Supercapacitive behavior of microporous carbon derived from zinc based metal-organic framework and furfuryl alcohol

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ABSTRACT

Microporous carbon materials are obtained by carbonizing a mixture of Zn—BTC MOF [Zn_2(BTC)$_3$ {BTC; 1, 3, 5-benzenetricarboxylic acid}] and polyfurfuryl alcohol (Zn—BTC MOF/PFA) at different carbonization temperatures. The obtained samples are characterized by PXRD, XPS, SEM, TEM, gas sorption and Raman spectroscopic analysis. The maximum BET surface area of 1455 m^2 g^{-1} is recorded for the porous carbon obtained at 950 °C. The incorporation of furfuryl alcohol in the 3D channels of Zn—BTC MOF results in creation of three distinct pore-regions; ultra-micropores (0.45—0.9 nm), micropores (0.9—2 nm) and mesopores (2—3.7 nm) exist with total pore volume of 2.03 cm^3 g^{-1}. The MPC-950 exhibits an enhanced specific capacitance of 471 F g^{-1} at 2 mV s^{-1} and 375 F g^{-1} at 0.75 A g^{-1} and retains ca. 96% of its initial capacitance over 3000 cycles.

Introduction

Electric double layer capacitors (EDLCs) or supercapacitors are energy storage devices that are superior to modern secondary batteries. Supercapacitors are used in electric vehicles, military weapons, space equipment, memory devices, digital cameras, and laser techniques [1]. Carbon based materials like carbon nanotubes (CNTs), graphene; graphene oxide, activated carbon and nanoporous carbon [2—7] are the promising electrode materials used in supercapacitors. A supercapacitor works on the principle of accumulating electrolyte ions in the electrical double layer developed by the electrostatic force. The capacitance (energy stored by an electrode) largely depends on the surface interaction of electrode and electrolyte. However, the surface which can be electrochemically accessed by the solvated ions only makes contribution to the capacitance. The pore size of the electrode materials should be properly matched with the size of the solvated ions for good capacitance. Hence, it is a general consideration that the

capacitance of a capacitor depends on surface area, pore size distribution, pore volume, surface wettability and electrical conductivity of the carbon based electrode [1,8,9].

The surface area and porosity of carbon largely depends on the synthetic procedures; for example, carbonization temperature, chemical activation with KOH/ZnCl$_2$, use of the catalyst, and the selection of the carbon precursors. In recent years, different researchers have thermally converted synthetic polymers into porous carbon materials for supercapacitor applications [10–15]. It has been observed in the reported work that the specific surface area of the resultant carbon material largely depends on chemical activation with KOH and the pore size distribution can be tuned via change in carbonization temperature. A variety of carbon structures like 3D sponge-like nanoporous carbons [16], nitrogen-doped hierarchical mesoporous/microporous carbon (NMMC) [17], highly porous carbon nanosheets [18,19], and porous carbon foam [20] with the BET surface area of greater than 1000 m^2 g^{-1} are synthesized by using various precursors. All these structured carbon material have demonstrated promising electrochemical performance when used as electrode materials in supercapacitors. Catalytic carbonization and chemical activation process were used for the synthesis of activated carbon [21] and mesoporous carbon nanosheets (CNSs) [22] with exceptionally high specific surface area and wide range of porosity. Natural carbon precursors like tobacco wastes [23], waste coffee grounds [24], peanut shell and rice husk [25], ginkgo shells [26], the stem bark of *Broussonetia papyrifera* (BP) [27], and humic acid (HA) [28] were also used for the preparation of porous activated carbon and tested for supercapacitor applications. However, the above mentioned reports with multistep synthetic procedures suffer the limitations like chemical activation and harsh thermal treatment procedures. Efforts have been made to design new synthesis protocols with no or limited drawbacks. Nanocasting (template carbonization) is one amongst the various synthetic procedures reported so far [29–34], which involves a porous template and organic precursor for the synthesis of nanoporous carbon materials.

