochemical studies demonstrated that the Tb^{III}-MOF has impressive long-term cycling stability and reversibility, with a high specific capacitance of 346 Fg⁻¹ at 1 Ag⁻¹ current density and an outstanding capacitance retention of 93 % after 2000 cycles [178]. Coordination polymers with porous properties, such as large specific surface area, excellent stability, and organic functionality, have long been referred to as metal-organic frameworks (MOFs), which are produced by organic linkers and metal ions. These features have resulted in their widespread application in electrochemical devices [179–181]. In 2021, Bao and co-workers investigated the electrochemical performance of rGO, Zn-MOF, and PANI composites as supercapacitors electrodes to study and identify the influence of PANI and Zn-MOF of the electrode materials. The obtained specific capacitance at a current density of 0.1 Ag⁻¹ was recorded to be around 372 Fg⁻¹ and the retention of >80 % was observed after 5000 cycles. These performances were attributed to the varied composites fabrication of electrode materials [182]. Tetrathiafulvalene (TTF) and its derivatives in MOFs, on the other hand, are redox active SBUs that have been investigated because of their unique physical characteristics and wide range of applications, including electrochemical sensors, magnetic materials, energy storage devices, and microporous conductors [183]. In 2019, Su et al. reported a high electrical conductivity 2D MOF with intrinsic supersonic

