

# Electrochemical capacitance of self-ordered mesoporous carbon

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## Abstract

The capacitance properties of the self-ordered mesoporous carbons (CMK-3), from a template of hexagonal self-ordered mesoporous SiO<sub>2</sub> (SBA15) using sucrose as the carbon source, have been investigated. The pore distribution was narrow with a diameter of 3.90 nm and a surface area of 900 m<sup>2</sup>/g. Rectangular shape of the cyclic voltammetry was observed even if the scan rate is increased to about 5 × 10<sup>-2</sup> V/s. Self-ordered mesoporous carbon exhibited an electrochemical double-layer capacitance of 60–90 F/g in scan rate from 5 × 10<sup>-4</sup> to 5 × 10<sup>-2</sup> V/s between 1.5 and 3.4 V (Li/Li<sup>+</sup>). The specific capacitance of 10 μF/cm<sup>2</sup> was similar to that of the typical value of EDLC. After the 100th cycle, the capacity decreased 20% in comparing with that of the first one.  
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## 1. Introduction

Recently, regularly arrayed mesoporous carbons have been synthesized [1,2] and become the current topics. Among them, the self-ordered mesoporous carbon, first reported by Ryoo et al. [3] in 1999 through carbonizing sucrose inside the pores of the self-ordered mesoporous silica template, has attracted much attention in applications as methane and hydrogen storage, adsorbents, catalyst supports in addition to electrochemical double-layer capacitors (EDLC) [4–8].

The EDLCs can be used as pulse power sources for digital communication devices and electric vehicles. The mechanism of EDLC is to store charges in an electrochemical double-layer formed at the interface between electrode and electrolyte. Various methods have been reported for producing electrochemical double-layer capacitive materials such as activated carbon black, carbon aerogels and carbon nanotubes [9–12]. The self-ordered mesoporous carbon, with high surface area, uniform pore size and controlled structure, will be a good candidate for EDLC's application.

In 1999, Hyeon and co-workers presented the preliminary results on the EDLC performance of the self-ordered mesoporous carbon (SUN-1) [13], which performed using aluminum-implanted MCM-48 as the template and phe-

nol and formaldehyde as the carbon source. In order to avoid the difficulty for synthesizing of template MCM-48 material, hexagonal mesoporous aluminosilicate (HMAIS) was used as template to prepare self-ordered mesoporous carbon (SUN-2) [14] by the same research group. Some simple preliminary results on cyclic voltammetry (CV) performance were also demonstrated. The CV of SUN-1 was carried out both in organic electrolyte (1 M Et<sub>4</sub>NBF<sub>4</sub> in propylene carbonate, potential range of 0.0–3.0 V versus Li/Li<sup>+</sup>) and an aqueous electrolyte solution (2 M H<sub>2</sub>SO<sub>4</sub>, 0.0–0.7 V versus SHE). The self-ordered mesoporous carbons of SUN-1 and SUN-2 have both relatively small pore sizes. SUN-1 has interconnected 2 nm pore arrays separated by 2-nm thick carbon walls. Meanwhile, SUN-2 from hexagonal self-ordered mesoporous aluminosilicate (HMAIS) exhibited a bimodal pore size distribution, that is one peak from micropores at 0.6 nm and the other one from the templating effect of self-ordered mesoporous Al-HMS at 2.0 nm. So, the SUN-2 is formed by mixing micropores and self-ordered mesopores carbon. In fact, the small diameter micropore cannot be accessible to electrolyte solution because the ions, especially those big organic ions, are too big to enter those micropores, so the surface area of those non-accessible micropores will not be contributed to the total electrochemical double-layer capacitance [12]. The larger pore-sized is important for the mesoporous carbon being used in organic electrolyte, it enable the organic ions to enter the mesopore interface more easily.

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Herein, we synthesized one kind of hexagonal self-ordered mesoporous carbon (CMK-3) using hexagonal mesoporous silica (SBA-15) as a template [3,15], and investigated in detail about the EDLC properties of this material. The pore size distribution data calculated from the  $N_2$  gas adsorption–desorption isotherm curve showed that the pores are uniform with an arranged pore size of 3.90 nm.

