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Review

Metal-organic frameworks and their composites as efficient electrodes for supercapacitor applications

Shashank Sundriyal [a,b], Harmeet Kaur [a,b], Sanjeev Kumar Bhardwaj [a,b], Sunita Mishra [a,b], Ki-Hyun Kim [c,*], Akash Deep [a,b,*]

[a] CSIR-Central Scientific Instrument Organisation (CSIR-CSIO), Chandigarh 160030, India
[b] Academy of Scientific and Innovative Research (AcSIR-CSIO), Chandigarh 160030, India
[c] Department of Civil & Environmental Engineering, Hanyang University, 222 Wangsimni-Ro, Seoul 04763, Republic of Korea

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ABSTRACT

Metal-organic frameworks (MOFs) belong to a novel class of materials with several advantages (e.g., ultrahigh porosity, tunable pore size distribution, convenience of synthesis, and structural tailorability). However, the insulating nature of MOFs is often recognized as a limiting factor in the extension of their applications, especially in electronic fields. In light of such limitations, various functional or conductive materials have been mixed/intercalated with MOFs to improve their potential for such applications (e.g., rechargeable batteries, optoelectronics, and supercapacitors). Lately, many of these composite materials have been recognized as next-generation electrodes for the development of efficient supercapacitors. In this review article, we have critically reviewed the recent advancements in supercapacitor applications of MOFs and their derived composite structures. Further, we have also discussed the application of various categories of electrolytes (e.g., aqueous, organic, ionic liquids, solid-state, and redox electrolytes) and their impacts on the development of MOF-based supercapacitors.

Contents

Abbreviations: MOF, metal-organic framework; SC, supercapacitor; CNT, carbon nanotubes; R_s, series resistance; R_{ct}, charge transfer resistance; E_S, energy density; P_s, power density; NPC, nano-porous carbon; BDAC, biowaste derived activated carbon; TMDs, transition metal dichalcogenides; CP, conducting polymers; BTC, benzene tricarboxylic acid; BDC, benzene di-carboxylic acid; EDLC, electrochemical double layer capacitor; ZIF, zeolitic imidazolate frameworks; PANI, polyaniline; PEDOT, polyethylene dioxythiophene; HKUST, Hongkong University of Science and Technology; PVA, polyvinyl alcohol; GPE, gel polymer electrolytes; ESR, equivalent series resistance; PC, propylene carbonate; $TEABF_4$, tetra ethyl ammonium tetra fluoro borate; RTILE, room temperature ionic liquid electrolyte; MIL, Material Institute Lavoisier; HEV, hybrid electric vehicle; GCD, galvanostatic charge discharge; CV, cyclic voltammetry; EIS, electrochemical impedance spectroscopy; POAP, poly ortho amino phenol; POM, poly oxometalates; AC, activated carbon; Ppy, polypyrrole; FA, furfuryl alcohol; MHCF, manganese hexacyano ferrate; IRMOF, isoreticular metal organic framework; TMO, transition metal oxides; nMOF, nanocrystalline metal organic framework.

* Corresponding authors at: CSIR-Central Scientific Instrument Organisation (CSIR-CSIO), Chandigarh 160030, India (A. Deep).
E-mail addresses: kkim61@hanyang.ac.kr (K.-H. Kim), dr.akashdeep@csio.res.in (A. Deep).

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1. Introduction

Limitations in renewable energy resources and the pollution stemming from the consumption of fossil fuels has catalyzed the demand for clean and green sustainable energy. To address this issue, a large community of researchers has actively been involved in the development of devices for the efficient conversion and storage of energy such as solar and wind energy [1–3]. Undoubtedly, the exploitation of solar energy is a preferred choice. Many types of solar cells (such as silicon, dye sensitized and perovskite cells) have been developed over the years to efficiently convert solar energy into electricity.

