

Metal-organic frameworks and composites on their basis: structure, synthesis methods, electrochemical properties and application prospects (a review)

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Abstract

Various types of metal-organic frameworks (MOF) and their structural parameters have been reviewed and their classification has been presented. Most widely used synthesis methods and approaches for MOF and composites on their basis have been discussed. MOF structure is a regular 3D lattice formed by organic linkers and metallic clusters. It has been shown for an example of literary data on MOF synthesis and structural studies that the types of bonds and metals can strongly affect the spatial structure and dimensions of MOF crystals: they can have nano-, micro- and meso-dimensions, be dense or porous, bulk or layered. This variety of structural parameters determines the wide range of their properties and potential applications.

Prospects and methods of controlling the shapes of the crystals, their size and spatial bonds between organic components and metal ions have been reviewed.

Major attention has been paid to zeolite-like frameworks (ZIF) as the most promising ones from the viewpoint of structure, synthesis and electrochemical current source applications. Discussion has touched on possible modifications and methods of controlling the properties of those MOFs and composites on their basis and introduction of impurities, including those having magnetic properties. Possible synthesis options of complex composites through controlled MOF pyrolysis have been presented, for either small-batch or scalable processes. The effect of heat treatment conditions on the final properties and electrochemical applications of those materials has been demonstrated.

ZIF-67 structured MOF doping with one more metal has been presented as variant of modifying the properties of MOF and composites on their basis. For example, the Authors have implemented cobalt MOF synthesis wherein cobalt is partially substituted for manganese at the synthesis stage. Furthermore, a simple water solution co-deposition synthesis technique has been modified with ultrasonication thus reducing the time consumption of the process. Electrochemical studies have shown that the unit electrochemical capacity of pyrolyzed MOF electrodes with partial

cobalt substitution for manganese is appreciably higher as compared to the manganese-free materials. The unit capacity and energy density increase with manganese content in the MOF. MOF manganese doping delivers a considerable improvement in the electrochemical parameters of the electrode materials for hybrid supercapacitors on their basis (from 100 to 298 F/g at 0.25 A/g current density). The results suggest that cobalt substitution for manganese is an effective method of improving the electrochemical parameters of MOFs.

It has been demonstrated that the development of new approaches to the design of MOF based composite materials and the study of the physicochemical regularities of their interaction with various carriers is an important task.

Keywords

metal-organic frameworks, ZIF-67, organic ligands, metal ions, hybrid supercapacitor electrodes, metal/carbon nanocomposites, pyrolysis

1. Introduction

Metal-organic frameworks (MOF) are a new type of materials pertaining to the class of coordination polymers. Those materials are formed by bonds between metal ions and organic linkers. MOF can have unit surface areas exceeding 4000 m²/g [1], controlled pore size and chemical stability [2].

Analysis of literary data on the synthesis, structure and properties of various MOFs showed them to be quite promising materials for multiple applications such as a gas adsorption and separation [3–5], catalysis [6, 7], medical applications and drug delivery [8–11], energy storage materials [11–19] and electromagnetic radiation absorbing materials and coatings [20, 21].

Due to their special properties such as large unit surface area, high porosity, catalytic and sorption capacity, MOFs are good candidates for industrial application. However, the use of MOFs is currently limited to small-batch production [22], probably due to their granulometric composition (soft powders). It is therefore an important task to develop new approaches to the design of MOF based composites and to study the physicochemical regularities of their interaction with various carriers.

Currently the number of MOF materials possessing unique properties is more than 99,075 as per the Cambridge Structural Database (CSD) [23].

One of the most promising subclasses of MOFs combining practically important properties, e.g. simplicity and environmental friendliness of synthesis, chemical stability in alkaline media, controlled porosity, possibility of synthesizing a core-shell structure etc., are zeolitic imidazolate frameworks (ZIF) composed of tetrahedral metal cations M (where M is substantially zinc and cobalt) and imidazolate ligands which are imidazole derivatives (Im) [24, 25]. A distinctive feature which gave the name to this subclass of materials is the structure of the ZIF materials. Due to the ~145 arc deg angle between the metal ions (M–Im–M) which equals the angle between the silicon ions in zeolites (Si–O–Si), the structure of most ZIFs has a tetrahedral topology which is

similar to that of typical zeolites [26]. As compared to ordinary zeolites, ZIF open up new research and technological opportunities. They organically combine the advantages of zeolites and MOFs such as large unit surface area, homogeneous pore distribution, elevated thermal and chemical stability and large number of active centers [27–29].

The ZIF-67 zeolitic imidazolate framework (Co(2-MeIm)₂) consists of a cobalt ion (Co²⁺) and 2-methyl-imidazolate anions acting as linkers, and has a cubic crystal symmetry with unit cell parameters $a = b = c = 1.69589$ nm [30]. ZIF-67 has a large unit surface area (SBET > 1700 m²/g), accounting for the presence of a large number of active centers and micropores in ZIF-67 (pore diameter ~0.34 nm) which favor the reactions due to their high affinity to “guest” molecules [31–33]. Furthermore, it was shown that high concentrations of coordinated unsaturated metallic centers (CUS) embedded into the ZIF-67 framework provide for high activity to multiple guest molecules. ZIF-67 derivatives such as metal oxides and metal/carbon composites can deliver fundamentally new properties that are not typical of ZIF-67. For example, metal/carbon nanocomposites (MCNC) derived from ZIF-67 by annealing solve the ZIF-67 electrical conductivity problem while retaining the initial porosity, whereas reduced cobalt gives a substantial contribution to the oxidation–reduction processes [34–36]. The abovementioned advantages of ZIF have enabled their electrochemical applications.

2. Metal-organic frameworks and their electrochemical application prospects

Environment protection and shortage of fossil energy sources require the use of stable and environment friendly energy storage. It is therefore a top priority task for the industry to develop high-efficiency energy storage and conversion devices [37–39].

Supercapacitors have gained widespread use in recent years as a new type of recoverable energy storage devices due to a tangible improvement in their unit capacity, energy density, power density, good chemical and thermal stability, simple technology, low cost and large number of charge/discharge cycles per lifetime that is hardly achievable with standard batteries and capacitors [40, 41].

There are two large groups of devices that are typically distinguished in this field, i.e., electric double-layered capacitors (EDLC) and pseudocapacitors [42]. EDLC technologies typically use electrochemically inert materials having large electrode unit surface areas so to keep the charge on the top of the electrode or at the electrolyte boundary. EDLC exhibit long charge/discharge cycles and high power density but their energy density and capacity are limited by the effective electrochemical surface area of the electrode active material [43]. On the other hand, pseudocapacitors, unlike EDLC, mainly accumulate the charge at the outer side of the electrode material due to reversible and fast Faraday reactions. They have higher unit capacity and energy density but usually lower power density [42].

Transition metal sulfides such as Co_3O_4 , MoS_2 , Fe_2O_3 , Fe_3O_4 and RuO_2 are typically used as pseudocapacitor electrode materials in supercapacitors [44–47]. Synthesis of electrode materials for prospective energy storage devices requires producing large unit surface area matrices suitable for the synthesis of tunnel-thin insulators and chemically active materials. Development of this carbon tissue based electrode material referred to as Busofit using a thin-film technology allows reducing the internal resistance of electrolytic cells by orders of magnitude and improving their operational safety [48].

Moreover, further increase in the electrochemical parameters of supercapacitors requires development and discovery of new transition metal compounds, e.g. cobalt and manganese. Hollowed nanostructures featuring internal cavities and high surface to volume ratio reduce the charge mass transfer path and provide for easier electrolyte access to the active centers and sufficient contact area between the electrode and the electrolyte. Those specific features make them promising materials for supercapacitor electrodes with the possibility to improve their electrochemical parameters [49].

However, the limited porosity of most transition metal compounds offsets their advantages thus limiting the device capacity [50]. Therefore developing new electrode materials is a key strategy to the improvement of supercapacitor electrochemical parameters.

Supercapacitors with ZIF-67 electrodes have high power density, short charge/discharge time and long lifetime and are considered among the most promising candidate materials for energy storage and conversion devices. However, their widespread application is currently hindered by the lack of efficient synthesis techniques that could enable large-scale industrial MOF production [51].

Various MOFs (ZIF-8, ZIF-67, ZIF-69, ZIF-11, HKUST-1, MIL-100 etc.) have been suggested as potential supercapacitor electrode materials due to their high porosity and homogeneous pore size distribution providing for charge transfer and storage [52]. However, some MOFs initially have insufficient electrical conductivity and therefore electrodes made from them do not provide for effective charge transfer to the current collector. This MOF limitation can be overcome by synthesizing MOF-based composites in combination with other conductive materials such as conducting polymers, graphene etc. followed by metal/carbon nanocomposite fabrication on the basis of the composites. The presence of MOFs delivers greater unit surface area of the conductive composites which is an advantage over electrode materials currently used in the industry, e.g. graphene, carbon nanotubes and other carbon forms.

The type and structural features of the electrode material are of great importance for the supercapacitor output parameters such as unit capacity, cyclic stability and energy/power density. Supercapacitor electrolyte is also important for device performance [53, 54]. The performance of water and organic electrolytes can be improved by using redox active additives (potassium hexacyanoferrate (III), hydroquinone and potassium iodide) which can be combined with conventional water electrolytes (e.g. H_2SO_4 , Na_2SO_4 and KOH) [53]. There are indications [54–59] of an improvement in the electrochemical parameters of product devices as a result of the use of redox additive electrolytes (RAEs).

Simple environment-friendly acid-free mixing synthesis of ZIF-67/GO high-porosity composite was reported [60]. Since ZIF-67 has large unit surface area, its application onto graphene oxide (GO) results in the formation of a highly porous electrically conductive hybrid composite. The ZIF-67/GO composite provides more efficient electron transfer and ion diffusion in electrolyte as compared to pure ZIF-67 [61]. It is of interest to explore ZIF-67/GO composite application as supercapacitor electrode material in optimized electrolyte solutions with redox additives (RAE), i.e., 0.2 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 1 M Na_2SO_4 . The ZIF-67/GO-RAE system with redox electrolyte delivers high unit capacity (326 F/g at 3 A/g current density) and energy density (25.5 (W·h)/kg), combined with high cyclic stability (99.9% of initial unit capacity after 1000 continuous charge/discharge cycles) [60].

An essential limitation on the practical use of supercapacitors is their low energy density E_d which depends on the squared voltage V and the unit capacity C_s . Thus, in order to achieve high energy density one should use optimized combinations of high unit capacity electrodes with wide working potential range electrolytes delivering structural compatibility and having electrolyte pore sizes matching the electrolyte ion sizes [62].

