

Recent Advances in Nickel and Cobalt-Based Metal-Organic Frameworks for High-Performance Supercapacitor Electrodes

Usama Zahid^{1*}, Fasiha Kashif¹, Iqra Saleem¹, Farzeen Dilshad¹, Jabir Shahbaz¹, Samra Arshad¹, Kiran Qasim², Ghdeer Abbas¹, Tahreen¹, Zunaira Kashif¹

¹Department of Physics, University of Agriculture, Faisalabad, Pakistan

²Department of Physics, Riphah International University, Lahore, Pakistan

DOI: <https://doi.org/10.36347/sjet.2024.v12i12.007>

| Received: 10.11.2024 | Accepted: 17.12.2024 | Published: 24.12.2024

*Corresponding author: Usama Zahid

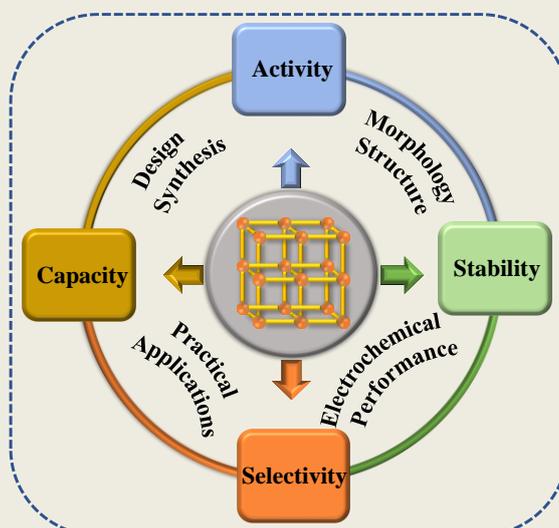
Department of Physics, University of Agriculture, Faisalabad, Pakistan

Abstract

Original Research Article

Energy sustainability has become a pressing concern in material science due to the growing demand for scalable, efficient, and eco-friendly energy storage solutions. In recent times, supercapacitors have become a central focus in the field of advanced electrochemical energy storage system. For supercapacitor electrodes, metal-organic frameworks (MOFs) are one of the most talked materials due to their multiple structures, suitable functionalities, and similar metal centers resulting in broad applications. This review provides a comprehensive overview of the recent advancements in the fabrication of Nickel-based MOFs (Ni-MOFs) and Cobalt-based MOFs (Co-MOFs) and their applications as electrode materials in high energy supercapacitors. Ni-MOFs and Co-MOFs have garnered significant attention in energy storage systems due to their exceptional properties including remarkable durability, highly porous nature, high specific capacitance, rich active sites, robust redox activity, excellent performance, and eco-friendliness, making them ideal for advancing supercapacitors to meet the increasing demand for efficient electrochemical energy storage devices.

Keywords: Nanomaterials, Metal-organic frameworks, Supercapacitor, Nickel-MOF, Co-MOF, Specific capacitance, Energy density, Power density.



Graphical Abstract

Copyright © 2024 The Author(s): This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CC BY-NC 4.0) which permits unrestricted use, distribution, and reproduction in any medium for non-commercial use provided the original author and source are credited.

INTRODUCTION

Nanotechnology has gained significant attention globally, with various revolutionary advancements, media coverage, and investments,

making it an important field of research. It is a versatile field that enables progress across various scientific disciplines, leading to new innovations. Its applications can potentially create better, cheaper, cleaner, smarter,

Citation: Usama Zahid, Fasiha Kashif, Iqra Saleem, Farzeen Dilshad, Jabir Shahbaz, Samra Arshad, Kiran Qasim, Ghdeer Abbas, Tahreen, Zunaira Kashif. Recent Advances in Nickel and Cobalt-Based Metal-Organic Frameworks for High-Performance Supercapacitor Electrodes. Sch J Eng Tech, 2024 Dec 12(12): 380-393.

and faster products with improved manufacturing processes [1]. The term "nanotechnology" simply means "technology at the nanoscale". The word "nano" is derived from Greek term "nanos", which indicates a dwarf or something very small. A nanometer (nm) is equivalent to one billionth of a meter or one-millionth of a millimeter. Nanotechnology involves manipulating matter at the atomic and molecular levels within the range of 1 to 100 nanometers [2]. It refers to the capacity to control and fabricate materials at a nanoscale level, as well as to observe, measure, manipulate, and manage them while Nanoscience refers to the interdisciplinary field that combines materials science, physics, and biology to study the modification and designing of materials at nanoscale [3]. Nanotechnology has shown promising results in reducing pollution and creating productive and economical energy solutions. For instance, nanotechnology can be utilized to minimize the pollution generated during material production, manufacture affordable solar cells, and eliminate volatile compounds from the atmosphere. Nanotechnology is transforming the scientific landscape through its exceptional characteristics [4]. Nanotechnology is often linked with materials and systems that possess advanced chemical, physical, and biological properties due to their nanoscale components and structures. The progress of fresh theoretical and practical approaches for study, as well as the discovery of new materials, phenomena, and processes at the nanoscale, give new opportunities for the advancement of imaginative nanostructures in the materials and nano systems [5].

1.1. The Imaginative Pioneers of Nanoscience

Nowadays, nanoparticles (NPs) have gained considerable interest due to their numerous applications in different fields. The roots of nanoscience were laid in 1950s to 1960s, a period when scientist began examining materials at molecular and atomic levels. In 1959, during a conference held by the American Physical Society, Richard Feynman gave a talk called "There's Plenty of Room at the Bottom" at the California Institute of Technology (Caltech) [6]. In his research, he proposed the concept that weaker micro-level forces such as Van der Waals and gravity become dominant at the nanoscale, while significant effects of other forces are negligible. This talk is often cited as a seminal moment in the history of nanoscience and nanotechnology. During the 1970s, the progress made in microscopy and other technologies allowed scientists to observe and control materials at the nanoscale with greater accuracy.

In 1974, Norio Taniguchi coined the term "nanotechnology" into the scientific community. Eric Drexler wrote his first book "Engines of Creation: The Coming Era of Nanotechnology" in 1985. The United States initiated its first nanotechnology program under the National Science Foundation in 1991 and it was approved in 2001. China, South Korea, Japan, Germany, and other nations are increasingly focusing on the development of nanotechnology. Numerous fields of research have benefited from the use of nanotechnology to enhance various goods [7].

1.2. Classes and applications of nanomaterials

Nanostructured material plays a crucial role as a fundamental component within the realm of nanotechnology. The chemical and physical features of nanostructured materials, also known as nanomaterials, are strongly influenced by their morphology, or shape. There are four main classes of nanostructured materials, which include organic, inorganic, carbon-based, and composite materials. The categorization of nanostructures by dimensions was redefined by Pokropivny and Skorokhod. These structures were divided into four categories based on their size named as 0D, 1D, 2D, and 3D [5].

Nanotechnology relies on a variety of nanomaterials that differ in their nature, size, and morphology such as nanoparticles (NPs), nanospheres, nanocomposites, nanoflakes, nanotubes (NTs), and nanowires (NWs). Nanoparticles (NPs) are tiny materials, usually measuring between 1 to 100nm, and can be categorized based on their properties, dimensions, and shapes [8]. Common classes of NPs include carbon-based, lipid based, polymers, semiconductor, and ceramics. NPs have a significantly greater surface area compared to larger particles, which enables them to interact with various chemical groups, increasing their chemical affinity [9]. The morphological features of NPs are highly significant as they determine the major properties of NPs. NPs have many applications in the field of biomedical and pharmaceuticals. NPs are widely utilized in industrial applications, like lubricants, adhesives, and coatings owing their exceptional mechanical properties, including high Young's modulus, strain, and stress capabilities. NPs have various applications in the field of photodegradation, and many nanomaterials are used for this purpose as demonstrated in Fig. 1. Additionally, NPs are utilized in energy storage systems at the nanoscale in various ways [10].



Fig 1: Applications of nanomaterials in different fields

1.3. Properties of nanomaterials

The nanoscale size of nanomaterials leads to remarkable chemical and physical properties, such as magnetism, optical absorption, electrical and thermal

conductivity, fluorescence, melting point, and catalytic activity, that differ significantly from their bulk counterparts. Structuring materials at the nanoscale can lead to a wide range of property adjustments [11].

Table 1: Variable properties and examples of Nanomaterials

Characteristics	Examples
Electrical	Enhanced electrical conductivity in magnetic nanocomposites and ceramics, along with higher resistance in metals
Mechanical	Enhanced alloy’s resilience and hardness, as well as increased ceramic ductility and superplasticity.
Sterical	Optimized selectivity, hollow spheres for targeted drug delivery, with regulated release capabilities.
Catalytic	Improve catalytic performance with higher surface area relative to volume
Magnetic	Elevated magnetic properties up to a particular grain size, leading to superparamagnetic effect
Biological	Improved biocompatibility and enhanced permeability via biological barriers.
Optical	Improved semiconductor crystal’s quantum efficiency, attributed to changes in fluorescence and optical absorption qualities.