Rectangular-shaped cyclic voltammograms were kept over a wide range of scan rate from  $5 \times 10^{-4}$  to  $5 \times 10^{-1}$  V/s in the range from 1.5 to 3.5 V (versus Li/Li<sup>+</sup>). Properties of electrochemical capacitors were analyzed and the detail electrochemical capacitance data was provided.

## 2. Experimental

The synthesis process of self-ordered mesoporous silicate, SBA-15, was as same as described anywhere under acidic condition [15]. The process of producing carbon was similar to that reported by Ryoo and co-workers except for the method of carbonization [5]. Generally, 1.25 g of sucrose was added into a mixture of 0.14 g  $H_2SO_4$  and 5 g of  $H_2O$ . After mixed fully, the mixture was put into a drying oven for 6 h at 373 K, then the temperature was increased to 433 K, held at that temperature for 6 h. After, added 0.8 g of commercially available sucrose ( $C_{12}H_{22}O_{11}$ ), 0.09 g of  $H_2SO_4$

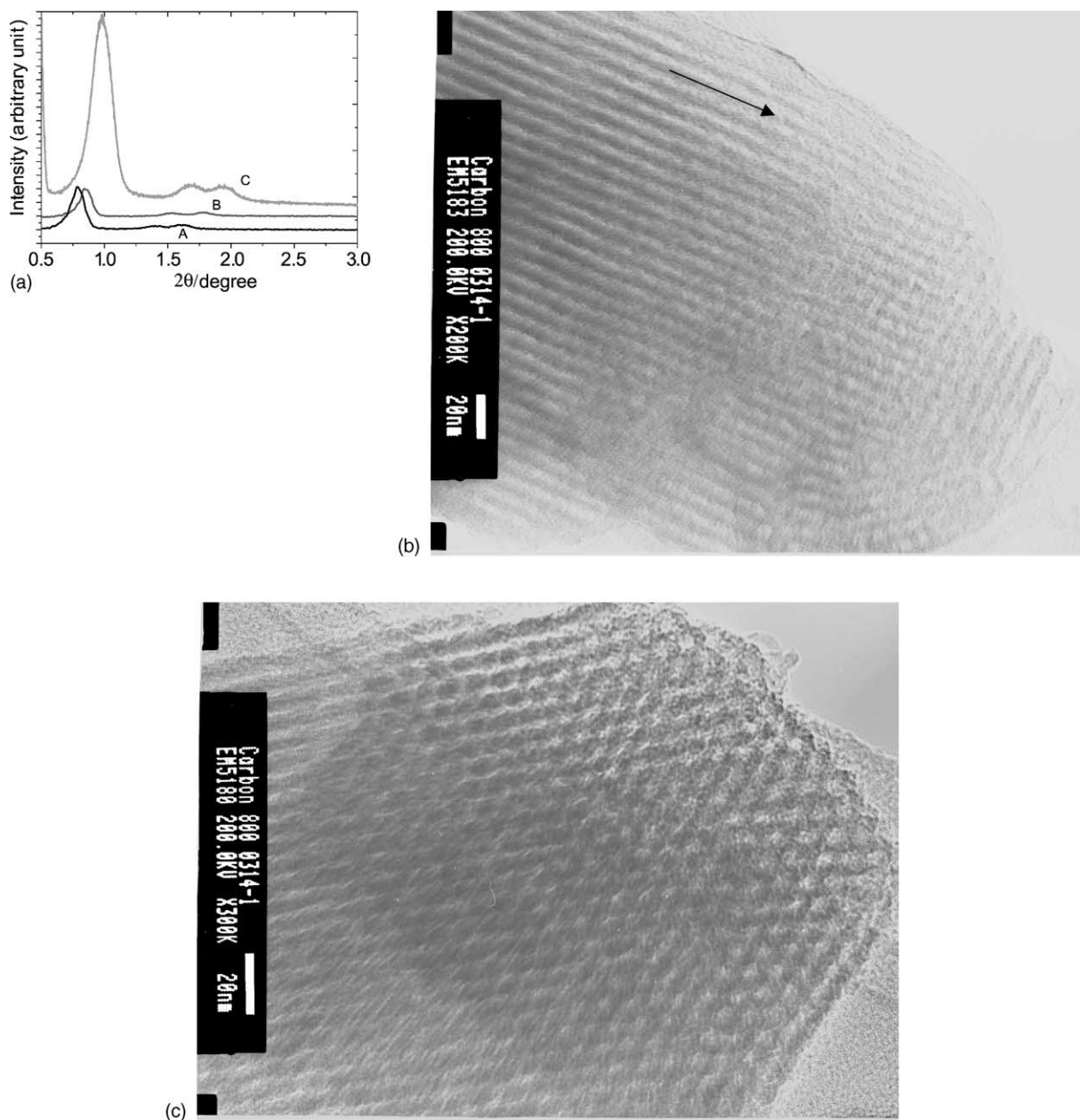


Fig. 1. (a) Powder X-ray diffraction patterns for: (A) the SBA-15 before calcinations; (B) the SBA-15 after calcinations; and (C) the CMK-3 mesoporous carbon. (b) The TEM of CMK-3 along the direction of the hexagonal pore arrangement. An arrow shows the pore channel direction of the CMK-3. (c) The TEM of CMK-3 perpendicular to the direction of the hexagonal pore arrangement.

and 5 g of H<sub>2</sub>O, the mixture was treated again at 373 and 433 K successively. The carbonization was complemented by heating the mixture up to 873 K under nitrogen gas environment. The silica template was removed using 5 wt.% hydrofluoric acid (HF) at room temperature.

The fundamental characteristics of the self-ordered mesoporous carbon were investigated by X-ray diffraction (XRD), N<sub>2</sub> gas adsorption–desorption technique and transmission electron microscopy (TEM). For electrochemical measurement, the samples were mixed and ground with 5 wt.% poly(tetrafluoroethylene) (Teflon) powder as a binder. The mixture was spread and pressed on a nickel mesh. The CV performance of the material was investigated in a three-electrode cell using lithium metal as a counter and reference electrodes. The electrolyte was 1 M LiPF<sub>6</sub> in EC + DEC (EC/DEC = 1 (v/v) ratio). Cell assembly was carried out in a glove box under an argon atmosphere.