MOFs such as ZIF-67 are good candidate materials to solve this problem due to their controlled pore sizes, large unit surface area, adjustable morphology, availability

of various functional groups and broad possibilities of synthesizing different structures on their basis [23].

3. Structure and specific features of metal-organic frameworks

For developing MOFs and materials on their basis, it is useful to discuss MOF structure, specific features and methods of controlling their properties. Specific features of MOFs include:

- structural and morphological parameters: regular crystal structure, high porosity and large unit surface area;
- chemical composition and functionality of hybrid materials.

By analogy with zeolites, MOFs can be represented in the form of elementary building units (blocks), or modules. The organic building unit is a polydentant ligand or linker, whereas the inorganic building unit is a metal cluster or ion. MOFs exhibit properties that associate them with highly ordered inorganic materials, i.e., highly ordered structure based on a 3D framework, large unit surface area, regular accessible pore system and homogeneous pore size and shape distribution. MOFs also have unique physical and chemical properties distinguishing them from highly ordered inorganic materials: wide range of possible chemical composition variation, flexibility and capability of forming “interweaving” (catenane-like) structures. The modular or block structure of the MOFs facilitates the control of their 3D structure as well as the shape and functionality of pores in those materials through optimized choice of inorganic and organic building units and linking methods.

When solving design optimization problems, one can discern building units of specific types and hence draw an analogy with zeolites [26] or coordination polymers [63]. Table 1 presents a summary of the above two MOF aspects.

In accordance with the S. Kitagawa concept [64], MOFs pertain to a large group of metal-organic coordination polymers. Those hybrid polymers can be in the form of chains (1D), layers (2D) or spatial frameworks (3D), i.e., MOFs. Homogeneous pore size and shape distribution is typical of MOFs as highly ordered materials since pores/channels are constituents of the construction blocks (i.e., repeated structural units) of MOFs [65]. Homogeneous porosity is an important advantage of MOFs since it allows controlling the mass transport inside the crystalline space.

The hybrid nature of MOFs favors the flexibility of their framework and delivers the possibility of significant structural transformations [66].

MOF structural components are linked by coordination bonds which have lower energy than the strong Si/Al–O bonds that form the frameworks of microporous zeolites and mesoporous silicates of the MCM type [67]. This provides for the lowered thermal stability of MOFs as compared to inorganic carriers [68].

The decomposition temperature of most MOFs is within 300–500 °C which delivers MOF stability at “guest” molecule desorption temperatures [69].

The “primary building units” of the MOF framework are considered to be organic ligands and metal ions. A combination of inorganic structural components with rigid organic units produces the desired MOF structure [70], whereas “secondary building units” (SBU) are simple geometrical shapes representing the structure of

Table 1. Comparison of metal-organic frameworks with silicon and aluminum based porous inorganic materials

Carrier, composition	Porous structure description	Pore size (nm)	Unit surface area (BET) (m ² /g)	Stability	Applications
Zeolites, including derivatives formed as a result of Al, Si, O, exchange as well as H ⁺ , Li ⁺ , Na ⁺ , K ⁺ , Ba ²⁺ , Ca ²⁺ , Mg ²⁺ , Ag ⁺ , etc.	Micropore frameworks with regular and homogeneous pore structure containing one or two cation types with different localization	0.3–1.0	340	High thermal stability, to 800 °C. High hydrothermal stability	Acid catalysis. Oxidation-reduction (Redox) catalysis. Metal ion carriers. Gas phase catalysis
Mesoporous silicates, Si, O	Amorphous frameworks containing non-intersecting hexagonal channels	Controlled size channels, within 2–10 nm	1100	High thermal stability, to 800 °C. Lowered hydrothermal stability as compared to zeolites	Acid catalysis. Oxidation-reduction (Redox) catalysis. Incorporation of active centers in silicate walls or active particle application on inner walls of materials
MOFs, various organic and inorganic building units	Micro- and mesoporous frameworks with regular crystal structure and homogeneous pore size and shape distribution	0.5–3.4	300–4900	Some MOFs are thermally stable at up to 550 °C. Some frameworks are stable in air for months	Active centers in inorganic sites and in organic linkers. Acid catalysis. Oxidation-reduction (Redox) catalysis. Electrochemical applications

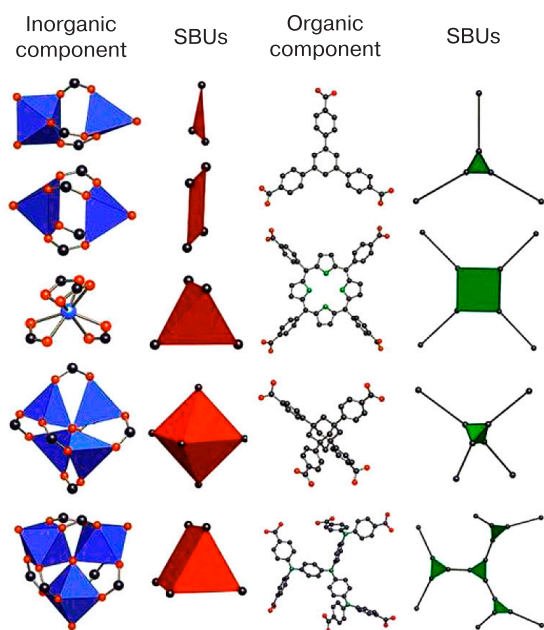


Figure 1. Examples of SBU in carboxylate MOFs [71]

the inorganic clusters or coordination shells of the metal ions interconnected into a specific framework by organic linkers (Fig. 1) [71].

Along with the large unit surface area, MOF synthesis produces similarly shaped pores with a narrow size distribution. The pore sizes (0.2–3.0 nm) and shapes can be controlled over a wide range by choosing appropriate organic linkers [72]. The pore shapes in MOFs can vary, e.g. squares, rectangles and triangles [73].

Synthesis of MOFs as functional materials requires MOF activation, i.e., MOF separation from reactant and solvent molecules captured during synthesis. MOFs are activated at lower temperatures than conventional porous materials, e.g. zeolites, since MOF synthesis does not require template molecules or structure-forming agents which should be annealed. As a rule, it is sufficient to vacuum-treat MOFs at 25–190 °C for removing solvent molecules or surplus reactants from the channels and cavities.

The possibility of activating MOFs at within 190 °C allows producing various types of hybrid materials on their basis. The soft activation conditions favor the formation of continuous MOF layers on porous carriers in the fabrication of integrated membranes. The moderate process temperature does not trigger the formation of cracks or breaks in the selective layers, unlike for zeolite-based materials [74].

4. Classification of metal-organic frameworks

In accordance with the simplest accepted classification, MOFs can be divided in the following subgroups [75]:

- isorecticular MOFs (IRMOF) which are microporous octahedral crystalline materials in which the ligands

are different aromatic carboxylates and $[\text{Zn}_4\text{O}]_6 + (\text{IRMOF-3})$ [76];

- zeolite-like MOFs (ZIF) which are synthesized with the use of elements containing valence electrons and imidazole derivatives. They are topologically similar to zeolites, which is reflected in their name. The most known materials of this class are ZIF-7, ZIF-8, ZIF-67, ZIF-71, ZIF-90, ZIF-L [77]. ZIF contain pores the sizes of which allow accommodating guest molecules, and good thermal and chemical stability making ZIF promising precursors for metal-organic nanocomposite (MCNC) synthesis [78];

- porous coordination networks (PCN) which are stereo-octahedral materials well-known examples of which are PCN-333 [79];

- MOF materials of Lavoisier Institute (MIL) the synthesis of which uses elements having valence electrons and ligands containing two carboxylate groups. Well-known materials of this group are MIL-101[80];

- porous coordination polymers (PCP). Those materials can be synthesized from carbonic acid, pyridine, its derivatives as ligands and transition metal ions [81];

- MOFs of Oslo University (UiO) synthesized on the basis of dicarboxylic acid as ligand and Zr salts. The most remarkable representative of this group is UiO-66 [82];

- biological MOFs (Bio-MOF) [83].

However, at the time being, this classification does not allow one to identify MOFs. To solve this problem and improve the efficiency of search for appropriate MOFs, new methods and tools have been developed based on analysis of a large number of data, and attempts have been made to develop algorithms based on the description of the key chemical and physical properties of MOFs. Those algorithms can subdivide MOFs into subgroups depending on their building units thus facilitating the search for whole MOF families [84]. Elements of advanced data analysis and the high-level Python programming language enabled a new classification on the basis of the Cambridge Structural Database, providing the possibility to itemize and include in the search such important parameters as surface chemistry or family of metallic clusters. For simplifying data analysis, an interactive Web site was developed that allows data visualization¹ [23]. The newly developed classification system can be used by researchers for finding required compounds in the abovementioned classes or by individual MOF properties.

Analysis of literary data on the topic suggests that the most widely used inorganic building units for framework building are the following metal ions: Zn^{2+} , Cu^{2+} , Co^{2+} , Cr^{3+} and Fe^{3+} , while among the most widely used organic ligands there are benzene-1,4-dicarboxylic acid (H2bdc), 2-amino-benzene-1,4-dicarboxylic acid (H2abdc), benzene-1,3,5-tricarboxylic acid (H3btc) and 2-methylimidazole (2-Melm). The structural formulas of those compounds are shown in Fig. 2.

1. CSD MOF subset explorer. http://aam.ceb.cam.ac.uk/mof-explorer/CSD_MOF_subset

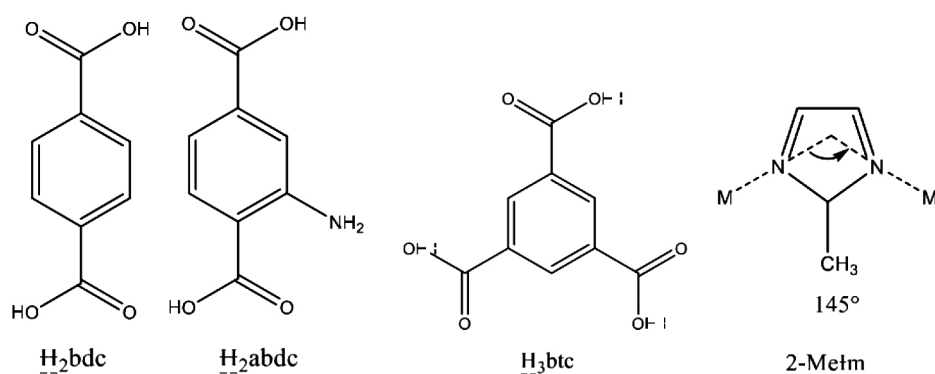


Figure 2. Organic building units used for synthesis of MOF with preset structure

5. Optimized design of metal-organic frameworks

Design of new MOFs is a promising domain of effort due to the almost infinite structural variety, architecture and unique properties of MOFs.