2. Metal-Organic Frameworks (MOFs)

Discovering novel materials that exhibit higher stability and efficacy is a challenging task in the advancement of storage systems and sustainable energy conversion technologies. MOFs are the class of porous materials made up of metal ions or clusters that are linked with organic ligands, creating a 3D crystalline structure. Usually, MOFs are composed of organic ligands that have two or more binding sites that coordinate with metal ions, forming a well-organized network with high surface area and pore volume [12-14]. These porous crystalline materials have a unique structure where the metals are arranged in a closed position, creating a rigid and porous geometry that is held together by various organic groups (Fig 2). Due to their flexible structure, controllable pore size, and large surface area, MOFs have wide range of applications in different fields including separation [15, 16], sensing [17, 18], gas storage and adsorption [19, 20], catalysis [21, 22], drug delivery [23,

24], luminescence [25, 26], molecular recognition [27], and energy storage [28-30]. The 3D porous and tunable channels of MOFs make them highly useful for separation, storage, and molecular conversion based on their dimensional properties. In general, MOFs can be classified as a type of coordination polymer family. However, MOFs are more specific as compared to coordination polymers due to their porous structural crystalline networks in two or three dimensions. MOFs are sometimes called porous coordination polymers (PCPs) because of their porous nature and coordination polymer structure [31].

The pores in MOFs provide an immense internal surface area, estimated to be around 7800 square meters per gram of MOF, which is enough to cover an entire football ground. Besides much larger internal surface areas, MOFs have an advantage over zeolites due to their ability to modify organic units in a predictable

manner to create materials that are customized for specific applications. Recently, researchers have made significant efforts to improve the stability of MOFs.

Enhancing the stability of MOFs can expand their practical applications [32].

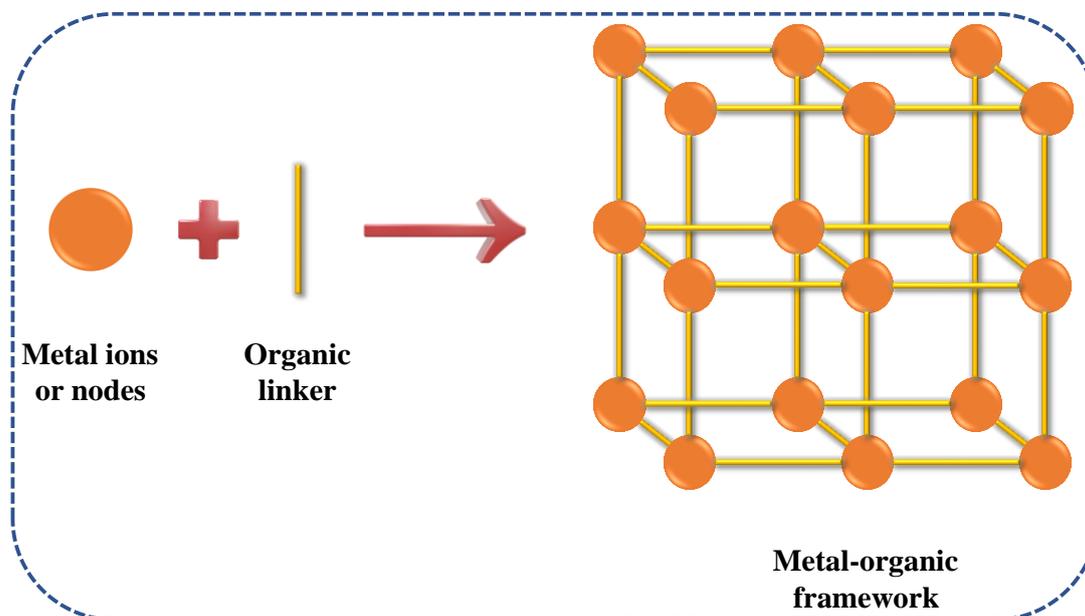


Fig 2: Representation of MOF building blocks and resulting porous, crystalline structure

2.1 Historical developments

The idea of using organic ligands to coordinate metal ions and create extended networks was initially proposed during the 1960s. Coordination polymers fabricated using di- and tetrapotic carboxylic acid linkers coordinated to di-, tri-, or tetravalent metals were first reported by Tomic in 1965 [33]. He studied the thermal stability of these polymers and found that it was linked with both the valency of the metal and the binding sites on the linker. Hoskins and Robson suggested that a vast array of scaffold-like materials could be fabricated, adjusted, and potentially beneficial [34]. The first report on MOFs was published by Leonard MacGillivray and Michael L. Gross in the journal *Science* where they synthesized a porous 1D coordination polymer of copper (II) ions and 4,4'-bipyridine. Yaghi *et al.*, later formed a 3D crystalline material by using hydrothermal synthesis technique and introduced the term MOF [35]. At the same time, Kitagawa *et al.*, conducted research on the potential of MOFs for the storage of methane gas [36]. During the 2000s, the field of MOFs grew rapidly with the discovery of numerous new materials and applications. Over the years, the field of MOFs has continued to grow and diversify. Researchers have made significant advancements in comprehending the fundamental properties of MOFs, including their stability and mechanical characteristics, and have devised new techniques for synthesizing and functionalizing MOFs.

2.2 Structural aspects of MOFs

The primary building units (PBUs) and secondary building units (SBUs) define the structural characteristics of MOFs. Within MOFs, PBUs and SBUs

are distinct levels of organization that contribute to the distinctive properties and functionalities of these materials.

2.2.1. Primary building units (PBUs)

Primary building units (PBUs) are the essential building blocks of MOFs, consisting of an organic ligand linked to individual metal ion or network of metal ions. Metal ion or cluster acts as the basic coordination site, whereas the organic ligands act as the coordination bonds that connect the PBUs to form the MOF framework. The arrangement of metal ions decides the structure, geometry, and dimension of the pores in MOFs. These organic compounds and metal ions which are utilized in the development of MOFs are known as the Primary Building Units of MOFs. Transition metal ions from the first row such as Co^{2+} , Fe^{3+} , Cr^{3+} , and Zn^{2+} are commonly used as connectors in the construction of MOFs. Examples of common PBUs include octahedral, tetrahedral, and trigonal prismatic coordination geometries [37].

2.2.2. Secondary building units (SBUs)

SBUs are larger units that are formed when two or more PBUs coordinate through metal-ligand bonds. The overall architecture of a MOF is determined by the connectivity and arrangement of SBUs, which can be formed by identical or different PBUs. Designing and engineering the properties of MOFs frequently involve the use of SBUs to control factors such as pore size, stability, and capacity for gas adsorption. Examples of common SBUs include Linear SBUs, Planar SBUs, and Cage-like SBUs [38].

2.3. Synthetic technologies of MOFs

MOFs are synthesized via hydrothermal, solvothermal, sonochemical, chemical vapor deposition, mechanochemical, and solvent-free methods. The majority of these techniques are carried out in a liquid medium, where the inclusion of a solvent allows for easier mixing and organization of metal salts and organic ligands, resulting in the formation of well-structured and

crystalline arrangements. Choosing an appropriate solvent is crucial as it plays a significant role in determining the synthesis conditions such as reactivity, stability constant, solubility, and redox potential. These factors are important in achieving the desired outcome of the synthesis process [39]. The complete schematic representation of synthesis techniques is shown in Fig 3.

