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Review Article

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Role of metal-organic frameworks (MOFs) in electrochemical energy storage devices including batteries and supercapacitors

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Abstract: Better energy storage systems are becoming more and more in demand as electric cars, portable electronics, and renewable energy sources become more prevalent. Supercapacitors and batteries, such as lithium-ion batteries (LIBs), sodium-ion batteries (NIBs), lithium sulfur/air batteries, and lithium selenium batteries, are major components of these technologies; yet, stability, cycle life, and energy density are some of the challenges they face. MOFs have emerged as a new material that can solve the problems with unique structural properties. Large surface area and porosity are properties of MOFs which improve the energy density, life cycle and stability of energy storage devices when MOF are used as alectrode material in these devices.This paper analyzes and focuses on the application of MOFs in supercapacitors, LIBs, and SIBs, in which it emphasizes improvement in terms of stability and performance. This review article ends with an overview of the important challenges and the prospects for future research to fully meet the promise of Metal organic frameworks in energy storage applications.

Keywords: MOFs; energy storage devices; Na-ion batteries; Li-ion batteries; Li–O_2 batteries; supercapacitors

1 Introduction

Global energy needs have significantly increased as a result of the fast economic growth, while severe environmental pollution and resource shortages have worsened due to the exploitation of fossil fuels. In order to address these energy and environmental issues, research into renewable energy sources and environmental battery technology has become a global priority. To lessen the energy danger, a number of rechargeable energy storage systems, such as supercapacitors, lithium-ion batteries, lithium-sulfur batteries, and sodium-ion batteries, have been created. A type of materials known as MOFs, which have a three-dimensional, highly porous structure, are made up of metal ions or clusters bound to organic ligands. These materials are distinguished by their high surface area, adjustable porosity, and capacity to accommodate a wide range of guest molecules in their pores. MOFs can improve the performance of electrolytes, anodes, and cathodes in energy storage devices such as lithium-ion batteries due to their special structural characteristics. They are also used in sensing, catalysis, gas storage, and other fields.[1–9] MOFs that are chemically stable, especially those that remain stable in aqueous, basic, and acidic environments, as well as in the investigation of their potential uses in a number of developing environmental, food safety and energy storage applications. Stable MOFs can be obtained by different strategies given below.

(a) Assembling high-valent metals (hard acid, like Zr^{4+}, Al^{3+}) with carboxylate ligands (hard base) for acid-stable MOFs;
(b) Combining low-valent metals (soft acid, like Co^{2+}, $Ni^{2+)}$ with azolate ligands (soft base, like pyrazolate) for alkali-resistant MOFs;
(c) Improving building unit connectivity;
(d) Rigidifying or contracting the ligand;
(e) Raising the framework's hydrophobicity; and
(f) Replacing unstable building units with stable ones (like metal metathesis) to produce robust MOFs.[10–15]

Because lithium-ion batteries and sodium-ion batteries share a similar chemistry and there are many salt sources in nature,

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SIBs are considered an inexpensive alternative to battery technology for possible electrical power systems.[16–19] Furthermore, because of their excellent power density, extended cycle life, and cost-effectiveness, supercapacitors have received a lot of attention and are frequently used in electric vehicle and aircraft systems.[3,20,21] It has shown tremendous potential to overcome current barriers in supercapacitors, LIBs, and SIBs by using MOFs.[22,23] Further improving these batteriesperformance and safety is the application of MOFs as solid electrolytes or stabilizing agents. In order to construct the energy storage devices previously indicated, electrode materials are essential and are currently the subject of intensive research.[15,24–27] Through the process of intercalation & DE intercalation chemistry, LIBs, SIBs collect and release energy. Supercapacitors are powered by the action of ion adsorption and desorption in an electrolyte.[28–30] MOFs can boost energy storage capacity in supercapacitors by offering high surface area electrodes that expedite ion transport. Thus, the criteria for electrode materials used in LIBs, SIBs, and supercapacitors are outstanding electrical conductivity, large surface area and desired pore size.[31,32] It has been proposed that MOFs, which have low density and large specific surface area, are very promising materials for the development of next-generation rechargeable batteries and supercapacitors. These special properties of MOFs allow for enhanced electrochemical performance, which makes them good candidates for advanced electrode applications; their structural flexibility allows for the optimization of charge storage and conductivity, which greatly increases the lifespan and efficiency of energy storage devices. As Figure 1 illustrates,

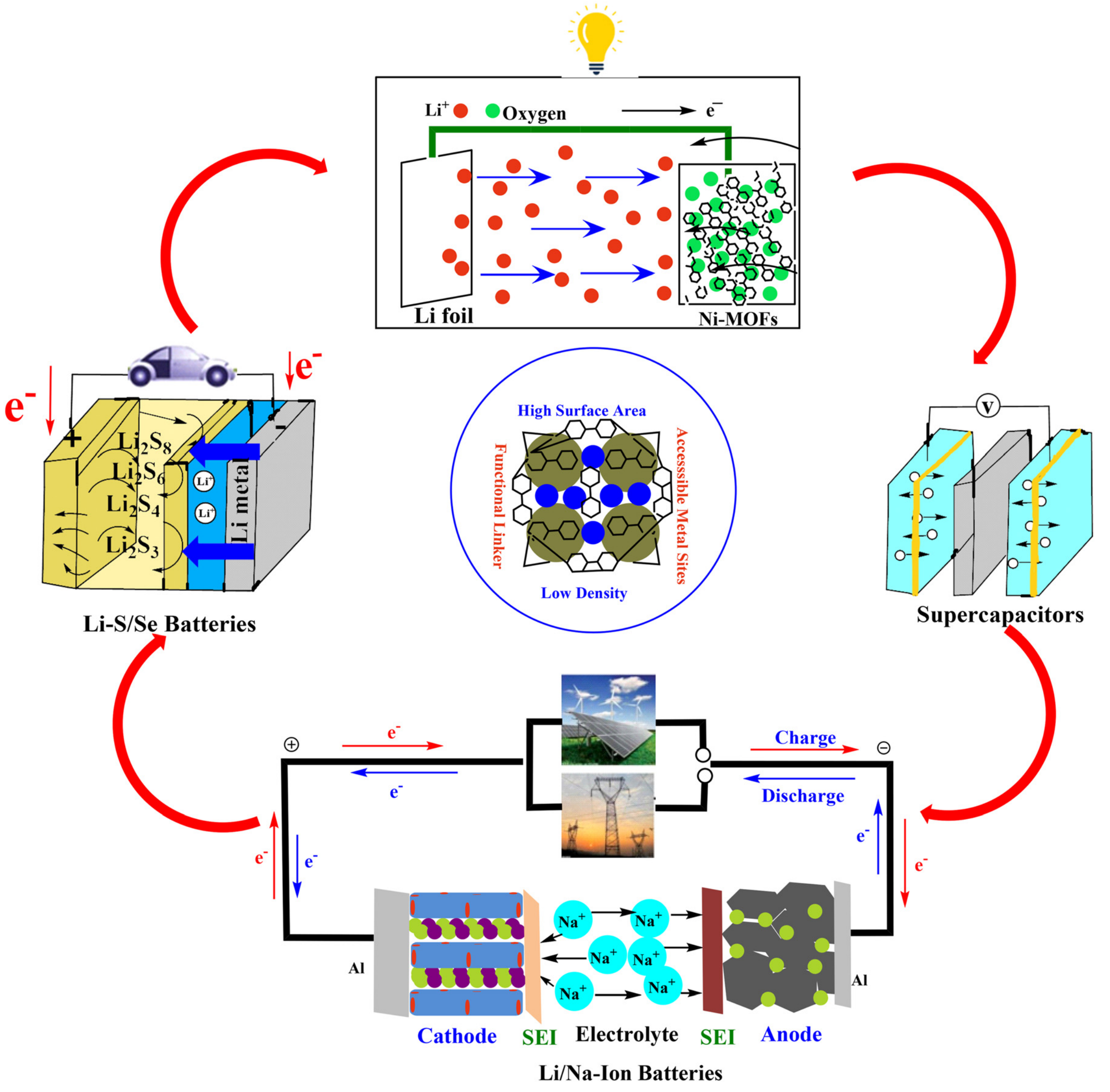

Figure 1: An overview of MOFs' function in electrochemical energy storage systems, including supercapacitors, Li–S/Se batteries, and Li/Na-ion batteries. Redrawn on ChemDraw ultra 21.0 from source.[47,48]

the potential of MOFs in this context highlights their role in spurring innovation in energy storage technologies and paving the way for more effective, sustainable solutions in the field.[33–36] Batteries possess an excellent energy density, but a low power density. Supercapacitors, on the other hand have low energy density and high power density. By choosing certain metal sites and modifying their pore widths, MOFs may be made more suitable for the requirements of the applications for which they are designed.[37–39] The chemical interaction between metal sites and functional linkers in MOFs and polysulfide improves by the cycling performance of Li-SB.[40–42] Because MOFs exhibit catalytic activity in both biological linkers and metal centers, they are superior electrodes material for higher-energy density Li–O_2.[43–46]

2 Modern battery technologies using MOFs

2.1 Parts of lithium ion batteries

An electrolyte, an anode electrode and cathode electrode are the three main parts of LIBs. When LIBs are charging, lithium ions are released from the cathode electrode. After that, lithium ions that have been de intercalated pass through electrolyte and intercalate at anode electrode. In the course of this process, LIBs acquire and retain energy.[49–52] Lithium ions return to the cathode electrode during LIBs discharging, which releases the energy that the LIBs have stored. Anode and cathode materials have been the subject of several investigations. The major weaknesses of the typical electrode materials lie in short cyclability, low energy/power density, and difficult synthesis process.

