Supercapacitive Performance of Ordered Mesoporous Carbon (CMK-3) in Neutral Aqueous Electrolyte

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ABSTRACT: *Ordered Mesoporous Carbon (OMC) represents an interesting material for electric double layer capacitors which have the high surface area, easily accessed ordered pore channels and lower production cost. In this work, CMK-3 as promising OMC has been fabricated using the ordered mesoporous silica SBA-15 as a template. The structure and morphology of CMK-3 are characterized by X-ray diffraction, nitrogen adsorption/desorption, and scanning electron microscopy. CMK-3 is sprayed on the surface of highly conductive three-dimensional nickel foam and characterized as an electrode for electric double layer capacitors. When this electrode is soaked in a neutral aqueous electrolyte solution, reaches a specific capacitance as high as 285 and 167 F/g, at a current density of 10 and 34 A/g, respectively. CMK-3 shows excellent long-term stability with >90% capacitance retention after 10000 cycles, as well as high power (37 kW/kg) and energy density (98 Wh/kg).*

KEYWORDS: *Mesoporous carbon; Supercapacitor; Neutral aqueous electrolyte; High power; Symmetric.*

INTRODUCTION

Carbon has been often declared as one the most important elements with tremendous importance in the life science, energy [1], climate change [2], water treatment and etc. [3]. Fossil fuels are an important source of energy for mankind and carbon is the main element constituent of these fuels. Carbon materials play an important role in energy storage devices such as batteries [4], capacitors [5, 6] and fuel gas storage (natural gas and hydrogen) [7, 8]. In each case, the properties of the carbons are important and the different forms of carbon have been used (e.g., granular, fiber, sheet and tube).

Supercapacitors are a class of electrochemical energy storage devices that are used traditionally and commercially from carbonaceous materials, for the fast storage of energy. In the first patent describing the concept of an electrochemical capacitor [9], carbon materials have been used for the manufacture of electrodes and

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so far no element has been used as much as carbon in supercapacitors. Carbon nanostructured materials have high potential in the development of energy storage systems. Carbon nanomaterials based on various dimensions ranging from zero to three such as fullerenes, nano-onions, carbon nanotubes, nanofibers, nanorods graphene nanosheets, and porous carbons are used in designing and fabrication of nanostructured supercapacitor electrode [10]. For example graphene with the high specific surface area and excellent electron mobility can be synthesized by different method [11, 12] is a good choice for EDLCs [13, 14].

Ordered Mesoporous Carbons (OMCs) are one of the most popular forms of carbon with many articles published on its manufacturing methods and applications [15-17]. Some properties such as high specific surface areas, large pore volumes, chemical inertness, and good mechanical stability lead to the widespread use of OMCs. OMCs mostly have been used as a composite with other materials such as metal compounds (oxides, sulfides, and metal-organic frameworks, etc.) [18-20] and conductive polymers [21-23]. However, it has been rarely investigated as a pure material for electrochemical energy storage devices [24].

In this paper, one of the OMCs (CMK-3) has been synthesized and its super capacitive properties have been investigated in a neutral aqueous electrolyte. Most studies have been done in acidic and alkaline solutions [25-27] or in non-aqueous solvents [24, 28, 29]. Therefore, in this study, a less corrosive electrolyte was used and an appropriate performance was obtained.

EXPERIMENTAL SECTION

Preparation of CMK-3

At first, SBA-15 was synthesized by Zhao method as a template [30]. Briefly, 2 g of triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, 5800) was dissolved in 75 mL 2 M HCl solution at 40 °C and then 4.16 g of TEOS ($Si(OCH_2CH_4)_4$) was added. After the solution was stirred at 40 °C for 24 h, the mixture was transferred to an autoclave which was kept at 100 °C for 48 h. The resulting material was filtered and washed with distilled water. Subsequently, the sample was heated at 550 °C in the air for 6 h.

CMK-3 was prepared according to *Jun et al.* [31]. 1 g SBA-15 was added to 5 ml aqueous solution containing 1.3 g sucrose and 0.3 mL H_2SO_4. The resulting mixture was heated in an oven at 100 °C for 6 h and then at 160 °C for another 6 h. It was then carbonized in an argon flow at 900 °C for 6 h. Finally, CMK-3 was obtained by removing the silica matrix using a 4 M NaOH solution at room temperature followed by filtration, washing, and drying at 120 °C for 4 h.