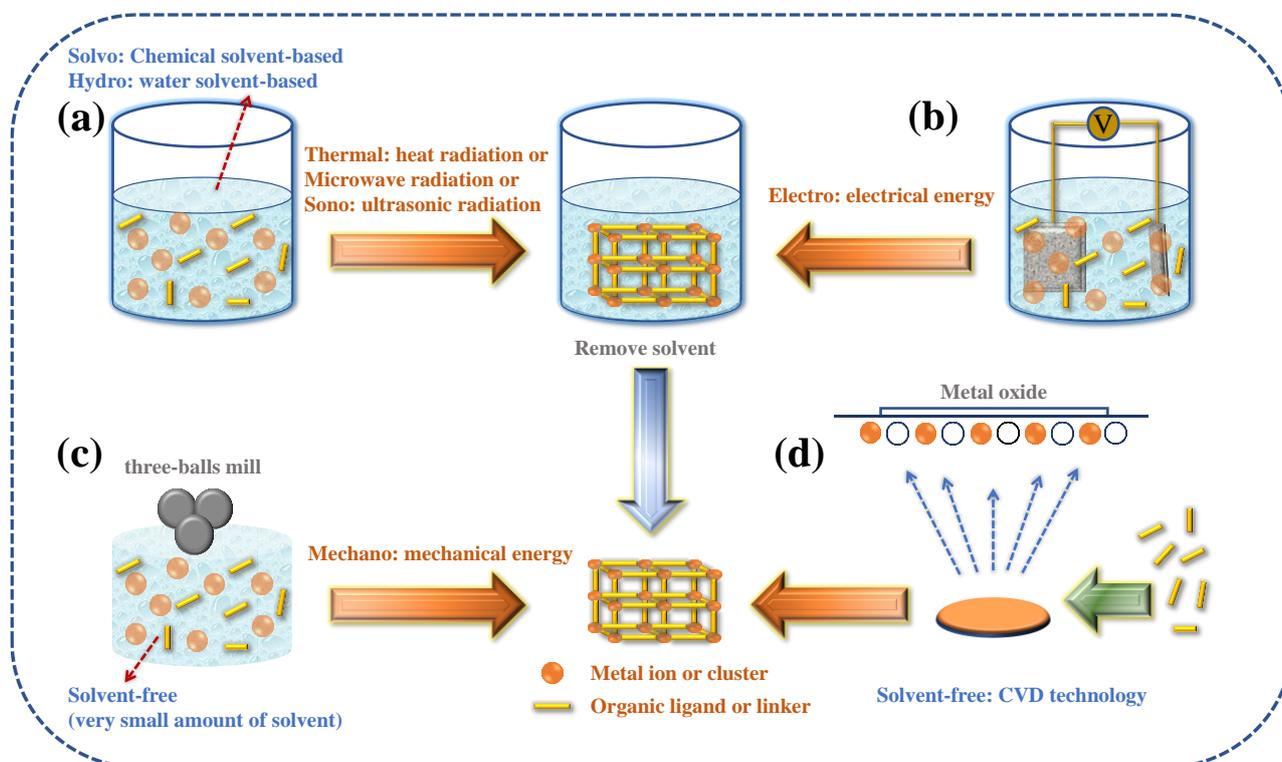


Fig 3: Schematic representation of various synthetic techniques of MOFs

3. Nickel Nanomaterials

Nickel was actually discovered by Axel Fredrik Cronstedt in 1751. Nickel is a transition metal that appears as a shiny metallic silver in its pure form. It is hard and ductile, and it has a slow rate of oxidation, which gives it good corrosion resistance. The crystal structure of nickel is face-centered cubic (FCC), which is frequently observed in other metallic elements. The lattice parameter of nickel is about 0.352nm and its density is about 8.908 g/cm³. Nickel atoms are bonded together primarily through metallic bonding, where valence electrons are shared among all the atoms in the crystal lattice. Due to the presence of metallic bonding, nickel possesses a high melting point, electrical conductivity, and ductility. Nickel has an atomic radius of about 0.124 nm, which falls between the atomic radii of iron and copper. Nickel can exist in various oxidation states ranging from -2 to +4. The most stable and common oxidation states of nickel are +2 and +3 [40].

Nickel metal-organic frameworks (Ni-MOFs) refer to a group of porous materials that composed of metal nodes, often nickel ions, and organic ligands that are linked together through coordination bonds to form a

3D network structure. The formation and properties of Ni-MOFs are significantly influenced by the distinctive characteristics of nickel, including its coordination chemistry, oxidation states, and electronic properties. Coordination bonds that form in a Ni-MOF can either be covalent or electrostatic, and the potency of these bonds can impact the stability and porousness of the resulting material. Due to their inexpensive cost, good abundance, improved catalytic activity, and electrochemical characteristics, nickel (Ni) ions are a widely used transition metal ion of interest. Ni-based MOFs are also used in different types of applications such as electrochemical sensing, drug delivery, electrical energy storage, and electrocatalysis [41].

4. Cobalt nanomaterials

Cobalt (Co) can be obtained from various types of ores, including cobaltite, erythrite, glaucodot, and skutterudite. The electronic configuration of cobalt is (Ar) 3d⁷ 4s². Cobalt possesses several distinct properties that make it valuable in numerous applications. Cobalt is a metallic element that has a hard, shiny, and silver-white appearance. It is ferromagnetic, which means it can be magnetized and has a high MP and BP of 1495°C and

2870°C, respectively. These include its magnetic properties, high-temperature stability, and catalytic activity. Cobalt is known for its remarkable mechanical characteristics including high tensile strength, good thermal conductivity, and impressive corrosion resistance. In addition, cobalt is also known for its catalytic activity and biocompatibility, which makes it a valuable material for various applications. Nanoscale Cobalt Particles usually have surface area between 30-70 m²/g and a size range of 20-60 nm. Cobalt is a well-known element that has been used for centuries to produce brilliant blue pigments for coloring paint and glass. Cobalt is also known for its ferromagnetic characteristics and it is used in the fabrication of high-strength superalloys. Co-60 is a radioactive isotope that has commercial importance and can be used as a source of gamma rays and as a tracer material [42].

At room temperature and atmospheric pressure, cobalt exhibits a face-centered cubic (FCC). Under high pressure, cobalt can undergo a phase transformation and adopt a hexagonal close-packed (HCP) crystal structure. Cobalt is a ferromagnetic material, which means that it retains a magnetic field even when no external magnetic field is present. The magnetic properties of cobalt are due to the alignment of electron spins in its atoms. Due to the presence of 27 protons in its nucleus, cobalt has a higher atomic number, which results in a greater electron density in its outermost electron shell [43].

5. Supercapacitors

The increasing global concern about environmental pollution and energy scarcity has led to a rising demand for sustainable and renewable sources of energy. Solar, wind, and tidal energy are some examples of clean energy sources that are gaining popularity as alternatives to traditional fossil fuels. These energy sources are typically converted into electricity for storage and future use. To meet the required efficiency

levels, various types of electrical energy storage systems are being developed. Supercapacitors (SCs) have been given significant attention among these devices due to their charge and discharge capabilities, power density, and cycling stability [44]. A supercapacitor typically consists of three main components: a high surface area electrode, a separator (which serves to prevent short circuits among two electrodes) and an electrolyte (which can be aqueous or organic). To determine the performance of a supercapacitor the electrode is a crucial element [45]. It can be seen that SCs have an electrical storage capacity many times greater than that of fuel cells and batteries. They demonstrate efficient and speedy charging and discharging capabilities, with a significant amount of power released. This feature has drawn the attention of researchers in energy storage field. The performance and properties of supercapacitors are influenced by their material composition, and several potential materials have already been utilized, including pristine carbon-based materials like graphene, as well as active carbon, conductive polymers [46].

Currently, there is a significant amount of scientific research being conducted on supercapacitor devices. These devices can be divided into two categories based on the electrode material and charging/discharging mechanism [47].

- The electrical double-layer capacitor (EDLC)
- Pseudo-capacitors

EDLC relies on the electrostatic interactions between the electrolytic ions and the conductive surface of the electrodes to save energy. While Pseudo-capacitors primarily rely on faradaic reactions, which involve oxidation-reduction reactions, intercalation processes, and electro-sorption through electron charge deliver among the electrodes and electrolyte (Fig 4).

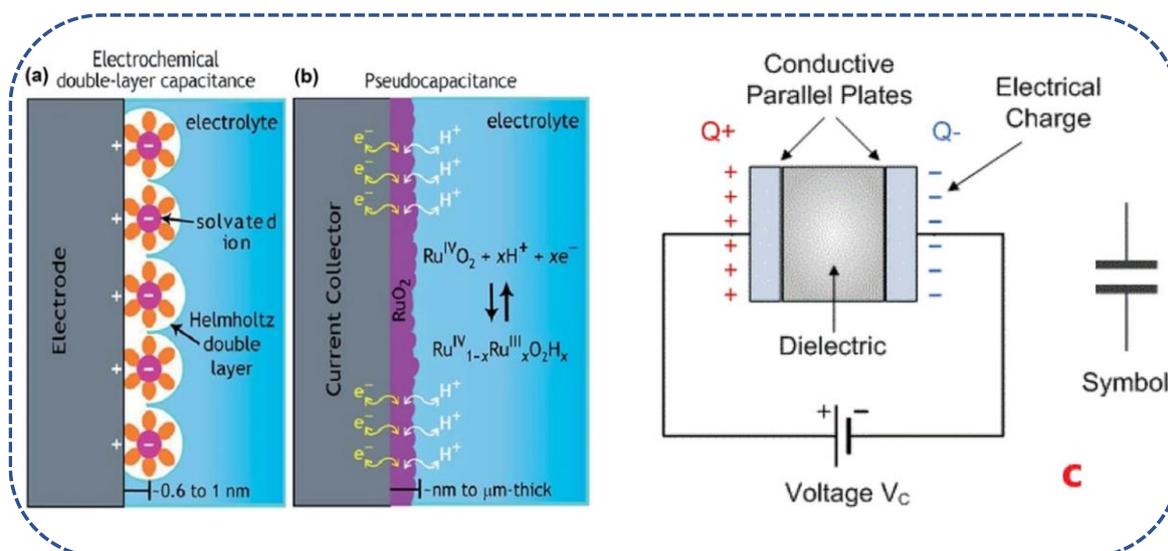


Fig 4: Schematic demonstration of capacitor type; (a) EDLC, (b) pseudocapacitor, (c) conventional capacitor [48]