2.2 Role of MOFs as electrode material in Li-ion batteries

Because of their great surface area, distinct structural characteristics, developed porosity, and high lithium storage capacity, metal-organic frameworks are therefore becoming more and more attractive options for lithium-ion battery electrode materials. Such a large surface area makes it much easier for the ions in the electrolyte to interact. In return, it enhances charge transfer rates as well as the general performance of the battery. Moreover, due to its unique architecture, MOFs make it easy for lithium ions to diffuse through because of their requirement in fast cycles of charging and discharging. They are particularly very effective at optimizing energy density owing to their tunable porosity, which may change for maximum storage capacity among lithium ions. Long-term study and improvement of such materials with MOFs can significantly enhance the life cycle and effectiveness of lithium-ion batteries.[53–55] Metal cations and ions can be introduced or removed from MOFs in an efficient and reversible manner. MOFs are active sites for redox reactions. Fe^{3+} $(OH)_{0.8}F_{0.2}[O_2–C–C_6H_4–CO_2]$ was reported by de Combarieu et al.[56] as a cathode material by reversibly injectings Li^+ into MIL-53(Fe). MOFs are suitable cathode materials for LIBs because, as per the experimental results, they enable up to 0.6 Lithium/Iron III to intercalate into MIL-53(Fe) at C/40 without causing structural changes. MOFs can be employed as LIB anode materials in addition to cathode materials. A basic solvothermal technique was used by Maiti et al.[57] to create Mn-1,3,5-benzenetricarboxylate MOFs (Mn-BTC MOFs). A crucial function for the Li^+ insertion/extraction is performed by the COO groups in Mn-BTC MOFs (Figure 2). Electrochemical properties and MOF-based electrode material for Lithium ion batteries shown below in Table 1.

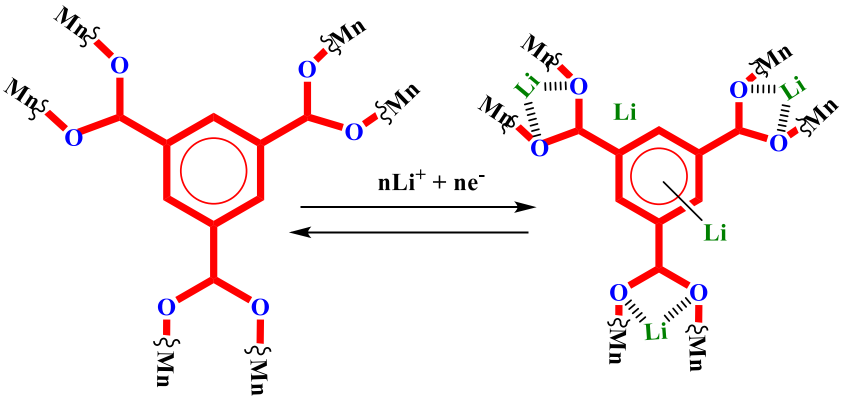

Figure 2: Li + insertion/extraction sites for Li coordination on the Mn-BTC MOF organic fraction are given. Redrawn on ChemDraw ultra 21.0 from source.[57]

Table 1: MOF-based electrodes material for LIBs and their basic electrochemical properties.

Sr. No	MOFs	1st Discharge capacity (mAh g $^{-1}$)	Overall charge capacity (mAh g $^{-1}$)	Current density(mAh g $^{-1}$)	Cycles	Ref.
1	UiO-66	118	<85	38.8	100	58
2	Fe-BTC MOF	1,765	1,021	100	100	59
3	MOF-177	400	105	50	50	60
4	Ni-BDC MOF	1,984	620	100	100	61
5	Co-BTC MOF	1,739	750	100	200	62
6	Ti-MOF	1,590.4	296	200	200	63

The highly specific capacity of 694 mAh g^{-1} that was produced, along with around 83 percent capacity retention over hundred cycles at 103 mAg^{-1}, showed that Mn-BTC MOFs had exceptional electrochemical performance.[57,64] Presented by Lin et al.[65] the bimetallic (BMOF) exhibited remarkable chemical and thermal stability and was both hydrophobic and polar functionalized. It was shown that pores in BMOF were the main source of lithium ion storage. The high specific capacity of BMOF was also attributed to the N atoms in the amine groups.[66–68]

As a result, increasing BMOF's particular area of surface, volume of pores, and reactive nitrogen-rich functionality content can boost its specific capacity even further using 3,3,5-tetramethyl-4,4-bipyrazole (H_2Me_4bpz) and Nickel chloride hexahydrate in a solvent-based reaction, a flexible multilayer MOF based on nickel (Ni–Me_4bpz: $C_{20}H_{24}Cl_2N_8Ni$) was created by An et al.[69] For a framework with repeating quadrilateral units and a lower energy state, there is flexibility in the rotation of adjacent pyrazolate rings. (Figure 3a and b). Furthermore, the vertex and edge action from the Ni(II) ion and H_2Me_4bpz ligands results in a sql topology (Figure 3c).[70,71]

The reason for NiMe_4bpz's initial specific capacity of 320 mAh g^{-1} at 50 mA g^{-1} and its sustained performance of 120 mAh g^{-1} over 100 cycles was its layered structure, flexibility and more stability.[71,73] Han et al. state that a hydrothermal reaction and subsequent annealing process were used in order to produce metallic-1,4,5,8 naphthalenetetracarboxylates (Metal = Li or Ni).[72,74] The chemical stability of metal-organic frameworks, known commonly as MOFs, is significantly restricted by increasingly more challenging barriers that arise in the intricate and complex electrochemical environment associated with lithium-ion batteries, known as LIBs. In order for LIBs to cycle effectively and efficiently in a variety of practical applications, it is, therefore, of utmost importance to greatly value and prioritizes the, thermal, structural and chemical stabilities of MOFs. Furthermore, electrical conductivity determines the particularity and rate performance of MOFs. Ideal electrode materials for LIBs are MOFs with conductive qualities and stability.[75–77]

2.3 Role of MOFs in lithium sulfur batteries (LSBs)

Lithium sulfur batteries (LSBs) are gaining popularity because they have a greater energy density and specific capacity than LIBs that are sold commercially. The commercialization of lithium-sodium batteries, or LSBs for short, is beset with a number of major obstacles arising from the

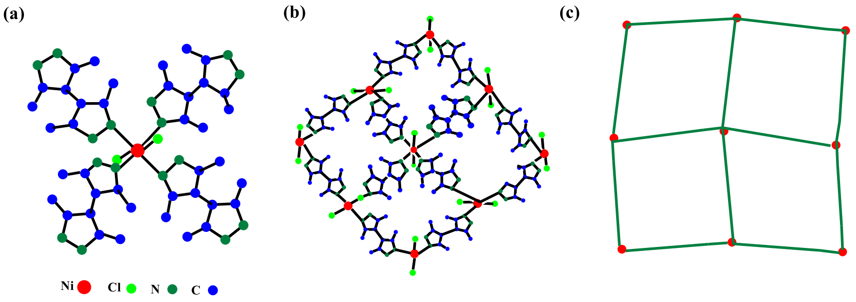

Figure 3: The MOF (Ni–Me4bpz) crystal structure's coordination mode, planar structure, and sql topological structure are depicted in (a), (b), and (c), respectively. Blue is C, dark green is N, light green is Cl, and red is Ni. Redrawn on Chemdraw ultra 21.0 from source.[69,72]