Characterization

The XRD patterns were obtained at room temperature on a Bruker D8 (Germany) diffractometer with a CuKα (0.15406 nm) radiation source in the 2theta range from 0.5 to 5, with a step size of 0.02°. N_2 adsorption-desorption isotherms were recorded using a Quadrasorb SI analyzer (Japan) at 77 K. The specific surface area was measured according to the Brunauer–Emmet–Teller (BET) model. The morphology of samples was obtained by Scanning Electron Microscopy (SEM) (TESCAN VEGA3) (Check).

Electrochemical measurements

The electrochemical measurements were done using a two or three-electrode system with an aqueous solution of 1 M Na_2SO_4 as the electrolyte. The CMK-3 was used as the working electrode, and a Pt rod electrode and an Ag/AgCl electrode as the counter and reference electrodes, respectively. The working electrodes were prepared by mixing 85% wt CMK-3 with 10% wt carbon black and 5% wt PVDF dissolved in ethanol. This dilute slurry was then sprayed onto a Ni foam (1 cm × 1 cm) and dried in a vacuum oven at 90 °C for 8 h. Each working electrode contained about 0.5–1.0 mg of CMK-3. Galvanostatic charge/discharge, life cycle measurements, Cyclic Voltammetry (CV) measurements were performed using an AUTOLAB PGSTAT30 (Eco Chemie, Netherlands). In a two electrodes system, asymmetric supercapacitor was employed. CV measurements were obtained at different scan rates and galvanostatic charge/discharge curves were carried out at various current densities to evaluate the specific capacitance. A potential window of 0.0-1.2 V for CVs test and 0.0-1.1 V for charge/discharge tests was selected in two electrode system measurements and a cellulosic paper was used as separator.

RESULTS AND DISCUSSION

The low-angle XRD patterns of the SBA-15 and CMK-3 are compared in Fig. 1. For SBA-15, three well-resolved peaks at 0.82°, 1.46°, and 1.7°, indexed as (100),

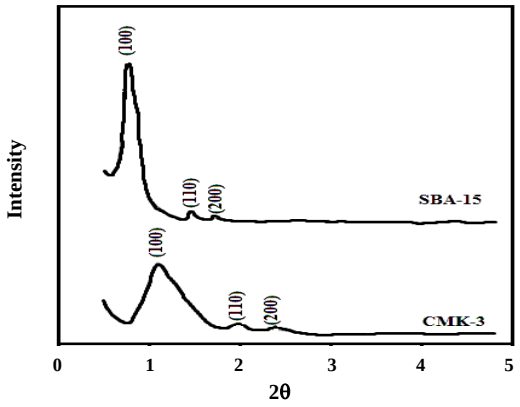

Fig. 1: Low angle XRD patterns of the SBA-15 and CMK-3.

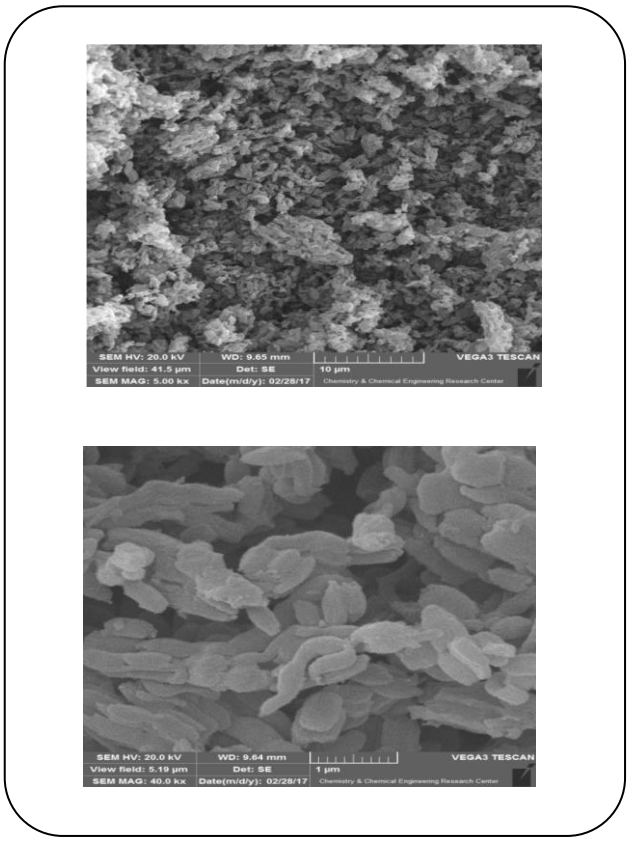

Fig. 2: SEM images of CMK-3.

