จุฬาลงกรณ์มหาวิทยาลัย

ทุนวิจัย

กองทุนรัชดาภิเษกสมโภช

รายงานผลการวิจัย

การพัฒนาตัวเก็บประจุไฟฟ้าชนิดที่เก็บพลังงานได้มากเป็นพิเศษ จากวัสดุคอมพอสิทของคาร์บอนแอโรเจลที่ได้จากเบนซอกซาซีน

โดย

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ชื่อโครงการวิจัย การพัฒนาตัวเก็บประจุไฟฟ้าชนิดที่เก็บพลังงานได้มากเป็นพิเศษจากวัสดุคอมพอสิทของคาร์บอนแอโรเจลที่ได้จากเบนซอกซาซีน

ชื่อผู้วิจัย ธัญญลักษณ์ ฉายสุวรรณ์ ปรวี กตัญญูตะ และ นันทิยา มหิงสุพรรณ

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บทคัดย่อ

พอลิเบนซอกซาซีนซึ่งเป็นเรซินที่มีประสิทธิภาพสูงถูกนำมาใช้เตรียมขั้วไฟฟ้าคาร์บอนแอโรเจลของขั้วเก็บประจุไฟฟ้า พอลิเบนซอกซาซีนถูกทำให้แห้งด้วยการอบที่อุณหภูมิห้องภายใต้ระบบสูญญากาศซึ่งเป็นการประหยัดค่าใช้จ่ายและเหมาะแก่การใช้งานเชิงพาณิชย์ ได้คาร์บอนแอโรเจลหลังจากเผาภายใต้ไนโตรเจน พื้นที่ผิวของคาร์บอนแอโรเจลมีค่าประมาณ 360 ตารางเมตรต่อกรัม ในการเปรียบเทียบคุณสมบัติทางกายภาพและทางเคมีไฟฟ้า ได้มีการศึกษาคาร์บอนแอโรเจลที่มีการกระตุ้นพื้นที่ผิว ซึ่งมีค่าพื้นที่ผิวเพิ่มขึ้นมากกว่าสองเท่าของคาร์บอนแอโรเจลที่ไม่ได้มีการกระตุ้นพื้นที่ผิว จากการศึกษาคุณสมบัติทางเคมีไฟฟ้าโดยใช้ไซคลิกโวลแทเมททรี ชาร์จ/ดิสชารจ์ และอิเล็กโตรเคมิคอลอิมพีแดนซ์ ผลปรากฏว่าคาร์บอนแอโรเจลที่สังเคราะห์จากพอลิเบนซอกซาซีนมีคุณสมบัติทางเคมีไฟฟ้าที่มีประสิทธิภาพที่ดี คาร์บอนแอโรเจลมีค่าความจุไฟฟ้าจำเพาะ 30 ฟารัดต่อกรัม ที่ความหนาแน่นกระแสไฟฟ้า 5 มิลลิแอมต่อตารางเซนติเมตร คาร์บอนแอโรเจลที่มีการกระตุ้นพื้นที่ผิวมีค่าความจุไฟฟ้าจำเพาะเพิ่มขึ้นเป็น 78 ฟารัดต่อกรัมที่ความหนาแน่นกระแสไฟฟ้าเดียวกัน นอกจากนี้ ยังพบว่าคาร์บอนแอโรเจลที่ผ่านการให้ความร้อนที่อุณหภูมิ 300 องศาเซลเซียสให้คุณสมบัติทางเคมีไฟฟ้าที่ดีที่สุด โดยให้ค่าความจุไฟฟ้าจำเพาะสูงถึง 109 ฟารัดต่อกรัม พฤติกรรมทางเคมีไฟฟ้านี้ถูกยืนยันด้วยไซคลิกโวลแทมเมททรีและอิมพีแดนซ์สเปกโตรสโกพี

Research Title: Development of Supercapacitors from Carbon Aerogel Derived from
Polybenzoxazine

