

## **A REVIEW MOF BASED APPLICATION IN BATTERIES**

**Meena Devi**

[milunain46@gmail.com](mailto:milunain46@gmail.com)

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### **Abstract**

A group of hybrid inorganic and organic linkers that are all tightly coupled to metal ions make up the metal organic framework class of supramolecular solid materials. This class of compounds has attracted a lot of interest due to its larger surface area, variable pore size advantage, and diverse and attractive structure. The following review article has examined structural characteristics, classification, synthesis methods, numerous factors impacting synthesis and stability, properties, and applications. The discipline has recently made strides, and new research initiatives have been developed to investigate the potential uses and scope of MOFs. Super-capacitors and rechargeable batteries with high energy densities have shown a lot of interest in metal-organic frameworks (MOFs). This paper outlines their expanding diversity, chemical compositions, and molecularly-tunable structural variations. Additionally, it attempts to assess how their naturally porous structure affects electrical and ionic transportation during lithium-ion battery charging and discharging cycles. We have outlined the several synthesis routes used to create a specific metal-organic framework in this review. The utilization of viable anode and cathode materials for lithium-particle batteries (LIBs) made of metal-natural structures is generally examined in this paper, alongside an assessment of their impacts on cycle steadiness and release limit.

**Keywords:** Metal Organic Framework, coordination polymers, synthesis, Application in Batteries,

### **1. INTRODUCTION**

Metal particles or metallic groups act as the hubs in Metal Natural Structures (MOFs), a class of strong permeable materials, and polydentate natural ligands act as the linkers associating the hubs. Metal particles or metallic groups act as the hubs of association, and natural ligands interface the metal habitats through coordination bonds, bringing about one-, two-, or three-layered networks. The major primary qualities of MOFs are their high porosity, tremendous volume of pores, which can represent 90% or a greater amount of the translucent volume, enormous explicit surface region, and superb warm security because of the presence of solid bonds. The Isorecticular Metal Natural Structures (IRMOFs), a critical subclass of MOFs, were made interestingly by the Yaghi bunch [1].The foundation of the

archetypal IRMOF-1 was a network with a pcu topology composed of 1, 4-benzenedicarboxylic acid coupled to octahedral Zn-O-C clusters. The various organic linkers used in the series of IRMOFs, which maintain the pcu topology and have different pore volumes and surface areas, produce these differences. MOFs fall within the category of coordination networks, which in turn fall under the category of coordination polymers, as per the terminology formally adopted by IUPAC in 2013 [2]. Through the use of recurrent coordination entities, coordination networks can span one, two, or three dimensions. MOFs are dynamic systems whose structures can shift in response to external stimuli such as temperature and pressure; hence they are not necessarily crystalline.

The science of MOFs has progressed rapidly as of late, making it conceivable to alter the surface region, network geography, and pore size and shape to fit the MOFs' designs and properties to the requests of different applications. With the end goal of a thoroughly examined union of novel MOFs with wanted physical and substance properties as per Gem Designing standards, information on particle or potentially intermolecular cooperation's inside the three-layered game plan is fundamental. The coordination connections between metal particles and natural ligands are instances of atomic communications, rather than the frail associations intervened by intermolecular contacts. Many scientists have argued that, just as it is hard to regulate every aspect of a chemical reaction, so too does the carefully orchestrated synthesis of MOFs require ultimate command of every aspect of the materials and apparatus used. On the other hand, the case may be made for the intended synthesis of IRMOFs, which is founded on MOF-5 and yielded a substantial series of solids.

Critical effect on the primary qualities of MOFs is applied by elements like the mathematical properties, adaptability, and utilization of oligonuclear metal bunches as hubs (optional structure units, SBUs), the quantity of coordination calculations embraced by the metal particles, the job of the counterions, and the response dissolvable [3-7]. The organization geography and dimensionality of MOFs are inseparably connected to the different coordination calculations that the metal hubs can embrace, which shift with the electronic design of the metal particles. Progress metal particles, particularly those of the main column, lanthanides, and antacid earth metals, have been utilized for this reason as a result of the engineered and underlying variety they offer by righteousness of their tremendous scope of coordination numbers, calculations, and oxidation states. Since adaptable ligands offer a bigger number of levels of opportunity than unbending ones and can bring about startling gem developments [8], they are an ideal choice while building a MOF.