5.1 MOF as a supercapacitor

In recent years, valuable research work has been focused on investigating MOFs as potential electrode materials for SCs. This is because MOFs possess redox-active metal ions and large surface areas that makes them promising candidates for use in supercapacitors. Sundriyal *et al.*, have suggested that utilizing electrode material in supercapacitors can be advantageous when using MOFs. These advantages include their ability to provide extremely high porosity, adjust the distribution of pore sizes, undergo convenient synthesis, and exhibit robust structural adaptability [45]. The exceptional properties of MOFs have drawn valuable attention for their potential in SCs advancements in recent times. Additionally, MOFs have the capability to be combined with various other materials, including metal nanoparticles, metal oxides, polyoxometalates, carbon-based materials, and polymers to create composites with enhanced properties [46]. MOFs are composed of organic linkers like imidazole and carboxylic acids and different metal ions including Fe, Co, Ni, Zn, Mn, etc. that have been used for many applications including memory backup devices, consumer electronics, and energy storage devices [49]. Díaz *et al.*, were the first to investigate the supercapacitive behavior of a pure or pristine MOF, specifically Co8-MOF-5. However, the results showed that Co8-MOF-5 had a very low specific capacitance [50]. Following this initial study, Yaghi *et al.*, examined 23 different nanocrystalline MOF materials as potential electrode materials for supercapacitors. Their findings revealed that the Zr-

MOF exhibited a higher areal capacitance than commercially available activated carbon, indicating the promising potential of MOFs for supercapacitor applications [51].

6. Nickel and Cobalt MOF for supercapacitors

6.1. Pristine Nickel MOFs

MOFs based on transition metals, especially Ni-MOF, have garnered considerable interest in energy storage systems due to flexible structures, extensive surface area, and organized meso-porosity, which distinguish them from other MOFs [52]. Over the past several years, extensive studies have demonstrated that Ni-MOFs are excellent precursors for active materials in energy storage systems. While pristine Ni-MOFs may not provide adequate electronic conductivity when used as electrodes, their large specific surface area (SSA) and uniform pore structure can enhance electron and ion transport. Compared to pure MOFs, Ni-MOF-derived structures exhibit a substantial improvement in electrical conductivity while maintaining high SSA [45]. To date, a wide array of Ni-MOF nanostructures has been synthesized through diverse chemical methods and reaction conditions, for example, Khan *et al.*, [53] developed Ni-MOF by hydrothermal approach utilizing terephthalic acid as an organic ligand which exhibited a specific capacitance (C_s) of 565.32 Cg^{-1} at a current density of 1.2 Ag^{-1} . Moreover, the assembled asymmetric supercapacitor (ASC) device demonstrated remarkable energy density (ED) and power density (PD) which were 45.56 Whkg^{-1} and 850 Wkg^{-1} , respectively (Fig 5).

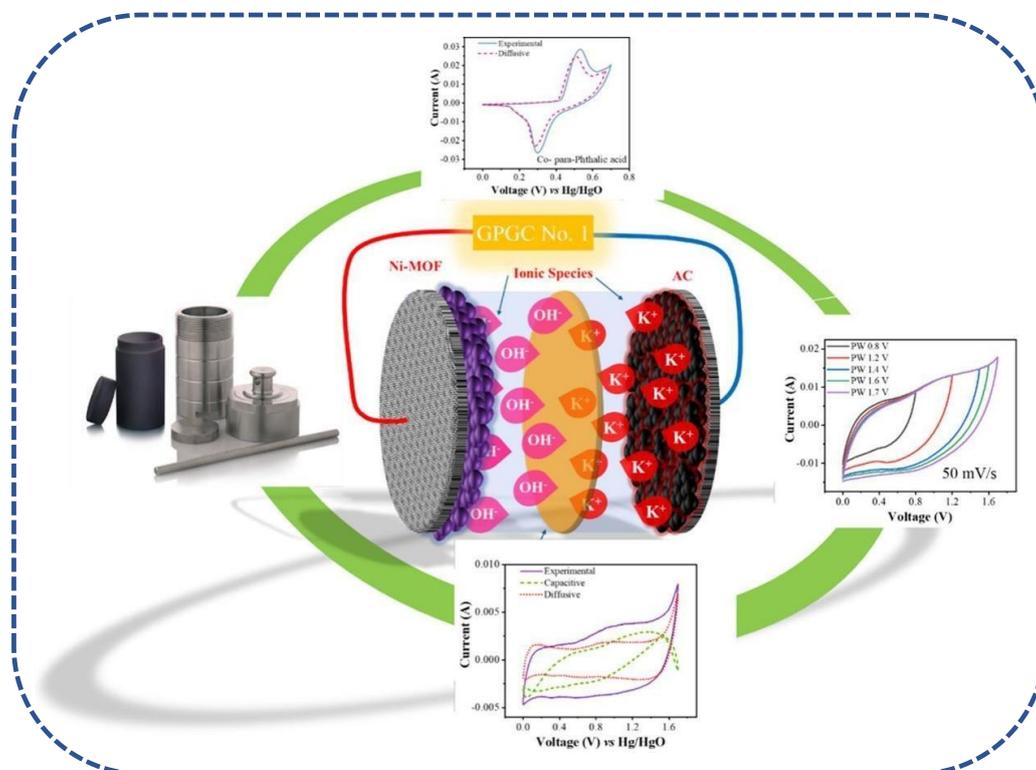


Fig 5: Schematic illustration and electrochemical performance of Ni-MOF. Reproduced with permission from Ref. [53]. Copyright 2024, Elsevier

Furthermore, Bhoite *et al.*, [54] designed thin films of binder free Ni-MOF by utilizing solvothermal method. These nanosheets like fabricated MOF showcased excellent electrochemical performance by achieving a Cs of 850.42 Fg^{-1} at 1 mAcm^2 . Additionally, Ni-MOF electrode exhibited an impressive ED of 18.66 Whkg^{-1} at a PD of 1671 Wkg^{-1} . Wang *et al.*, [55] presented a novel method for synthesizing composite NiO/Ni-MOF electrodes for supercapacitors. The amount of H_2BDC was dissolved in hydrothermal

approach that was found to be able to conveniently tune the conversion degree of NiO/Ni-MOF (Fig. 6). It was used to produce an ASC, which had a high degree of cyclic stability and a higher ED of 31.3 Wh kg^{-1} at a PD of 374.2 W kg^{-1} . These results highlight Ni-MOF as well-designed and environmentally friendly option for electrode materials in next-generation energy systems, contributing to the development of sustainable energy technologies.

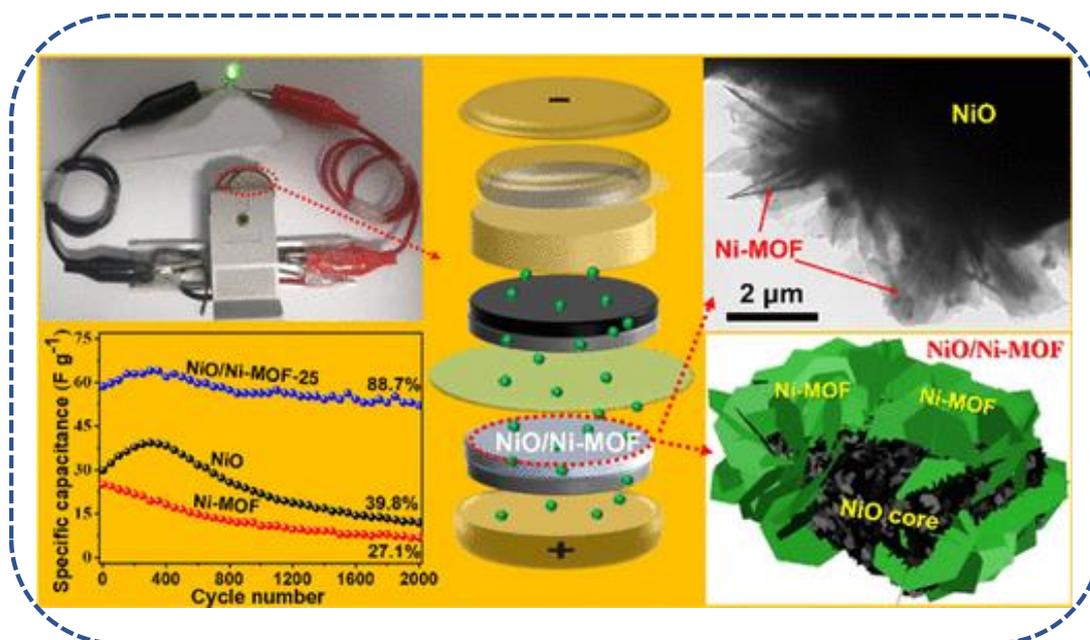


Fig 6: Device fabrication and capacitance retention of NiO/Ni-MOF electrode. Reproduced with permission from Ref. [55]. Copyright 2021, American Chemical Society