considerable discrepancies between the theoretical capacity and the actual capacity seen in real-world applications. These problems become worse by inadequate energy density and inadequate cycle stability, both of which are essential components of battery performance. Sulfur is a plentiful and non-toxic mineral, so adding it to the mixture is one viable way to overcome these challenges. By adding sulfur, battery manufacture may be able to lower its manufacturing costs, which would increase its marketability.[15,78] Lithium-sulfur batteries (LSBs) are particularly noteworthy among the top contenders for advanced energy storage technologies because of their superior characteristic features. One of the most impressive features of these batteries is their large specific capacity, which has a maximum capacity of 1,675 mA h g^{-1}. This means that LSBs have a large energy storage capacity relative to their weight, which makes them ideal for lightweight and efficient power sources for a variety of applications. In addition to their large capacity, LSBs have an impressive energy density that can reach up to 2,600 W h kg^{-1}. Because of their increased energy density, LSBs can be more powerful for longer periods of time, it makes them excellent for several applications like as electric cars and portable devices. LSBs have the potential to be crucial for the development of energy storage technologies going forward as research and development continue. These features position LSBs as a type of secondary battery with considerable potential. Its positive electrode is sulfur and its negative electrode is lithium. LSBs have become the most significant next-generation batteries because sulfur is an inexpensive, abundant, and environmentally beneficial material.[79–81] Combining antiferroelectric perovskite dimethyl ammonium zinc type MOFs with conductive carbon nanotubes results in a powerful molecular filter that reduces polysulfide (PS) migration in LSBs.[9,32,82–85] The composite MOF-based electrode exhibits an impressive specific capacity of 1,260 mA h g^{-1}, at a current rate of 0.05 °C and at 0.1 °C it continues to function well with a specific capacity of 1,007 mA h g^{-1}. It further demonstrates extremely low degradation by losing its capacity of 0.07 % after 120 cycles with a S loading of 5 mg cm^{-2}. These findings demonstrate the electrode's exceptional efficiency and stability, which make it a viable option for cutting-edge energy storage applications. The processing ability of the LSBs based on a hierarchically porous TiO_2–S cathode demonstrates much greater coulombic efficiency and specific capacity.[86–89] It is reported that the newly developed TiO_2–S hybrid cathode has a diffusion rate of Li-ions approximately 17 times smaller than Li-ion diffusion due to Titinium-Sulphur chemical bonding that occurs in the charge/discharge process.[90–92] The N-doped dual carbon conducting network encapsulated Ni/Co bimetallic phosphides prepared by high-temperature phosphorization and annealing of the Ni-ZIF-67 precursor. LSBs functioning flawlessly with the cells, an initial rating of 1,083.44 mA h g^{-1} at 0.5 °C outstanding cycle durability, with an approximate rate of degradation of about 0.09 % per cycle for 300 cycles.[93–95]

To help the lithium polysulfide (LiPS) surface-mediated reaction, a carbon nanocage made of a nitrogen-rich metal-organic framework and strengthened with an iron single atom catalyst (FeSA-CN) is added. This advanced catalyst effectively stores and distributes energy, as indicated by its exceptional specific capacity of 1,123 mA h g^{-1} at a current density of 0.2 °C. Furthermore, at a significantly higher current density of 4.0 °C, the FeSA-CN/S electrode has remarkable rate capability, yielding 605 mA h g $^{-1}$. Its remarkable low capacity loss maintaining only 0.06 % degradation each cycle over 500 cycles highlights its durability and efficiency in battery applications. The FeSA-CN/S electrode is a strong contender due to its great performance and stability for next-generation energy storage technologies.[96,97] Li–S battery is shown schematically in Figure 4. When used as a separator, nickel-based hexa-iminotriphenylene MOFs improved overall conductivity and showed a strong capacity to absorb for lithium polysulfides." The 2D structure of these MOFs has an enormous specific surface area and an organized microporous. The manufacturing of $Ni_3(HITP)_2$/PP, a separator utilized in lithium sulfur batteries, is shown in Figure 4 above.[98–100]

2.4 Role of MOFs in lithium-air batteries ($Li–O_2$)

An very promising candidate for lithium-ion batteries that provides a remarkable energy density is an oxide cathode paired with a lithium metal anode. By storing more energy and delivering larger capacities, this design improves LIBs overall performance. This design, as seen in Figure 5, demonstrates the advantages of mixing cutting-edge materials to maximize battery longevity and efficiency. The utilization of oxide cathodes enhances the electrochemical characteristics, and the lithium metal anode provides a means of storing more energy, thereby making this arrangement a viable path for further advancements in energy storage technology.[39,101,102] For example, Co_3O_4 carbon microfibers hybrids made from ZIF-9 by thermal treatment and electrospinning show exceptional durability and work as LAB cathodes, which suggest that they may find use in electrical energy storage systems.[103–106]

Characterization of Cobalt-10/MCu-BTC in an aprotic $Li–O_2$ battery reveals that mesopores enhance the capacities at discharge with around 7,000 mA h g^{-1}. This is due to

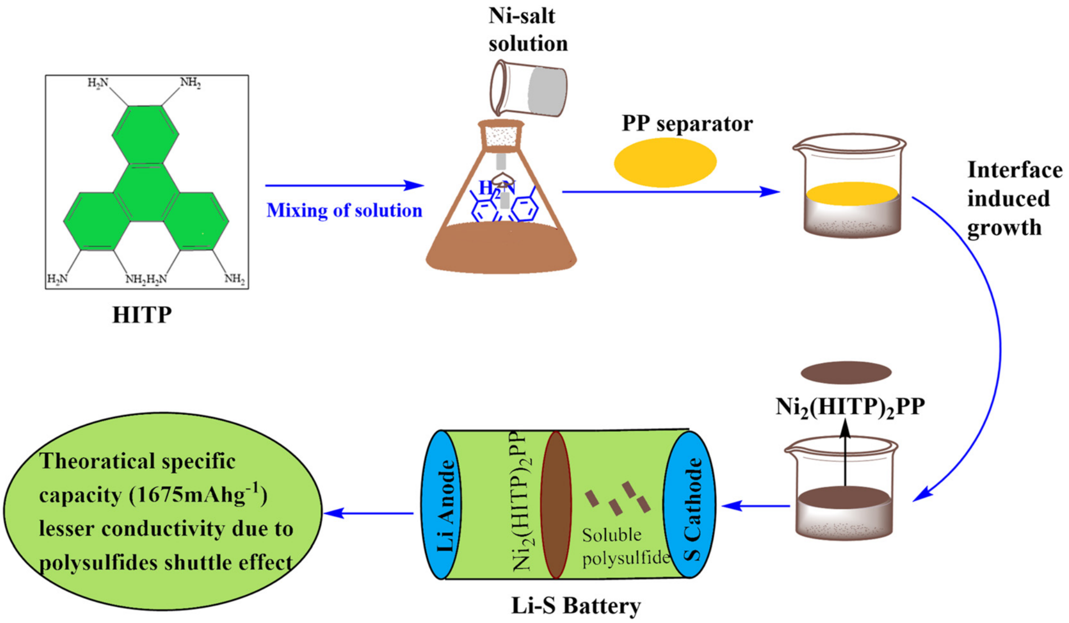

Figure 4: Schematic of MOFs in Li–S batteries. Redrawn on ChemDraw ultra 21.0 from source.[98]

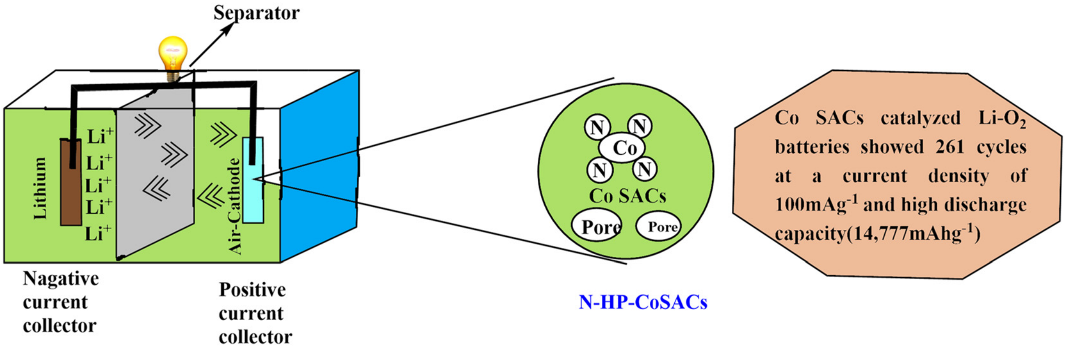

Figure 5: Role of MOFs in Li–O_2 battery. Redrawn on ChemDraw ultra 21.0 from source.[107]

electrolytic attack and mass as well as charge transfer by these pores that offer a larger area to store the discharge product.[108–110] By the use of electrospinning and post-thermal processing, a standalone binder-free ZIF-9 Co_3O_4/carbon microfiber composite was produced that will be used as a cathode in non-aqueous Li–air battery. Carbon nanofiber composites made of Co_3O_4 have exceptional performance in energy storage applications, having a capacity for initial discharge above 760 mA h g^{-1}. On the other hand, discharge capacity of pure carbon nanofiber, is much lower only 72 mA h g^{-1}. This notable variation emphasizes the improved electrochemical qualities that the Co_3O_4 component imparts, which are essential for raising the composite material's overall capacity and efficiency. By incorporating Co_3O_4, energy storage capacity is increased and new materials that can satisfy the increasing needs of high-performance energy devices can be developed.[78,105,111] The conductive metal organic framework (c-MOF) is distinguished by its ability to induce the formation of nanocrystalline Li_2O_2 with amorphous areas. Direct charge transfer provides an extended cycle life (100–300 cycles) having a minimum charge potential of 3.7 V, extended capacity (1,000–2,000 mA h g^{-1}) and high current densities (1–2 A g^{-1}).[105,107,112]

2.5 Role of MOFs in sodium ion batteries (SIBs)

Because they are inexpensive and in high demand worldwide, SIBs are used extensively in the development of consumer gadgets and electric cars. Figure 6displays the sodium