Researchers: Thanyalak Chaisuwan, Porawee Katanyoota, and Nuntiya Mahingsupan,

Project Completion: July, 2012

Abstract

Polybenzoxazine, a high-perfomance phenolic resin, was used as a precursor for carbon aerogel electrode of supercapacitors. A cost-effective ambient drying was used for benzoxazine aerogel preparation. After the pyrolysis of benzoxazine aerogel under a nitrogen atmosphere, carbon aerogel was obtained. The BET surface area of the carbon aerogel was approximately 360 m^2/g. The activation of the carbon aerogels was also investigated in order to compare the physical and electrochemical properties. The BET surface area of the activated carbon aerogels increased more than twice in comparison with the unactivated one. The electrochemical behaviors were studied by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The results showed that the polybenzoxazine-derived-carbon aerogel exhibited good electrochemical performance. A specific capacitance of the carbon aerogel electrode was 30 F/g obtained at current density 5 mA/cm^2. The specific capacitance increased to 78 F/g at the same current density after carbon dioxide activation. Moreover, the best electrochemical behaviors with the specific capacitance of 109 F/g were obtained from the electrode prepared from carbon aerogel which underwent heat treatment at 300 °C in air. The electrochemical impedance spectroscopy as well as cyclic voltammetry was also confirmed those electrochemical behaviors.

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1. Introduction

Currently, energy demand is increasing in our life; therefore, energy storage devices—batteries, capacitors and fuel cells—have been received great attention because they are good alternative power sources for electronic devices, electrical vehicles, digital telecommunication systems, and memory back-up systems, etc. Some problems found in these devices are low energy density, short life time and durability, high cost and toxic waste which limited their use.

Electrochemical supercapacitors are energy storage devices, which have a high specific capacitance and long life cycle. These devices can be categorized into two types according to their operation mechanisms: electrical double-layer capacitors (EDLCs) and pseudocapacitors. The former is based on charge separation at the electrode/electrolyte interface, whereas the latter is based on Faradaic redox reaction in the electrode surface formed with electroactive materials [1]. The materials studied for capacitors have been mainly of three types: carbon, metal oxide, and conducting polymers. Carbon aerogels are promising materials as electrodes for EDLCs due to their high performance and low cost [2].

Carbon aerogels normally are obtained via polycondensation of resorcinol and formaldehyde using acid or base as a catalyst [3]. However, costly raw materials and tedious preparation time are the limitations for a commercial application. In this study, polybenzoxazine, a high-performance phenolic resin, is considered to be a precursor for carbon aerogel preparation because of its unique characteristics such as excellent dimensional stability and low water absorption [4]. Moreover, the facile synthesis approach adapted from the solventless method reported by Ishida *et al*. allows for scale-up production. Additionally, the surface characteristics of carbon aerogels—pore volume, pore size distribution, and specific surface area—can be varied by changing concentration and type of precursors of benzoxazine and/or catalyst.

The purposes of this work are to fabricate the carbon aerogel electrodes for supercapacitors by using polybenzoxazine, a high-performance phenolic resin, as a precursor. The physical and electrochemical properties of the electrodes will be investigated. In order to compare the electrochemical properties, the activated carbon aerogel will also be studied.

2. Survey of Related Literatures

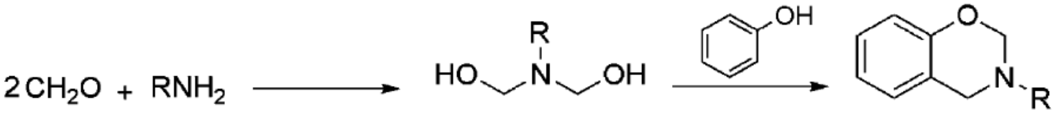
Benzoxazine

Polybenzoxazines as a novel type of phenolic resin offer many advantages in comparison with the traditional phenolic resins. Their precursors can be easily prepared from inexpensive raw materials, and polymerized without using strong acid or basic catalysts and without producing any by-products. Polybenzoxazines also provide unique characteristics like low water absorption and high dimensional stability due to near-zero shrinkage upon curing [5]. Therefore, they are widely applied in various fields such as protective coatings for circuits in television studios and computer chips, airplane bodies, materials for airplane interiors, curing agents for other synthetic resins and varnishes which form films with a good resistance to water, alkali and solvents. The major disadvantages of the typical polybenzoxazines are their brittleness and a high temperature needed for the polymerization. Various studies have been reported aiming at performance improvement of polybenzoxazines. Generally, for performance enhancement, the preparation of novel monomers, copolymers, polymer alloys, and fiber reinforced composites have become increasingly attractive to overcome the shortcoming of the typical polybenzoxazines.

