

Cobalt doped carbon xerogels as efficient supercapacitor electrodes

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ABSTRACT

Carbon xerogel and cobalt doped carbon xerogel are successfully prepared from resorcinol-formaldehyde monomers by the sol-gel process. N₂ adsorption/desorption isotherms technique are used to characterize the surface texture and pore size distribution of prepared samples. The measured BET specific surface areas for the carbon xerogel and the cobalt doped carbon xerogel are 796.9 and 701.9 m².g⁻¹, respectively. These materials were tested as electrodes in a symmetric supercapacitor two-electrode configuration using 1M H₂SO₄ electrolyte by means of cyclic voltammetry technique. The cobalt doped sample exhibits relatively high specific capacitance of 231 F.g⁻¹ (at 0.1 A.g⁻¹). The presence of cobalt species inside the carbon structure of xerogel lead to lowering the specific surface area, increasing the mesoporosity and consequently enhancing the accessibility for electrolytic ions inside the pores of the cobalt doped samples.

Key words: Cobalt-doped carbon xerogel; Supercapacitors; mesoporosity.

INTRODUCTION

Nowadays the renewable energy conversion devices such as solar cells, fuel cells and wind turbines^[1], as well as the energy storage devices like lithium ion batteries^[2] and supercapacitors acquire a great interest of researchers all over the world. Supercapacitors are environmental friendly electrochemical energy storage devices that attracted a lot of attention due to their high power density, long life cycle, high charge discharge rates, and wide ranges of operating temperature^[3-5]. The supercapacitors can play a vital role in complementing the gap between the high energy storage functions of batteries and fuel cells and the high power density of the traditional dielectric capacitors^[6, 7].

Super capacitors consist of two electrodes separated by insulator di-electrical material. The specific surface area, pore structure, and chemical stability of electrode materials are very important parameters for determining the performance of the supercapacitors. Recently, carbon materials such as carbon nanotubes^[8], carbon gels^[9, 10] and graphene^[11, 12] are intensively used in designing the supercapacitor electrodes. In addition, the carbon materials have high electrical conductivity, chemical inertness, abundance, and low cost^[13, 14].

For instance, carbon gels, including aerogel, cryogel and xerogel, are characterized by a controllable large specific surface area through adjusting the micro - meso pores ratio. The micropores are essential for increasing the surface area and providing the place for storing the ions of the dissociated electrolyte. However, the meso pores offer channels for the electrolyte to pass through and reach the entire micropore structure with sufficient amounts. Consequently, carbon xerogels are good candidates for many recent energy applications such as fuel cells^[15-17], hydrogen storage adsorption^[18, 19], lithium ion batteries^[20-22] and supercapacitors^[23-26]. Carbon xerogels can be doped with active materials such as Mn, Ni, Fe, Pd^[27] or metal oxides^[17] in order to enhance its activity.

Although, cobalt metal is intensively used in energy devices, it was not tested as a dopant for the carbon gels in supercapacitor applications to the best of our knowledge. The aim this work, is focused in preparing carbon xerogel with a high surface area and doping it with cobalt metal as a promising highly efficient supercapacitor electrode. In addition, the performance of the prepared xerogels is compared with some similar published electrodes.

EXPERIMENTAL

1. Synthesis of carbon xerogel (X)

Carbon xerogel was synthesized by polycondensation of resorcinol and formaldehyde in molar ratio of 1:2 respectively in the presence of aqueous solution of Na_2CO_3 as catalyst. All these chemicals were of analytical grade and were purchased from the ADWIC laboratory chemicals (Egypt). The components were mixed and stirred well to get clear solutions. Then the mixture was divided into equal portions, poured into glass tubes and sealed from both sides to minimize solvent evaporation. The glass molds were dried at 40°C overnight; then, maintained constant at 80°C for 5 days. The obtained organic gel was then soaked for 5 days in acetone and dried in microwave oven. Finally, Carbon xerogel (X) was obtained after carbonizing the resultant xerogel at 900°C in nitrogen atmosphere in a special tube furnace^[28-30].