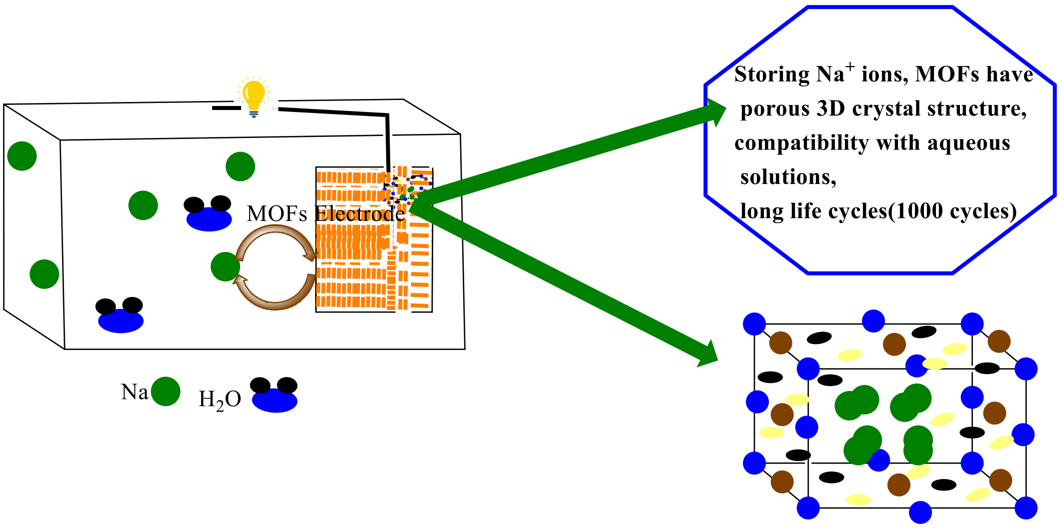

Figure 6: Shows role of MOFs in Na-ion batteries. Redrawn on ChemDraw ultra 21.0 from source.[116]

ion battery that uses MOF as an electrode. Due to its seamless operation at room temperature, SIBs are becoming more and more important. Furthermore, SIBs are prospective LIB substitutes since sodium is highly available and requires less money for extraction, which is an advantage over LIBs. Lithium ion migration is a feature of LIBs, while sodium ion mobility characterizes SIBs. The essential elements and general structure of SIBs and LIBs, however, are very similar, notwithstanding this distinction. To improve the longer cycle life of SIBs, materials must include porosity. A new calcium metal organic framework could be effectively produced by an easy-to-use technique termed ion exchange. The produced calcium terephthalate ($C_8H_4CaO_4$) exhibits a voltage plateau of 0.5 V, which is adequate for storing sodium ions. When the current density is 0.2 A g^{-1}, it can also deliver a specific capacity of 235.2 mA h g^{-1}. The bimetallic Ni–Co-ZIF served as the first building block for the synthesis of Ni-doped Co/CoO/N-doped carbon (NC) composites.[17,113] As an anode material for sodium-ion batteries (NIBs), this Ni-doped Co/CoO/NC hybrid has shown remarkable performance, attaining a noteworthy capacity of 218 mA h g^{-1}at a high current density of 500 mA g^{-1}. Its remarkable cycling stability is demonstrated by the fact that, after 100 cycles, it maintains a discharge capacity of 218.7 mA h g^{-1}or about 87.5 % capacity retention. Furthermore, the composite makes use of a nitrogen-enriched microporous carbon substrate that comes from zeolitic imidazolate framework-8, which contains microscopic amorphous red phosphorus. At a current density of 0.15 $mAhg^{-1}$, P@N-MPC composite demonstrated an extraordinary reversible specific capacity of 600 $mAhg^{-1}$. Furthermore, MOF-836 was used to synthesize monodispersed 30 nm Bi–Sb alloy nanoparticles; the antimony (Sb) content in MOF-836 was modified for precise compositional analysis. With a little loss of 0.055 % every cycle, the MOF-836 alloys' capabilities demonstrate remarkable retention, attaining 180.9 mA h g^{-1} at 1 A g^{-1} over 1,000 cycles [114,115]

Metal-organic frameworks were employed as the electrode in the development of an aqueous sodium-ion rechargeable battery. As seen in Figure 6, MOFs are the microscopic structure of the metal hexacyanometallate (NaP [R(CN_6)]), where P and R are transition metals.[117] Aonther example is the effective synthesis of a conductive single-crystal 2 dimentional nanoribbon Co-HITP MOF utilizes *in situ* sodiation-stimulated electrochemical rebuilding. A thin layer with a large layer disparity that resembles graphene assembles the 2 dimention nanoribbon as shown in Figure 7. Superior electrochemical performance is demonstrated by the conjugated single-crystal structure with high conductivity and the expanded layer spacing (high initial charge capacity of 576.6 mA h g^{-1}, superb rate performance, and ultra-long cycling stability of ≈0.001 % decay rate per cycle after 15,000 cycles at 8 A g^{-1}). This work not only establishes a framework for investigating the process of MOF sodium storage, but it also offers suggestions for creating novel long-cycle electrode materials.[117,118]

2.6 Role of MOFs in supercapacitors

Between conventional capacitors and secondary batteries, the supercapacitor, also known as electrochemical capacitor, is a special energy storage device. Supercapacitors have several advantages over normal capacitors because they

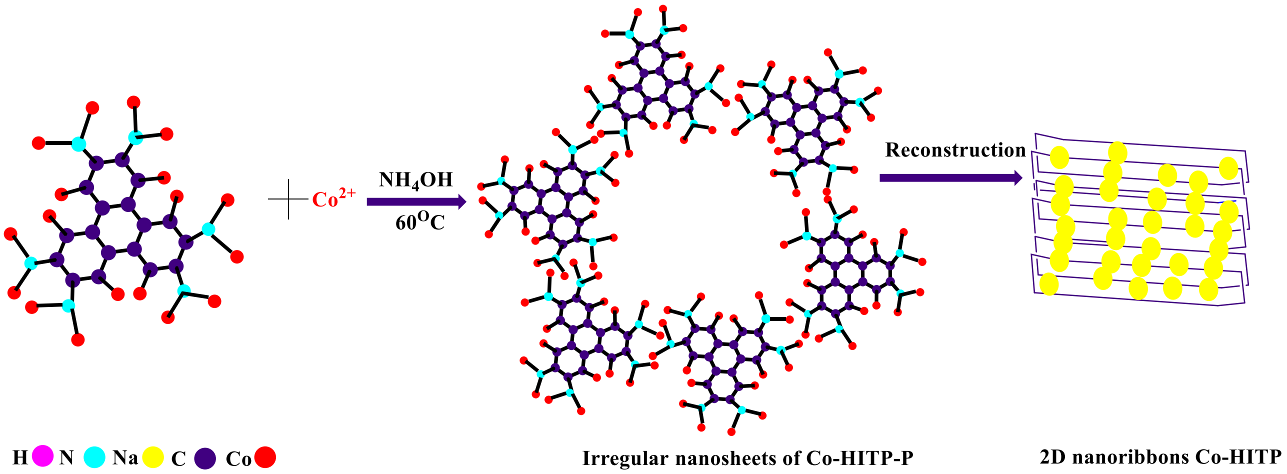

Figure 7: Synthetic procedure of Co-HITP MOF. Redrawn on ChemDraw ultra 21.0 errors and omissions are possible for more detail please see citation.[117]

combine the high power density of traditional capacitors with the high energy density characteristics of secondary batteries, including higher rate performance, excellent reliability, prolonged lifespan, and ecological sustainability.[119–121] Supercapacitors are currently extensively used in a variety of industries, such as the automotive and uninterruptible power supply sectors, and have garnered a lot of interest from both the academic and business worlds. In order to achieve capacitance storage, supercapacitors store energy in two main ways: the first step is the separation of charges that arise at the interface between electrolyte ions and electrode. Another technique for storing energy that the Faraday capacitor uses is a reversible redox reaction that occurs in bulk phase or on the electrode surface. These days, the electrode materials have a major influence on how well supercapacitors work. Owing to a number of benefits, carbon is currently the most popular electrode construction in the supercapacitor industry, such as being readily available, environmentally acceptable, having strong electrical conductivity and huge specific surface area.[119,122–125] Carbon materials require the proper pore size and a structure with a big specific surface area in order to achieve high capacitance. Due to the separation of ion charges in the electrolyte, carbon materials are able to store energy through the formation of a double layer of electrical charge on their outermost layer.[123,126,127] Even though certain organic precursors can be converted through physical or chemical activations into carbon materials with high specific surfaces, these carbons' pore structures frequently contain various defects that can cause kinetic issues with ions' transmission and lower the material's rate performance.[128–130] The materials that are highly porous and partially graphitized carbon have shown that they may increase the exploitation of a specific surface area, decrease high-rate polarization, and provide an electrode material that performs well for supercapacitors. The carbon materials made from MOFs are a good fit for the aforementioned specifications because they are porous and have regular nanopore structures and large specific surface areas that can be adjusted.[131–134] This provides a basis for the creation of highly active electrode materials.[135–137] Carbon materials generated from MOFs do, however, come with certain disadvantages. In the case of MOF precursors, for instance, the related carbon materials essentially preserve the microporous structure because they own the majority of the microporous structures.[138–143] As a result, the pore structure impedes the electrolyte ions' ability to diffuse and penetrate quickly, which reduces the effective contact area and performance. Recently, there has been an increasing trend in utilization of hollow porous carbon hybrids based on MOF precursors. The primary reason for this is that the region of contact between hollow porous carbon materials and solid microporous carbon materials is higher. As a result, the electrode's ionization transmission speed rises and its reaction kinetics are enhanced. It also adapts to volume fluctuations during operation.[144–146]