(110), and (200) reflections related to *p6mm* hexagonal symmetry were observed, indicative of the ordered mesoporous structure of SBA-15 [31]. The XRD pattern of CMK-3 also shows reflection peaks similar to the *p6mm* hexagonal symmetry of the SBA-15 template. This indicates that CMK-3 is a replica of SBA-15. The d-spacing of (100) from the low-angle diffraction peak is 7.80 nm, and the unit cell parameter is 8.97 nm for CMK-3.

The morphology change of CMK-3 is investigated using SEM. The SEM images of CMK-3 are shown in Fig. 2, where they reveal that the CMK-3 consist of many worm-like shapes with relatively uniform sizes of 300 nm in diameter and 1-2 µm in length. The SEM results correspond with the observations of other researchers [32-34].

To determine the pore-size distribution and Brunauer-Emmett-Teller (BET) surface area, the adsorption and desorption isotherms of the CMK-3 (Fig. 3a) was measured. Also, both the N_2 sorption isotherms are typical type IV isotherms with loops, indicating that both CMK-3 have mesoporous structure [34, 35]. Textural properties such as specific surface area, pore volume, and pore diameter are derived from these isotherms. CMK-3 shows the BET surface areas 980 m^2/g, while the pore volume is 193 cm^3/g for CMK-3. Also utilizing the BJH method CMK-3 has a mean pore size of 3.6 nm (Fig. 3b).

The electrochemical performance of the CMK-3 as electrodes for supercapacitors was measured by CV in a three-electrode system with a neutral aqueous solution of 1 M Na_2SO_4 as the electrolyte. Fig. 4 shows the CV curves of CMK-3 at a different scan rate of 10 - 100 mV/s. These CV curves show a quasi-rectangular shape in the voltage window from −0.5 V to 1.0 V, indicating that the CMK-3 have ideal double layer capacitive behavior. It is obviously shown in these CV curves that CMK-3 at the high scan, rates have relatively quasi-rectangular areas with good shapes, indicating the electrochemical performance as electrode materials.

Fig. 5a presents their CV profiles at scan rates of 5-300 mV/s in 1 M Na_2SO_4 solution by using a two-electrode quasi-capacitor. CMK-3 shows a typical rectangular-shaped CV curve in the voltage window from 0.0 to 1.2 V, indicating that the composites have ideal capacitive behavior with good charge propagation and easy ion transport in the electrode materials. It can be seen that at different sweep rates, CVs of CMK-3 retain a similar shape even at a high sweep rate, indicating low equivalent series resistance (ESR) and fast diffusion of ions from the electrolyte into the CMK-3.

In order to demonstrate the cyclic stability of CMK-3 as electrode active material, we measured CV curves of the prepared electrode at the scan rate of 100 mV/s after 10000 cycles. As shown in Fig. 5b, a small drop in capacity occurs, suggesting the high stability for

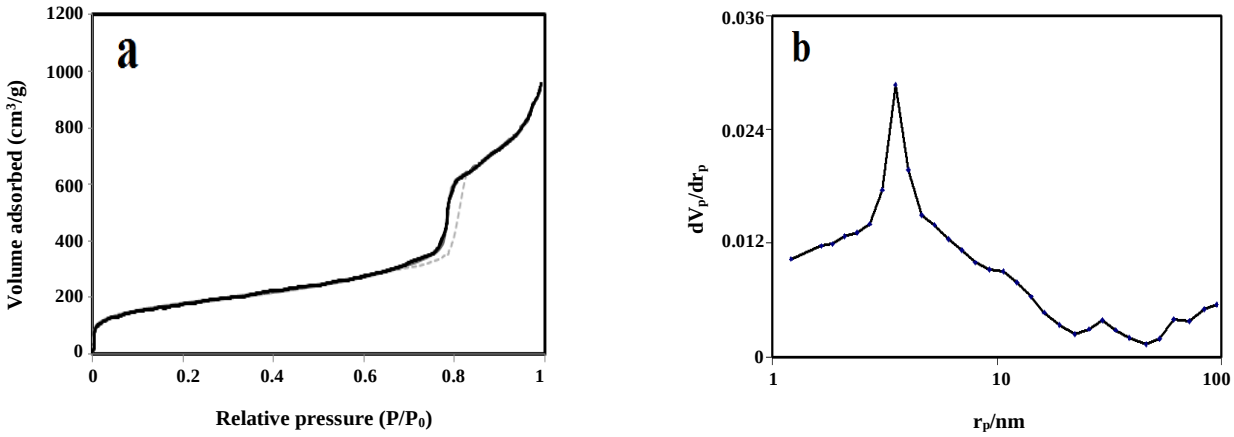

Fig. 3: N_2 adsorption/desorption isotherm for CMK-3 (a) and pore size distribution (b).

