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Review article

Advanced metal-organic frameworks (MOFs) and their derived electrode materials for supercapacitors

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HIGHLIGHTS

- MOFs and their derivatives are promising electrode materials for supercapacitors.
- Controllable structure of MOFs contributes to high surface area and large pore volume.
- Various derivative of MOF-5, ZIF-8/67, UiO-66 and MOF-74 as electrodes are introduced.

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ABSTRACT

Metal-organic frameworks (MOFs) and their derivatives are promising electrodes materials because of their various modular and controllable structures as well as their high specific surface areas and large internal pore volume. This review elaborates the recent advances in MOFs and MOF-derived materials for supercapacitor applications. Derivatives based on several typical MOFs are discussed with a focus on material synthesis strategies and corresponding supercapacitor performances if applied as electrode materials. Challenges and opportunities in MOFs-derived materials as supercapacitors are also highlighted, and further research directions are proposed to facilitate research and development in this area.

1. Introduction

Increasing global energy consumption and fossil fuel usage with the associated environmental pollution has stimulated intense exploration into renewable and environmentally-friendly energy sources. To efficiently utilize these new sustainable energy sources, efficient energy storage systems must be developed [1–3]. Among the various existing energy storage technologies, electrochemical methods such as batteries, supercapacitors, water/CO_2-electrolysis and so on are recognized to be one of the most efficient and reliable technologies. And of these, supercapacitors are especially promising because of their high power density, fast charge/discharge rate and long cycle life [4–9]. Generally, supercapacitors can be classified into the following three categories: (1) electrochemical double-layer capacitors (EDLCs) in which the electrodes are mainly composed of carbon materials, and the inside charge storage is at the electrode-electrolyte interface without any electron transfer process from the electrode (electrolyte) to electrolyte (electrode); (2) faradaic pseudocapacitors in which the electrodes are composed of conductive polymers, metal oxides and metal nitrides/carbides, and the charge storage is through the fast and reversible faradaic reaction with electron transfer from the electrolyte (electrode surface) to electrode material surface (electrolyte); and (3) hybrid supercapacitors (HSCs) in which one cell contains two electrodes, one is EDLC electrode and the other is the battery electrode [4,10,11]. However, the utilization of supercapacitors does possess challenges, with a major one being low energy density, limiting their application in many cases, particularly in cases where high energy capacity is required. To increase supercapacitor energy density, two approaches have been intensively explored by researchers recently: one is to develop high capacitance electrode materials, and the other is to develop electrolyte materials with wide potential windows [12–17]. In general, carbon-based materials, conducting polymers and metal oxides/hydroxides are three main electrode materials used in supercapacitors [9]. Among them, carbon-based materials with very large surface area ($\sim$2180–3100 $m^2\,g^{-1}$) possess the specific capacitance value of 100–300 $F\,g^{-1}$ [18–22]. Both conducting polymers and metal oxides/

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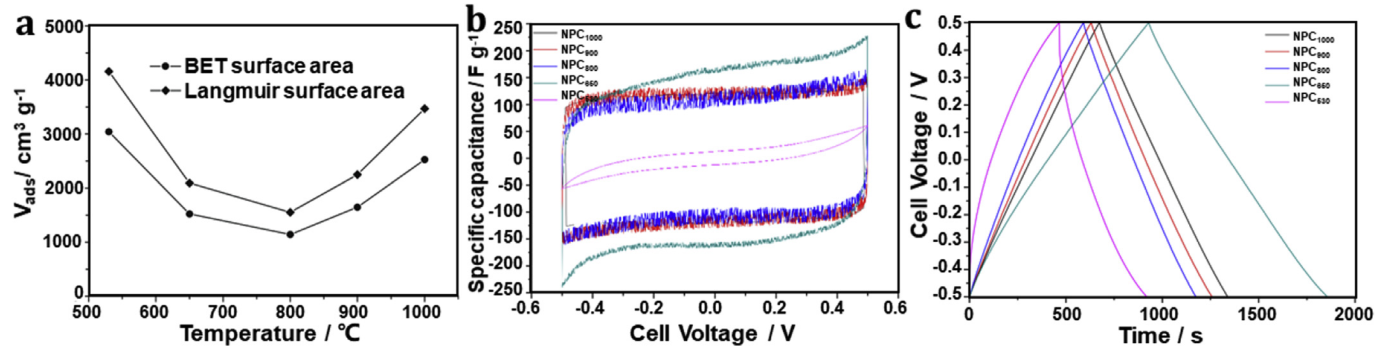

Fig. 1. (a) Relationship between surface areas and temperatures for MOF-5 derived NPC samples. (b) Cyclic voltammograms at 5 mV s^{-1} for five NPC samples carbonizing at different temperatures. (c) The galvanostatic charging/discharging curves at 100 mA g^{-1} for five NPC samples [53].

hydroxides are both faradaic materials, of which the specific capacitance could up to as high as ∼ 1500 F g^{-1} [23–26].