Zeolitic imidazolate framework-8 is a precursor that is commonly used in the production of porous carbon materials meant for use in supercapacitors. Its increased nitrogen content, which improves the electrochemical qualities of the resultant carbon compounds, is the main cause of this choice. ZIF-8 also has advantages in terms of synthesis ease, enabling more productive production methods. It's consistent and well-defined shape makes it easier to create homogeneous porous structures, which are essential for maximizing conductivity and charge storage in supercapacitors. These characteristics can be used by researchers to create sophisticated carbon materials that greatly

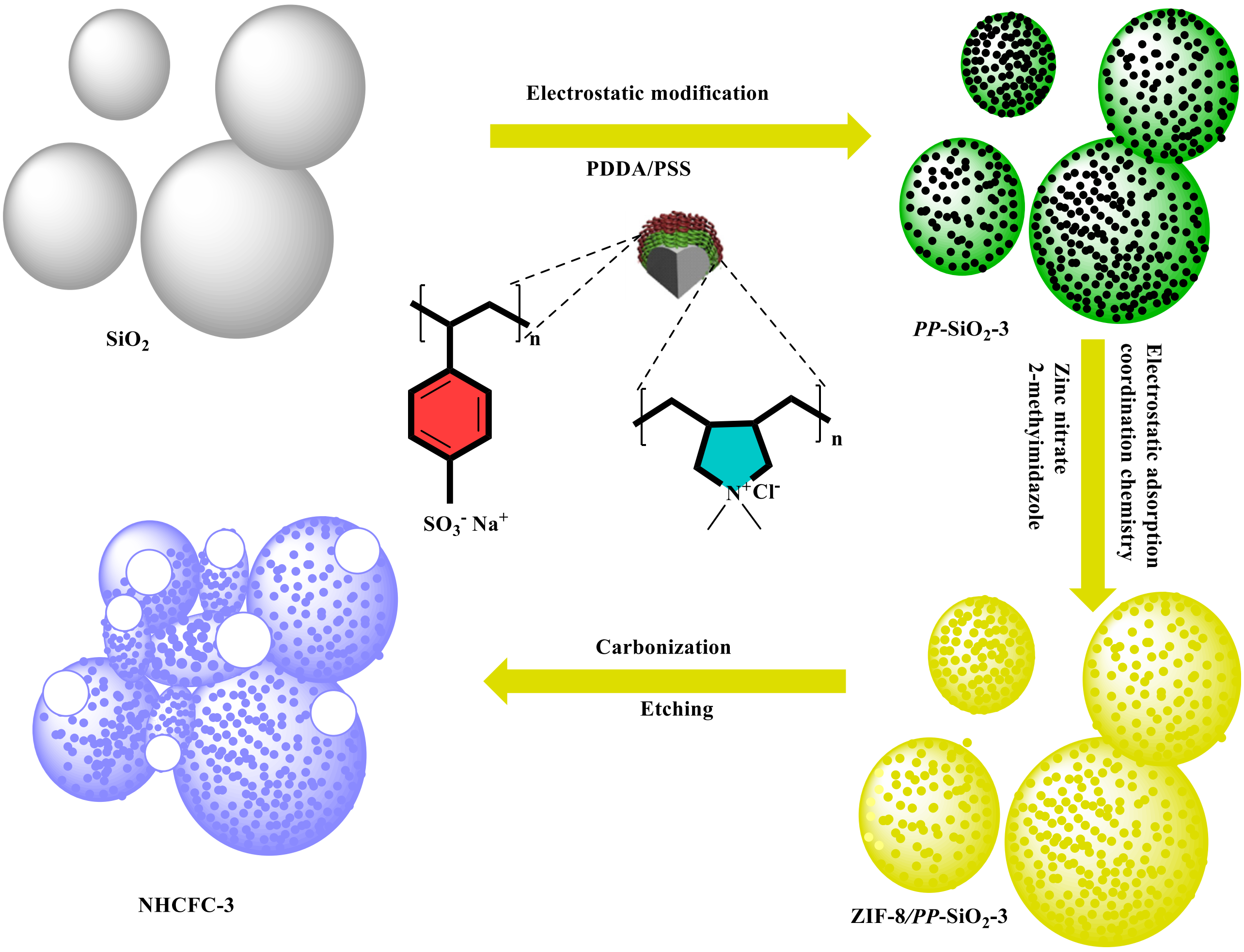

Figure 8: Illustrating how NHCSF-3 is made from ZIF-8/PP-SiO_2-3 precursor. Redrawn on Chemdraw ultra 21.0 and errors are possible, for more details please see citation.[148]

increase the effectiveness and performance of energy storage devices.For example, Li et al. synthesized ZIF-8 on the surface through the deposition in Figure 8below where an electrolyte-modified silicon dioxide is taken as a template.[147]

A hollow carbon shell after removing the template and carbonization process, a nitrogen-doped framework was produced. After 20,000 cycles, the generated carbon material showed a particular capacitance retention rate of 92.1 %, indicating that it could find use as a material for electrodes for supercapacitors. Maintaining an electrode's specific capacitance at 79 % could be achieved with a current density of 1.0 A g^{-1}, resulting in an enhanced current density of 50.0 A g^{-1} it reached 253.6 F g^{-1}. Furthermore, a symmetrical supercapacitor made with this carbon material produced from ZIF-8 showed a high voltage of 1.6 V and an energy density of 13.3 Wh kg^{-1} in a 1 molL^{-1} Na_2SO_4 electrolyte. ZIF-8 nanoparticles were successfully dispersed in a polyacrylonitrile (PAN) solution dissolved in N,N-dimethylformamide (DMF) by Wang et al.[149] to create a composite fiber. They then prepared a hybrid fiber with ZIF-8 and PAN. The composite thus obtained was subjected to high-temperature carbonization to yield one-dimensional nitrogen-doped porous carbon fibers (NPCF). During carbonization, the ZIF-8 nanoparticles transformed into hollow cubic shells, which bonded tightly to the 1D carbon fibers formed as a result of the pan pyrolysis. This novel technique optimizes the electrochemical properties of the fiber while enhancing their structural integrity, thus rendering them ideal candidates for application in a wide array of energy storage devices, among them supercapacitors. The electrochemical performance of NPCF far surpassed that of the pure carbon material obtained from ZIF-8 as a result of its characteristic 1D hollow fiber structure. Due to large value of conductivity NPCF is a very strong contender to advance supercapacitor technology and improve energy storage application performance. Under the current density, the specific capacitance was 332 F g^{-1} at 1.0 A g^{-1}, and after 5,000 cycles, the capacitance retention rate was 98.9 %. Later, zeolite imidazole framework-8 and PAN were utilized as precursors by Chen et al.[150] who also prepared nitrogen-doped carbon fibers with hollow nanoparticles by electrospinning. The supercapacitor displays remarkable specific capacitance values when its electrode material is nitrogen-doped porous carbon fibers (NPCF). The specific capacitance of the supercapacitor can exceed 307.2 F g^{-1} at the current density of 1.0 A g^{-1}. The high capacitance of the electrode implies that a substantial amount of electrical energy may be stored by it. The supercapacitor retains a good specific capacitance of 193.4 F g^{-1} even at a higher current density of 50.0 A g^{-1}. The NPCF electrode's remarkable stability and rate capability are proven by the retention of a significant capacitance at various current densities, suggesting that this material is a viable choice for high-performance energy storage applications. At 25,000 Wkg^{-1}, the highest energy density is 10.96 Wh kg^{-1}. After 10,000 cycles at a current density of 5.0 A g^{-1}, the loss rate was only 1.8 %, fiber electrode also demonstrated exceptional cycling stability. Apart from the standard nitrogen atom doping, the addition of sulfur, phosphorus, and other heteroatoms can also enhance the hydrophilicity of carbon materials. For instance, Zhu et al.[151] used the dual-solvent method to introduce thiourea into MIL-101-NH_2, afterwards, pyrolyze the entire mixture in an inert environment to produce porous carbon composites that are co-doped with sulfur and nitrogen and resemble hollow nanocapsules. The carbon materials multiphase pore structure, which is made up of macropores, mesopores, and micropores, is essential to improving its electrochemical performance. The variety of pore design provides an efficient contact area to the electrode-electrolyte, facilitating a rapid charge transfer. It allows electrolyte ion entry through macropores while increasing surface area for charge storage via meso pores and micro pores that enhance ion diffusion kinetics. This complex way of pores thus gives ease and provides great battery and supercapacitor applications in terms of superior electrochemical properties for the carbon material. With superior contact area and good charge transfer processes through that macroscale configuration, it seems that energy will be better overall. The supercapacitor electrode recorded a specific capacitance of 240 F g^{-1} at a current density of 10 A g^{-1}. Utilizing the ionic liquid as an electrolyte, the cell's energy density was 46.7 Wh/kg, while its power density was 8250 W/kg. Zhang et al., have developed a new, carbon-based material called ZIF-8@PZS-C. The S, P and N doping of a hollow polyhedral porous carbon proceeded well following carbonization and acid washing. Acid washing and carbonization with a painstaking method were developed for the synthesis of this new substance. The conversion of the precursor into porous carbon during carbonization allows for three important dopants-nitrogen, phosphorus, and sulfur-to be incorporated into the carbon framework. Such dopants boost its electrochemical properties making it amenable for energy storage uses. Due to its large surface area and efficient ion transport, the facade of a hollow polyhedral shape enhances its performance considerably. The promise of customized carbon materials for cutting-edge uses in batteries and supercapacitors is highlighted by this synthesis method. The surface of ZIF-8 nanoparticles was grown with organic polymers to achieve this. ZIF-8@PZS-C demonstrated an enhanced hydrophilic surface, increased conductivity, and a larger specific surface area when compared to ZIF-8-C, the pure ZIF-8-derived carbon material.[148,152,153] The specific capacitance of ZIF-8@PZS-C material was found higher than that of ZIF-8-C, irrespective of the sweep speed, which indicated better work of ZIF-8@PZSC as a double-layer capacitor. The ZIF-8@PZS-C material exhibited remarkable cyclic stability, as evidenced by its constant current charge-discharge curve, which remained essentially unchanged after 10,000 cycles at current density of 10.0 A g^{-1}. These exceptional qualities are mostly the result of numerous heteroatom doping and the unique structure working together effectively.[148,154,155]