### 3. Results and discussion

The X-ray diffraction patterns for: (A) SBA-15 before calcinations; (B) SBA-15 after calcinations; and (C) the CMK-3 self-ordered mesoporous carbon, respectively, are shown in Fig. 1(a). All of them show a hexagonal structure. The unit length of the CMK-3 self-ordered mesoporous carbon is about 10.5 nm. The TEM images parallel and perpendicular to the pore direction are shown in Fig. 1(b) and (c), respectively. The morphology of CMK-3 is a reverse hexagonal structure [3–5]. But, the unit length seems decreased comparing with that of SBA-15 according to the XRD results.

The capacitance of an EDLC depends on the surface area of the materials used in the electrodes. The N<sub>2</sub> adsorption–desorption isotherm, which are shown in Fig. 2(A), was used to determine the surface area of the self-ordered mesoporous carbon. The uniform pores with an average pore-size of about 3.90 nm are developed as shown in Fig. 2(B). So, the thickness of the carbon wall is estimated to be about 6.6 nm (10.5–3.9). The BET surface area is about 900 m<sup>2</sup>/g and the total pore volume is about 0.87 cm<sup>3</sup>/g. The *t*-plotting curve of the N<sub>2</sub> isotherm shows that micropores contributed very little to the surface area.

Cyclic voltammetry (CV) measurements were used to examine the influence of operational parameters (sweep rate and cycling) on the capacitance of carbon. The capacitor performance has been investigated by voltammetry techniques, ranging from  $E = 1.5$  to 3.4 V (versus Li/Li<sup>+</sup>).

The influence of sweep rate on the performance of the carbon electrodes is shown in Fig. 3(A) and (B) at various scan rates changed from  $5 \times 10^{-4}$  to  $1 \times 10^{-1}$  V/s. The absence of Faradic peaks indicates capacitive charging and discharging at a constant rate over a complete cycle.