1. Chemical methodologies for systhesis of benzoxazine monomer

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached. These substituting groups can provide additional polymerizable sites and also affect the curing process. Consequently, polymeric materials with desired properties may be obtained by tailoring the benzoxazine molecular structures. In this section synthesis of different benzoxazine monomers is discussed.

Holly *et al.* (1944) [6] first reported the condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two-steps. Later Burke *et al.* (1949) [7] found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge. In 1965, the same group systhesized Mannich condensation for benzoxazine synthesis in a solvent proceeds by adding amine to formaldehyde at lower temperatures at first to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring (Scheme 1) [8].

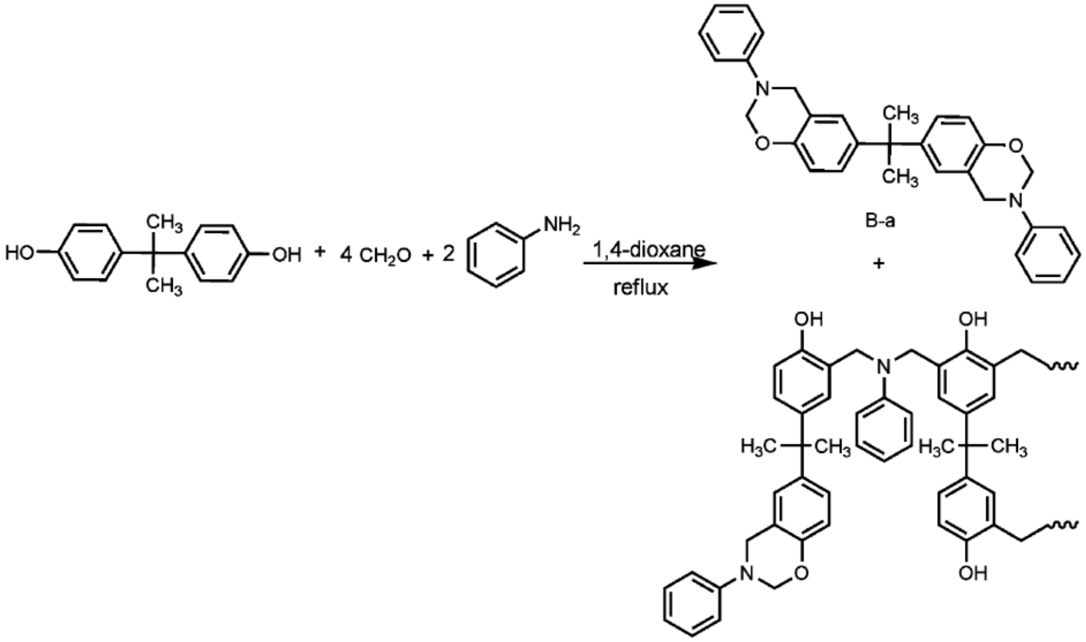


Scheme1. Synthesis of 3, 4-dihydro-2H-1,3-benzoxazines.

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with an average molecular weight around 1000 Da. Thus, no materials could be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high-molecular weight linear structures were unobtainable [9]. To overcome this limitation, Ishida and coworkers in 1995 have developed a new class of difunctional or multifunctional benzoxazine monomers, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The precursor was synthesized using bisphenol-A, formaldehyde and aniline in 1,4-dioxane solvent and the pure monomer was referred as B-a and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a were analyzed by 1H-NMR measurements. The overall synthetic procedure is shown in Scheme 2. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by NMR, FTIR and SEC. It was observed that the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility.To achieve successful processing, cure kinetics of this material was investigated by using DSC, which indicated that the curing of benzoxazine precursors is an autocatalyzed reaction until vitrification is occurred, and diffusion begins to control the curing process.