2. Synthesis of cobalt doped carbon xerogel (Co-X)

Preparation of cobalt doped carbon xerogel (Co-X) was achieved in the same manner as X, but with replacing Na_2CO_3 by cobalt acetate $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich, USA) that works as the catalyst and the dopant as well. The molar ratio of resorcinol-formaldehyde mix to cobalt acetate was 100:1.

3. Characterization of surface texture:

The surface texture of the prepared samples was characterized by N_2 adsorption/desorption at -196°C using a BET-Surface area analyzer, Gemini VII 2390 Analyzers, Micromeritics, USA, instrument. The samples were previously degassed for two hours under Helium as flow at 110°C .

a. Electrochemical characterization

Electrochemical measurements of supercapacitor performance were achieved using a Swagelok two-electrode cell setup. The electrodes were prepared by mixing the electroactive X material and polytetrafluoroethylene (PTFE) (60% suspension in water) as binder with a mass ratio of 90:10. The mixture was dried in oven at 100°C for 24 hrs. A portion of 4 mg of the resulted paste was loaded and pressed onto a graphite disc with diameter of 0.8 cm which employed as a current collector. The samples were soaked in 1M H_2SO_4 for 72 hrs prior to the electrochemical measurements to ensure complete diffusion of electrolyte ions into the pores of the active material. The capacitor cell was built up of two composite discs electrodes separated by filter paper witted with electrolyte in the Swagelok system. All electrochemical measurements were performed using Gamry Reference 3000 electrochemical workstation. The electrochemical cyclic voltammetry (CV) technique was used to estimate the performance of the prepared electrodes in a potential range from 0 to 0.8 V with different scan rates of 100, 50, 20, 10, 5, 3, 1 and $0.5 \text{ mV} \cdot \text{s}^{-1}$.

RESULTS AND DISCUSSION

1. Surface characterization and pore size analysis:

The typical N_2 adsorption/desorption isotherms at -196°C for X and Co-X are shown in Figure (1) and the data extracted from the isotherms including BET specific surface area

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(S_{BET}), total pore volume (V_{P}) and the average pore diameter (d) are compiled in Table (1). The adsorption-desorption isotherm obtained from X sample can be considered as a composite of types I and IV with a very narrow H4 hysteresis behavior based on the IUPAC classification indicating that such carbon matrix has a combined micro-mesoporous structure^[31]. This is consistent with the high S_{BET} of $796.9 \text{ m}^2 \cdot \text{g}^{-1}$ and its (d) value of 2.88 nm which is slightly higher than the micropore diameter borderline (Table 1).

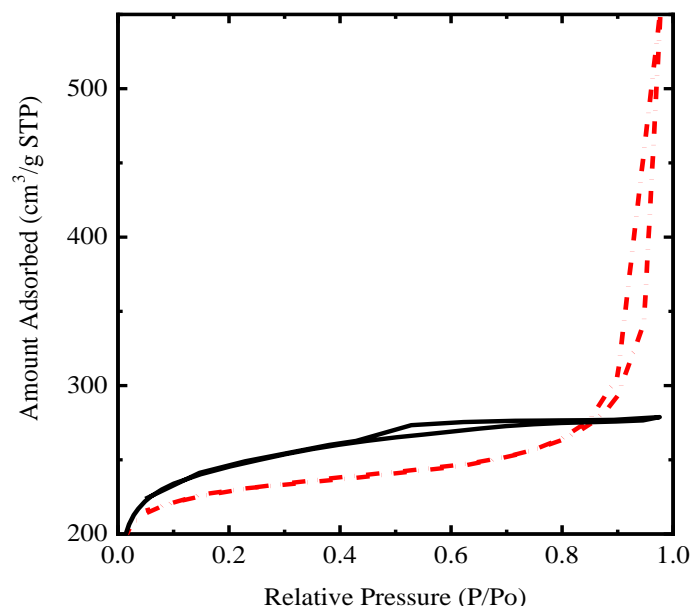


Fig. 1. N_2 adsorption/desorption isotherms for Xerogel sample; X (black solid line) and cobalt/Xerogel sample; Co-X (red dashed line).