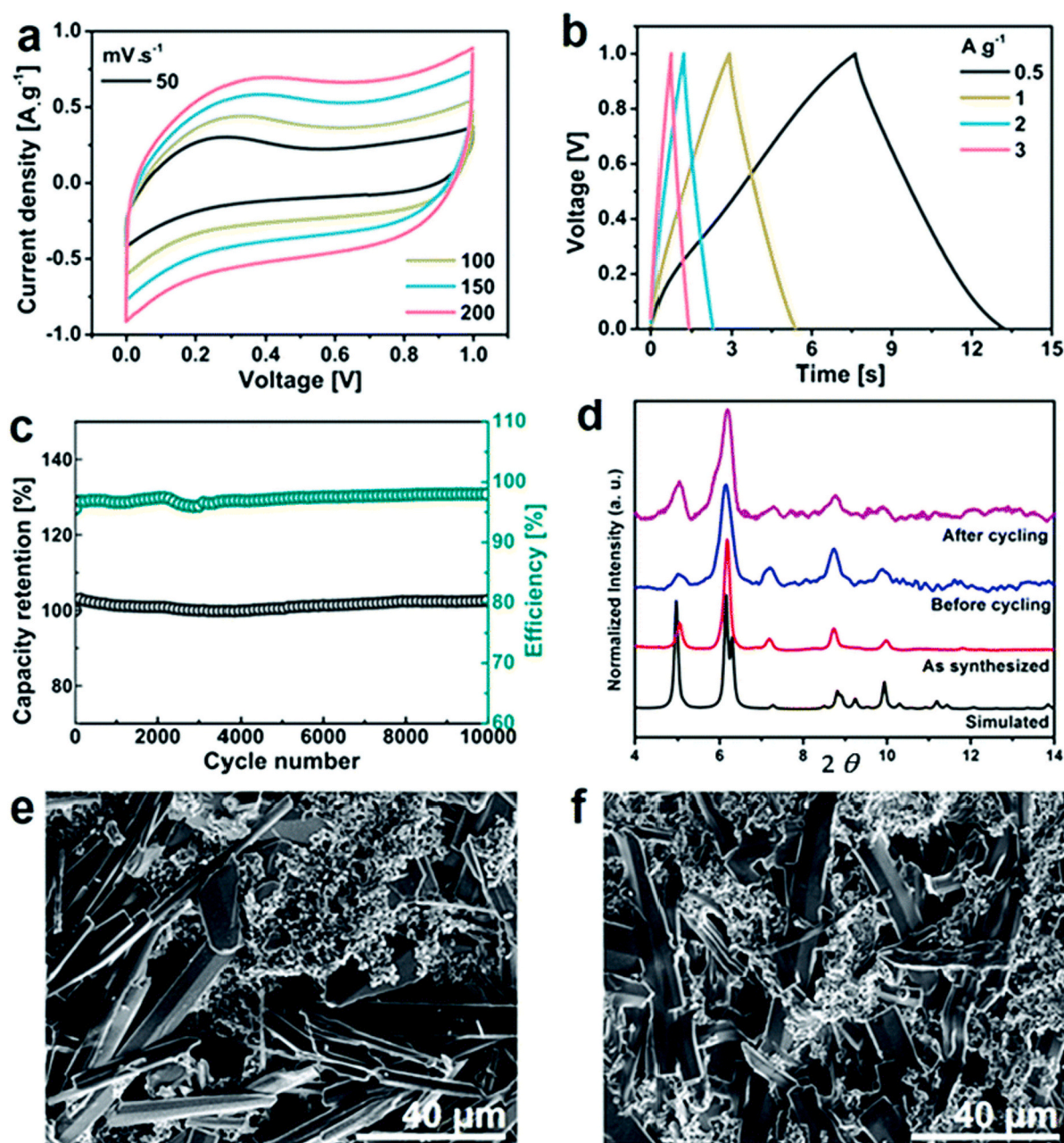


Fig. 10. (a) CV curves of Zr-NDI-BPy-sco-MOF device. (b) GCD curve of Zr-NDI-BPy-sco-MOF. (c) Cyclic performance for Zr-NDI-sco-MOF (black) and Zr-NDI-BPy-sco-MOF (blue). (d) PXRD pattern before and after stability for Zr-NDI-BPy-sco-MOF. SEM images for the Zr-NDI-BPy-sco-MOF electrode before (e) and after (f) stability tests [25]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

conduction and interfacial pseudo-capacitance properties. They combined $[\text{In}(\text{COO})_4]^-$ metal nodes and tetratopic tetrathiafulvalene-based linkers to fabricate two 2D MOFs with ultrahigh proton conductivity. They observed that the redox-switchable nature of TTF-based ligands allows for electrical conduction at the MOF-metal contact. A new approach for harnessing the ionic conductivity of MOFs to build functioning electronic devices is provided by the novel charge-transport mechanism referred to as protonic/pseudo-capacitance coupling [184].

6.3. MOFs with both redox-active metals and organic linkers

MOFs with both redox-active metal nodes and organic linkers have been extensively studied in recent years [185–187]. MOFs possessing redox-active metal nodes and linkers have been used largely because of their exceptional properties, such as high electrical conductivity, charge

storage capacity, and tunable redox-active properties [188–190].

Incorporation of redox-active metal nodes or organic linkers can introduce special features such as conductivity, electrocatalyst, and electrochromic behavior in MOFs. These frameworks have shown great potential in various applications such as energy storage devices, photocatalysis, gas storage, separation, electrochemical sensing, electrocatalysis, and photocatalysis [185,186,190]. However, the insulating nature of organic linkers and the instability of the framework to the redox process have hindered the study of electroactive MOFs until the last decade and there is a surge of interest in understanding their mechanism of charge transfer [186]. Recent studies have explored the design of MOFs with redox-active metal centers, such as rare-earth lanthanide ions, cobalt, nickel, copper, and electron-rich linkers. The greater oxidation state of the redox-active metal centers is stabilized by the electron-rich linkers, thereby increasing their electrocatalytic

activity. [189,191]. Designing MOFs with multiple redox-active units has been extensively explored to trigger their potential high specific capacities. However, these frameworks are fragile during long-term cycling owing to the weak metal-ligand coordination bonds and exhibit poor electrochemical stability. Therefore, developing MOFs that integrate both multiple redox centers and robust frameworks is an ideal design philosophy to achieve high-performance electrode materials [185,192]. Due to the formation of the coordination structure, which affects the redox potentials and transitions between the valency states of metal ions, the linking organic ligands have significant effects on the electrochemical features [193]. For example, Weng et al. (2022) synthesized a redox-active MOF containing copper nodes and tetrathiafulvalene-functionalized organic linkers, tetrathiafulvalene-Co-MOFs (TTF-Co-MOFs), and examined them for a high pseudo-capacitive negative lithium-ion capacitor.

Similarly, Iqbal et al. successfully reported the synthesis of a redox-active MOF involving copper nodes with bi-linkers of pyromellitic acid and 2-methylimidazole and its utilization for advanced hybrid supercapacitor that showed high capacity and cyclic stability in battery-supercapacitor applications. The bi-linkers Cu-MOF displayed high specific energy and power densities of 52 Wh/kg and 4000 Wkg⁻¹ respectively. The cyclic stability of hybrid-supercapacitor device was also conducted and approximately 93 % capacity was retained after 300 cycles [194]. In 2023, Iqbal et al. also reported another bi-linker redox-active MOF containing a cobalt node and two organic ligands of pyridine-3,5-dicarboxylic acid and 1,2,4,5-benzene-tetra-carboxylic acid was prepared and specifically applied for the construction of hybrid supercapacitor applications. A three-electrode configuration was used to investigate the electrochemical behavior of the bi-linker Co-MOF (B-H-MOF), and a single device hybrid supercapacitor was fabricated

with the Co-B-H-MOF//AC configuration. The device showcases excellent high specific energy and power densities of 42.5 Wh/kg and 4250 W/kg with stability capacity retention of 93 % after 3000 cycles. The authors employed Dunn's model to theoretically extract the regression parameters and capacitive-diffusion contribution of the battery-supercapacitor. They concluded that Co-B-H-MOF could be a potential material for futuristic energy storage applications [115,116]. The collaborative influence of metal node engineering with different organic mixed-linkers in the synthesis of redox-active Cu-MOF was reported for energy storage applications by Rozveh et al. They evaluated the effect of mixed metal and mixed-linkers on the electrochemical properties of Cu-MOF, and the best performing electrode was reported to provide maximum specific energy and power densities of 3.39 Whkg⁻¹ and 750.0 Wkg⁻¹ with capacitance retention of 86 % after 10,000 cycles [195].