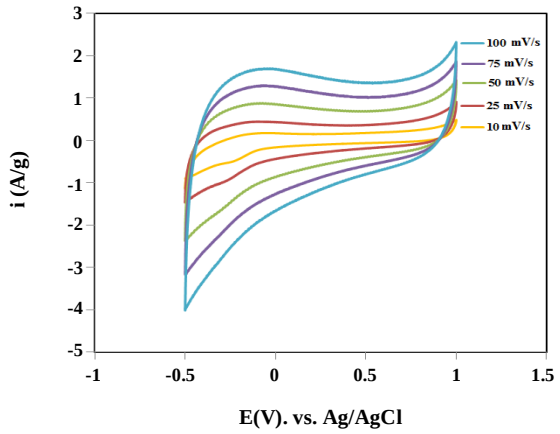

Fig. 4: Cyclic voltammograms (in a three-electrode system) of CMK-3 at different scan rates in 1 M Na_2SO_4.

the CMK-3 based symmetrical supercapacitor. A minor change in channels size, due to soaked in electrolyte, may be occurred and cause to fade capacity.

Fig. 6a exhibit the galvanostatic charge/discharge curves of CMK-3 at different current densities of 10 to 34 A/g in the voltage window from 0.0 to 1.1 V. It can be seen that all curves are highly linear and symmetrically close to triangle shapes, indicating typical characteristics of Electric Double-Layer Capacitors (EDLCs).

Fig. 6b shows the rate and cycle performances of CMK-3. After 500 cycles, current density constantly changes. The specific capacitance of the electrode was calculated from the following equation [36]: $C=I\Delta t/\Delta V$, where C is the specific capacitance (F/g) of electrode materials from two electrode configuration, i is the discharge current density (A/g), Δt is the discharge time (s), ΔV is the voltage change (V) from the end of IR drop to the end of the discharge process. As shown in Fig. 6b, the CMK-3 electrode exhibited a specific capacitance (on average during the 500 cycles) of 285, 218, 200, 185, 171 and 167 F/g at current densities of 10, 16, 20, 24, 30 and 34 A/g, respectively. The gradual decline in specific capacitance with the increase of the current density is related to the reduced surface area accessible to the electrolyte at high current density. After discharged at 34 A/g for 500 cycles, the cell regained a capacity of 277 F/g at a current density of 10 A/g. Only about 3% loss in capacity is observed after 3500 charge/discharge cycles at high current densities.

The specific energy and power of the symmetric supercapacitor were calculated and the results are shown as a Ragone plot in Fig. 7. The specific energy (E) and power (P) were estimated according to the [36]: $E= 0.5 C\Delta V^2$, and $P= E/\Delta t$, where C (F/g) is the specific capacitance. The symmetric supercapacitor can deliver a specific energy of 98 Wh/kg at a specific power of 11 kW/kg and still maintain 56 Wh/kg at a high power density of 37 kW/kg.

CONCLUSIONS

In summary, we have reported CMK-3 based supercapacitor to achieve a high specific capacitance (285 F/g), excellent cycling stability (9% capacitance decay over 10000 CV circles), high energy and power density (98 Wh/kg and 37 kW/kg, respectively). The high specific surface area and order mesoporous structure of the CMK-3 give a large active surface area and full