On the other hand, the adsorption-desorption isotherm of cobalt-doped sample (Co-X) is typically type II with type H1 hysteresis. Moreover, introducing the cobalt dopant leads to a slight decrease in S_{BET} of Co-X to $701.9 \text{ m}^2 \cdot \text{g}^{-1}$, and enlargement of its (d) to 4.33 nm (Table 1) indicating the enhancement of the mesoporosity. This is consistent with the increase of the adsorbed volume at high relative pressure (P/P^0) due to the mesopores saturation. This development of mesoporous structure of the carbon xerogel matrix may be related to the incorporation of the cobalt species into the X micro-mesopore system. It is worth noting that increasing the mesoporosity in xerogel matrix improves its availability for the electrolyte through providing networks for fast ion transport^[32]. Meanwhile, the micropores supply a large surface area together with strong adsorption ability to improve capacitance and act as ion traps for energy storage as well^[32,33].

Table 1: Surface area and pore size analysis of the prepared materials

Sample	Specific surface area (S_{BET}) $\text{m}^2 \cdot \text{g}^{-1}$	Pore volume (V_{P}) $\text{cm}^3 \cdot \text{g}^{-1}$	Pore diameter (d) nm
CX	796.9	0.267	2.88
Co-CX	701.9	0.163	4.33

2. Cyclic voltammetry characterization of the carbon xerogel (X) and cobalt doped carbon xerogel (Co-X) composites:

The cyclic voltammetric behavior of the X and Co-X samples at different scan rates are shown in Figs. 2 and 3 respectively. The CVs exhibit a rectangular shaped profile characteristic of an ideal capacitive behavior. This behavior remains stable in the studied range of scan rates. The integrated area of the CV of X is lower than that for Co-X. This indicates a better capacitive performance of Co-X. For instance, the specific capacitances measured for X and Co-X at scan rate (v) of $1 \text{ mV} \cdot \text{s}^{-1}$ are 159 and $231 \text{ F} \cdot \text{g}^{-1}$ respectively. Table (2), summarized the calculated specific capacitances of both X and Co-X samples at different values of scan rates. The results revealed that the capacitance of both samples increases by decreasing the scan rate due to ion exchange mechanism. At lower scan rates the ions have enough time to intercalate and de-intercalate, which facilitates storing more charge^[34].

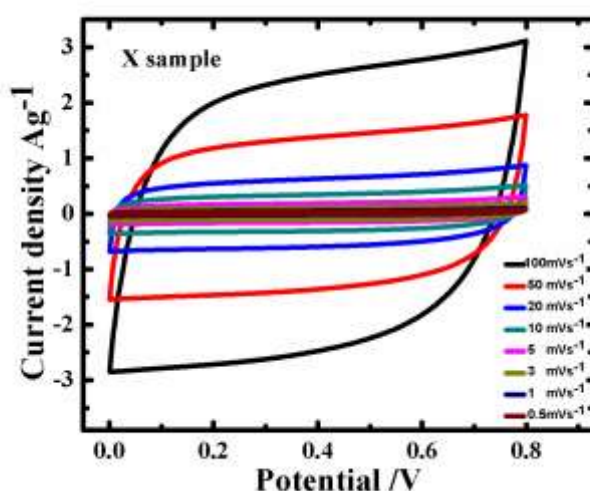


Fig. 2 CV curves in $1\text{M H}_2\text{SO}_4$ for Xerogel electrode at different scan rate values.