Natural mixtures with at least one N-giver or O-benefactor particles are by and large utilized as ligands to join the metal particles in MOFs. Carboxylates (either aliphatic or sweet-smelling with at least one rings), pyridyl (for instance, pyrazine and 4,4'-bipyridyl subordinates), cyano, polyamines created from imidazole, oxalic corrosive, and benzene, phosphonates, sulfonates, and crown ethers are probably the most frequently utilized ligands. To neutralize the positive charge of cationic MOFs, anions either direction to the metal particles or fill the pores of the supramolecular structure [9]. Natural cations are facilitated inside the pores of anionic MOFs and can be traded with different cations, very much like  $\text{Me}_2\text{NH}_2^+$  cations and solvate atoms are facilitated inside bio-MOF-1, which keeps up with its crystallinity in dissolvable trade tests and during the capacity and arrival of cationic medication particles [10]. Metal cations are normally organized to the first organization, changing its underlying angles [11], yet anionic metallic bunches require enormous permeable geographies and, in outstanding cases, can be traded by different cations for sensor applications. Through steric impacts, the response dissolvable can impact the organization engineering and crystallization energy. It can also fill metal ion coordination sites, seal MOF pores, and take part in weak intermolecular interactions that support the lattice's crystal and thermal stability.

## 2. Lithium-Ion Battery Development

Clinical embed innovation, the necessity for high-energy and high-power sources in military applications, and the dangerous development of the compact gadgets industry are factors pushing battery innovative work forward. The advancement of lithium-particle batteries throughout recent years is portrayed in Fig. 1. It records each huge strategy created to accomplish more prominent execution and expanded limit. Early 1960s medical equipment, such as pacemakers, relied on the zinc-mercury batteries that were in use at the time [12]. Then, a breakthrough was made when lithium, which had a theoretical capacity of  $3860 \text{ A h kg}^{-1}$  compared to  $820 \text{ A h kg}^{-1}$  for zinc, was identified as a leading option for an electrode material. Practical challenges must be overcome in order for lithium batteries to have this much capacity. The incompatibility of lithium with moisture is its primary drawback. Therefore, lithium-based battery topologies necessitate the use of non-aqueous electrolyte solutions due to their greater stability. Lithium, when mixed with other reactive and active replacements, sparked the first wave of innovation. Lithium was utilized as the anode and iodine as the cathode in lithium-iodine batteries, which were several times more potent than zinc-mercury batteries and had an energy density of  $250 \text{ W h kg}^{-1}$ . Thus, the era of high-capacity lithium-anode batteries was ushered in. Liquid reagents like thionyl

chloride (SOCl<sub>2</sub>) or sulfuryl chloride, as well as soluble reagents like sulphur dioxide (SO<sub>2</sub>), are examples of the unique cathode materials that have been tested by researchers (SO<sub>2</sub>Cl<sub>2</sub>). In the 1970s, lithium was widely employed in electronic devices including watches, cameras, toys, and portable electronics. 13 All of these needs can be met by a LIB that is made in the form of a coin cell battery and uses manganese dioxide for its cathode. All of these systems are considered main batteries, from which secondary battery systems evolved. The development of intercalation electrode types later in 1978 paved the way for numerous secondary or rechargeable LIBs[13]. For the first half of the battery's cycle, lithium ions are absorbed inside the host matrix's open structure via the intercalation process and then released for the second half of the cycle. In the late 1970s, the American company Exxon followed the intercalation phenomenon by creating the first viable rechargeable lithium battery utilising a TiS<sub>2</sub> cathode. 18 In a similar vein, a Canadian company by the name of Moli Energy developed lithium batteries using MoS<sub>2</sub> in the cathode. Overheating and, in outrageous cases, blasts were seen in lithium batteries with a known SEI (strong electrolyte interphase). 20 Out of 1978, specialists initially began thinking about involving polymer electrolytes as an answer for this issue. Polymeric electrolytes are a perplexing mix of a lithium salt and a planning polymer have. The idea of rocker batteries arose in the last part of the 1970s [14, 15] as a piece of intercalation-based lithium batteries, the veracity of which was eventually settled during the 1980s.