As shown in Fig. 3(A), rectangular-shaped CV curve is obtained even at the scan rate of  $1 \times 10^{-2}$  V/s. The rectangular-shaped CV curve gradually collapses as shown in Fig. 3(B) when the scan rate exceeds over  $5 \times 10^{-2}$  V/s.

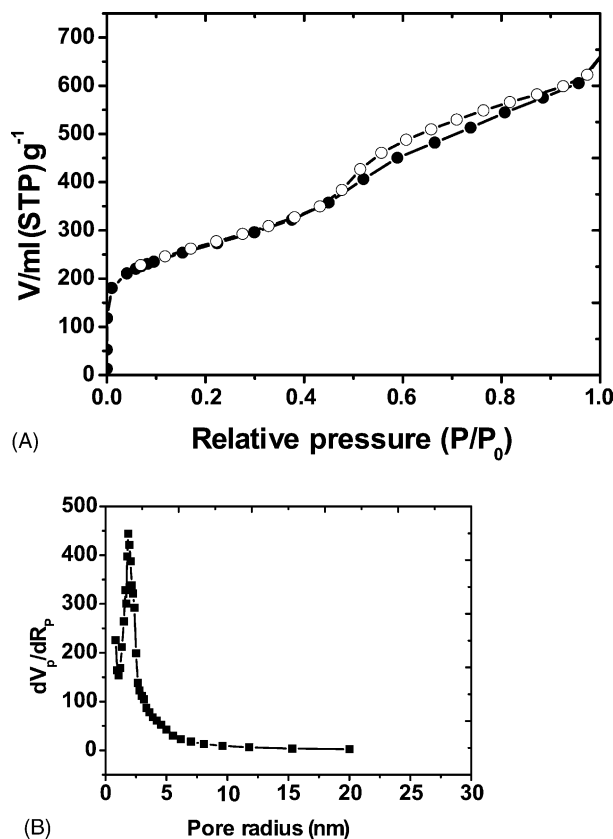
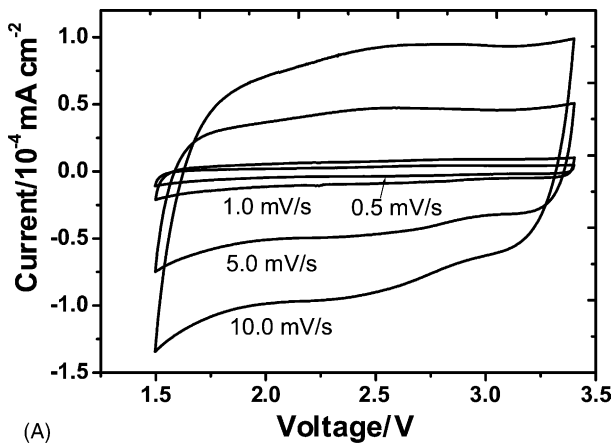


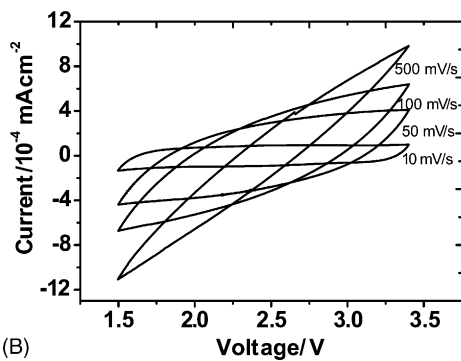
Fig. 2. (A) The N<sub>2</sub> gas adsorption–desorption isotherm. The square and circle are adsorption and desorption curve, respectively. (B) The pore size distribution of CMK-3.

This is because the actual resistance between working and counter electrodes was a few 10 Ω and capacitance 1 F in our experimental conditions. Then relaxation time after potential reversal which is expressed as RC can be estimated to be about 10 s, corresponding to 0.5 V at the sweep rate of  $5 \times 10^{-1}$  V/s. The rectangular-shaped cycle voltammograms were also observed in the extending potential range from  $E = 1.0$  to 3.75 V (versus Li/Li<sup>+</sup>) as shown in Fig. 3(C). If the potential range exceeded the range of 1.0–3.75 V the rectangular-shaped cycle was collapsed as shown in Fig. 3(C) because of the decomposition of the electrolyte.