Important features of MOFs are the fine-tuning possibility of the framework structure, the functionality of pores (surface) by choosing inorganic and organic building units, as well as linking method. This provides for the MOF advantages over conventional porous materials, i.e., activated carbon and zeolites.

Currently, increasing attention of researchers is attracted by the synthesis of MOFs with practically promising structures and properties (porosity, variegated topology, physical and chemical stability and pore surface functionality) including those for direct use as hybrid functional materials. Also considered is the possibility of MOF basis modification for improving the existing properties or attaining new ones.

MOF properties can be modified using three methods of incorporating functional molecules: 1) incorporation into the organic linker, 2) incorporation into the inorganic site and 3) arbitrary incorporation inside the crystalline lattice space [85–87]. This strategy implies the following approaches:

- incorporation of molecules containing potential catalytic and adsorption centers in the building units of MOFs;
- using the framework for the stabilization of active nanoparticles that are unstable under other conditions;

– encapsulation of functional molecules in porous metal-organic structures (Figs. 3 and 4) [88].

The implementation of the above three MOF modification options is possible due to the unique properties of porous MOFs [90–93]:

- presence of large-diameter pores/cavities, with many frameworks having channel and pore sizes matching the sizes of functional molecules or particles to be encapsulated;
- high and controlled adsorbability;
- possibility of forming active centers, including by modification of inorganic sites and organic linkers;
- high ion exchange capacity;
- specific electronic properties;
- possibility of varying the size and functionality of pores.

Upon the incorporation of guest molecules and particles in the porous structure, specific properties (catalytic, adsorption, optoelectronic etc.) of the active component of the composite material can be used for effective modification of the carrier, and the modified properties of the active particles can be improved due to the “limiting” effect of the host matrix. Thus, encapsulation provides for the integration of functional centers with the porous matrix.

If the size of active modifying particles is greater than that of the carrier pores, their encapsulation can be achieved through imbibition, i.e., incorporation of preliminarily formed particles or molecules into the matrix. Then the active particles are incorporated using the following methods. 1) Formation of active particles

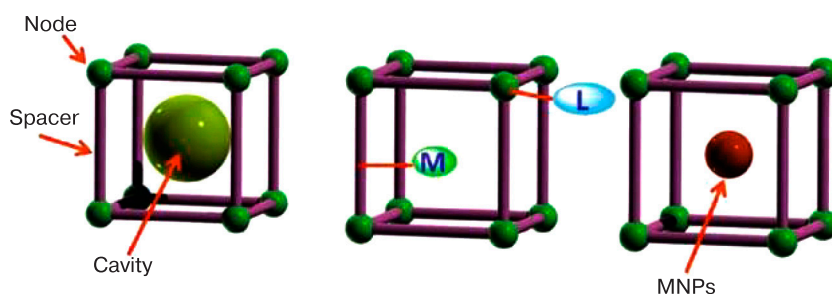


Figure 3. Synthesis of active centers in MOFs (left) Schematic representation of MOF unit cell, (center) active centers in inorganic building unit and organic building unit; (right) incorporation of metal nanoparticles in MOF pore [88]

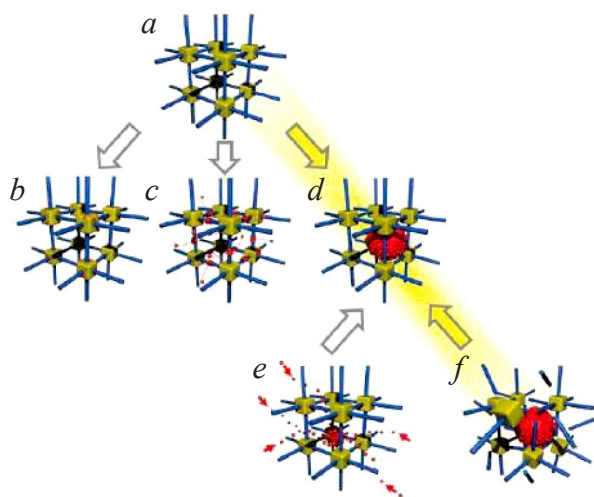


Figure 4. Different methods of introducing desired functions in MOF framework [89]: (a) MOF framework; (b) incorporation of doping molecules in coordination centers; (c) post-synthesis modification of organic linkers; (d) incorporation of functional molecules or particles in the inner crystal space of the framework; (e, f) methods of incorporating functional molecules or particles in MOF matrix (e) is post-synthesis modification (imbibition or infiltration) and (f) is encapsulation of particles or molecules during self-assembly (single-stage approach)

inside the pores of synthesized MOF. This *ex situ* approach implies assembling active particles inside carrier pores. For example, metal-organic compounds with labile ligands were incorporated into a porous MOF structure by MOCVD and then metal nanoparticles were formed on their basis [94]. 2) Carrier formation around active particles or template in situ synthesis (direct introduction of functionality into porous structure), i.e., carrier assembly around active particles during MOF synthesis [95].

Encapsulation methods are chosen based on the chemical nature of the carrier and the functional molecule or particle. If the active particle can be formed using a simple synthesis technique, it is then preferable to form it inside the carrier pores. The carrier should be stable under the conditions of the respective reaction. Otherwise, if the active particle is stable but its synthesis is complicated, it is preferable to assemble the carrier around the active particle, and then the particle itself should be stable during carrier synthesis [96].

The optimum carrier, i.e., a matrix for the encapsulation of active particles and functional molecules, should possess the following properties:

- accessible cavities of appropriate size for the encapsulation of one guest molecule per cavity to provide disperse guest molecules at a molecular level;
- appropriate opening of pores or “windows” providing for diffusion of reactants and reaction products;
- simple one-stage (achievable) MOF synthesis under soft conditions providing for simultaneous encapsulation of guest molecules;
- integrity and stability of synthesis conditions [94].

Thus, the choice of combinations of various organic groups for the modification of MOF structures with different topologies and pore sizes and shapes is dictated by the specific properties of MOFs as the basis for the synthesis of inorganic/organic hybrid materials. This possibility of optimum design delivers the advantages of MOFs over conventional porous materials, activated charcoals and zeolites [97].

6. Control of shape and size of metal-organic framework crystals

MOF crystal size control is an important task since changing MOF size one can optimize their physical properties [98]. For example, MOF particle size is the key parameter determining the physical properties of functional materials formed on their basis (rheology, reactivity, outer surface area etc.) [99].

Carrier modification can include developing the required parameters of materials and task-oriented modification of the initial properties of surfaces and phase boundaries such as hydrophilic, optical, electric etc. [100]. Example of targeted modification of surface parameters is the generation of defect-free crystalline films on the basis of MOFs [101].

The adsorption properties of MOFs originate from the high porosity and the presence of structural metal cations and functional groups on the inner pore surfaces. Analysis of recent literary data on the topic suggests that targeted construction on a molecular level opens broad opportunities for the successful application of ordered MOF crystal clusters.

The broad variety of MOF structures and topologies stems from the following key factors [102]:

- choice of framework building units, i.e., metal ions (inorganic framework sites) and organic ligands;
- variation of synthesis parameters including composition (reactant molar ratios and solvent types) as well as thermodynamic parameters (temperature, heating method (thermal, RF reaction mass activation), and pressure (solvo-thermal synthesis at elevated atmospheric pressure).

The properties of organic linkers (bond angles, ligand chain length, volume, chiral properties etc.) are known to play a key role in the formation of MOF types. In turn, MOF structure and topology are determined by the coordination number of the metal ions.

7. Key methods and approaches to synthesis of metal-organic frameworks and composites on their basis

MOF synthesis includes transition metal ion reaction (inorganic framework building unit) with organic linker

which is the bridge ligand, forming an infinitely long chain. Due to the kinetic lability of the coordination bonds and the presence of molecular components, i.e., organic linkers in the MOF structure, optimized MOF design obeys the principles of molecular self-assembly [103].

New approaches to the synthesis of hybrid materials are developed at different levels:

- molecular level: modification of the framework porous structure through optimum choice of building units (organic molecules and inorganic sites);
- supramolecular level: incorporation of “guest” molecules and particles into MOF cavities;
- microscopic level: synthesis of MOF crystal clusters on the surface of solid substrates and polymer matrix modification with MOF nanoparticles.

ZIF-67 synthesis methods should deliver important MOF parameters such as morphology and surface area, quantity of active centers, pore sizes and distribution. MOF can be synthesized using different methods: solvothermal, surfactant, sol-gel, microwave, ultrasonic etc. Those methods not only provide for the synthesis of pure ZIF-67 but also enable effective control of crystal and pore sizes in the product ZIF-67 by modifying synthesis parameters (temperature and time) [33, 104].

7.1. Solvothermal synthesis

The solvothermal method implies dispersion of primary building units in polar solvents (DMFA, methanol, acetonitrile) followed by autoclave treatment at up to 200 °C for 12 h. The solvothermal method allows one to overcome the reactant solubility related limitations that are typical of the slow diffusion method. Solution polarity, solvent–ligand exchange kinetics and crystal formation rate can be controlled by using several solvents.

For example, ZIF-67 was synthesized [105] using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-Melm which were solved for 4 h in two different organic solvents, i.e., dimethylformamide (DMFA) and methanol at 60 °C. Scanning electron microscopy (SEM) and N_2 adsorption-desorption tests showed that the solvent plays an important role in MOF crystallization processes. For example, ZIF-67 synthesized in methanol has a microporous structure whereas similar-composition materials synthesized in DMFA have a hierarchical structure. Nanosized ZIF-67 crystals were successfully synthesized [106] in methanol at room temperature for a longer time (24 h). The product ZIF-67 had a more homogeneous and monodisperse rhombic dodecahedron morphology (Fig. 5).

However, the above synthesis method limits ZIF-67 applications due to its high cost and the toxicity of most solvents.