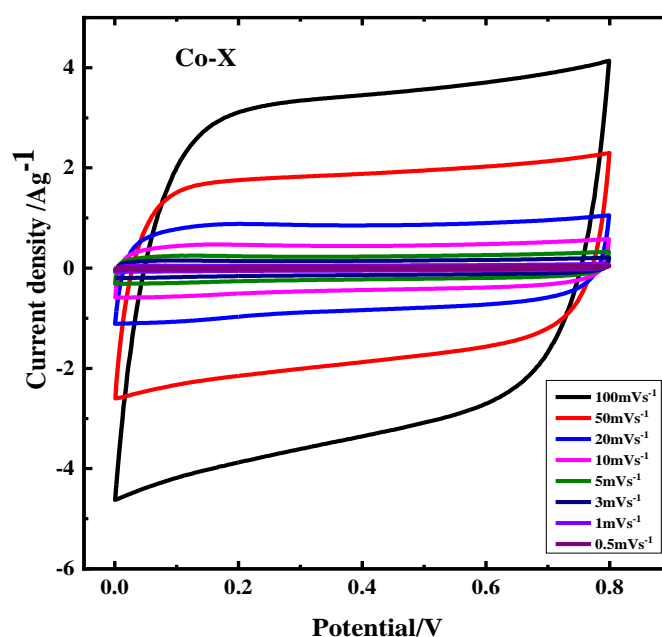


Fig.3. CV curves in $1\text{M H}_2\text{SO}_4$ for Co-X electrode at different scan rates values.

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Also, the obtained results together with those of Fig.1 and Table 1, lead to the conclusion that cobalt doping in carbon xerogels enhances the electrochemical activity due to faster ionic accessibility inside the pores (owing to improving the mesoporosity) and creation of new cobalt active sites.

Table 2: Effect of scan rate on the specific capacitance of X and Co-X samples.

Scan rate mVs^{-1}	Specific capacitance F.g^{-1}	
	X	Co-X
100	90	142
50	102	161
20	116	185
10	125	198
5	134	208
3	139	215
1	159	231
0.5	188	243

Moreover, it is worth noting that the present X and Co-X electrodes have higher capacitance values than almost all published electrodes as shown in the rough comparison of Table 3. Accordingly, our Co-X represents a hopeful highly efficient material as a supercapacitor electrode.

Table 3: Comparison between the present X and Co-X electrodes and other electrodes.

Electrode Material	Electrolyte	Capacitance F.g^{-1}	Scan rate v/mV s^{-1}	Reference
10 wt% Ni-X	6M KOH	103	1	[35]
X	30% wt KOH	210	1	[36]
X	1 MH_2SO_4	159	1	present work
Co-X	1 MH_2SO_4	231	1	present work

Conclusions:

Two carbon network samples namely, carbon xerogel (X) and cobalt doped carbon xerogel (Co-X) were prepared by the sol-gel prior to hydrothermal processes and well characterized by some surface and electrochemical techniques. The analysis of N_2 adsorption/desorption isotherms revealed that the specific surface area of Co-X is slightly lower than that of undoped sample. However, the porous structure of Co-X is enlarged to the mesoporous scale due to the invasion of cobalt species through the porous carbon network. Moreover, cobalt doping in carbons xerogels enhances the electrochemical activity and increases its capacitance due to faster ionic accessibility inside the pores (improving the mesoporosity) and creation of new cobalt active sites.

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تحسين كفاءة الكربون زيروجيل بواسطة تطعيمه بالكوبلت لاستخدامه كقطب في المكثفات الفائقة

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المستخلص

تم تحضير الكربون زيروجيل من الريسورسينول و الفورمالدهايد و كذا الكربون زيروجيل المطعم بالكوبلت بنجاح بواسطة طريقة سول جيل. وقد تم دراسة الخواص السطحية من خلال تعيين مساحه السطح (S_{BET}) والخواص المسامية لها. وقد أظهرت النتائج أن قيم مساحه السطح للعينات 796.9 و 701.9 متر مربع لكل جرام لكل من الكربون زيروجيل والكربون زيروجيل المطعم بالكوبالت على الترتيب. تم اختبار هذه المواد كأقطاب كهربائية في مكثف متماثل ثنائي القطب باستخدام محلول حمض الكبريتيك بتركيز واحد مولار بواسطة تقنية قياس الجهد الدوار. وقد تميزت عينة الكربون زيروجيل المطعم بالكوبالت بسعة تخزين عالية نسبياً بلغت قيمتها 231 Fg^{-1} وذلك بسبب وجود الكوبلت داخل الهيكل الكربوني للزيروجيل مما أدى إلى تقليل مساحه السطح المحددة ، وزيادة نصف قطر المسام والذي بدوره يعزز إمكانية وصول الأيونات داخل مسام العينات المطعمه بالكوبلت.