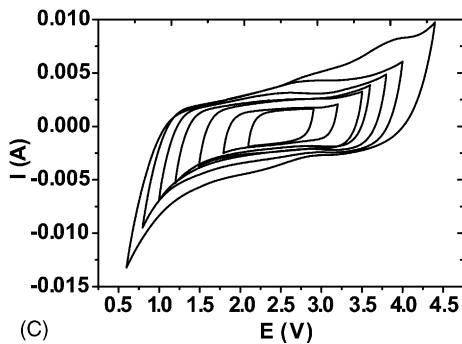
The values of capacities were calculated on the stabilized capacitors. The results are demonstrated in Fig. 4. The capacity of charge reaches 95 F/g at scan rate  $1 \times 10^{-3}$  V/s, the capacity of discharge is a little less than that of charge, but also reaches about similar level. It is found that the capacities of charge and discharge are kept in a constant value in the range of 60–95 F/g in a wide scale of the scan rate from  $5 \times 10^{-4}$  to  $5 \times 10^{-2}$  V/s, which indicates a typical EDLC capacitor characteristic. The specific capacitances of charge and discharge are in the range of about 8–10 μF/cm<sup>2</sup> in this scan range. Then, the capacities decrease with increasing scan rate at the scan rate above  $5 \times 10^{-2}$  V/s. It means the charge–discharge rates cannot follow the fast scan rate in this range. Here, the mesoporous carbon gives a similar specific



(A)



(B)



(C)

Fig. 3. (A) Cyclic voltammograms of CMK-3 in 1 M LiPF6 in EC/DEC electrolyte in the potential range from 1.5 to 3.4 V (vs. Li/Li<sup>+</sup>) at the scan rates from 0.5 to 50 mV/s. The specific current (mA/cm<sup>2</sup>) is obtained by dividing the current with the surface area of the mesoporous carbon. (B) Cyclic voltammograms of CMK-3 in 1 M LiPF6 in EC/DEC electrolyte in the potential range from 1.5 to 3.4 V (vs. Li/Li<sup>+</sup>) at the scan rates from 50 to 500 mV/s. (C) Cyclic voltammograms of CMK-3 at various potential regions performed in 1 M LiPF6 in EC/DEC electrolyte.

capacitance (10  $\mu\text{F}/\text{cm}^2$ ) value as the commercially available active carbon. This value seems a little higher than the capacitance of carbon nanotube (CNT) [16,17] as EDLC. Both the self-ordered mesoporous carbon and CNT have uniform pore and similar pore size, but the conductivity of the self-ordered mesoporous carbon is lower than that of the CNT although the surface area of self-ordered mesoporous carbon is higher than that of CNT. The heat treatment under

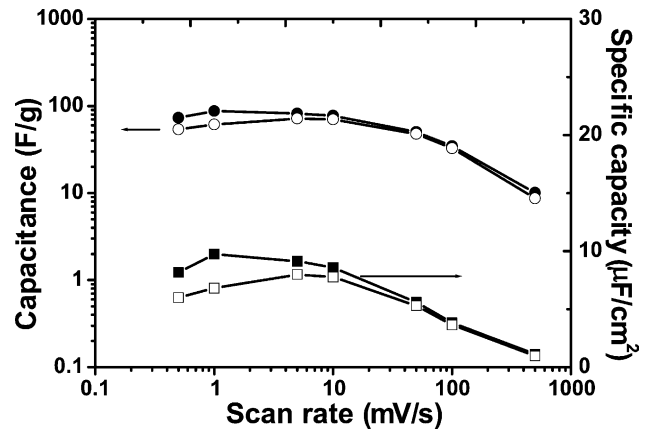


Fig. 4. The dependence of capacitance on the scan rates. The square and circle are capacitance and specific capacities of charge and discharge curves, respectively.

nitrogen gas environment in high temperature can improve the conductivity of self-ordered mesoporous carbon by increasing the graphite domain in the framework. Such treatment can make the self-ordered mesoporous carbon suitable for EDLC's application. The problem is how to keep the self-ordered structure and high surface area remaining after the heat treatment.