6.2. Pristine Cobalt MOF

Cobalt, being transition metal, offers redox active sites and is an ideal choice for designing MOFs with excellent electrochemical performance. Additionally, the diverse oxidation states of cobalt contribute to surface redox reactions, providing better electrochemical activity compared to other MOF-based materials. Ramachandran *et al.*, [56] investigated the systematic synthesis of Co-MOFs in various solvents and mixtures by using the solvothermal approach. The Co-MOFs were characterized for detailed information about their crystal nature by XRD, morphology by FESEM, and porosity by BET. In 3M KOH, the electrochemical characteristics of Co-MOFs were examined for SCs as an electrode material (Fig 7(a)). At a current density of 2

Ag^{-1} , Co-MOF can reach a maximum Cs of 958.1 Fg^{-1} at 2 Ag^{-1} . Even after 3000 cycles, the capacitance retention was kept at a high level of 92.3%. Moreover, Zheng *et al.*, [57] used one-pot hydrothermal synthesis method by a facile surfactant-assisted to prepare ultrathin 2D Co based MOF nanosheets (NS). Due to their extraordinary thinness, the resulting 2D Co based MOF had exceptional electrical and optical transparency. For improved capacitance and stability, their distinctive nanostructures made them suitable choices for high-performance supercapacitors. More significantly, the electrode maintains 96.7% of specific capacitance and shows very minimal capacitance decay after 6000 cycles (Fig 7(b)).

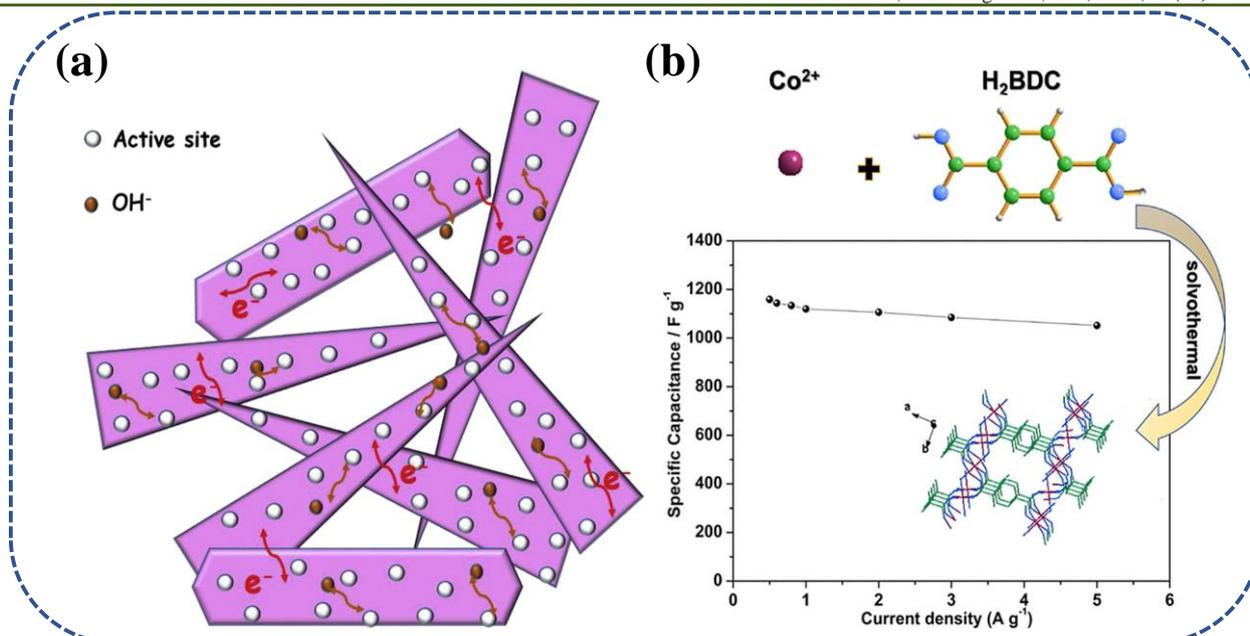


Fig 7: (a) Charge storage mechanism of Co-MOF. Reproduced with permission from Ref. [56], Copyright 2018, Elsevier. (b) Synthesis illustration and Retention of Co-MOF. Reproduced with permission from Ref. [57], Copyright 2019, Elsevier.

6.3. Nickel and Cobalt MOF-based composites (NiCo-MOF)

The drawbacks of having a single metal active site and limited electrical conductivity lead to the poor performance of single MOF materials in supercapacitor. Compared to monometallic MOFs, bimetallic MOFs offer quicker redox retraction, leading to improved stability on the applications of supercapacitor. The synergistic interaction between bimetallic ions improves ion and electron transport, while tuning the properties of different metal ions can enhance the electrochemical performance of MOF materials for energy storage. For example, Zhou *et al.*, [58] developed Ni/Co-MOF-NPC derived from Nickel and Cobalt which showed unique structural characteristics and outstanding electrochemical efficiency and had the best choice for electrode material. In a three-electrode test system, CoO had a Cs of only 104.3 F g^{-1} at 1 A g^{-1} . However, the fabricated material exhibited a Cs of 1214 F g^{-1} , that was significantly higher than CoO. Even after 6000 cycles at a current density of 10 A g^{-1} , the capacitance of the

electrode still retained 98.8% of its initial value. The device also demonstrated an extremely maximum ED of 55.4 Wh kg^{-1} at a PD of 758.5 W kg^{-1} and retained a stable performance over a long period of cycling. Liang *et al.*, [59] fabricated a series of bimetallic MOFs by using a hydrothermal method that possessed a layer-and-channel frameworks (Fig 8). The capacitive behavior of the bimetallic series of $\text{Ni}_n\text{Co}_m\text{MOFs}$ was remarkable due to the combined effect of Ni and Co. $\text{Ni}_1\text{Co}_1\text{MOF}$ showed exceptional capacitive performance with a capacitance of up to 1333 F g^{-1} at 2 A g^{-1} . Moreover, even at 10 A g^{-1} , it maintained 83% of its capacitance, that was greater than the equivalent monometallic MOFs. An ASC was assembled by pairing $\text{Ni}_1\text{Co}_1\text{MOF}$ with activated carbon (AC). The device demonstrated a remarkable capacitance of 97 F g^{-1} when tested at 0.5 A g^{-1} . The ASC device demonstrated a maximum ED of 28 Wh kg^{-1} at a PD of 444 W kg^{-1} . The electrochemical properties of the bimetallic MOFs made them a promising material for supercapacitor electrodes.