Co/Mn-ZIF-67 composites were synthesized [107] using the single-stage methanol deposition strategy. The electrochemical parameters were evaluated using a standard three-probe test assembly in a 3M KOH water electrolyte solution. The tests showed high unit capacity

(926 F/g at 0.5 A/g). Practical applicability was checked using asymmetrical Co/Mn-ZIF-67 MOF / activated carbon composites with a unit capacity of 73.54 F/g at 0.5 A/g, an energy density of 53 (W·h)/kg and a power density of 1080 W/kg/ The device exhibited good cyclic stability, retaining 51% of initial unit capacity after 1500 charge/discharge cycles at 10 A/g.

7.2. Hydrothermal method

In order to solve the solvent-related problems inherent to the solvothermal method, environment-friendly ZIF synthesis in water solvent was first suggested [27, 33].

ZIF-67 crystals were synthesized in a pure water solution at room temperature [33]. Nitrate hexahydrate in a quantity of 0.45 g was dispersed in 3 ml deionized water and then 5.5 g 2-Melm was dissolved in 20 ml distilled water. The two solutions were mixed and stirred with a magnetic stirrer for 6 h at room temperature, and the residue was then collected by centrifugation, rinsed in water and methanol and vacuum-dried at 80 °C for 24 h. ZIF-67 crystal particle size could be controlled in a range of 228 nm to 5.2 mm. Furthermore, the thermal and chemical stability of the synthesized crystals was tested [33]. Three main ZIF crystal water growth mechanisms were identified, i.e., hydrolysis, coordination and deprotonation, which allow controlling the properties of the material by modifying the synthesis conditions [108].

Figure 6 shows an X-ray diffraction pattern and X-ray phase analysis data, a SEM image, a TGA curve and nitrogen sorption isotherms for the synthesized ZIF-67 specimen. The product is single-phase ZIF-67 (Fig. 6a). The SEM image (Fig. 6b) suggests that the particles are polyhedral crystals with an average size of 228 nm. The synthesized ZIF-67 readily disperses in methanol to form a stable suspension and can be stored for several weeks without sedimentation. The TGA curve of the synthesized specimen (Fig. 6c) suggests that the weight loss at below 350 °C is as low as 3% due to compound activation [109].

It was shown [33, 111] that the size and morphology of ZIF-67 crystals can be controlled by varying the solution concentration.

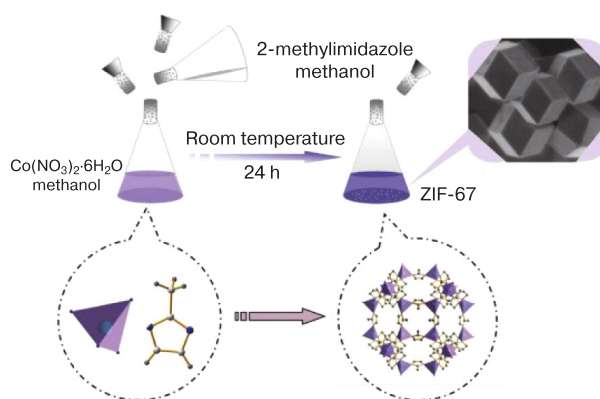


Figure 5. ZIF-67 solvothermal synthesis process [106]

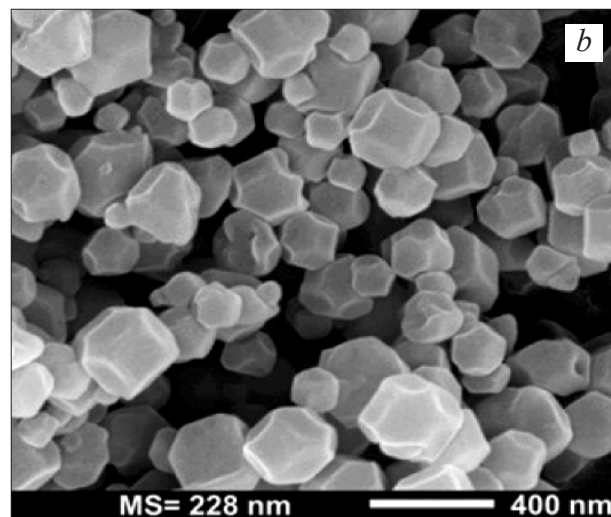
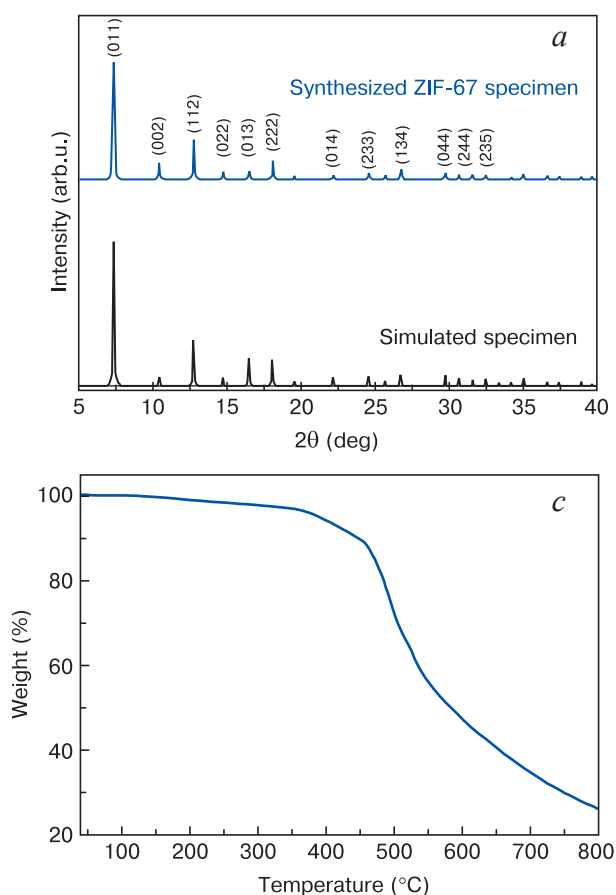


Figure 6. (a) X-ray phase analysis data, (b) SEM micrographs and (c) TGA curve for synthesized ZIF-67 nanocrystals [110]

Along with solution concentration, the structure and morphology of ZIF-67 can be controlled by varying the precursor molar ratio, synthesis time and synthesis media pH [111]. ZIF-67 synthesis and processes accompanying $\text{Co}(\text{NO}_3)_2$ mixing with 2-MeIm in water media were studied and a model of the ZIF-L-Co transition phase was developed [111]. The phase and morphology of the specimens can be controlled by varying the molar ratio of the source precursors. Increasing the 2-MeIm/ Co^{2+} molar ratio from 8 to 24 changed the morphology of the structure from leaf-shaped to rod-shaped ones (Fig. 7 a–c). With an increase in the 2-MeIm/ Co^{2+} molar ratio from 32 to 48 (Fig. 7 d–f), noticeable changes toward a tetrahedral topology typical of ZIF took place.

The experiments also showed that decreasing the ZIF-67 precursor concentration due to water dilution of the media increases the average size of the ZIF-67 particles. Attempting to explain that regularity, the authors hypothesized that reactant concentration reduction decelerates the nucleation reaction and accelerates the growth of the crystals thus developing auspicious conditions for the growth of larger crystals with a deformed morphology.

Precursor heating in vacuum or in water steam media leads to ZIF-67 crystallization by the solid state transformation mechanism. Water media plays an important role in the acceleration of ZIF-L-Co transformation to ZIF-67. Furthermore, low 2-MeIm/ Co^{2+} molar ratios and high reactant concentrations facilitate the crystallization and transition to ZIF-67.

In another work [112] the electrode materials were deposited onto a graphene oxide (GO) carrier for MOF synthesis in distilled water. The electrochemical parameters were evaluated using a standard three-probe assembly in 1 MH_2SO_4 electrolyte. The tests showed a good unit

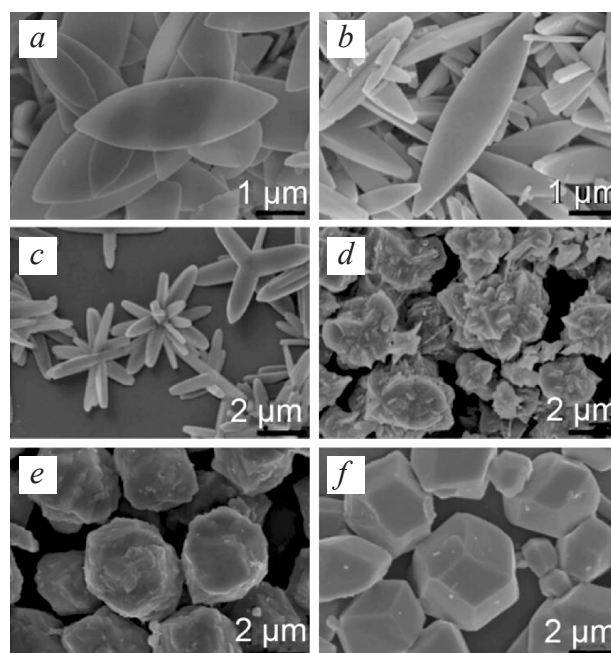


Figure 7. SEM images of specimens synthesized at different 2-MeIm/ Co^{2+} molar ratios: (a) 8, (b) 16, (c) 24, (d) 32, (e) 40 and (f) 48

capacity of 304 F/g at 0.5 A/g. The synthesized material was also tested in a symmetrical supercapacitor assembly. The device had the following energy and power densities: 21.5 (W·h)/kg and 1000 W/kg, respectively. Furthermore, the device had a good cyclic stability, retaining 87% of initial unit capacity after 4500 charge/discharge cycles.

7.3. Surfactant synthesis

This method accelerates the formation of ZIF-67 crystals by fast dispersion of source precursors due to additional active centers acting as catalysts [113, 114]. Along with synthesis acceleration, varying the type and quantity of surfactants allows controlling the morphology and structure of ZIF-67 [115]. For example, addition of cetyltrimethylammonium bromide (CTAB) to the water solution containing typical ZIF-67 precursors reduced the reaction time to 5 min. Varying the quantity of CTAB one could control the particle size within 50–320 nm during crystal formation [116]. It was also noted that polyvinylpyrrolidone (PVP) addition has two important effects: it allows controlling the size of the ZIF-67 crystals and acts as a linker for increasing the ZIF-67 affinity to other materials [117].

Surfactants can also be used as structure controlling agents (SCA) for developing hierarchical porosity and synthesizing hierarchical structures in MOF materials [118–120]. For example, surfactants facilitate linker coordination with Co^{2+} ions to form mesoporous and macroporous channels during crystal growth [121].