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, Ishida *et al.* [10] developed a solventless synthesis in the melt state.

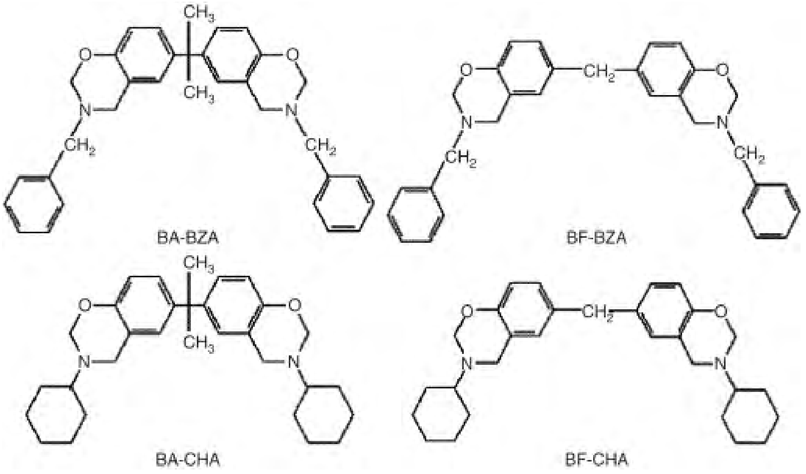
The reaction mechanism and kinetics of this solventless synthesis were proposed by Liu *et al.*[11] In a typical synthesis, the reactants, i.e., aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. It should be pointed out that formaldehyde is not typically used as it evaporates easily and causes stoichiometric imbalance. Instead, paraformaldehyde is used. The choice for phenols and amines provides the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless synthetic method are improvement of reaction times compared with the traditional synthetic route and formation of fewer unwanted intermediates and by-products.



Scheme 2. Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.

Garea et al. [12] systhesized four different benzoxazine monomers bis(4-benzyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BA-BZA), bis(4- ciclohexyl-3,4-dihydro-2H-1,3 benzoxazinyl) isopropane (BA-CHA), bis(4-benzyl-3,4-dihydro-2H-1,3-benzoxazinyl) methane

(BF-BZA), bis(4-ciclohexyl-3,4-dihydro-2H-1,3-benzoxazinyl) methane (BF-CHA) led to products, which include oligomers revealed by ^{1}H NMR and GPC.



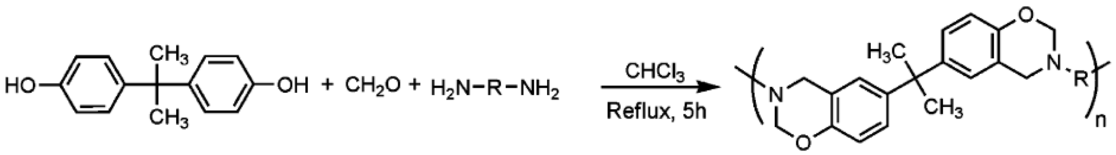
Scheme 3. Four different benzoxazine monomers

The quantity of oligomers mainly depends on the basicity of the oxygen and nitrogen atoms from the oxazine cycles, which influences the possibility of oxazine cycles opening and, thus, the formation of oligomers. Therefore, the benzoxazine monomers obtained from BA exhibit a higher concentration of oligomers than for those based on BF. The effective thermal polymerization of the benzoxazine monomers may be followed by GPC, which shows that there are two main factors which influence the polymerization reaction: the basicity of the N and O atoms from the oxazine cycles and the oligomers already existing in the monomers from their synthesis, which may act as a catalyst through the phenolic groups. FTIR proved the gradual formation of the tetrasubstituted aromatic rings within the polymer, the process depending on time and, again, on the initial concentration of the oligomers in the monomers. The T_g values of the obtained polybenzoxazines, as determined from tan δ-temperature curves, depend mainly on the nature of the phenolic component and less on the amine component. The dependence of ionic conductivity against time during the polymerization of the benzoxazine monomers gives the value for the gel time and, therefore, the reactivity of each of the benzoxazine monomer. The major difference in the reactivities for monomers based on BA and BF is due to the initial concentration of oligomers in each monomer, while the minor difference in the reactivities of the monomers based on the same phenol but with different amines is explained in terms of the electron density at the nitrogen atom from amine.