Kannangara et al. synthesized three redox-active multilayered supercapacitor electrodes (Zn-pPDA MOF-5, Zn-pPDA MOF-8, and Zn-pPDA MOF-12) utilizing the modified liquid-liquid interfacial reaction, and for the first time employed MOF materials in energy storage devices [196]. Zn-pPDA MOF-5, Zn-pPDA MOF-8, and Zn-pPDA MOF-12 are 2D nanosheets, as seen by the SEM pictures. Fig. 11a and b depict the layered morphology of Zn-pPDA MOF-5, where the 2D structure is most prominently seen, demonstrating that multi-layered structures may be successfully synthesized via the liquid-liquid interfacial interaction. Compared to the other two Zn-pPDA MOFs, Zn-pPDA MOF-5's multi-layered structure, which offers a greater surface area, leads to improved electrochemical performance.

MOF supercapacitors have superior energy and power densities of 62.8 Wh/kg and 4500 W/kg, respectively (Fig. 12). Furthermore, after 2000 cycles, there is high cyclability with 96 % capacitive retention. We

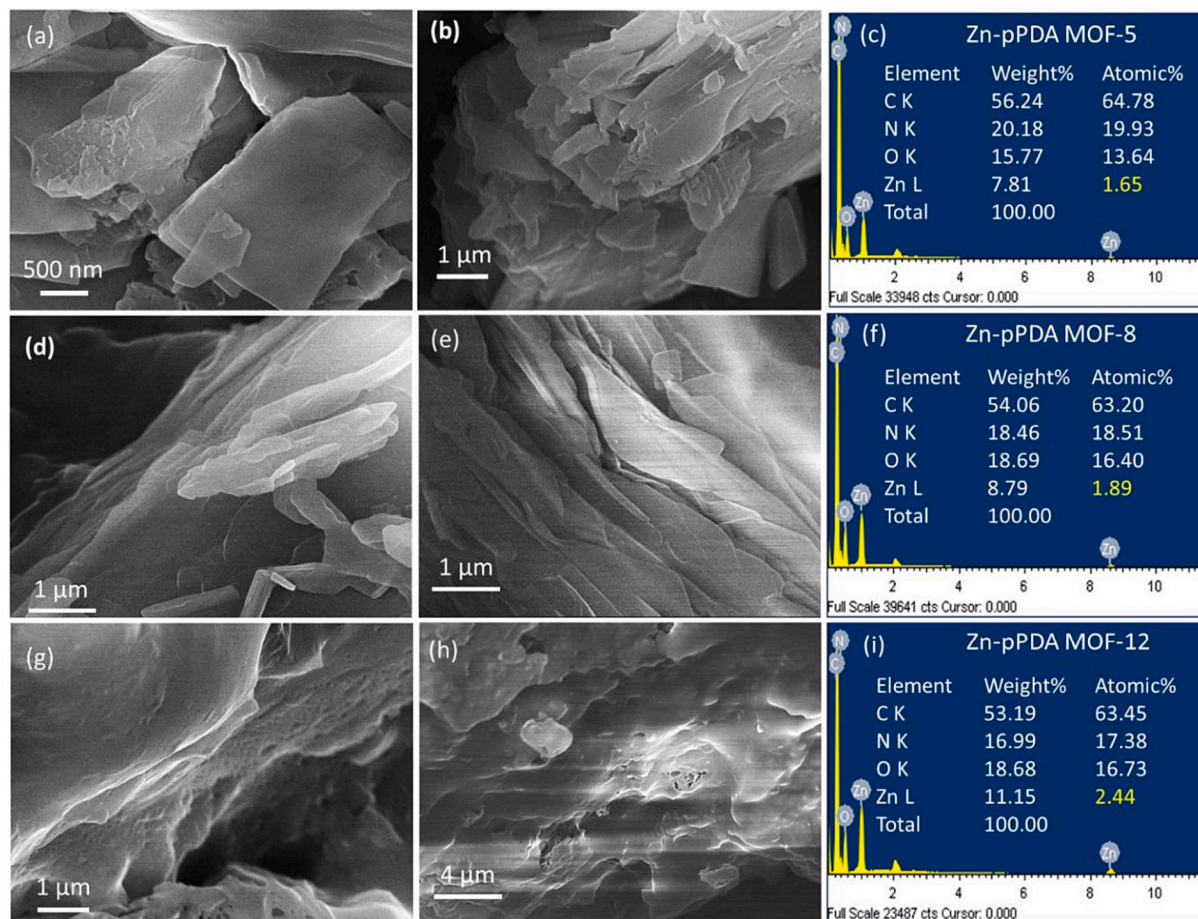


Fig. 11. SEM images of (a,b) Zn-pPDA MOF-5, (d,e) Zn-pPDA MOF-8, and (g,h) Zn-pPDA MOF-12, and (c,f,i) the corresponding EDS spectra [196].

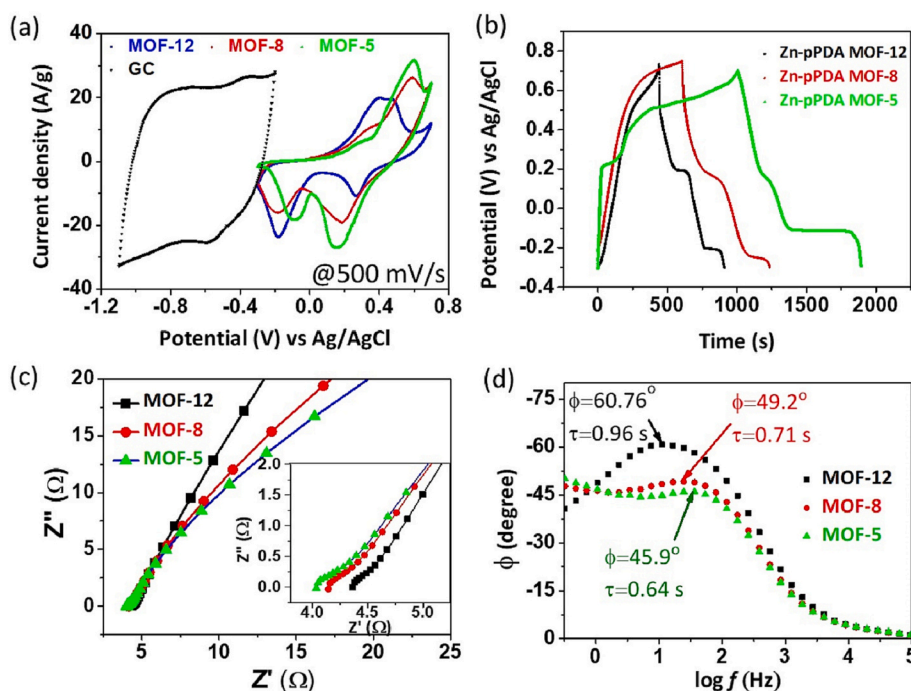


Fig. 12. Electrochemical performance of single Zn-pPDA MOF-5, Zn-pPDA MOF-8, and Zn-pPDA MOF-12 electrodes. (a) CV curves of the positive and negative electrodes at 500 mV/s (b) GCD curves, (c) Nyquist plot, with magnified high-frequency region in the inset, and (d) Bode plots obtained between 0.01 Hz– 10^5 Hz. ('MOF-#'s in legends represent 'Zn-pPDA MOF-#'s.) [196].

demonstrate that the synthesis approach can pave the way for the development of pPDA-ligand-based MOFs, and that the Zn-pPDA MOF is a potential material for future energy storage devices [196].