Zeolite Co-MOF materials were synthesized using the solvothermal method in DMFA without surfactants and in the presence of CTAB, and electrochemical measurements with a standard three-probe test assembly were conducted in a 3M KOH water electrolyte solution [122]. The results showed that CTAB addition to the reaction solution improves the unit capacity from 236.2 F/g to 334 F/g at a similar current density of 1 A/g. The unit capacity loss was also reduced from 35.96% to 22.08% after 3000 charge/discharge cycles.

A disadvantage of the above method is the high cost of the surfactants used which hinders its industrial application at the moment.

7.4. Sol-gel method

The sol-gel technology is a method providing the possibility to control the molecular composition and framework size of materials [123]. Interaction with coagulants occurs during the formation of a colloidal suspension of submicron-sized particles from MOF precursors. Then the gels having a specific spatial structure are transformed to solid particles by means of heat treatment. Sol-gel process for 3D GO/ZIF-67 aerogel was described [124]. The main specific feature of that process was sequential mixing of ZIF precursor solutions with prepared GO rather than simultaneous mixing. Taking into account the high adsorptive properties of GO relative to metal ions, cobalt

ions were adsorbed on the GO surface and combined with 2-MeIm. 3D GO/ZIF-67 aerogel was obtained by freeze drying.

7.5. Microwave synthesis of metal-organic frameworks

MOF structure synthesis with microwave radiation allows process implementation in a wide range of temperatures, reduces synthesis time, delivers high product output with high purity and homogeneous particle size distribution and provides the possibility of controlling the morphology and size of MOF crystals [125–127]. Crystals with homogeneous pore distribution form in a short time due to instantaneous and homogeneous rise of the precursor solution temperature wherein heating is provided by the solution itself rather than from an external source. These conditions favor the formation of secondary building units, delivering a significant reduction in the crystal growth time [128]. MOF specimen synthesis under microwave radiation is a multi-factor process controlled by temperature, reaction time and radiation power.

Microwave synthesis gradually replaces the conventional solvothermal MOF synthesis method based on thermal convection.

However, the microwave synthesis method is a high energy-consuming process which furthermore requires complex equipment design and labor-consuming equipment setting for fast crystallization, thus increasing production costs [129]. Nevertheless, this method is currently the most efficient MOF nanoparticle synthesis technique [130–132].

Layered Ni-Co (Ni-CoLDH) double hydroxides were synthesized from ZIF-67 by microwave treatment of precursor solution for 30 s [133]. Electrochemical parameters were measured on a three-probe test assembly comprising a Pt counter-electrode and an Hg/HgO reference electrode in 2M KOH water electrolyte. The tests showed a high unit capacity (2369 F/g at 0.5 A/g) due to a synergetic interaction between nickel and cobalt ions during mass transport processes, high unit surface area and accessible active cobalt centers. Practical applicability was tested for asymmetrical MOF “Ni-No layered double hydroxides (LDH) / activated coal” with a unit capacity of 68.1 F/g at 0.5 A/g, an energy density of 21.28 (W·h)/kg and a power density of 375 W/kg. The device had a good cyclic stability, retaining 83.6% of initial unit capacity after 10,000 charge/discharge cycles.

7.6. Ultrasonic synthesis

Along with microwave ZIF-67 synthesis method, ultrasonic ZIF-67 synthesis has been attracting increasing attention in recent years. Ultrasonic synthesis features high local rise in temperature (5000 K), pressure (1800 atm) and cooling rate (1010 K/s) due to acoustic cavitation mechanisms which auspice the generation of excited states, bond breakage, free radical formation, mechanical impacts and high shear gradients thus enabling reactions

that could hardly be achieved earlier with other methods. Cavitation reduces synthesis time, produces small-sized crystals and increases phase purity [134–136].

This method has found increasingly wide application in recent years both as an independent synthesis process and as a post-processing technique. ZIF-67/polyvinylidene fluoride (PVDF) ultrasonic synthesis was reported [137] for use in batteries. The ZIF-67/PVDF battery energy density was 0.58 J/cm³ while that of a PVDF battery is 0.49 J/cm³.

Ultrasonication was used for the synthesis of GO–GO/ZIF-67 electrodes [42]. All electrochemical experiments were conducted in a 6M KOH solution with a conventional three-probe setup. The unit capacity of the composite was 210 F/g at a 1 A/g current density which is far higher than that for ZIF-67 at the same current density (103.6 F/g).

8. Synthesis of ZIF-67 based materials

ZIF-67 based metal-carbon nanocomposites (MCNC) are synthesized by exposing ZIF-67 to an inert gas flow (N₂ or Ar) at room temperature for 30 min for air removal from the chamber, the furnace then being heated to the carbonization point (700–1000 °C) at a 3 K/min rate. Upon reaching the carbonization point the furnace maintains the required temperature for 5 h and is then cooled down to room temperature.

ZIF-67 is thermally stable up to 350 °C which is sufficient for most cyclic applications. Although the thermal stability of ZIF-67 is inferior to that of ZIF-8 (~500 °C) [27], it is still higher than those of many MOF compounds [138]. Carbonization also favors its high thermal and chemical stability.

The chemical suability of ZIF-67 nanocrystals was studied by suspending the synthesized specimens in boiling methanol [110]. The results proved that ZIF-67 nanocrystals are resistant to boiling methanol for 5 days. X-ray diffraction and SEM surface morphology studies of ZIF-67 nanocrystals showed no changes in the nanocrystals after 5-day exposure as compared to the as-synthesized specimen. The chemical stability of ZIF-67 is comparable with that of ZIF-8.

Thermogravimetric – differential scanning calorimetry (TG-DSC) tests were conducted for determining the calcination temperature of ZIF-67. TG data for ZIF-67 powder (Fig. 8a) suggest that weight loss takes place in three stages [139]. The first weight loss stage (10%) occurs in the range from room temperature to 250 °C and is mainly associated with the evaporation of absorbed molecules of water and residual molecular solvents. At the second (250–276 °C) and third (276–298 °C) weight loss stages, 62% weight loss can be accounted for by the release of H₂O, NO_x and CO₂ gaseous products during thermal decomposition of ZIF-67 precursors as confirmed by

the presence of an exothermic peak in the DSC curve at 250 °C (Fig. 8b) [140]. After heating to 298 °C the weight of the ZIF-67 powder remained constant suggesting the complete ZIF-67 transformation to Co₃O₄. Thus, the required calcination temperature is above 250 °C. For the ZIF-67@C composite (ZIF-67 deposited onto carbon tissue), weight remains almost completely stable after 310 °C suggesting the complete transformation and thermal stability of the product oxides upon pyrolysis. The endothermic DSC peak at 291 °C originates from the thermal reduction of Co³⁺ to Co²⁺. The final weight loss stage occurs at ~450 °C and is caused by the oxidation of the surrounding carbon matrix. Thus, to achieve controlled Co³⁺/Co²⁺ content and adequate ZIF-67 transformation to Co₃O₄ the calcination temperature should be from 250 to 310 °C.

Combinations of nitrogen doped porous carbon materials with cobalt oxide as active material in MOF are also promising [141].

ZIF-67 pyrolysis leads to the formation of MCNC with cobalt nanoparticles homogeneously distributed in the porous matrix [142]. X-ray phase analysis data after thermal decomposition of the materials [142] also confirm MCNC formation. These results are of great importance for further studies of the properties and potential practical applications of the materials.

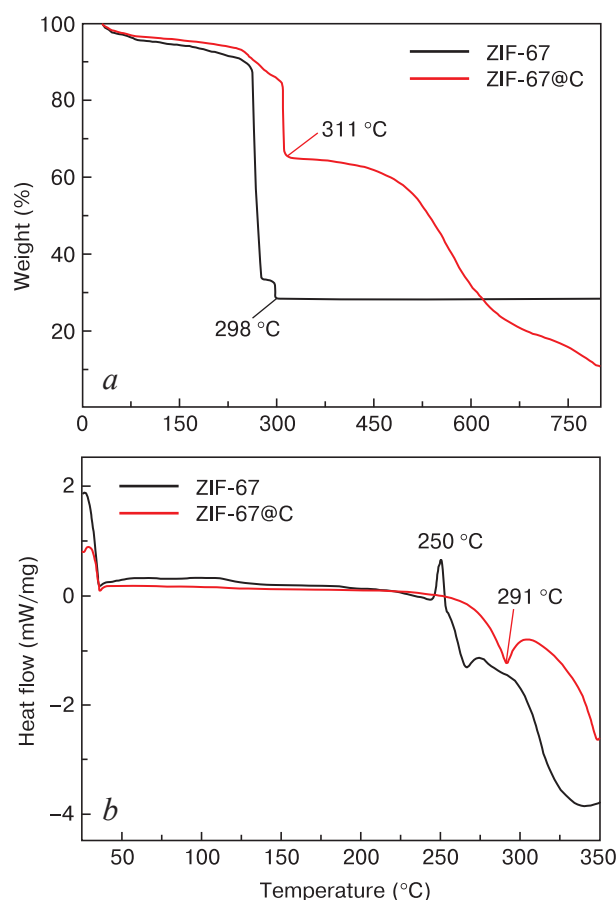


Figure 8. (a) TG and (b) DSC curves of ZIF-67 specimen and self-assembling ZIF-67@C specimen in air

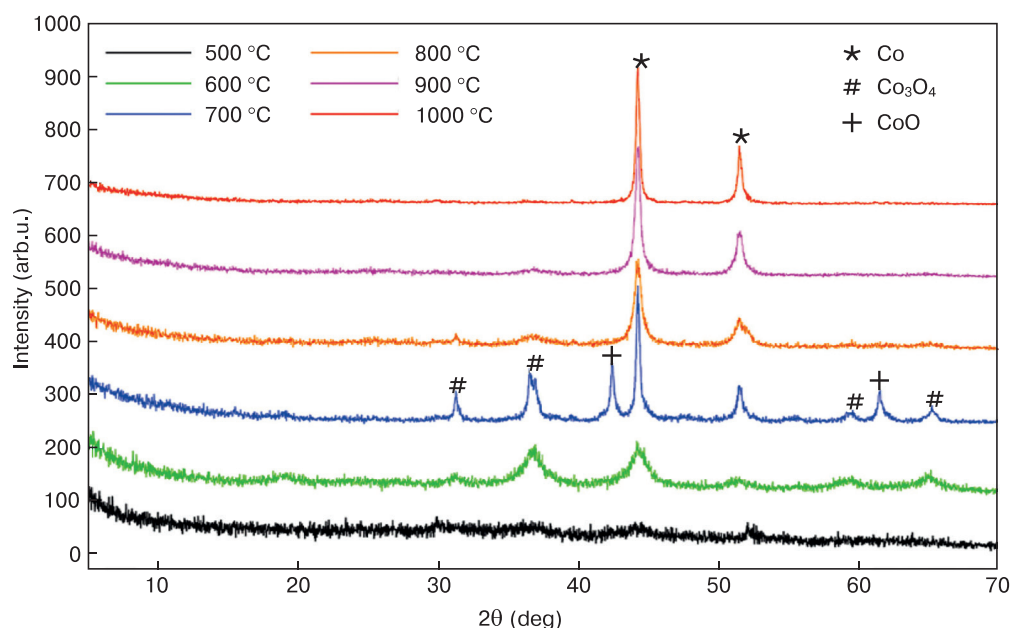


Figure 9. Diffraction patterns of Co/C MCNC synthesized from ZIF-67 by pyrolysis [144]

It should be noted that metallic cobalt particles are important for the improvement of electrode parameters participating not only in oxidation–reduction reactions but also in the carbonization of carbon acting as catalysts. This allows one to obtain layered graphite structure for synthesis of MCNC with high sp^2 -bound carbon content having high intrinsic electrical conductivity [143].