2. Preparation of high molecular weight benzoxazine precursors

Preparation of high molecular weight benzoxazine precursors would result in gel or insoluble solid because of the ring-opening polymerization of the once-formed cyclic ring. If it is possible to obtain soluble high molecular weight polybenzoxazine precursors, processing into thin films should become very easy, and application into the fields for which the low molecular weight cyclic monomer has not been used will be realized.

High molecular weight benzoxazine oligomers have been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde (Scheme 3). The precursors were obtained as soluble white powder. The structure of the precursors was confirmed by IR, ^{1}H NMR and elemental analysis, indicating the presence of cyclic benzoxazine structure. The precursor solution was cast on a glass plate, giving transparent and self-standing precursor films, which were thermally cured up to 240 °C to give brown transparent polybenzoxazine films. The toughness of the crosslinked polybenzoxazine films from the high-molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were as high as 238–260 °C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability [13].



Scheme 4. Synthesis of polybenzoxazine precursors.

Agag et al. [14] prepared polybenzoxazine matrix through high molecular weight polybenzoxazine precursors. They have used AB-type aminophenols instead of amines and phenols separately. The self-standing thin films from were obtained the precursors before curing by casting the precursor solutions onto glass plates. After the thermal treatment of the AB polybenzoxazine precursor films up to 250 °C, reddish-brown, transparent polybenzoxazines have been obtained. Both viscoelastic analyses and TGA have indicated that the thermosets derived from these novel AB precursors have excellent thermomechanical properties as well as high thermal stability. This enhancement in the thermal properties can be attributed to the increase in the crosslinking density and hence suggests that the use of AB precursors is an effective approach for obtaining a novel polybenzoxazine matrix with excellent thermomechanical properties.

Carbon aerogels

Carbon aerogels, discovered by Pekala et al. in 1989, compose of particles with sizes in the nanometer range, covalently bonded together. They are highly porous materials consisting of a continuous rigid solid framework. Carbon aerogels can be used in many application such as gas adsorption devices, for heavy metals and ions removal, purification of drinking water, electronic capacitors, fuel cell electrodes, parts for inertial confinement fusion targets, catalyst support and chromatographic packing.

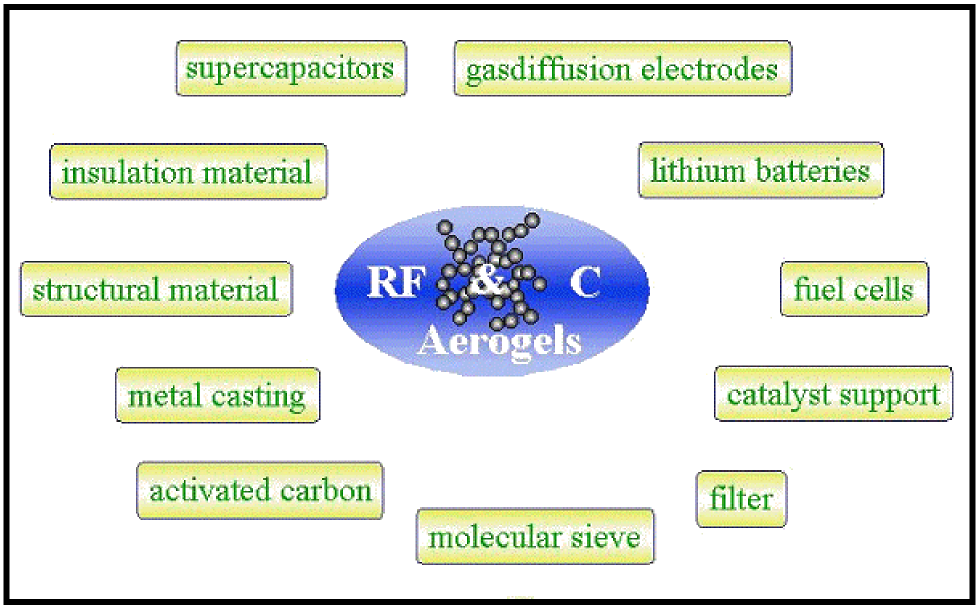


Fig.1 General application of carbon aerogels

Preparation of carbon aerogels

Carbon aerogels have been generally synthesized from resorcinol-formaldehyde, phenol resorcinol-formaldehyde and prepared in four steps namely sol–gel formation, solvent exchange, a supercritical drying and pyrolysis , all of these steps affect the structure of carbon aerogels .