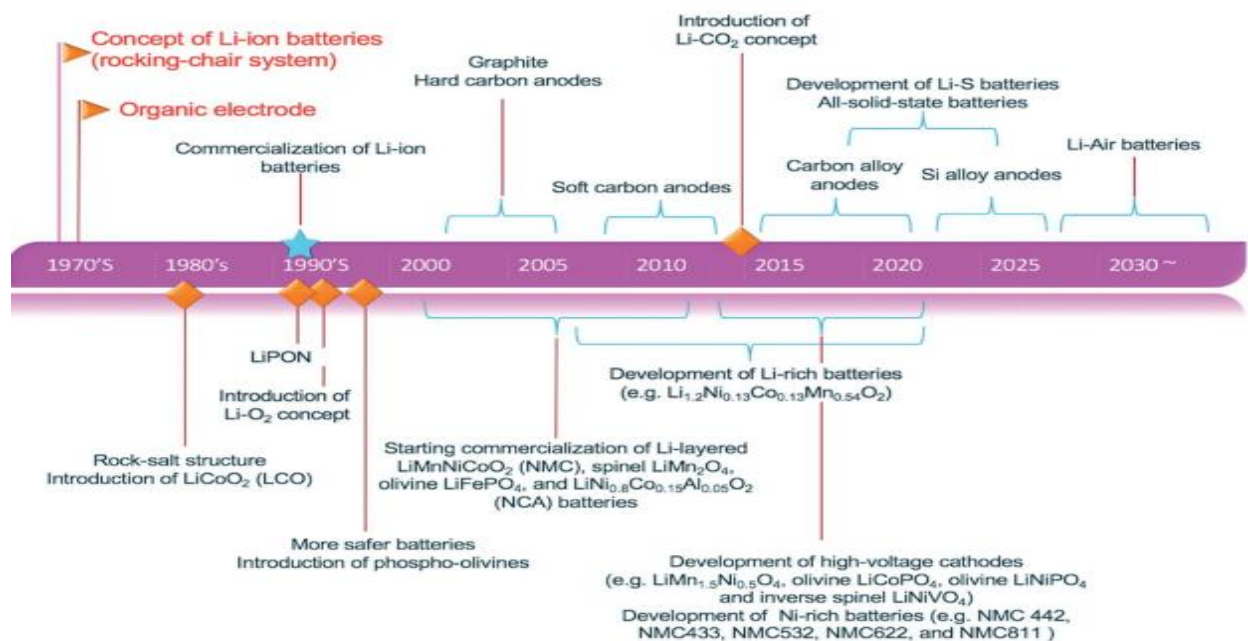
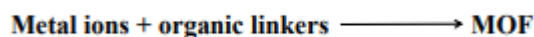


Fig. 1 shows the development and historical progression of lithium-ion batteries. Reproduced from Reference 2 with the Royal Society of Chemistry's permission under 2013 Copyright.

### 3. MOF Synthesis

Metal ions and organic linkers (sometimes called bridging ligands) are the two main components of MOFs. Traditionally, metal ions and organic linkers are combined under mild circumstances to create MOFs, which have a crystalline and porous network structure. “Modular Synthesis” is the word used for this.



Over the past 20 years, a variety of synthetic strategies have been developed and applied to the production of these substances [16]. These can generally be categorized as, Solvothermal techniques, both conventional and unconventional

#### 3.1. Standard Solvothermal, Hydrothermal, And Non-Solvothermal Techniques

In traditional solvothermal synthesis, a solvent-based mixture of metal ions and organic linkers is heated either in glass vials (for temperatures below 400 K) or in autoclaves or bomb reactors lined with Teflon (for temperatures above 400 K). If water is used as the solvent, the procedure is called a hydrothermal technique. A variety of synthesis variables, including pressure, temperature [17, 18], solvent composition, reagent concentration, and others, are controlled to achieve a desired structure. Adjusting the reaction temperature is a crucial step in the production of MOFs. Under typical research facility conditions, a nonisothermal response can occur when the temperature of the response is lower than the limit of the dissolvable, and a solvothermal response happens when the temperature of the response is higher than the edge of boiling over of the dissolvable. The expression "direct precipitation response" can be utilized to portray this strategy too. The gems framed have their shape intensely impacted by the response temperature.