Mixed-metal based MOFs have garnered significant attention in an effort to enhance the electrochemical energy storage performance of supercapacitors when compared to single-metal solo MOFs [197]. These hybrid metallic species provide enhanced conductivity and several oxidation states. They also quicken the transfer of charges from organic ligand to metals, increasing the efficiency of energy storage. In contrast to solitary MOFs, which have poorer redox chemistry and fewer active sites, mixed metals-based MOFs with different dimensional micro-nano structural morphologies have been produced using a variety of synthetic growth techniques and have shown enhanced energy storage capabilities and cycle stability [198]. Mixed-metal MOFs were used in a study by Jiao et al. to produce supercapattery applications. As previously mentioned, MOFs' special qualities offer a clear benefit when it comes to their use as cutting-edge materials in the field of energy storage.

According to Kazemi et al., a cobalt-and manganese-built mixed metal–organic framework (MOF) was fabricated using a straightforward solvothermal process and used as the supercapacitor's electrode material [199]. A Co–Mn MOF electrode stood out for having a sizable surface area and great cycling stability—after 1500 cycles, the capacitance retention was still above 95 %. Additionally, the Co–Mn MOF electrode in the basic electrolyte showed improved pseudocapacitive behavior, with an extraordinary areal capacitance of 1.318 F cm^{-2} which was later assembled in a device to produce an energy density of 30 W h kg^{-1} at 2285.7 W kg^{-1} and a specific capacitance of 106.7 F g^{-1} at 10 mV s^{-1} [199].