2.6.1 Nanoporous carbon as electrode material in supercapacitors

The production of nanoporous carbon for use as an electrode material in electric double-layer capacitors (EDLCs) was first accomplished in 2008 by Xu's research group using zinc-based metal-organic framework MOF-5.[84,156–158] A significant reason in the success of this novel technology in energy storage applications was the production of nanoporous carbon, which has an amazing surface area of 2,872 m^2 g^{-1}. Carbon-based EDLCs possess high electrochemical characteristics such as great surface area, which contain nature because of charge stabilization and ion mobility too. The discovery exercised made way for a formation of a more promising dating on optimization and inquisition of carbon-based materials for a number of energy storage mechanisms, while it is also pointed to the possibilities of the metal-organic frameworks in creating complex electrode materials. Specific capacitance between room temperature was found to be 258 Fg^{-1} at the current density of 25.0 mAg^{-1}. Again, various experiments were performed to examine how particular surface area, electrical conductivity, and pore size distribution of MOF-5 were influenced by raising its carbonization temperature from 530 to 1,000 °C. In brief, the goal of this work was to gain insight into the structural and functional changes that nanoporous carbon material underwent when systematically rising the carbonization temperature. Elevated temperature certainly will increase carbonization, leading to increased specific surface area and thus even greater charge storage capacity. This work is also aimed at assessing temperature effects for the conductivity, which is one of the crucial components of efficient electrode performance in energy storage applications. The porosity of materials is essential to observe how these ions diffuse through the materials and lead to the electrochemical performance of the resulting carbon electrodes. In terms of carbon material optimization for supercapacitors and other energy storage devices, this study presents insightful discussions. The porous carbon produced under high-temperature conditions from MOF-5 had excellent conductivity, high mesoporosity, and good electrochemical performance.[159,160] In the present study, vapor-injected furfuryl alcohol into the MOF-5 pores was taken to be the carbon precursor. This sets the framework for thorough infiltration and subsequent polymerization. Other carbon precursors, used in a different study, were carbon tetrachloride, ethylenediamine, and phenolic resin, which were further varied in structure and texture of MOF-5. In this manner, the electrochemical performance properties of materials have been enhanced by generating a range of pore topologies. The characteristics of the resulting carbon compounds can be customized by researchers using various precursors, making them ideal for particular applications in energy storage and catalysis. This innovation demonstrates the versatility of MOFs as platforms to fabricate complex porous carbon structures.[161–165] The electrochemical performance of porous carbon in both organic and aqueous electrolytes was studied. The resulting mesoporous network carbons demonstrated strong performance and capacitance stability ratios with regard to both organic and aqueous electrolytes. In particular, capacitances were obtained of $156\ \mathrm{F\ g^{-1}}$ for organic electrolytes and $271\ \mathrm{F\ g^{-1}}$ for aqueous electrolytes. When it comes to energy storage, these materials showed remarkable gravimetric energy densities of $9.4\ \mathrm{Wh\ kg^{-1}}$ for organic electrolytes and $31.2\ \mathrm{Wh\ kg^{-1}}$ for aqueous electrolytes. The materials' potential for effective energy storage in a variety of applications is indicated by their high energy densities. These mesoporous carbons' adaptability and efficiency point to their potential for usage in cutting-edge supercapacitors and emphasize their capacity to improve energy storage technologies in a variety of settings. Moreover, zeolite-type MOFs have demonstrated significant promise for the production of porous carbons. ZIF-8 can be directly carbonized at varying temperatures to produce nanoporous carbon.[166–168] Both the surface area and micropore volume increase with increasing annealing temperature. The resulting samples capacitances were clearly increased with greater carbonization at higher temperatures when their electrochemical performance was assessed in 0.5 M H_2SO_4 aqueous solutions.[169,170] Furfuryl alcohol was used as an extra carbon source for ZIF-8 in a different investigation. When used as an electrode in electric double-layer capacitors (EDLCs), this material showed remarkable specific capacitances of $200\ \mathrm{F\ g^{-1}}$ at a current density of $250\ \mathrm{mA\ g^{-1}}$. This remarkable performance was attributed to the synthesis process, which produced an incredibly significant surface area of $3{,}405\ \mathrm{m^2\ g^{-1}}$. The high surface area of the electrode material contributes to its overall effectiveness by improving charge storage capacity and facilitating efficient ion transport. These results highlight the possibility of combining furfuryl alcohol with ZIF-8 to produce improved carbon composites for high-efficiency energy storage uses. Future developments in this area could lead to more effective supercapacitors. Furthermore, ZIF-7 has been modified with various carbon sources, including glucose, ethylene glycol, glycerol, and furfuryl alcohol. The glucose-modified ZIF-7 achieved the largest specific capacitance of $228\ \mathrm{F\ g^{-1}}$ at current rate of $0.1\ \mathrm{A\ g^{-1}}$, the best sustained rate capability of $178\ \mathrm{F\ g^{-1}}$ at current rate of $10\ \mathrm{A\ g^{-1}}$, and the highest stable cycling, maintaining 94 % of the capacitance after 5,000 cycles.[171–173]

It was believed that the carbon obtained from glucose assisted in the removal of remaining Zn impurities, inhibited the development of macropores, and produced structures resembling graphene, all of which improved the electrochemical performance. Some research has concentrated on the design of the particular structure of porous carbon frameworks due to the significance of the pore's influence [170,174–176] ZIF-8, which was produced by ultrasonication, was carbonized to create 3D hierarchical porous carbon frameworks containing micro, meso and macropores. Here, interconnecting small holes inside larger ones help buffer ions to reduce the electrolytes diffusion lengths to the inner surfaces, which improves ion mobility and charge storage even more.[176–178] Yu et al.[179] have published another outcome that is comparable. Figure 9 illustrates the method of creating porous carbon with bimodal porosity. The precursor contained silica colloids that were integrated either inside or in between aggregated crystals. Mesopores were formed together with the creation of micropores from intrinsic ZIF-8 following an annealing process and silica removal. After 2000 cycles, the hierarchical porous carbon shows excellent capacitance retention (92–97 %), low resistance, and high capacitance. A seed-mediated growth method has been used to create core–shell ZIF-8@-ZIF-67 nanocomposites as shown in Figure 9a, which merge the features of the distinct ZIF-8 and ZIF67 MOFs Figure 10(b).[176] The benefits and drawbacks of ZIF-8 and ZIF-67 are displayed in Figure 10(a) and (b), respectively. The scientists produced