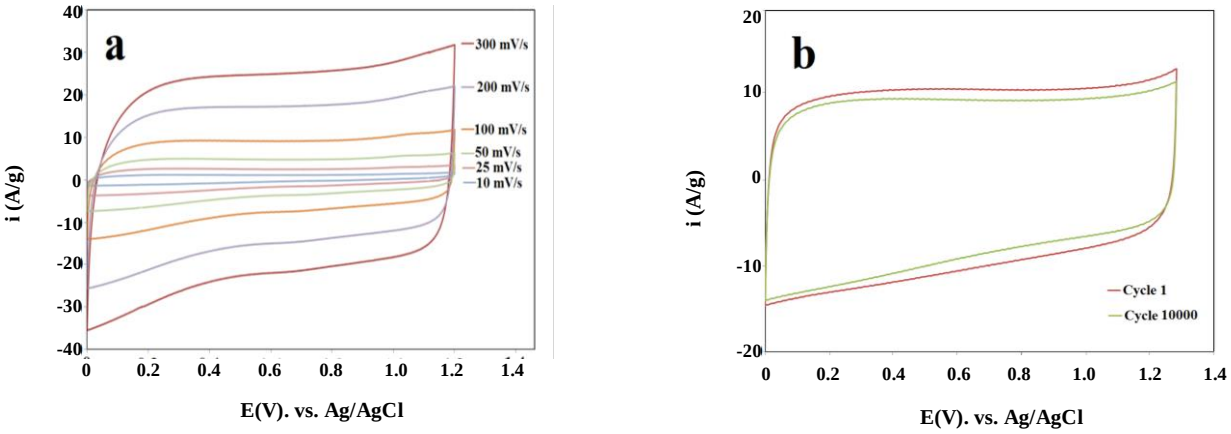

Fig. 5: Cyclic voltammograms (in a two-electrode system) of CMK-3 (a) at different scan rates in two electrode system (b) at the first and 10000th cycle number at a scan rate of 100 mV/s in 1 M Na_2SO_4.

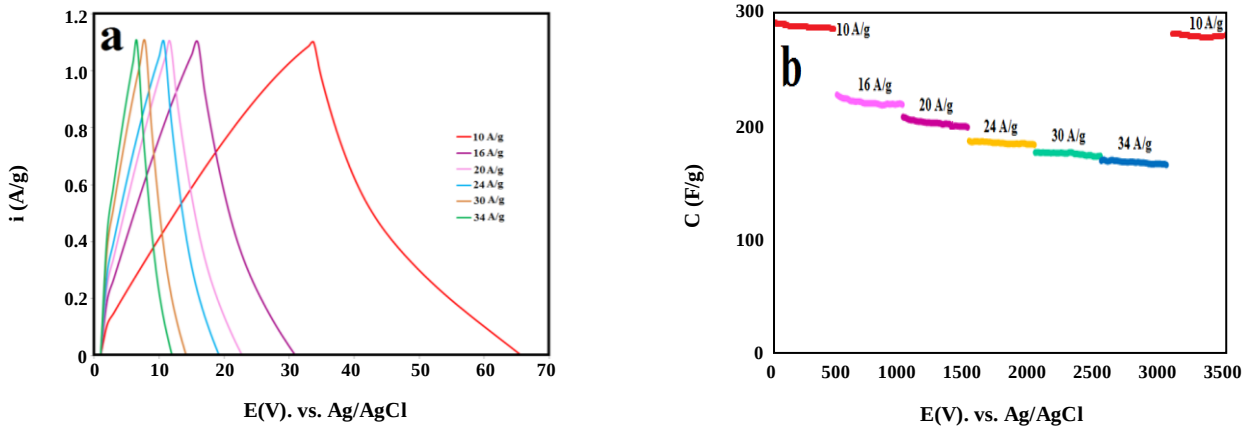

Fig. 6: (a) Galvanostatic charge/discharge curves of CMK-3 at different current densities, (b) specific capacitance of CMK-3 as a function of current density and cycle number.

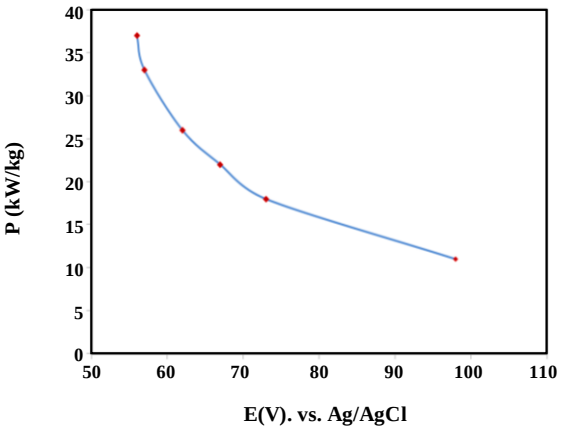

Fig. 6: Ragone plot of the CMK-3 supercapacitor.

accessibility for the electrolyte charged ions. On the basis of these attractive features, the high-performance electrochemical behavior of the CMK-3 electrode renders it a promising candidate for a supercapacitor. Furthermore, the simple and low-cost assembly of this supercapacitor can largely extend the potential applications of CMK-3 based devices.

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