7. Critical assessment of redox-active MOFs for supercapacitors

Energy storage electrode materials made of redox-active MOFs are currently in the early stages of study. Redox-active MOFs are attractive options for high-performance energy storage because of their high specific surface areas and integrated redox-active sites. The prerequisite for quick charge storage and supercapacitor application is adequate

electrical conductivity. The ligand and redox metal center composition of MOFs greatly influences their charge storage mechanism. While it is critical to incorporate redox activity into MOFs, it is equally important to ensure that the redox-active MOFs are conductive to meet with the requirements of high performance in supercapacitors. One hot topic for potential application in supercapacitor electrodes is the best design of MOF-based nanomaterials with a large specific surface area, strong redox activity, and good conductivity. Through the incorporation of various metal ions, Wang and colleagues designed unique bimetallic MOFs (PPNF@M-Ni MOF, M = Co, Zn, Cu, Fe) with flower-like nano-sheets that offer superior electrochemical qualities. The produced PPNF@Co-Ni MOF typically shown a high specific capacitance of 1096.2 F g^{-1} (548.1 C g^{-1}) at a current density of 1 A g^{-1} . Interestingly, with a power density of 1600.0 W kg^{-1} , an asymmetric solid-state supercapacitor with PPNF@Co-Ni MOF and KOH-activated carbon nanofibers modified with rGO may reach a maximum energy density of 93.6 W h kg^{-1} [200].

MOFs have inherent drawbacks as an electrode material, including poor electrical conductivity and stability which lead to poor utilization of active sites and poor rate performance. There is dispute regarding the structural stability of the MOF following repeated charge-discharge cycles when the metal ion is involved in the solid-state redox process. The majority of redox active MOF electrode examples are currently restricted to two-dimensional frameworks. When used as electrode materials, low electrical conductivity remains one of the most significant obstacles for a highly porous MOF, particularly for 3D MOFs. Recent findings, however, indicated that doping tiny molecules or polymers into the pore structure could significantly boost the electrical conductivity of such highly porous frameworks. Such a doping strategy may be beneficial since it preserves the materials' inherent high porosity while significantly increasing their electrical conductivity. For use as electrodes in energy storage, redox-active MOFs could benefit from the same doping method that improved the stability and electrical conductivity of MOFs.

It is an intriguing and practical idea to increase the conductivity of MOFs by doping or infiltrating tiny molecules through their pores. This tactic does, however, have certain drawbacks. For these tactics to be

widely successful, the MOF needs to have open metal sites in order to coordinate with a tiny molecule that can transfer charges. For the guest molecule to work with two metal centers to promote the charge transport, the pore size must also match that of the guest molecule. The quantity of MOFs and dopants that can be employed is thus restricted. For instance, to specifically develop a cathode with enhanced performance for energy storage, a redox-active tetrazine moiety is immobilized within a metal-organic framework (MOF) by Li and co-workers. The redox activity of the Tz moiety is preserved in the nanoporous MOF Tz-Mg-MOF-74, which is made using a 1,2,4,5-tetrazine (Tz) functionalized ligand. When Tz's redox activity and a MOF's porosity were combined, a Tz-Mg-MOF-74-based cathode with noticeably better electrochemical performance was created. This method effectively combines MOFs and electrochemical activity produced from redox-active moieties, opening up new possibilities for the creation of efficient materials for energy storage.

Adding inorganic components to MOFs is another way to increase their electrical conductivity. Maintaining the long-term stability of the doped material was difficult, despite studies on iodine-doped MOFs and the resulting modest improvements in their electrical conductivity. For instance, Zhang et al., showed that when treated by iodine, a redox-active 2D TTF-Cu $[(\text{CuCN})_2(\text{TTF}(\text{py})_4)]$ (1) ($\text{TTF}(\text{py})_4$ = tetra(4-pyridyl)-TTF) MOF shows a five-fold increase in electrical conductivity along with a high specific energy of 62.9 Wh kg^{-1} at 1.1 kW kg^{-1} [201]. A strong broad signal at $g = 2.019$ is seen in the solid-state electron

paramagnetic resonance (EPR) spectra of 1-ox and 1-ox', which can be explained by coupling between the strong TTF^+ radical cation and trace Cu^{2+} spins. The very weak signals of Cu^{2+} at $g = 2.06$ and TTF^+ at $g = 2.008$ (Fig. 2a) are caused by surface partial oxidation by air. The crystalline and structural integrity of the 1-ox' and 1-ox frameworks is maintained, as evidenced by the powder X-ray diffraction (PXRD) patterns, which, while similar to those of other iodine-treated MOFs, show that some of the PXRD peaks of 1-ox' and 1-ox (Fig. 2b) become wider and weaker and most peaks appear but shift slightly from the original positions of pristine 1. A TTF^+ radical cation is indicated by an amplification of absorption in the 800–1100 nm area when compared to the UV-vis absorption spectra of the $\text{TTF}(\text{py})_4$ ligand and 1. Because there are more TTF^+ radical cations in 1-ox' than in 1-ox, the electrical conductivity of 1-ox has improved [201]. (See Fig. 13.)