The effect of Co^{2+} doped ZIF-67 pyrolysis temperature on the final MOF electrochemical parameters was studied in a standard three-probe setup [144]. The results showed that the carbonization temperature has a great effect on the purity and crystallinity of the active materials. Figure 9 shows X-ray phase analysis data for Co-MCNC specimens synthesized at 500, 600, 700, 800, 900 and 1000 °C.

As can be seen from Fig. 9, the specimen synthesized at 500 °C has little if any diffraction features suggesting low carbonization. At a higher carbonization temperature (700 °C) there are clear peaks of the fcc metallic cobalt phase at $2\theta = 44.22^\circ$ and 51.52° , and cobalt oxide phases are eliminated. With a further increase in the pyrolysis temperature from 700 to 1000 °C the cobalt crystals grow

significantly from 2.1 to 14.8 nm due to cobalt oxide (II) reduction reaction to metallic cobalt at a higher carbonization temperature. Further increase in the carbonization temperature has but little effect on cobalt crystallinity but increases the Co/C composite grain size. TEM studies showed that the specimen synthesized at 1000 °C inherits the porous structure of Co-ZIF-67 which is favorable for ion diffusion during the electrochemical reaction.

Figure 10a shows cyclic CV curves in the 0.5 to 1.3 V range at a 50 mV/s scanning rate for all the test specimens. The CV curves of the specimens carbonized at 800 °C or higher contain two oxidation/reduction peaks, probably associated with the following reversible reaction:

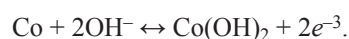


Figure 10b shows discharge curves of the test specimens for a 100 mA/g current density. It can be seen from Fig. 10b that the discharge curves of the specimens synthesized at 500 and 600 °C are substantially linear and exhibit typical MCNC electrochemical behavior, suggesting that cobalt compounds take little if any part in the

Table 2. Comparison between electrochemical parameters of ZIF-67 based materials

Electrode material	Synthesis method	Electrolyte	Unit capacity (F/g)	Energy density ((W·h)/kg)	Power density (W/kg)	Reference
Co/Mn-ZIF-67 // AC*	Hydrothermal	3M KOH	73,54	53	1080	[107]
ZIF-67/GO	Solvothermal	1 M H_2SO_4	304	21.5	1000	[112]
Ni-Co LDH	Microwave	2M KOH	68.1	21.28	375	[133]
GO/ZIF-67	Ultrasonic	6 M KOH	210	–	–	[42]
Co/C (ZIF-67)	Pyrolysis (800 °C)	0.5 M H_2SO_4	62	19.6	700	[143]
Co/C (Co-ZIF-67)	Pyrolysis (1000 °C)	1M KOH	511	–	–	[144]

*Activated carbon

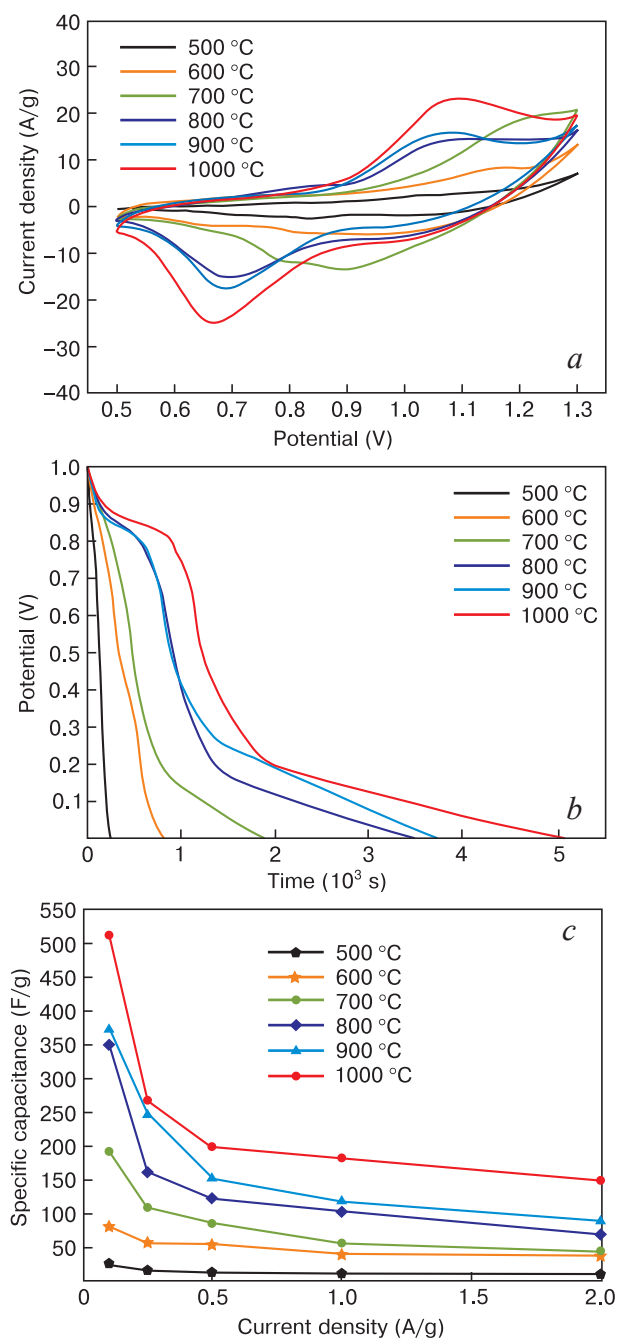


Figure 10. (a) 50 mV/s CV curves for Co/C specimens, (b) 100 mA/g galvanostatic charge/discharge curves for Co/C specimens and (c) unit capacity of composite electrode at different current densities [144]

electrochemical reaction. The relation between the unit capacity and the charge density is shown in Fig. 10c suggesting that the unit capacity decreases with an increase in the discharge current density. This is because the resistivity of electrode materials increases the potential drop at high discharge current densities. But moreover, low ionic permeability can hinder fast and sufficient oxidation/reduction reactions at high current densities.

As can be seen from Fig. 10c the material has the highest unit capacity 511 F/g at 1000 mA/g current density after 1000 °C pyrolysis. The electrochemical parameters

were measured in a standard three-probe setup in 1M KOH water electrolyte.

MCNC synthesis from ZIF-67 and supercapacitor electrode fabrication were reported [143]. Standard three-probe tests were conducted in a 0.5 M H₂SO₄ electrolyte solution with MCNC-coated graphite working electrode, a Pt counter-electrode and an Ag/AgCl reference electrode. The unit capacity calculated from the CV curves obtained in the above-described measurement setup was 238 F/g at a 20 mV/s scanning rate which is more than twofold that of commercial activated carbon (112 F/g) under the same conditions. The unit capacity of the symmetrical supercapacitor fabricated using that process was calculated from the galvanostatic charge/discharge curve to be 62 F/g at a 2 A/g current density. The energy density of the MCNC-based supercapacitor was as high as 19.6 (W·h)/kg at a power density of 700 W/kg. Table 2 presents a comparison between the parameters of various ZIF-67 based materials.

Over the last decade, new approaches to the synthesis of hybrid MOF materials have been developed and intensely studied. Solvothermal, hydrothermal, surfactant, sol-gel, microwave and ultrasonic ZIF-67 synthesis methods have been developed and studied. The possibility of synthesizing carbon-based materials with branched hierarchical core-shell pore structures has been explored. Despite the variety of the methods, the most economically viable are currently microwave and ultrasonic ones since they are free from such drawbacks as the necessity to use toxic solvents, expensive equipment, high power consumption and slow synthesis reaction.

Setting up large-scale and economically profitable fabrication of metallic nanoparticles and highly porous ZIF-67 based nanocomposites requires special attention to environmental issues. ZIF-67 based MCNC materials can be synthesized via simple and cheap processes that can be both economically and environmentally effective. The general potential of using ZIF-67 as a supercapacitor electrode material is related to the development of industrial processes for high-quality ZIF-67 and its derivatives.

The following aspects should be taken into account and thoroughly studied before setting up industrial synthesis of ZIF-67 based materials:

- search for new processes that do not require expensive or toxic solvents;
- synthesis of ZIF-67 based hierarchic materials with different porosity levels (micro-, meso- and macro-) aimed at increasing diffusion rate;
- stability improvement of ZIF-67 based materials (chemical, thermal and mechanical);
- development of optimum design and synthesis process of ZIF-67 derivatives with controlled morphology and porosity;
- development of monolithic ZIF-67 based materials rather than conventional powdered ZIF-67 which can cause pollution and loss of purity during packaging;
- optimization of synthesis and scalable production costs.

Based on the existing experience of nanocomposite synthesis based on metal salt / polymer / solvent systems which has already been commercially developed [145, 146] and on the results of earlier works dealing with the synthesis and study of properties of FeCo/C, FeNi/C, NiCo/C etc. composites [147–153], we developed an IR pyrolysis MOF synthesis method.

The aim of the work is to develop partially manganese-substituted ZIF-67-structured MOFs and study their electrochemical properties in supercapacitor applications. To this end, we used an ultrasonic-modified water solution chemical deposition MOF synthesis method.

9. Synthesis of ZIF-67-like metal-organic frameworks

ZIF-Co was synthesized using a system consisting of organic 2-methylimidazole (2-MeIM) as the linker, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as the metal ion donor and double-distilled water ($\text{pH} = 5.5$, electrical conductivity 0.2 MS/m) as the solvent. The raw Co^{2+} , 2-MeIM and H_2O components were mixed up in a 1:223:8 molar ratio. This ratio was chosen based on earlier data [111] and adapted to the available equipment for maximum yield of ZIF-67 and its modifications.