#### 3.2. Innovative Techniques

To avoid the need of a solvent, the metal salt and organic linker are typically mixed together in a mortar and pestle or a ball mill. If any water or other volatile molecules were created during the grinding process, they are removed by gently heating the mixture. This method is referred described as the “mechanochemical approach” [19, 20]. In this process, mechanical force is used to disrupt intermolecular bonds, which is followed by a chemical change. Due to the method’s ability to produce a high yield of goods and lack of solvent use, it is well known to be environmentally benign. Short reaction periods, typically in the range of 10 to 60 minutes, can be used to generate quantitative yields of tiny MOF particles. Metal oxides were frequently chosen as the starting material instead of metal salts, leaving water as the only waste. Pichon et al. published the first study on the

mechanochemical synthesis of porous framework in 2006. Bipyridene-based COFs have been examined using both solvothermal and mechanochemical techniques, and it has been discovered that only COFs made using mechanochemical techniques display the proton conducting property. The term “liquid-assist edgrinding” refers to a mechanochemical process in which a tiny amount of solvent is introduced (LAG). Small amounts of solvents added to a reaction mixture speed up mechanochemical reactions by making the reactants more mobile.

### **3.3. Utilizing Electrochemistry**

This strategy is utilized broadly in the development of MOF powders. The metal particle is brought through anodic disintegration into response arrangements containing natural ligands and electrolytes [21]. When compared to the solvothermal method, the main benefits of this approach are the lower reaction temperatures and incredibly fast synthesis times.

### **3.4. Sonochemical Process**

Sonochemistry examines how molecules change chemically when exposed to intense ultrasonic radiation. When a reaction solution is exposed to ultrasonic radiation, bubbles are produced. These air pockets immediately become nearby problem areas with high temperatures and strain, advancing substance responses and the fast improvement of crystallization cores. Utilizing the sono-synthetic technique with 1-methyl-2-pyrrolidone as a dissolvable, top notch MOF-5 and MOF-177 precious stones with widths of 5-25 m and 5-20 m, separately, were delivered in a definitely decreased response time.

### **3.5. Modification after Synthesis**

Basically a substance change of the secluded MOFs, the cycle includes integrating the MOFs' ideal useful gatherings into the MOFs after their union (PSM, Post Engineered Change). This method has been used to produce several is structural MOFs with a wide range of tailorable physical and chemical characteristics. For example, by mixing with different anhydrides and isocyanates, the structural MOF IRMOF-3, which contains 2-amino-1, 4-benzenedicarboxylic acid, can be transformed into a MOF with a new set of functional groups. Post-synthetic alteration of MOFs includes replacing their primary structural components such ligands, metal nodes, and bridging ligands by methods like solvent-assisted ligand exchange (SALE) and direct ligand replacement, respectively (BBR, Building Block Replacement). By completely exchanging the organic ligands, the MOF can acquire new properties through the SALE process [22, 23]. Heterogeneous trade of ligands or metal particles happens during BBR processes by breaking and transforming

substance bonds inside the first MOF. At the point when it is beyond the realm of possibilities to straightforwardly blend a MOF with the ideal utilitarian capacities, like catalysis, specific gas adsorption, redox, or ionic conductivity, BBR methods are utilized to functionalize the pores or hubs inside the MOFs. The BBR reactions are only detectable on the surface or very close to the surface of the MOF crystals. The MOFs may be flawed due to post-synthesis alteration processes, including the loss of metal nodes or their replacement, or the partial or complete loss of organic linkers. These defects are not limited to the synthesized and development phases of MOF synthesis. At least two metal ions can be found in the framework of mixed-metal MOFs, which can be synthesized via post-synthetic methods, one-pot methods, or metalloligands. The addition of a second metal ion confers novel properties and activities on these substances. Since primary imperfections and inhomogeneities is generally associated with huge material properties, deformity designing has been really utilized to adjust and functionalize MOFs for applications in catalysis, gas sorption, partition, capacity, glowing, and attractive materials.

#### **4. ELECTRODE MATERIALS FOR LIBS BASED ON MOF**

##### **4.1. MofsasaLi-Ion Battery Electrode Material**

In the past decade, there has been a lot of interest in devices that can convert and store energy electrochemically. The most extensively researched of any such technology and energy options are LIBs. LIBs' history has been discussed in earlier chapters [24]. Here, we center basically on the examination of MOFs and the various sciences associated with or made from them as potential cathode materials.