Utilizing the TTF group's redox activity and planar moiety (CuCN)₂, the electrical conductivity significantly increased after iodine treatment. The specific capacity increased significantly as a result of the oxidized 1 (1-ox) electrical conductivity surging. High specific energy is displayed by the supercapattery based on the 1-ox battery-type positrode. Electrochemical impedance spectroscopy study confirms that the high conductivity and tightly aligned active sites resulting from oxidation are responsible for the good performances of 1-ox' and 1-ox as shown in Fig. 14.

To achieve tunable porosity and conductivity, a more universal method is to polymerize conductive polymer monomers in situ within

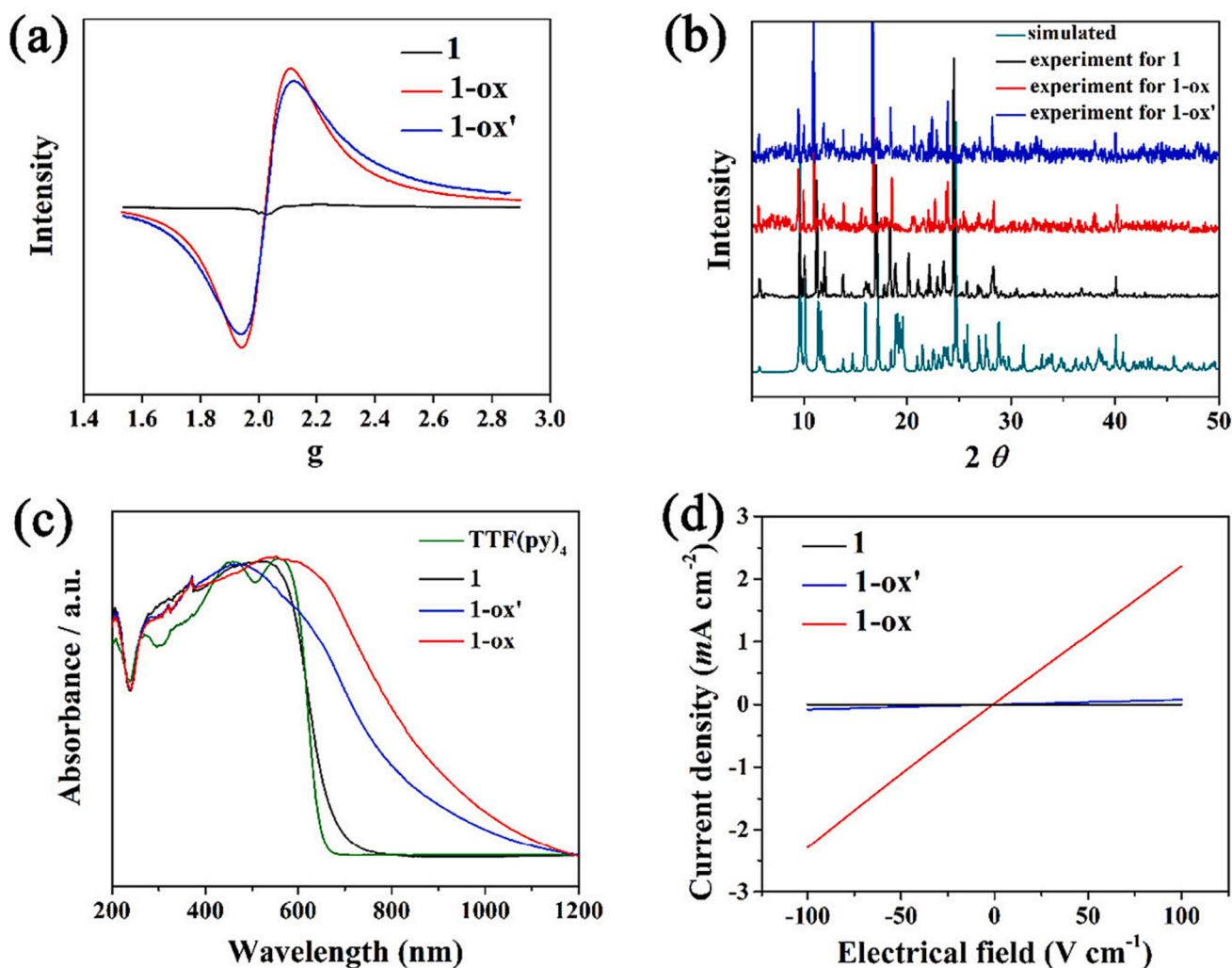


Fig. 13. (a) EPR spectra of 1, 1-ox, and 1-ox' measured at 110 K with the same parameters. (b) XRD patterns of 1, 1-ox', and 1-ox and the simulated pattern from