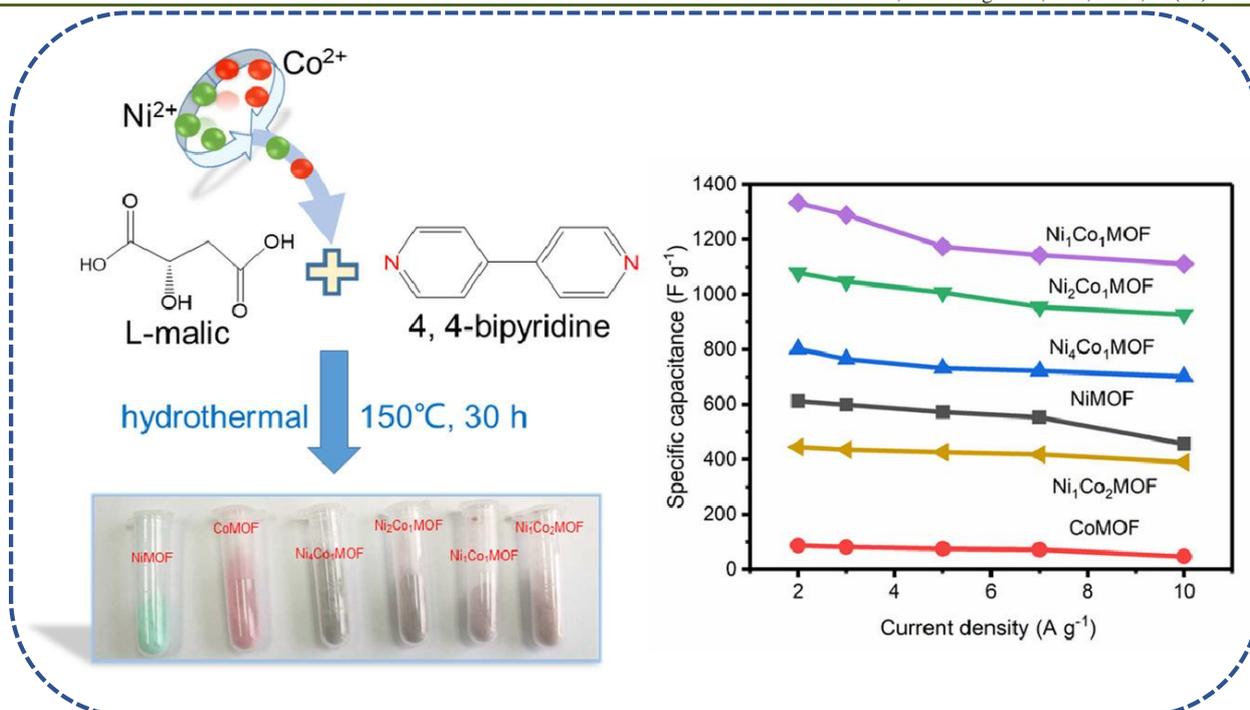


Fig 8: Fabrication of Ni_nCo_mMOFs and comparative capacitance graph. Reproduced with permission from Ref. [59], Copyright 2021, Elsevier

Chen *et al.*, [60] synthesized the Ni/Co-MOFs via etching Ni-based MOF microspheres in cobalt nitrate mixture and found that the amount of $Co(NO_3)_2$ and etching time played a critical role in their formation. The optimized material showed high capacitance at different current densities when utilized as electrode materials for SCs. The highest capacitances were achieved by the optimized Ni/Co-MOF-5, with values of $986.7 Fg^{-1}$ and $1220.2 Fg^{-1}$ observed with current densities of $10 Ag^{-1}$ and $1 Ag^{-1}$, respectively. The resultant Ni-Co-S electrode performed better after sulfurization, with specific capacitances of $1377.5 Fg^{-1}$ at $1 Ag^{-1}$. When the current density was raised to $10 Ag^{-1}$, the electrode showed a retention of 89.4%, indicating better rate capacity. Both the synthesized materials demonstrated exceptional cycling stability, retaining approximately 87.8% and 93.7% of their initial capacitances, respectively. Wang *et al.*, [61] prepared three-dimensional Co-doped Ni-based MOF by hydrothermal method. The addition of Co enhances the electrochemical characteristics of Ni-MOF, most special $Co_2-Ni-MOF$. Links between the electrolyte

ions and active sites were facilitated by the 3D flower-like microspheres that showed Co doping has an open hierarchical structure. At $1 Ag^{-1}$, it has an outstanding rate performance and a notable specific capacitance of $1300 Fg^{-1}$. After 3000 cycles, the $Co_2-Ni-MOF$ capacitance still holds 71% of its initial capacitance. The increased conductivity was caused by the combined impact of both Co^{2+} and Ni^{2+} ions. Moreover, the ASC device ($Co_2-Ni-MOF//AC$) showcased a remarkable Ed of $25.92 Whkg^{-1}$ at a PD of $375 Wkg^{-1}$.

Combining MOFs with conductive material can also enhance their electrochemical performance. Rahmanifar *et al.*, [62] reported the novel method for synthesizing water-stable Ni-based and Co-based MOFs, along with a composite material composed of reduced graphene oxide (rGO). The Ni/Co-MOF-rGO nanocomposite exhibited a specific capacitance of $860 Fg^{-1}$ at $1 Ag^{-1}$, indicating high performance (Fig 9). The ASC device demonstrated an excellent ED ($72.8 Whkg^{-1}$) and PD ($850 Wkg^{-1}$)

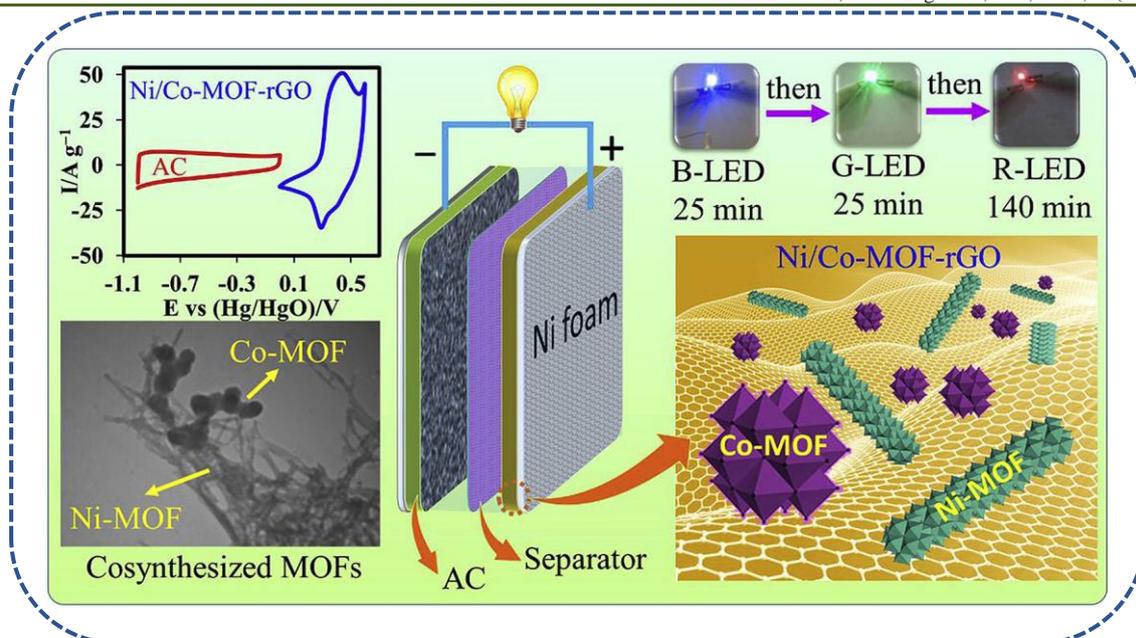


Fig 9: The electrochemical performance of Ni/Co-MOF-rGO. Reproduced with permission from Ref. [62], Copyright 2018, Elsevier

Table 2: Electrochemical performance of NiCo-based MOFs

Electrode Material	Specific Capacitance (Fg ⁻¹)	Retention (%)	Energy density (Whkg ⁻¹)	Power density (Wkg ⁻¹)	Refs.
NiCo ₂ -MOF	1070	91.1 % after 5k cycles	17.97	1075	[63]
NiCo-MOF//AC	1348	67 % after 10k cycles	46.6	800	[64]
Ni/Co-MOF 1-3	1230.3	92.1 % after 6k cycles	116	795	[65]
NiCo-MOF//AC	927.1	64.4 % after 200 bends	28.5	400.5	[66]
Ni ₂ Co-MOF//AC	1074.5 Cg ⁻¹	79 % after 5k cycles	66.1	800	[67]
NiCo-MOF: 8:2/rGO	113	97.7 % after 10k cycles	40	800	[68]
NiCo-MOF/rGO//AC	1320	90.6 % after 5k cycles	39.82	359.70	[69]
Co-Ni/rGO//3D rGO	5229	87.4 after 10k cycles	39.58	208.3	[70]

7. CONCLUSION

This review paper emphasizes the significant advancements in energy storage applications driven by Ni-MOF and Co-MOF nanoparticles. An in-depth examination of electrochemical performance of Ni-MOF and Co-MOF and their composite materials with conductive materials were carried out, with particular attention to the role of each component in improving the overall electrochemical efficiency. The scientific community is excited about the rapid progress being made in the development of agile and highly efficient Ni-MOF and Co-MOF-based nanocomposites for supercapacitor electrodes, foreseeing that the upcoming energy storage and conversion devices will be economically viable in the near future, contributing to solving global energy issues.