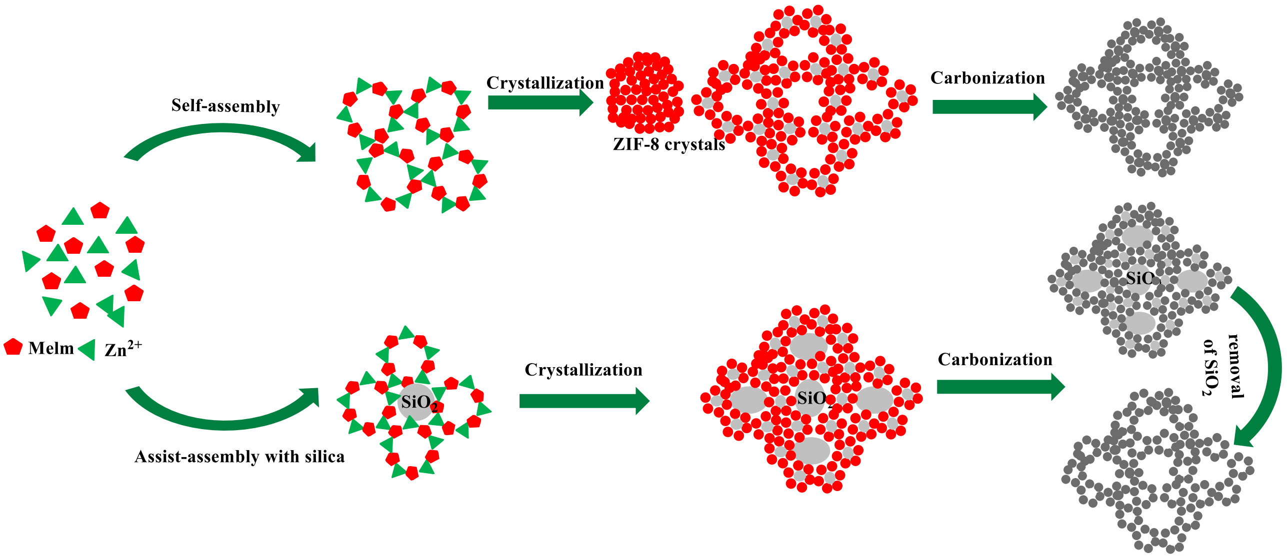

Figure 9: Shows the seed-mediated growth method of creating porous carbon with bimodal porosity. Redrawn on Chemdraw ultra 21.0 errors are expected for more details please see citation.[179]

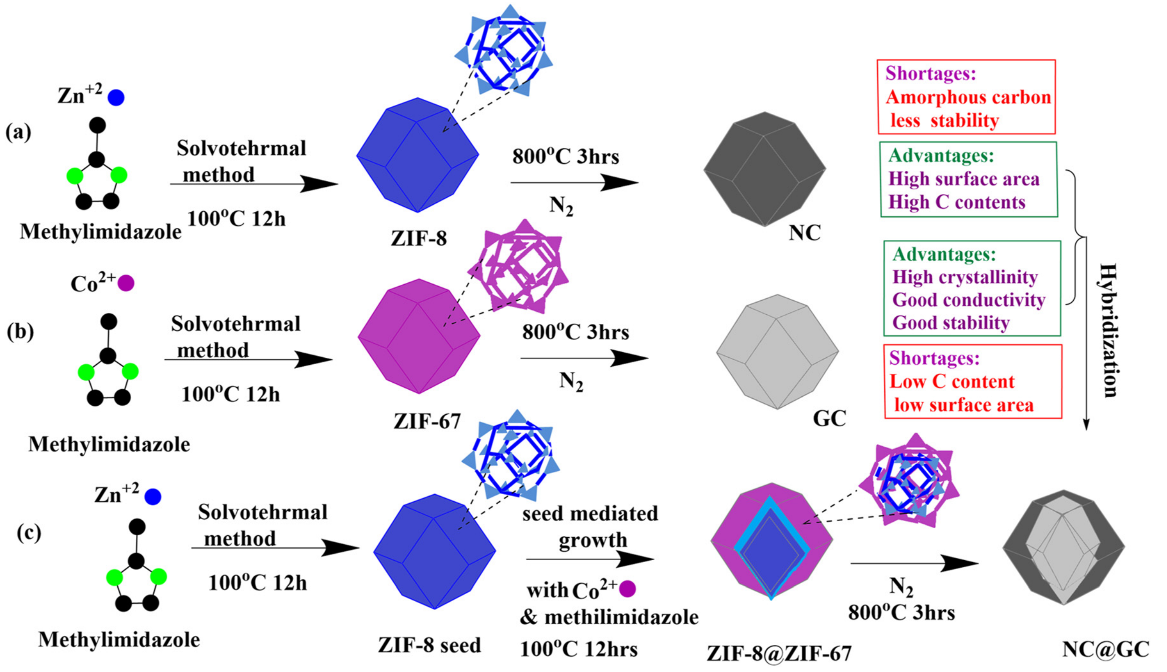

Figure 10: (a) Schematic synthesis of ZIF-8 crystals and NC, (b) synthesis of ZIF-7 crystals and GC, (c) illustrates core-shellZIF-8@ZIF-67 crystals and NC & GC. Redrawn on ChemDraw ultra 21.0 and errors are possible, for more details please see citation.[176]

functionalized nanoporous hybrid carbon materials containing highly graphitic carbon (GC) as the shell and nitrogen-doped carbon (NC) as the cores from ZIF-8 and ZIF-67 crystals after thermally treating the ZIF8@ZIF-67 crystals. The hybrid carbon material effectively combines the advantages of graphene (GC) and nitrogen-doped carbon (NC), with an ideal capacitance of 270 F g^{-1}. By combining the advantages of nitrogen doping's pseudocapacitive effects with graphene's high surface area and conductivity, this synergy enables the hybrid to attain improved electrochemical performance. Thus, the hybrid material provides increased stability and cycle performance in addition to increasing charge storage capacity. These developments demonstrate the possibility of creating sophisticated electrode materials that can greatly improve energy storage devices and make them appropriate for a range of contemporary technological applications.[177,178,180–183]

2.6.2 MOFs as electrode material for supercapacitors

Supercapacitors have gained increased interest due to high power and extended life cycle, as one of the most requiring energy storage technologies. Electrical double-layer supercapacitors (EDLCs) are one type of supercapacitor that typically uses high surface area and porosity carbon materials. Nonetheless, EDLCs have very poor energy densities and physical charge storage capacities.[126,184,185] Higher energy density pseudocapacitive materials as well as electrically active elements like transition-metal oxides and sulfides have gained popularity in recent years. It is possible and of advantage to apply supercapacitors containing huge surface areas, nanostructures, and tunable porosity in MOFs and their derived nanomaterials. In turn, MOFs make wonderful models and starting points for the production of metal oxides or sulfides and porous carbon, used in electrodes of double-layer electric capacitors and pseudocapacitors. MOFs porosity, large surface area and wide range of metal ions make them suitable for direct usage as supercapacitor electrode materials, much as how they are employed in LIBs. Cobalt 8-MOF-5 ($Zn_{3.68}Co_{0.32}O(BDC)_3(DEF)_{0.75}$) was first reported as an electrode for EDLCs in its early stages. Following that, researchers investigated the use of an alternative Co-based MOF sheet for supercapacitors. This specific capacitance reached 206.76 F g^{-1} and lost just 1.5 % of its capacitance after 1,000 cycles, this film demonstrated good pseudocapacitive performance.[127,186–189] Additionally, the same group has presented findings.[190,191] By using three distinct organic ligands with varying molecular lengths, pore size of Co-based MOFs was adjusted. The maximum capacitance, surface area, and pore size were all higher in the MOF with a longer organic linker [Co(bpdc)$(H_2O)_2$]H_2O, bpdc¼ 4,4-biphenyldicarboxylic acid]. A continuously connected microstructure resembling a leaflet with fewer structural interfaces is responsible for the improved electrochemical performance. In a separate study, the Wei group has shown how to create a multilayer Ni-based MOF electrode for use in supercapacitors. This design showed a high value of capacitance and rate capability of 1,127 and 668 F g^{-1} at speeds of 0.5 and 10 A g^{-1}, respectively, and design was stable during cycling. Recently, varied reaction temperatures were used to synthesize a new Zr-based MOF (UiO-66), which displayed variable degrees of crystallization and particle sizes.[192] At a scan rate of 5 mVs^{-1}, the sample obtained at 50 °C had the highest specific capacitance of 1144 F g^{-1} and the lowest particle size. A set of different distinct MOFs with a range of structural kinds, including MOF-5, nHKUST-1, nUiO-66, nMOF-177, nNi-MOF-74 and nMOF-867, were created by Yaghi's lab. About six times the capacitance of commercial activated carbon was demonstrated by the zirconium MOF (nMOF-867) among them, with areal and stacking capacitance values of 5.09 and 0.64 mF cm^2. MOFs can be employed right away to make the electrode materials for supercapacitors, as previously shown. Desired electrochemical properties can be obtained in MOFs with regulated particle and pore diameters by carefully selecting metal ions, organic linkers, and reaction conditions. Even though studies on the use of MOFs in supercapacitors remain in their early stages, more investigation is still required.[193–195]