Cobalt nitrate and 2-MeIM were dissolved separately in double-distilled water (in 10 and 30 ml, respectively). Then the cobalt nitrate solution was added to the 2-MeIM solution. Homogeneous component distribution was achieved by intense stirring of the two-component solution with a magnetic stirrer for 20 min at room temperature until the formation of a bright-violet color solution with partial sedimentation.

To accelerate coordination polymer synthesis and improve dispersion we ultrasonicated the two-component solution ($\sim 150 \text{ W/cm}^2$) for 20 min and held it for 12 h.

The solid residue was separated by centrifugation at 4000 rpm. The solid MOF residue was rinsed in double-distilled water and ethanol and dried at $\leq 70^\circ\text{C}$ for 24 h until constant weight.

10. Synthesis of substituted Co/Mn metal-organic frameworks

As a result of experimental work, several specimens of solid dark-violet residue with different ratios of substituted manganese in the system ($\text{Co:Mn} = 100:0, 95:5, 90:10, 80:20$) were synthesized. The synthesis process of substituted MOF (ZIFCo/Mn) was similar to that for ZIF-Co, i.e., liquid media deposition from a solution of cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), manganese chloride crystal hydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) and 2-methylimidazole (2-MeIM) in distilled water (40 ml). The molar ratio between the metal salts and 2-methylimidazole was 1:223.

The difference was, however, that initially cobalt nitrate and manganese chloride were jointly dissolved in double-distilled water for achieving a homogeneous metal ion distribution. The basic synthesis process was conducted with stirring of the metal salt solution and 2-MeIM with a magnetic stirrer for 20 min, followed by ultrasonication, 12 h holding, sedimentation and residue rinsing and drying.

11. Synthesis of porous metal-carbon nanocomposites

Porous MCNC were synthesized by MOF pyrolysis with IR heating. The pyrolysis temperature was 600°C . The process was conducted in a nitrogen gas atmosphere. The linear heating rate was 50 K/min with a 5 min exposure at the final temperature. The specimens were cooled to room temperature for 45–50 min in an inert gas flow using the cooling system of the IT furnace, and then crushed to a uniform fraction.

Pyrolysis was conducted in a MILA-5000 IR furnace having halogen lamps with a total power of 4 kW. The radiation intensity of the lamps is the strongest in the 0.8–1.2 mm range which is the optimum one for accelerated carbonization and decomposition of metal-organic compounds. The lamps are installed outside the reaction zone, at the exterior of the quartz reactor.

12. Experimental method

X-ray phase analysis (XPA) study of the materials was conducted at room temperature on a DIFRAY 401 diffractometer in CrK_α radiation. The average size of the coherent scattering region (CSR) was calculated from the XPA data using the Debye–Scherrer equations for the MOFs and the metal-containing phases in the nanocomposites.

The electrochemical parameters of the materials were measured using the two-probe method. The experimental symmetrical hybrid supercapacitor cell is shown in Fig. 11.



Figure 11. Appearance of experimental hybrid supercapacitor assembly

The electrodes were fabricated by depositing nano-composite suspension in ethyl alcohol on titanium foil followed by drying. The electrolyte was 2M KOH. The parameters of the experimental assemblies were measured with an Elins P-40X device.

The main objective of the electrochemical tests was to measure the electrochemical parameters (boundary potential, unit capacity, energy density and unit power) [112] of the symmetrical test assemblies made from pyrolyzed modified metal-organic compounds.

The unit capacity of the symmetrical supercapacitor assembly was calculated using the following formula:

$$C = \frac{4I\Delta t}{Um}, \quad (1)$$

where C is the unit capacity, F/g, I is the charge/discharge current, mA, Δt is the discharge time, s, U is the charge/discharge cycle voltage, mV and m is the weight of the active electrode material, g.

The energy density E (W·h)/kg of the symmetrical supercapacitor can be calculated using the following equation:

$$E = \frac{C\Delta V^2}{4 \cdot 2 \cdot 3.6}, \quad (2)$$

where C is the calculated unit capacity, F/g, and ΔV is the voltage drop, V.

The power density P (W/kg) of the symmetrical supercapacitor was calculated using the following equation:

$$P = \frac{E3600}{\Delta t}, \quad (3)$$

where E is the unit power of the supercapacitor, (W·h)/kg and Δt is the discharge time, s.

13. Structure of Mn-substituted metal-organic frameworks

We studied the synthesized ZIF-67 specimens using X-ray phase and structural analysis. Data on the crystal-line structure of the synthesized specimens confirmed the presence of the phase the reflections of which correspond to ZIF-67 [30, 33, 42].

The differences in the low diffraction angle region can be accounted for by the difference in the anode material used in the studies. In our experiments the anode was in chromium whereas a copper anode was used in the cited earlier works. This accounted for the absence of reflections at below 20 arc deg and could slightly shift the peaks towards higher angles.

Figure 12 shows the diffraction patterns of the synthesized MOF specimens with the component ratios Co:Mn = 100:0 (ZIF-67), Co:Mn = 80:20 and Co:Mn = 90:10.

The diffraction patterns of Mn-substituted MOFs have clear reflections typical of the ZIF-67 structure [30]. Noteworthy, a number of reflections typical of MOF without Mn substitution are absent or weak, indirectly suggesting partial cobalt substitution for manganese and the effect of manganese on the formation of MOF crystals. No 2-methylimidazole, metal salts or oxides were found.

Calculations showed that an increase in the manganese content in the MOF to 10% relative to cobalt provides for an increase in the crystal sizes from 28 to 38 nm. Further increase in the manganese content to 20% produces MOF with smaller average crystal size (32 nm).

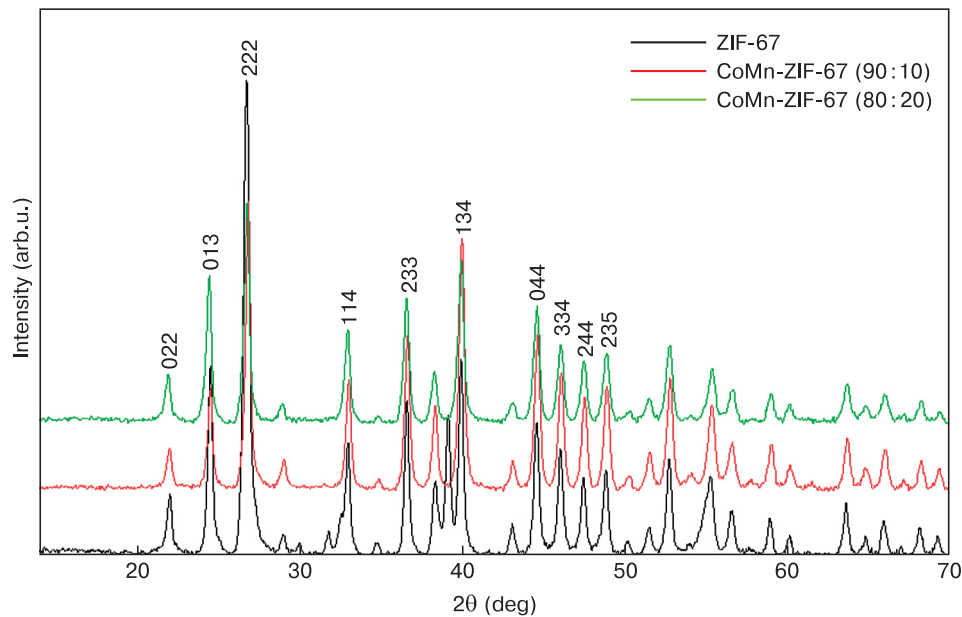


Figure 12. Comparison between synthesized specimens with different manganese contents

As discussed above, MOF pyrolysis produces MCNC with cobalt nanoparticles homogeneously distributed in the porous matrix.

XPA data on the Mn-substituted MOF heat-treated at 600 °C also indicate MCNC formation. Figure 13 shows diffraction patterns of MOF specimens having 100:0 and 90:10 Co:Mn ratios after pyrolysis.

Analysis of the XPA data shows that the most intense peaks of the two specimens correspond to the fcc structure of cobalt ($2\theta = 68.3^\circ, 80.6^\circ$ and 132.7°). Reflections typical of the initial MOF structure are absent, i.e., the organic component has undergone complete carbonization, accompanied by cobalt reduction to metal in the form of nanoparticles. Furthermore, low-intensity peaks at $2\theta = 53^\circ, 62^\circ, 94^\circ$ and 117° emerge, indicating the presence of the cubic MnO_2 phase in the specimens. Thus, cobalt substitution for manganese to a 90:10 ratio in the MOF does not produce a CoMn solid solution upon pyrolysis due to the absence of Mn reduction under the experimental conditions.

Calculations showed that Mn-substituted MOFs are distinguished by a growth of the average Co CSR size (from 6.2 to 11.7 nm). The experimental data suggest that pyrolysis of MOFs with cobalt substitution for manganese produces larger Co nanoparticles. The average MnO_2 CSR size was 28 nm.

Analysis of literary data [42, 107, 112, 143, 144] shows that MOF based experimental devices undergo medium intensity electrochemical reactions, probably due to the high internal resistance of the two-electrode assemblies caused by insufficiently close contact with the current collectors.

14. Electrochemical tests of metal-carbon nanocomposites with Mn-substituted metal-organic frameworks

The materials were tested in a two-probe experimental hybrid supercapacitor cell setup with both electrodes made from MOF based nanocomposites. The tests were conducted in potentiostatic mode (cyclic voltammetric analysis) and galvanostatic mode (galvanostatic measurements).

Figure 14 shows a cyclic voltammetric curve (CVC) for the -0.2 to 0.8 V potential range taken at a 20 mV/s voltage sweep rate.

The chosen voltage range is typical of electrode materials operating by the double electric layer principle in water electrolytes. Those materials have rectangular CVC loops. For our ZIF-Co based electrodes, the CVC loop also was close to rectangular. Deviation from the perfect rectangular shape can be accounted for by a high internal resistance of the cell due to insufficiently close contact between the active electrode material powder (pyro-MOF) and the titanium electrode core (current collector).