REFERENCES

- Hulla, J. E., Sahu, S. C., & Hayes, A. W. (2015). Nanotechnology: History and future. *Human & experimental toxicology*, 34(12), 1318-1321.
- Bhushan, B. (2017). Introduction to nanotechnology. *Springer handbook of nanotechnology*, 1-19.
- Silva, G. A. (2004). Introduction to nanotechnology and its applications to medicine. *Surgical neurology*, 61(3), 216-220.
- Roco, M. C. (2011). The long view of nanotechnology development: the National Nanotechnology Initiative at 10 years. *Journal of Nanoparticle Research*, 13, 427-445.
- Nasrollahzadeh, M., Sajadi, S. M., Sajjadi, M., & Issaabadi, Z. An introduction to nanotechnology. In *Interface science and technology 2019 Jan 1* (Vol. 28, pp. 1-27).
- Bayda, S., Adeel, M., Tuccinardi, T., Cordani, M., & Rizzolio, F. (2019). The history of nanoscience and nanotechnology: from chemical-physical applications to nanomedicine. *Molecules*, 25(1), 112.
- Newberry, D. (2020). The history of nanoscience and nanotechnology. In *Nanotechnology Past and Present: Leading to Science, Engineering, and Technology* (pp. 13-22). Cham: Springer International Publishing.
- Sadr, S., Lotfalizadeh, N., Ghafouri, S. A., Delrobaei, M., Komeili, N., & Hajjafari, A. (2023). Nanotechnology innovations for increasing the

- productivity of poultry and the prospective of nanobiosensors. *Veterinary Medicine and Science*, 9(5), 2118-2131.
9. Afolalu, S. A., Ogedengbe, T. S., Ikumapayi, O. M., & Adediran, A. A. (2024, April). Nanotechnology, Nanomaterials And Composites–An Overview. In *2024 International Conference on Science, Engineering and Business for Driving Sustainable Development Goals (SEB4SDG)* (pp. 1-9). IEEE.
 10. Khan, I., Saeed, K., & Khan, I. (2019). Nanoparticles: Properties, applications and toxicities. *Arabian journal of chemistry*, 12(7), 908-931.
 11. Findik, F. (2021). Nanomaterials and their applications. *Period. Eng. Nat. Sci*, 9(3), 62-75.
 12. Hou, Y., Hu, W., Gui, Z., & Hu, Y. (2017). Preparation of metal–organic frameworks and their application as flame retardants for polystyrene. *Industrial & Engineering Chemistry Research*, 56(8), 2036-2045.
 13. Abánades Lázaro, I., Chen, X., Ding, M., Eskandari, A., Fairen-Jimenez, D., Giménez-Marqués, M., ... & Forgan, R. S. (2024). Metal–organic frameworks for biological applications. *Nature Reviews Methods Primers*, 4(1), 42.
 14. Jin, H. G., Zhao, P. C., Qian, Y., Xiao, J. D., Chao, Z. S., & Jiang, H. L. (2024). Metal–organic frameworks for organic transformations by photocatalysis and photothermal catalysis. *Chemical Society Reviews*, 53(18), 9378-9418.
 15. Yang, H., Zhu, L., Zhou, Y., Xu, T., Zheng, C., Yuan, Z., & Si, C. (2024). Engineering modulation of cellulose-induced metal–organic frameworks assembly behavior for advanced adsorption and separation. *Chemical Engineering Journal*, 155333.
 16. Mohsenpour Tehrani, M., & Chehrizi, E. (2024). Metal–Organic-Frameworks Based Mixed-Matrix Membranes for CO₂ Separation: An Applicable-Conceptual Approach. *ACS Applied Materials & Interfaces*, 16(26), 32906-32929.
 17. Wang, X., Ma, T., Ma, J. G., & Cheng, P. (2024). Integration of devices based on metal–organic frameworks: A promising platform for chemical sensing. *Coordination Chemistry Reviews*, 518, 216067.
 18. Garg, N., Deep, A., & Sharma, A. L. (2024). Recent trends and advances in porous metal-organic framework nanostructures for the electrochemical and optical sensing of heavy metals in water. *Critical Reviews in Analytical Chemistry*, 54(5), 1121-1145.
 19. Yuvaraj, A. R., Jayarama, A., Sharma, D., Nagarkar, S. S., Dutttagupta, S. P., & Pinto, R. (2024). Role of metal-organic framework in hydrogen gas storage: A critical review. *International Journal of Hydrogen Energy*, 59, 1434-1458.
 20. Wei, K., Shi, Y., Tan, X., Shalash, M., Ren, R., Faheim, A. A., ... & Ge, S. (2024). Recent development of metal-organic frameworks and their composites in electromagnetic wave absorption and shielding applications. *Advances in Colloid and Interface Science*, 103271.
 21. Xu, W., Wu, Y., Gu, W., Du, D., Lin, Y., & Zhu, C. (2024). Atomic-level design of metalloenzyme-like active pockets in metal–organic frameworks for bioinspired catalysis. *Chemical Society Reviews*.
 22. Jiang, Z. W., Gong, X., Wang, Y., Li, Y. F., & Huang, C. Z. (2024). Engineering metal-organic frameworks-based nanozymes for enhanced biomimetic catalytic sensing. *TrAC Trends in Analytical Chemistry*, 117862.
 23. Khafaga, D. S., El-Morsy, M. T., Faried, H., Diab, A. H., Shehab, S., Saleh, A. M., & Ali, G. A. (2024). Metal–organic frameworks in drug delivery: engineering versatile platforms for therapeutic applications. *RSC advances*, 14(41), 30201-30229.
 24. Vikal, A., Maurya, R., Patel, P., Paliwal, S. R., Narang, R. K., Gupta, G. D., & Kurmi, B. D. (2024). Exploring metal-organic frameworks (MOFs) in drug delivery: A concise overview of synthesis approaches, versatile applications, and current challenges. *Applied Materials Today*, 41, 102443.
 25. Mohan, B., Gupta, R. K., Pombeiro, A. J., & Ren, P. (2024). Advanced luminescent metal–organic framework (MOF) sensors engineered for urine analysis applications. *Coordination Chemistry Reviews*, 519, 216090.
 26. Zhang, Z. C., Gu, Z. G., & Zhang, J. (2024). Host–Guest Metal–Organic Frameworks-Based Long-Afterglow Luminescence Materials. *Molecules*, 29(13), 2989.
 27. Jie, B., Lin, H., Zhai, Y., Ye, J., Zhang, D., Xie, Y., ... & Yang, Y. (2023). Mechanism, design and application of fluorescent recognition based on metal organic frameworks in pollutant detection. *Chemical Engineering Journal*, 454, 139931.
 28. Li, C., Yuan, Y., Yue, M., Hu, Q., Ren, X., Pan, B., ... & Zhang, Q. (2024). Recent advances in pristine iron triad metal–organic framework cathodes for alkali metal-ion batteries. *Small*, 20(23), 2310373.
 29. Chettiannan, B., Dhandapani, E., Arumugam, G., Rajendran, R., & Selvaraj, M. (2024). Metal-organic frameworks: a comprehensive review on common approaches to enhance the energy storage capacity in supercapacitor. *Coordination Chemistry Reviews*, 518, 216048.
 30. Letchumanan, I., Wani, A. A., Shaari, N., Beygisangchin, M., Kamarudin, S. K., & Karim, N. A. (2024). Metal–Organic Frameworks as a Catalyst and Catalyst Support in Fuel Cells: From Challenges to Catalytic Application. *Chemical Engineering & Technology*, 47(11), e202300580.
 31. Kitagawa, S., & Matsuda, R. (2007). Chemistry of coordination space of porous coordination polymers. *Coordination Chemistry Reviews*, 251(21-24), 2490-2509.
 32. Ding, M., Flaig, R. W., Jiang, H. L., & Yaghi, O. M. (2019). Carbon capture and conversion using metal–