The storage of electricity derived from solar energy is a major challenge to ensure the regularity, practicality, and reliability of such novel energy grids. Most energy storage devices are still not up to the desired standard levels of efficiency. Thus, it is still difficult to energize large systems (e.g., transportation systems and pulsed electronic devices) efficiently with solar energy. Newer transportation systems like hybrid electric vehicles (HEV) and their variants are definitely the future of clean and green technology vehicles and will help reduce the consumption of traditional fuels. Such transportation systems demand the deployment of electrical energy storage (EES) devices with sufficiently high energy and power density parameters that cannot be satisfied without high capacity batteries and supercapacitors [4,5]. Among these two options, batteries suffer from low power density and cyclic stability despite high energy densities. Supercapacitors, on the other hand, can offer very high-power density and cyclic stability but are subject to low energy density. Therefore, neither of these two devices can independently fulfill the desirable needs of high energy and power density along with cyclic stability [6].

Unlike the fuel cells and batteries, supercapacitors are electrochemical capacitors that store electric charge in electric double layers that are formed at the interface between the electrode and the electrolyte. Currently, supercapacitors find applications in memory backup systems, consumer electronics, and industrial energy/power management devices. One of the most fascinating recent applications of supercapacitors has been found in the emergency doors of the Airbus A380 [6]. This example supports the reliable and safe application of a new age supercapacitors [6–10]. A supercapacitor is made of a high surface area electrode, electrolyte (aqueous or organic), and a separator (which prevents short circuits between two electrodes). The electrode is a critical component for controlling the performance of a supercapacitor. The fabrication of a high-performance supercapacitor electrode material involves some critical properties such as high conductivity, large specific surface area, temperature stability, distribution of pores with optimized size, convenient processing, good corrosion resistance, and cost effectiveness [11–16]. Therefore, the selection of suitable materials and their optimized design for electrodes are key strategies to make supercapacitors more potent energy storage devices than batteries [17–23].

Metal-organic frameworks (MOFs) are a relatively new class of porous crystalline compounds which have outstanding material properties of high specific surface area, structural tailorability, and permeability to guest molecules [24–27]. As the synthesis of MOFs proceeds through the reaction between metal ions (or their clusters) and organic linkers, the judicious selection of such components can provide application-specific properties [28]. Further, the availability of a large variety of metal ions and organic linkers has facilitated the creation of several thousands of MOFs with various functionalities. As such, MOFs have been adopted in diverse fields of advanced technological applications, including drug delivery, sensors, catalysis, and storage/separation.[29–34].

As observed from recent research trends, MOFs and their hybridized nanostructures (e.g., metal oxides and porous carbons) have attracted attention in the development of electronic and electrochemical devices sensors, supercapacitors, solar cells, fuel cells, and Li ion batteries. Due to their very low intrinsic conductivities, the solitary use of MOFs for such applications is generally regarded as insufficient to obtain the desired results [35–39]. Consequently, MOFs tend to be infused with other suitable materials to attain the desired levels of charge transport. Nonetheless, the introduction of conductivity to MOFs should not lead to a deterioration in their basic properties (e.g., high porosity and stability) [29]. In this respect, it is noteworthy that the structures of MOFs can be modified in two different routes, either during their synthesis itself or through post-synthetic transformations. In the first approach, suitable materials are added during the synthesis of MOFs. This strategy provides an advantage that the added material undergoes superior bonding with either the metal component or the organic linker to help create more stable functional structures [30,40–46]. Composite formation may also help in boosting the properties of individual components to induce synergistic effects on the overall performance. This technique can help reach the desired levels of conductivity while also maintaining the inherent characteristics of MOFs [30,47–50]. Likewise, post-synthetic routes of modification are also reported to be useful to meet the desired specifications in many cases.

In this article, we offered a comprehensive review of the applications of MOF composites in supercapacitors for the first time. To this end, we discuss and analyze the available techniques for the realization of advanced MOF-based structures and composites for supercapacitor applications with respect to the critical parameters controlling their performance (e.g., specific capacitance, energy density, power density, cyclic stability, and bending stability) [51–54]. This review should help researchers understand the basic principles of material selection for improved design/tailoring of MOF structures with electrochemical characteristics [55–59]. In this respect, the potential for integration between MOFs and other novel materials (like quantum dots, carbon nanotubes, graphene oxide, reduced graphene oxide, conducting polymers, metal oxides, mixed metallic MOFs and transition metal dichalcogenides (TMDs)) was critically assessed [60–63]. A compilation of the