In regards to electrode materials with high energy capacities, metal-organic frameworks (MOFs) with high specific surface areas and large internal pore volumes have recently drawn increasing attention in supercapacitor applications aside from their usual applications in chemical sensing, renewable energy, separation, *etc*. [27–30] These MOF materials are suitable for applications as electrode materials of supercapacitors because of their controllable pore sizes and metal ions with redox activities [31–35]. However, because of poor electrical conductivities, most MOFs are generally used as sacrificial templates to prepare porous carbons [36–38], metal oxides [13,39,40] and metal oxide/carbon composites [41–44]. For example, Yamauchi et al. [45–48] reported various nanoporous carbon synthesized through the carbonization of ZIF-8, and used it as the electrode material for electrical double-layer capacitors (EDLCs). With deeper fundamental understanding through both theoretical and experimental approaches, researchers have come to realize that MOFs can be used as more than just sacrificial precursors for nano-porous carbon materials, and various pristine MOFs are being explored as potential electrode materials for supercapacitors. For example, Sheberla et al. [49] used a Ni-MOF ($Ni_3(HITP)_2$) as electrode material to form a two-electrode symmetrical supercapacitor without any other conductive additives or binders. This material was found to possess a specific capacitance of 111 F g^{-1} at 0.05 A g^{-1}, demonstrating that MOFs are feasible supercapacitor electrode materials. In another study, Yaghi et al. [50] investigated 23 different nanocrystal MOFs doped with graphene and separately incorporated these materials into supercapacitor devices. In the last several years, studies related to MOF applications for electrode materials are no longer being limited to MOF-5 materials and synthesis strategies for MOF-based electrode materials and associated fabrication of supercapacitors have become more diverse and in-depth.

In this review, a comprehensive overview of the development of different types of MOF-based electrode materials and their associated fabrication strategies for supercapacitor devices is provided. Several typical MOF-based materials are discussed in detail, including MOF-5, ZIFs, UiO-66, MOF-74 and other MOF-related materials. Furthermore, advantages and challenges as well as possible research directions to overcome technical challenges in the development of high-performance MOF-based materials for supercapacitors are discussed.

2. MOF-5 based materials for supercapacitors

In general, porous carbon materials can operate at very high charge/discharge rates with long cycle-lives if used as the electrode material for electrical double-layer capacitors (EDLCs) [50]. Based on the extensive application of such materials to supercapacitors, MOFs with high carbon contents and pore characteristics have been used as sacrificial templates for synthesizing nanoporous carbon materials [51,52], and the results have demonstrated that the porous carbon materials derived from these porous MOFs can exhibit tailorable pore textures and improved performance in supercapacitor applications. With respect to this, nanostructured MOF-5 materials with porous structures and high surface areas have been extensively applied as excellent carbon precursors for synthesizing supercapacitor electrode materials.

To explore the feasibility of applying MOFs to supercapacitors, Liu et al. [51] reported a MOF-5 derived nanoporous carbon (NPC) for EDLCs. In their study, furfuryl alcohol (FA) as a carbon precursor was treated with a dynamic vacuum pretreated process followed by a heat treatment process. The final NPC was subsequently obtained by carbonizing the PFA/MOF-5 composite. The specific capacitance of this obtained NPC was 204 F g^{-1} at 5 mV s^{-1} and was higher than that of the ordered mesoporous silica material SBA-15. Liu et al. [53] also investigated five additional NPCs as electrode materials for supercapacitors that were also prepared by MOF-5 at temperatures ranging from 530 °C to 1000 °C (Fig. 1). In this study, the researchers found that different heat treatment processes led to different final sample surfaces and because of this, they systematically studied the relationship between BET vs. temperature and the relationship between Langmuir surface areas vs. temperature. Here, it was found that the obtained NPC_{650} sample provided the highest specific capacitances of 167 and 222 F g^{-1} at 5 mV s^{-1} and 50 mA g^{-1}, respectively. To further study the effects of different carbon sources on the pore structure of derived porous carbons, Hu et al. [54] prepared porous carbons by using various MOF-5 based carbon sources for supercapacitor electrode materials and found that MAC-A samples; obtained by heating a mixture of MOF-5, carbon tetrachloride and ethylenediamine, followed by activation with KOH, produced high capacitances of 271 F g^{-1} and 156 F g^{-1} in aqueous and organic electrolytes respectively.

Díaz et al. [55] reported that a derivative of MOF-5; Co8-MOF-5, which was synthesized by the partial substitution of Zn by Co, can be directly used as the electrode material of supercapacitors. And although this Co8-MOF-5 material possessed much lower capacitance than commercial activated carbon, it provided support to the fact that MOFs themselves can be used directly as electrode materials rather than just as sacrificial precursors that need to be converted into nanoporous carbon before utilization in supercapacitors. After this discovery, various metal based MOFs have been explored as supercapacitor electrode materials [44,56–58]. For example, Yaghi et al. [50] investigated 23 different nanocrystal MOFs doped with graphene as electrode materials for supercapacitors and found 10 promising nanocrystals that possessed similar MOF-5 structures with three-dimensional pores and various mixed functionalities. These 10 isomorphic nanocrystal MOFs were synthesized by mixing different amounts of functionalized benzene-dicarboxylic acids with zinc acetate and although they could be directly used as the electrode material of supercapacitors, their capacitances were still lower than commercial activated carbon.