The two most common forms of electrochemical energy storage systems are rechargeable batteries and electrochemical capacitors. Lithium-particle batteries (LIBs) are a cutting edge battery type now the subject of examination and improvement in the field of energy stockpiling. LIBs' charging and releasing activity, where lithium particles are transported to and fro between two terminals, brings about high energy and power densities. Lithium particle batteries (LIBs) release their cathode after charging. The lithium particles are de-intercalated and afterward travel through the electrolyte to intercalate at the anode. Energy is obtained and stored by LIBs during this process. The lithium ions return to the cathode when LIBs discharge, and during this transition, the stored energy is released. The effectiveness of these processes determines the battery's overall effectiveness. The desirable characteristics of the anode and cathode materials support these operations. The optimum electrode material has been the subject of numerous studies in this area.

Traditional electrode materials have poor energy/power densities, low cycle lives, and a difficult production procedure. Materials like metal-organic frameworks (MOFs) are promising cathode materials for lithium-ion batteries (LIBs) because of their exceptional design, huge explicit surface region, advanced porosity, and high lithium stockpiling limit.

A few researchers from various regions of the planet have as of late noticed a shift towards MOF materials for use in electrochemical applications. Their greater surface area is one of the most crucial elements contributing to their improved electrochemical characteristics. MOF structures have a surface area between 1000 and 10,000 m<sup>2</sup> g<sup>-1</sup>, which is greater than the surface area of several porous conventional materials that are regarded as the best for electrochemical applications [25]. Consideration must also be given to pore size. Since the length of the natural ligand encompassing the metallic place might be changed, the normal pore size is 9.8 nm; but this figure is truly inconsistent.

When the metal centre and organic linker are chosen with care, MOFs can also provide redox-active sites. As a matter of fact, the explanation MOFs are so flexible in electrochemical applications is that scientists have made them utilizing various engineered techniques, browsing different dynamic metals and particular natural linkers to deliver MOF structures with different surface properties. Changing any of the planning parts of a MOF permits one to control its science and use it to work with the electrochemical cycles inside a battery. How a MOF is molded can significantly affect its surface region, the quantity of accessible dynamic locales, and the energy of the particle electrolyte collaborations. High surface regions, dynamic porosities, a great surface science, and redox-dynamic utilitarian gatherings are positive characteristics in LIB terminal materials. The increased surface area of MOF materials allows for optimal contact between the material and the electrolyte, resulting in high show rates. MOFs' high porosity and crystallinity make it possible to store lithium, as they provide more space for lithium ions and are more stable structurally.

#### **4.2. Metal Nanoparticle Composites Produced From MOFs For Use In Lithium Ion Batteries**

Many researchers were drawn to nanocomposites because of their huge surface area and potential for use in energy-related applications, particularly as electrodes for LIBs. Utilizing Sn-based metal-organic frameworks (MOFs), Shiva et al. [26] fostered an immediate combination technique for making Sn nanoparticles encased in a carbon grid. The NSn@C anode material showed an extremely high unambiguous capacitance of 1225 mF g<sup>-1</sup> and a 60% coulombic effectiveness. Along these lines, Yu et al. blended



NiMOF, changed it by including Sb metal, and pyrolyzed the subsequent compound to make Ni-Sb nanoparticles implanted in a carbon network. The alloy nonmaterial maintained its 58% coulombic efficiency and 497.3 mA h g<sup>-1</sup> discharge capacity after 100 cycles.

## 5. CONCLUSION

The preparation and testing of several carbon and metal-based materials as LIB electrodes has been examined. Over a long period of time, research and development have mostly concentrated on identifying practical and less expensive ways to create materials with controllable morphologies and assembly. Electrochemical execution in lithium-particle batteries further developed after metal-natural systems were utilized to make permeable, empty, and extraordinary center shell plans. Changing the underlying properties of MOFs and the mixtures produced using them has prompted the improvement of a few brilliant cathode materials, for LIBs as well as for some other battery sciences. Consolidating a nanomaterial as a composite with MOF or a nanomaterial produced from MOF, as shown in this work [27], gives a more noteworthy surface region and expanded porosity, bringing about better electrochemical execution. Involving metals with more prominent conductivity in perfect MOFs and producing metal combinations from bimetallic MOFs with empty permeable designs tackled the issue of frail conductivity of MOFs in lithium-particle batteries. The underlying solidness, conductivity, cyclic steadiness, diminished lithium dissemination lengths, higher lithium stockpiling limit, and improved electron take-up rates were all satisfactorily tended to by these adjustments. As a result, these have delivered exceptionally high rate capacities and coulombic efficiencies. That allowed them to be used in additional energy applications and in industrial testing. Research on metal-organic frameworks should continue to focus on improving the structure's chemical stability and kinetics for various energy applications.

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