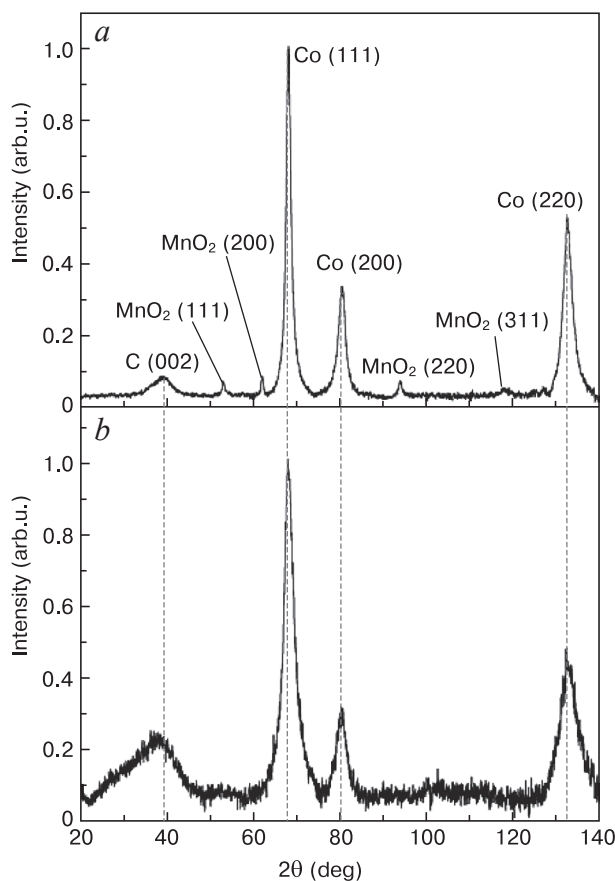


Figure 13. XPA data on MOF with different manganese content after 600 °C pyrolysis: (a) ZIF Co/Mn90:10; (b) ZIF Co

The typical rectangular CVC shape for pyrolyzed Mn-substituted MOF electrodes is heavily distorted due to reversible electrochemical oxidation-reduction processes. Their potential is the highest near -0.37 V. All the CVC indicate high reversibility of the electrochemical processes beginning from the third cycle and are almost constant within 30 cycles.

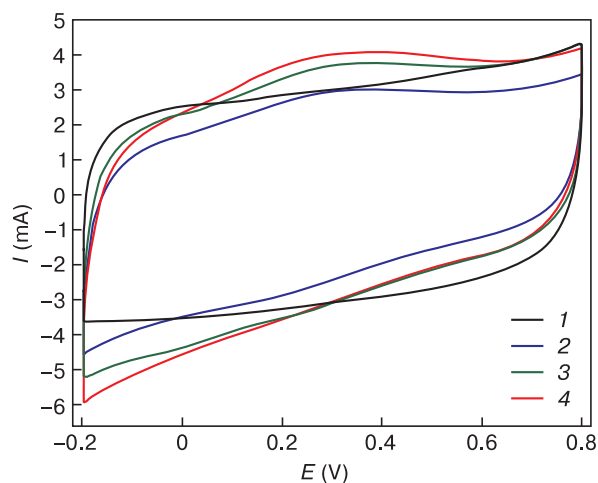


Figure 14. CVC for -0.2 to 0.8 V range of pyrolyzed MOF electrode cell with different Co/Mn ratios: (1) 100:0; (2) 95:5; (3) 90:10; (4) 80:20

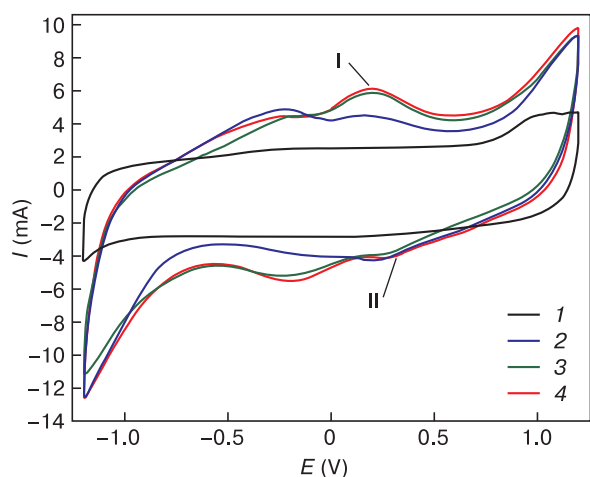


Figure 15. CVC of pyrolyzed Mn-substituted MOF electrode cell in $-1.2 - 1.2$ V range with different Co/Mn ratios: (1) 100:0; (2) 95:5; (3) 90:10; (4) 80:20

CVC of pyrolyzed Mn-substituted MOF electrodes in the $-1.2 - 1.2$ V range are shown in Fig. 15. The voltage sweep rate was 20 mV/s.

The pyrolyzed ZIF-Co specimen (Co/Mn: 100/0) has an almost rectangular CVC, as for the $-0.2 - 0.8$ V range, due to the large contribution of the double electric layer to the unit capacity. At a maximum potential of 1 V, an electrochemical process occurs that can be considered as

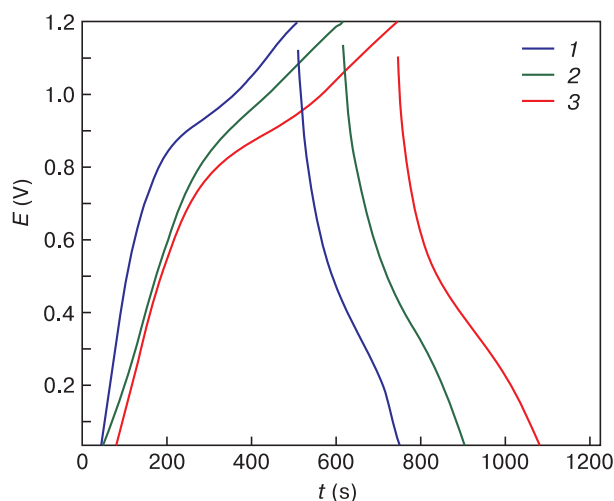


Figure 16. Comparison between galvanostatic data for specimens with different Co/Mn ratios: (1) 95:5; (2) 90:10; (3) 80:20

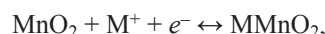
Table 3. Unit capacity calculated from galvanostatic data for 0.25 A/g current density

Specimen	Unit capacity (F/g)	Energy density ((W·h)/kg)	Power density (W/kg)
ZIF-Co	100	2.2	76.1
ZIF-Co/Mn (95/5)	213	10.7	157.6
ZIF-Co/Mn (90/10)	238	12	157.3
ZIF-Co/Mn (80/20)	298	15	172.3

a set of reversible oxidation-reduction reactions with Co nanoparticles.

Pyrolyzed Mn-substituted MOFs exhibit a different regularity. Along with electrolyte processes ($U \sim 1.2$ V) intense electrochemical processes occur at maximum potentials of 0.23 (point I) and 0.25 V (point II), see Fig. 15. Those processes seem to be attributable to manganese oxide nanoparticles. By analogy with pyrolyzed ZIF-Co, electrochemical processes occur at 1 V, but they are weak against the overall background. By and large, with an increase in the Mn content in MOFs the CVC area increases for comparable electrode weights.

The presence of the MnO_2 phase can favor the charge accumulation reaction:

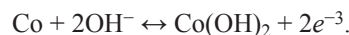


where M^+ was K^+ .

Cobalt oxide Co_3O_4 can also contribute to charge transfer by the following reaction:



Another working reaction occurring in the system is



It should be noted that Co(OH)_2 does not conduct charge but quite probably forms a layer on the cobalt nanoparticles thus preventing electron transfer from the Co particles. This increases the internal resistance at high voltages. Charge transfer occurs most likely through porous carbon layers with a heavily defective graphite structure (nanocomposite matrix) surrounding the nanoparticles and providing for charge accumulation in the double electric layer.

Then we carried out galvanostatic tests of pyrolyzed specimens with different manganese contents. Charge/discharge cycle measurement data are shown in Fig. 16. The current density was 0.25 A/g.

The shapes of the galvanostatic curves are typical of charge accumulation as a result of two factors: double electric layer at low voltages and Faraday pseudo-capacity at voltages of above 0.8 V. The process is repeatable within 5 cycles.

The unit capacity was calculated from the charge/discharge cycle curves using Eq. (1). The count started at a non-zero value due to a negative bias of the supercapacitor unit at the beginning of the measurements. The unit capacity was calculated based on discharge time. The results are summarized in Table 3.

Analysis of the data in Table 3 suggests that an increase in the manganese content leads to an increase in both the unit capacity and the power density of the materials, this difference being tangible as compared to ZIF-Co (172.3 against 76.1 W/kg).

It can be seen from Table 3 that manganese doping of MOFs greatly improves the electrochemical properties

of ZIF-Co. The improvement can be accounted for by the synergetic effect of cobalt and manganese oxide. Furthermore, manganese doping can change the morphology of the materials, e.g. increase their unit surface area and pore size redistribution, thus significantly influencing the kinetics of the electrochemical processes.

15. Conclusion

MOFs are a new class of materials possessing unique properties that make them promising for a wide range of applications. Aspects of synthesis, structure and properties of MOFs were analyzed, as well as their prospects for use as superconductor electrode materials.

The possibility was demonstrated to synthesize bimetallic CoMn ZIF-67-based MOF structures with different Co/Mn ratios: 95/5, 90/10 and 80/20. Ultrasonic modification of the synthesis process reduces synthesis time. It was shown that Mn-substituted MOF specimens match the structure of ZIF-67 MOFs.

Pyrolysis-based MOF synthesis methods were discussed. Pyrolysis can be conducted in various atmospheres and at different temperatures. Air pyrolysis produces porous cobalt oxide with a spinel structure whereas

nitrogen gas pyrolysis produces MCNC with reduced cobalt nanoparticles stabilized in the porous carbon matrix formed by carbonization of the organic MOPF component. Pyrolysis temperature has a tangible effect on the electrochemical parameters of the products.

It was shown that the IR pyrolysis of MOFs in a nitrogen gas atmosphere produces nanocomposite in the form of a porous carbon matrix with embedded Co and MnO₂ nanoparticles. MOF Mn doping noticeably increases the electrochemical parameters of the hybrid supercapacitor electrode materials (from 100 to 298 F/g at a 0.25 A/g current density). However, achieving optimum parameters require further studies of the effect of MOF carbonization temperature and heating rate on the porosity, unit surface area and composition of the nanoparticles. Another promising approach is to use Li polymer electrolytes at voltages of up to 5 V to significantly increase the supercapacitor energy density of MOF electrode supercapacitors.

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