the crystal data of 1. (c) UV-vis absorption spectra of py-TTF-py, 1, 1-ox', and 1-ox. (d) I - V properties of 1, 1-ox', and 1-ox [201].

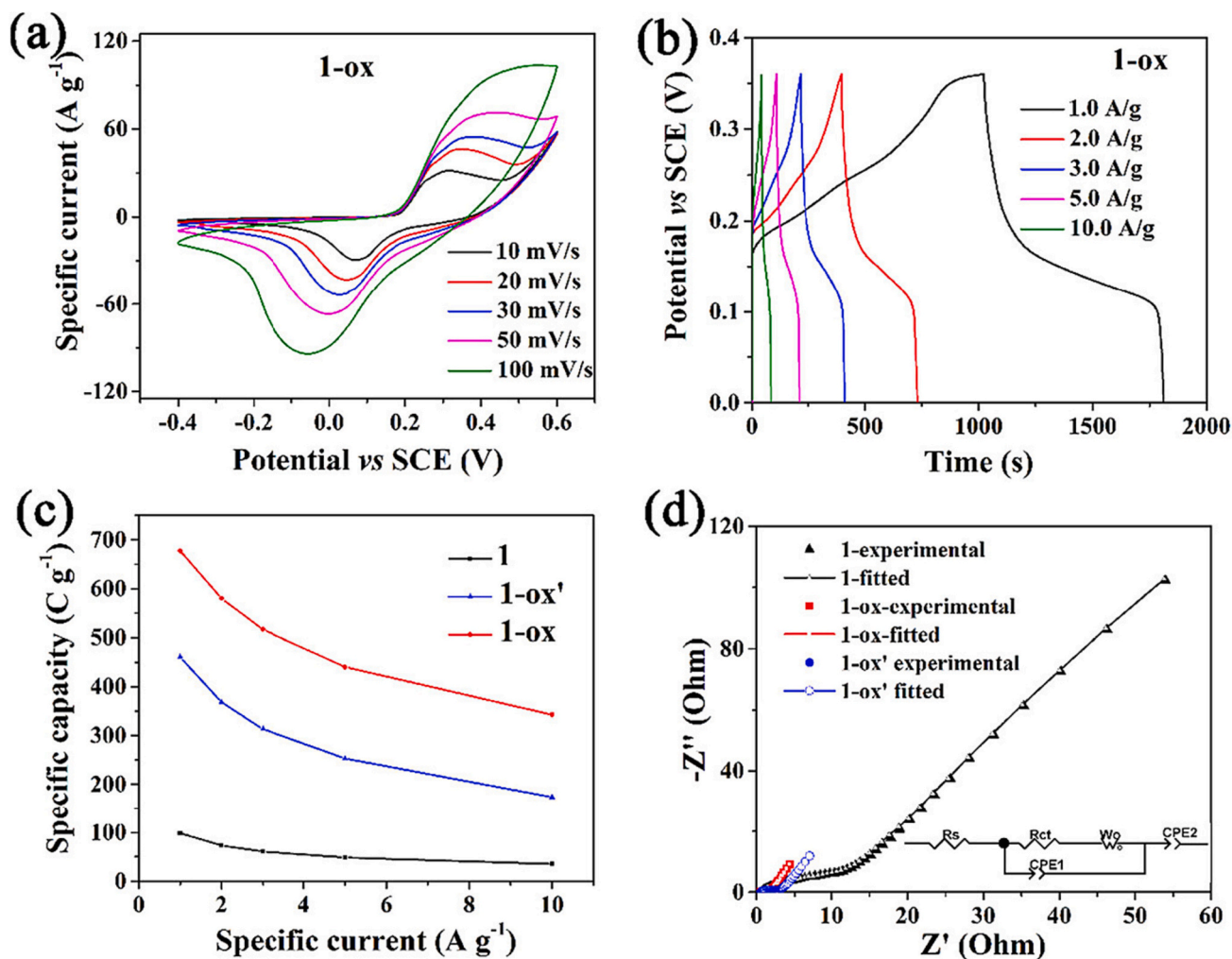


Fig. 14. Electrochemical performance of 1, 1-ox, and 1-ox' showing (a) CV at different scan rates (b) GCD at different current densities (c) specific capacity and (d) EIS [201].

the MOF pore structure. When in-situ synthesis is carried out, MOF or CP grows uniformly on the surface of its counterpart. By using this process, a chemically bonded structure with improved electrochemical performance is produced together with a fast charge transfer mechanism and a short ion diffusion length. For instance, Yao et al.'s study compares in-situ synthesis with physical mixing, demonstrating that the MOF@CP hybrid produced in-situ exhibited reduced charge transfer resistance, longer discharging periods, and a larger CV area [202].