Recently, porous metal-organic frameworks (MOFs) are emerged as an excellent template candidates for the fabrication of porous carbon [35–37]. Specifically, zinc based MOFs consisting of Zn metal as the secondary building unit with carboxylic acid or substituted imidazole linkers (struts) have been used as template and furfuryl alcohol (FA) as a precursor [38–42] for the synthesis of nanoporous carbon by different researchers. Liu et al. [38] for the first time reported the synthesis of porous carbon for supercapacitor application using Zn-based MOF as a template and furfuryl alcohol as carbon precursor. Yuan et al. [43] have obtained worm-like mesoporous carbon (MPC) by thermally treating glycerol/MOF–5 composite at different temperature for supercapacitor applications. Zn–imidazole frameworks (ZIFs), along with furfuryl alcohol have also been used for the synthesis of porous carbon materials for H$_2$ storage and supercapacitor applications [41,42]. Similarly, porous carbon materials for supercapacitive application were synthesized by Gao and co-workers [46] using MOF-5 as template and carbon precursor along with different additional carbon sources like phenolic resin or carbon tetrachloride and ethylenediamine. The direct carbonization of MOFs without any precursor for the synthesis of porous carbon has also been reported by numerous researchers [44–48].

Although lot of work in this field has been done recently; still the researchers are trying to tune the properties of obtained carbon materials via changing the experimental conditions, i.e., carbonization temperature, change in secondary carbon source, change in MOF template. For example, Banerjee and co-workers have carbonized Zn–BTC MOF directly without any precursor at 1000 °C for porous carbon synthesis (C–Zn–BTC) and evaluate the product for hydrogen storage and supercapacitor applications [49]. The obtained carbon material (C–Zn–BTC) showed specific capacitance value of up to 134 F g^{-1} at 1 A g^{-1}. In current study, we have found that FA is best suited secondary carbon source for this MOF. We are able to significantly tune the properties of obtained carbon product. During the synthesis process, three distinct pore regions were created which have resulted in superior electrochemical performance as 375 F g^{-1} of specific capacitance at 0.75 A g^{-1}. The addition of FA not only increased the yield (25–37%) of the product but also enhanced the capacitive performance of the carbon samples as compared to similar reported materials. The incorporation of FA in 3D channels of MOF has resulted in creating more diverse pores in the carbon matrix during the process of carbonization.

Materials & methods

Syntheses

Zn–BTC MOF

For the synthesis of Zn–BTC MOF, zinc acetate dihydrate [Zn(O$_2$CCH$_3$)$_2$·2H$_2$O (1.7 g, 7.76 mmol)] was dissolved in dimethylformamide (DMF, 20 mL). In the presence of triethylamine (Et$_3$N, 2 mL) base 1, 3, 5-benzenetricarboxylic acid [BTC; C$_9$H$_6$O$_6$ (0.21 g, 1 mmol)] was dissolved in DMF (20 mL). The resulting solutions were mixed and stirred at room temperature. The product, a white powder, was vacuum filtered, washed several times and dried in an oven at 70 °C. The product PXRD spectrum matched with the simulated pattern of reported Zn–BTC MOF (Fig. S1) [49].

Furfuryl alcohol/Zn–BTC MOF mixture

Zn–BTC MOF was vacuum dried at 200 °C and 280 mbar pressure (using Fistreem furnace with Vacuubrand 2008/05 vacuum pump) for 12 h to remove the solvent present in the pores. The evacuated Zn–BTC MOF (0.5 g) was mixed with furfuryl alcohol (5 mL) for 12 h under stirring to ensure complete saturation of template with precursor. After filtration furfuryl alcohol/Zn–BTC MOF (FA/Zn–BTC MOF) mixture was washed with absolute ethanol to remove any furfuryl alcohol adsorbed on the surface.

Carbonization of furfuryl alcohol/Zn–BTC MOF mixture (FA/Zn–BTC MOF)

The (FA/Zn–BTC MOF) was transferred to a ceramic boat which was placed in a quartz tube fixed in a tube furnace (Nabertherm B 180). Initially, air was flushed away by continuous flow of argon for 30 min followed by heating at