- organic frameworks and MOF-based materials. *Chemical Society Reviews*, 48(10), 2783-2828.
33. Tomic, E. A. (1965). Thermal stability of coordination polymers. *Journal of Applied Polymer Science*, 9(11), 3745-3752.
 34. Hoskins, B. F., & Robson, R. (1990). Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related frameworks [N(CH₃)₄][CuI₂ZnII(CN)₄] and CuI[4, 4', 4'', 4'''-tetracyanotetraphenylmethane] BF₄·x C₆H₅NO₂. *Journal of the American Chemical Society*, 112(4), 1546-1554.
 35. Yaghi, O. M., & Li, H. (1995). Hydrothermal synthesis of a metal-organic framework containing large rectangular channels. *Journal of the American Chemical Society*, 117(41), 10401-10402.
 36. Kondo, M., Yoshitomi, T., Matsuzaka, H., Kitagawa, S., & Seki, K. (1997). Three-Dimensional Framework with Channeling Cavities for Small Molecules: { [M₂(4, 4'-bpy)₃(NO₃)₄]·xH₂O }_n (M = Co, Ni, Zn). *Angewandte Chemie International Edition in English*, 36(16), 1725-1727.
 37. Kim, D., Liu, X., Oh, M., Song, X., Zou, Y., Singh, D., ... & Lah, M. S. (2014). Isorecticular MOFs based on a rhombic dodecahedral MOP as a tertiary building unit. *CrystEngComm*, 16(28), 6391-6397.
 38. Bour, J. R., Wright, A. M., He, X., & Dincă, M. (2020). Bioinspired chemistry at MOF secondary building units. *Chemical Science*, 11(7), 1728-1737.
 39. Huang, C. W., Nguyen, V. H., Zhou, S. R., Hsu, S. Y., Tan, J. X., & Wu, K. C. W. (2020). Metal-organic frameworks: preparation and applications in highly efficient heterogeneous photocatalysis. *Sustainable Energy & Fuels*, 4(2), 504-521.
 40. Harasim, P., & Filipek, T. (2015). Nickel in the environment. *Journal of Elementology*, 20(2).
 41. Khokhar, S., Chand, P., & Anand, H. (2023). Recent advancements in Ni-MOF template derived electrode materials for supercapacitor application: A mini review. *Results in Chemistry*, 101298.
 42. Hamilton, E. I. (1994). The geobiochemistry of cobalt. *Science of the total environment*, 150(1-3), 7-39.
 43. Slack, J. F., Kimball, B. E., & Shedd, K. B. (2017). *Cobalt* (No. 1802-F). US Geological Survey.
 44. Tian, D., Wang, C., & Lu, X. (2021). Metal-organic frameworks and their derived functional materials for supercapacitor electrode application. *Advanced Energy and Sustainability Research*, 2(7), 2100024.
 45. Sundriyal, S., Kaur, H., Bhardwaj, S. K., Mishra, S., Kim, K. H., & Deep, A. (2018). Metal-organic frameworks and their composites as efficient electrodes for supercapacitor applications. *Coordination Chemistry Reviews*, 369, 15-38.
 46. Liu, X., & Song, J. (2021, October). Metal-organic framework materials for supercapacitors. In *Journal of Physics: Conference Series* (Vol. 2021, No. 1, p. 012008). IOP Publishing.
 47. Xu, Y., Li, Q., Guo, X., Zhang, S., Li, W., & Pang, H. (2022). Metal organic frameworks and their composites for supercapacitor application. *Journal of Energy Storage*, 56, 105819.
 48. Patel, A., Patel, S. K., Singh, R. S., & Patel, R. P. (2024). Review on recent advancements in the role of electrolytes and electrode materials on supercapacitor performances. *Discover Nano*, 19(1), 188.
 49. Li, W., Zhao, X., Bi, Q., Ma, Q., Han, L., & Tao, K. (2021). Recent advances in metal-organic framework-based electrode materials for supercapacitors. *Dalton Transactions*, 50(34), 11701-11710.
 50. Díaz, R., Orcajo, M. G., Botas, J. A., Calleja, G., & Palma, J. (2012). Co₈-MOF-5 as electrode for supercapacitors. *Materials letters*, 68, 126-128.
 51. Choi, K. M., Jeong, H. M., Park, J. H., Zhang, Y. B., Kang, J. K., & Yaghi, O. M. (2014). Supercapacitors of nanocrystalline metal-organic frameworks. *ACS nano*, 8(7), 7451-7457.
 52. Manikandan, M. R., Cai, K. P., Hu, Y. D., Li, C. L., Zhang, J. T., Zheng, Y. P., ... & Wang, X. W. (2021). Influence of hydrothermal reaction time on the supercapacitor performance of Ni-MOF nanostructures. *Applied Physics A*, 127(6), 421.
 53. Khan, J., Ahmed, A., Saleem, M. I., & Al-Kahtani, A. A. (2024). Benzene-1, 4-dicarboxylic acid-based Ni-MOF for efficient battery-supercapacitor hybrids: Electrochemical behavior and mechanistic insights. *Journal of Energy Storage*, 100, 113455.
 54. Bhoite, A. A., Patil, K. V., Redekar, R. S., Patil, P. S., Sawant, V. A., & Tarwal, N. L. (2023). Solvothermal synthesis of binder free Ni-MOF thin films for supercapacitor electrodes. *Journal of Solid State Chemistry*, 326, 124192.
 55. Wang, G., Yan, Z., Wang, N., Xiang, M., & Xu, Z. (2021). NiO/Ni metal-organic framework nanostructures for asymmetric supercapacitors. *ACS Applied Nano Materials*, 4(9), 9034-9043.
 56. Ramachandran, R., Zhao, C., Luo, D., Wang, K., & Wang, F. (2018). Morphology-dependent electrochemical properties of cobalt-based metal organic frameworks for supercapacitor electrode materials. *Electrochimica Acta*, 267, 170-180.
 57. Zheng, Y., Zheng, S., Xu, Y., Xue, H., Liu, C., & Pang, H. (2019). Ultrathin two-dimensional cobalt-organic frameworks nanosheets for electrochemical energy storage. *Chemical Engineering Journal*, 373, 1319-1328.
 58. Zhou, P., Wan, J., Wang, X., Xu, K., Gong, Y., & Chen, L. (2020). Nickel and cobalt metal-organic-frameworks-derived hollow microspheres porous carbon assembled from nanorods and nanospheres

- for outstanding supercapacitors. *Journal of colloid and interface science*, 575, 96-107.
59. Liang, Y., Yao, W., Duan, J., Chu, M., Sun, S., & Li, X. (2021). Nickel cobalt bimetallic metal-organic frameworks with a layer-and-channel structure for high-performance supercapacitors. *Journal of Energy Storage*, 33, 102149.
 60. Chen, C., Wu, M. K., Tao, K., Zhou, J. J., Li, Y. L., Han, X., & Han, L. (2018). Formation of bimetallic metal-organic framework nanosheets and their derived porous nickel-cobalt sulfides for supercapacitors. *Dalton Transactions*, 47(16), 5639-5645.
 61. Wang, J., Zhong, Q., Xiong, Y., Cheng, D., Zeng, Y., & Bu, Y. (2019). Fabrication of 3D Co-doped Ni-based MOF hierarchical micro-flowers as a high-performance electrode material for supercapacitors. *Applied Surface Science*, 483, 1158-1165.
 62. Rahmanifar, M. S., Hesari, H., Noori, A., Masoomi, M. Y., Morsali, A., & Mousavi, M. F. (2018). A dual Ni/Co-MOF-reduced graphene oxide nanocomposite as a high performance supercapacitor electrode material. *Electrochimica Acta*, 275, 76-86.
 63. Bhoite, A. A., Sawant, V. A., & Tarwal, N. L. (2024). Solvothermal synthesis of Ni/Co-based metal-organic framework with nanosheets-like structure for high-performance supercapacitor. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 702, 134814.
 64. Yang, X., Zhang, X., Yang, N., Yang, L., Wang, W., Fang, X., & He, Q. (2023). NiCo-MOF Nanospheres created by the ultra-fast microwave method for use in high-performance Supercapacitors. *Molecules*, 28(14), 5613.
 65. Ren, F., Ji, Y., Chen, F., Qian, Y., Tian, J., & Wang, J. (2021). Flower-like bimetal Ni/Co-based metal-organic-framework materials with adjustable components toward high performance solid-state supercapacitors. *Materials Chemistry Frontiers*, 5(19), 7333-7342.
 66. Du, Y., Liang, R., Wu, J., Ye, Y., Chen, S., Yuan, J., ... & Xiao, P. (2022). High-performance quasi-solid-state flexible supercapacitors based on a flower-like NiCo metal-organic framework. *RSC advances*, 12(10), 5910-5918.
 67. Xu, F., Chen, N., Fan, Z., & Du, G. (2020). Ni/Co-based metal organic frameworks rapidly synthesized in ambient environment for high energy and power hybrid supercapacitors. *Applied Surface Science*, 528, 146920.
 68. Huang, S., Shi, X. R., Sun, C., Zhang, X., Huang, M., Liu, R., ... & Xu, S. (2022). Template-controlled in-situ growing of NiCo-MOF nanosheets on Ni foam with mixed linkers for high performance asymmetric supercapacitors. *Applied Surface Science*, 572, 151344.
 69. Salunkhe, A. D., Pawar, P. S., Pagare, P. K., & Torane, A. P. (2024). Facile solvothermal synthesis of Ni-Co MOF/rGO nanoflakes for high-performance asymmetric supercapacitor. *Electrochimica Acta*, 477, 143745.
 70. Wu, H., Li, S., Liu, Y., Mu, Q., & Shi, Y. (2024). Dual metal MOF derived Co-Ni/rGO as cathode material with synergetic effect for an asymmetric supercapacitor with enhanced performances. *Journal of Energy Storage*, 84, 110864.