8. Conclusion and future perspectives

The population of MOFs is expanding quickly, and so is the scope of their potential uses. MOFs have been used for energy applications including supercapacitors because of their high surface area, tunable porosity, and rich redox metal centers. The key drawbacks of MOFs as energy storage materials, however, are their poor conductivities and constrained energy storage capacities. Compositing MOFs with other functions via MOF-template strategy and/or functionalization have garnered significant attention to improve the electrochemical energy storage performance of supercapacitors when compared to pristine MOFs. The resultant MOF derivatives have enhanced conductivity, several oxidation states, and quicken the charge transfer from organic ligand to metals, increasing their capacity for energy storage. However, new applications of MOFs in energy storage require higher capacitances and higher energy density. To achieve this, electrodes exploiting redox

activity as described in this review must be developed. The development of redox-active MOFs for supercapacitors is thoroughly reviewed in this paper, with an emphasis on key features and operational modes in addition to the range of redox-active materials. By strategically integrating predesigned organic linkers with their desired activity, their tunability enables the incorporation of other capabilities, including redox centers, in their structure. Optimized MOF-derived electrodes have been shown to provide redox active materials that outperform the traditional electrode materials used in supercapacitors in terms of electrochemical performance. Rational design of the ligand struts and/or metal-based nodes that comprise the multidimensional framework can facilitate redox activity in MOFs. Transition metals provide a wealth of options for adjusting the redox activity in the metal nodes because of their abundance of stable oxidation states. Notwithstanding that the current review covers a limited number of redox-active MOFs, the survey continuously adds to the comprehensive outlook on the advances of MOF technology on energy storage. We have examined the most recent methods and achievements in introducing redox activity into MOFs, connecting the newly acquired properties to their potential use in supercapacitors.

Despite their remarkable performance and potential for SCs, redox-active MOFs are still in the early stages of research and cannot yet compete with the most advanced materials. The following is a list of the precise solutions required to overcome these challenges as quickly as feasible:

1. Pure MOFs and their composites often have limited electrical conductivity, which leads to low capacitance and poor rate capability. Naturally, the solution to this issue is to create redox-active MOFs with proven conductivity in otherwise inactive MOFs by choosing appropriate redox-active organic ligands and metal centers. Additionally, a thorough investigation of the precise conductive mechanism of MOFs materials is necessary, particularly for 3D-MOFs.
2. The relationship between the redox activity and the electrochemical storage mechanism of the redox-active MOF molecules is still unclear when it comes to ternary or multi-metallic MOFs. Thus, it might be possible to effectively clarify the electrochemical pathways by combining sophisticated experimental characterizations with calculations based on fundamental principles.
3. It is currently unclear how the electrochemical performances of redox-active MOFs relate to their structural architectures. Researchers must immediately conduct systematic studies to help them prepare superior redox-active MOFs-based materials. While it may take a lot of time to complete this task, artificial intelligence (AI) and machine learning (ML) may be introduced and used in the future in the fields of supercapacitors and redox-active MOFs-based materials.
4. The morphology, content, and structure of redox-active MOF electrode materials can vary depending on the kind of redox-innocent MOF precursors or strategy used, which can alter the supercapacitor's characteristics. Thus, in order to create high-performance supercapacitor electrode materials, MOF architectures and compositions must be carefully chosen.
5. Pseudocapacitive contributions to charge storage may result from adjusting MOF-electrolyte interactions or changing the functional groups of MOF linkers. The organic linker with multiple ion adsorption sites and the metal node(s) are the two potential redox-active sites in MOFs. These can be used to speed up redox reactions and improve capacitive performance. More work is needed to fully use the potential of such pseudocapacitive MOF electrodes, as they are presently underutilized in MOF-based supercapacitor systems.

Lastly, we believe that different redox-active MOFs with better supercapacitor performances and commercial potentials will be produced, provided that the issues that have been raised are properly addressed.

CRedit authorship contribution statement

Kabir O. Otun: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Azfarizal Mukhtar:** Conceptualization, Funding acquisition, Supervision, Visualization, Validation. **Sodiq A. Nafiu:** Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Ismaila T. Bello:** Conceptualization, Data curation, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Jibril Abdulsalam:** Conceptualization, Investigation, Validation, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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