2.6.3 Types of MOFs used in supercapacitors

2.6.3.1 Role of ZIFs based material in supercapacitors

Zeolitic imidazolate frameworks are a different class of metal-organic frameworks. Imidazolate ligands, being organic linkers, are linked with metal ions for the formation of these compounds. ZIFs, due to the unique structural attribute, offered a good combination of the tunability of MOFs with stability of natural zeolites, thus producing such materials with a remarkable surface area and porosity. Their unique composition makes ZIFs useful for a number of tasks, such as gas storage, catalysis, and building blocks for synthesizing porous carbon materials.[196,197] ZIFs have great versatility in Materials Science and Engineering because of their superb tunability for researchers to further adjust specific purposes through metal ions and organic linkers. They have some features and topologies similar to those of traditional inorganic zeolites, yet differ in others. Particularly as materials for electrodes in supercapacitors, the ZIFs and the material generated from them have garnered a great deal of attention lately because of their commercialization potential, adaptability, and modularity. The main starting materials of ZIFs for use in supercapacitors are ZIF-67 and ZIF-8, both of which have a sodalite framework. Sodalitenets are often the most prevalent due to the extensive variety of Metal-O-Metal angles present in zeolite MOFs, which create favorable circumstances for the formation of multi-structured derivatives. ZIF-8 is a commercially available, easily synthesized compound with strong thermal stability, and is made of zinc and methylimidazole.[198–200]

2.6.3.2 Role of Uio-66 in supercapacitors

The terephthalic organic ligands Zr 6 [$Zr_6O_4(OH)_4$] and Zr 12 provide these conventional UiO (Zr-terephthalic MOF) materials. The three-dimensional microporous architecture of

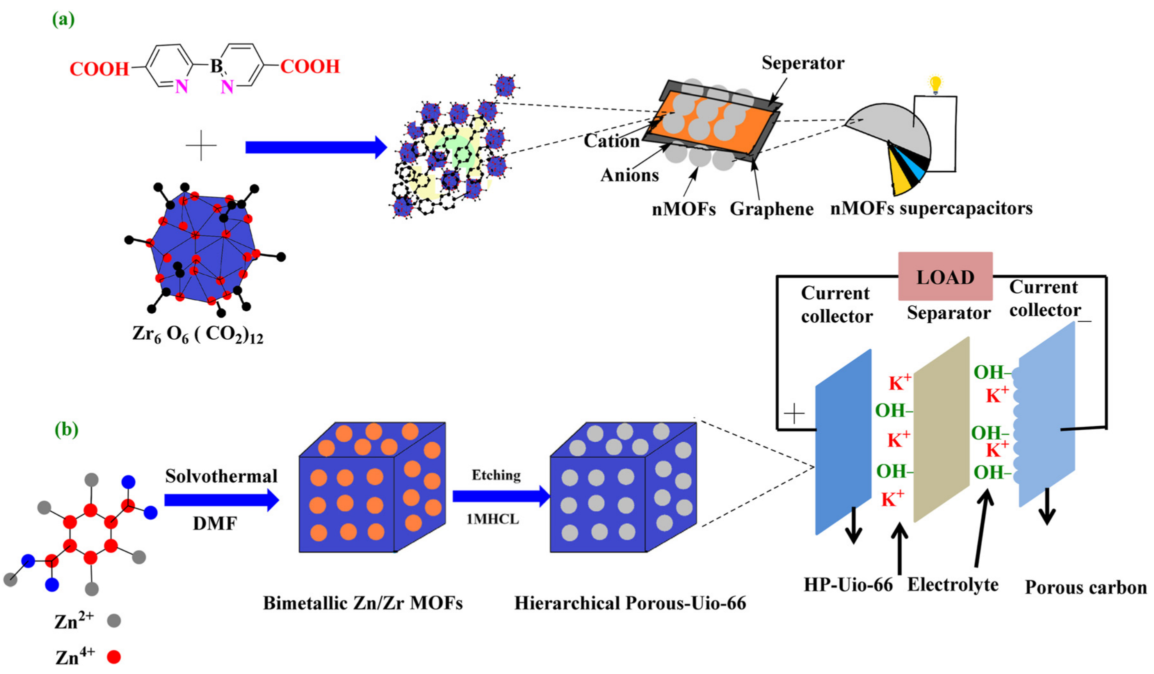

Figure 11: (a) Shows synthesis and designing of nMOF-867. HP-UiO-66 and PC/HP-UiO-66 ACS production processes are shown in Fig. (b). Redrawn on ChemDraw ultra 21.0, and errors are possible for more detail please see citations.[204]

this material consists of eight tetrahedral angle cages and an octahedral center cage. Because of its remarkable water durability and electrochemical activity, UiO-66 has garnered the most interest among these compounds. An analogous structure to UiO-66 has been found in a Zr-based nMOF-867 by Yaghi et al. It can reach real capacitance of 5.085 mF cm^{-2}, or about six times higher than the capacitance commonly available activated carbons used as supercapacitor standards. Moreover, it has a high stacking capacity of 0.644 F cm^{-3}. In Yaghi's study, films on Ti substrates were formed using a mix of several nMOFs and graphene, producing a coin-type supercapacitor for testing. One separating membrane was then positioned in between each of the two films (Figure 11a**)**. Other well-known MOFs, such as MOF-5, MOF-74, UiO-66, MOF-808, HKUST-1, MOF177, and ZIF-8 related materials, were also comprehensively considered in this work to help direct future research on MOF selection for supercapacitors. The test parameters were constant for each MOF. A specific capacitance of 849 F g^{-1} was demonstrated by hierarchically porous Zr-MOF, HP-UiO-66, at an applied current density of 0.2 A g^{-1}. To produce a bimetallic Zn/Zr MOF, their HP-UiO-66 was first synthesized. To produce the hierarchical porous structure, the Zn-MOF was later removed Figure 11b. Ni foam was coated with slurry including PVDF, conductive carbon black, and active components to create the working electrodes. At 240 W kg^{-1}, an aqueous ASC with an energy density of 32 W h kg^{-1} was created with porous carbon made from biomass acting as the negative electrode and as-synthesised HP-UiO-66 acting as the positive electrode. Using the method described in this paper, one can concurrently create mesopores and micropores in a hierarchical porous structure, which will improve the electrochemical efficiency of active substances by providing a sufficient number of surface flaws along with large specific surface areas.[201–203]

3 Challenges and future prospects

In the field of energy storage, Metal-Organic Frameworks are a state of art development that can improve stability and performance of sodium and lithium-ion batteries as well as supercapacitors. To completely achieve their potential, a few important obstacles must be overcome. A primary concern is the stability of MOFs in operational environments. Due to their sensitivity to moisture and ambient oxygen, many MOFs eventually experience degradation that negatively impacts both their structural integrity and functionality. Energy storage systems may not last as long as intended due to this instability, which reduces their appeal for industrial use. Low electrical conductivity remains another apparent problem limiting many metal-organic framework structures. Since this is a limitation, some sort of conductive additives should be added to alleviate this constraint. Unfortunately, the incorporation of such additives can render the synthesis process complicated and might result in lowered overall performance.

Additionally, the manufacture of MOFs remains difficult because the synthesis procedures remain complicated, costly, and time-consuming, thus hampering their mass manufacturing and commercialization. Compared to more conventional materials of energy storage, the market penetration capability of MOFs may be limited due to their complexity. Further issue for MOFs is the charge and discharge characteristics due to comparatively slow ion diffusion rates required for a battery and supercapacitance to achieve high efficiency. Challenges can be overcome through stabilization techniques, post-synthesis modifications, composite materials, and coating strategies.

With a multitude of ways to overcome these barriers, there is hope for the future of MOFs in energy storage. The invention of hybrid MOFs which integrate the advantages of organic frameworks and conducting materials is likely to happen indebtedness to the breakthroughs in material science improving their electrical conductivity and mechanical strength. In addition doping with sulphur, phosphorus and other heteroatom can enhance the hydrophilicity of carbon materials which can further improve the stability and have large capacitance at various current densities suggesting that this materials can be a viable choice for high performance energy storage applications. Another method is to enhance the conductivity of the material through doping with conductive materials such as graphene and optimizing the structure.

4 Conclusions

Metal-Organic Frameworks offer a promising way to improve the performance, power consumption efficiency and stability of energy storage devices, especially in lithium-ion, lithium sulphur, lithium air, sodium-ion batteries supercapacitors. Large surface area, tunable porosity and structural porosity makes them ideal for use in batteries technology. MOFs derived material which is being used recently as a solid electrode material in electrochemical energy storage devices significantly enhance the efficiency, charge discharge ability, energy conversion and life cycle of batteries and supercapacitors to a significant extent.

Notwithstanding the challenges pertaining to stability, conductivity, scalability, and ion diffusion, further research and development in the discipline of material engineering have the potential to successfully address these issues. As the field of energy storage prospects develops, MOF integration may be essential to developing more robust, long-lasting, and environmentally friendly energy storage systems, which will eventually assist to meet worldwide energy requirements and expand renewable energy technologies.

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Informed consent: Not Applicable.
Author contributions: KR: Drafting the work, UO: Analysis, AHR: Interpretation of data, AM: Analysis, MAI: Design of work & Final approval of the version to be published, MSA: Acquisition, GI: Interpretation of data, MAS: Revising it critically for important intellectual content, AR: Acquisition.
Use of Large Language Models, AI and Machine Learning Tools: Not Applicable.
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