Voltammetry measurements are also used to characterize the cycling behavior of the carbon. In the 1.5–3.4 V (versus Li/Li<sup>+</sup>) potential region, a sample was examined for up to 100 charge–discharge cycles at the same rate of 10 mV/s. By repeating this procedure, we examined electrochemical stability and reversibility for carbon. We show the results of the cycle performances in Fig. 5.

At the first process, the amount of charging was about 75 F/g and that of discharging was 68 F/g. After 100 cycles, the capacity decreased about 20% in comparing with the first one. It is the same as that of carbon aerogels (25%) [18]. This loss results from the irreversible reactions of electrolyte with C–H, C–O, and other adsorbed impurities on the surface of self-ordered mesoporous carbon, which could not be removed entirely by thermal treatment at 873 K in nitrogen.

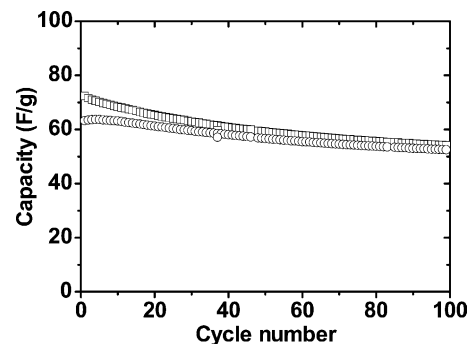


Fig. 5. The dependence of capacitance on the scan number. The square and circle are capacitance and specific capacities of charge and discharge curves, respectively.

#### 4. Summary

In summary, we have successfully prepared self-ordered mesoporous carbon (CMK-3) from SBA15 using sucrose as the carbon source, the pore size distribution was narrow and the pore size was homogeneous, reached 3.90 nm from the analysis of adsorption–desorption measurement. The surface area of the self-ordered mesoporous carbon produced was 900 m<sup>2</sup>/g.

The capacitance properties of the self-ordered mesoporous carbon have been investigated. Rectangular shape of the CV was observed even when the scan rate was increased to  $5 \times 10^{-2}$  V/s. When the scan rate was kept at 10 mV/s, the potential range of the rectangular-shaped could be reached between 0.75 and 3.75 V (versus Li<sup>+</sup>/Li). Self-ordered mesoporous carbon exhibited a capacitance of 60–95 F/g (about 8–10 μF/cm<sup>2</sup>) in scan rate from  $5 \times 10^{-4}$  to  $5 \times 10^{-2}$  V/s. The specific capacitance of 10 μF/cm<sup>2</sup> was similar to that of typical EDLC capacitor. After the 100th cycles, the capacity decreased to 20% in comparing with that of the first one. The specific capacitor of the self-ordered mesoporous carbon is much larger than some commercially available activated carbons with high surface area, which had been investigated and reported [12,19]. The capacitances of M-10, M-15A and M-30 series samples from Spectracorp are 56, 78 and 63 F/g with surface areas of 1370, 1800 and 2571 m<sup>2</sup>/g, respectively [12]. We can calculate their specific capacitors, by dividing the capacitance with the surface area of the activated carbon, are 4.1, 4.3 and 2.5 μF/cm<sup>2</sup>, respectively. These values are much less than 10 μF/cm<sup>2</sup> for a typical EDLC capacitor. So, the effective surface areas for EDLC in the commercially available activated carbon should be much less than the surface area from N<sub>2</sub> gas isotherm valuation. In fact, the small micropore, with diameter less than about 0.7 nm [20], could not be accessible to electrolyte solution, so the surface area of those non-accessible micropores will not be contributed to the total electrochemical double-layer capacitance [12].

The results suggest that self-ordered mesoporous carbon with uniform mesopore is promising for energy storage devices such as EDLC. As rectangular-shaped cyclic voltammograms over a wide range of scan rates is the ultimate goal in EDLC. Self-ordered mesoporous carbon presents attractive materials as electrodes for capacitors.

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