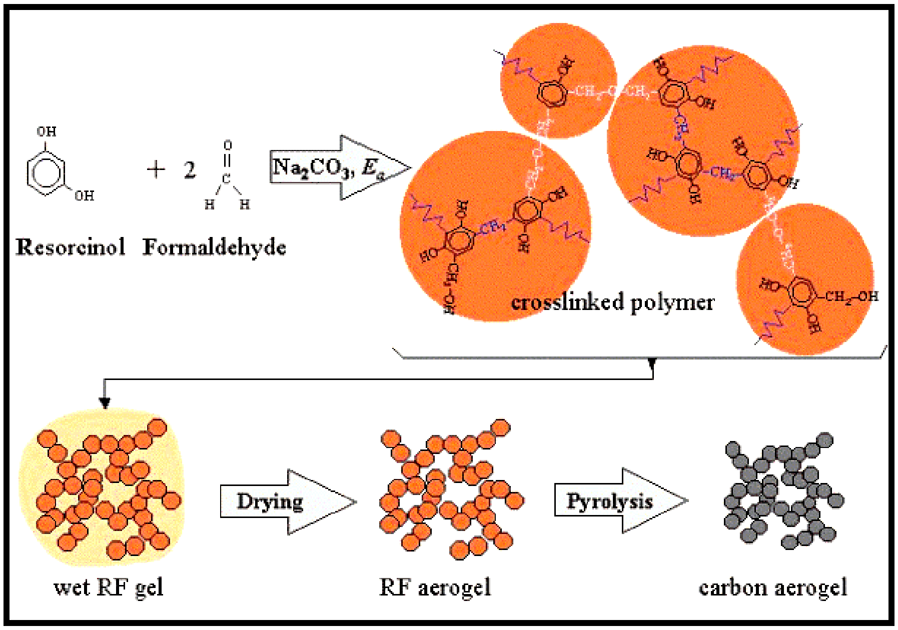


Fig.2 Schematic diagram of the reaction of Resorcinol with Formaldehyde

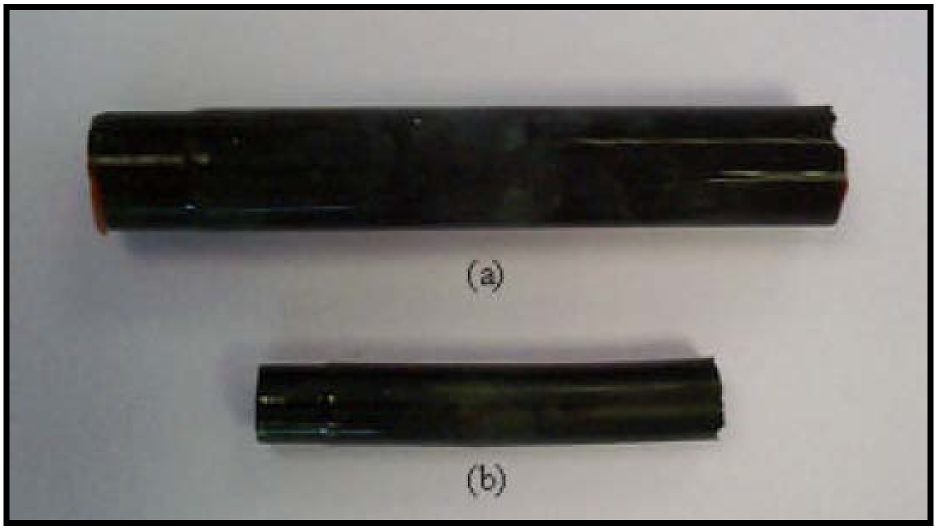


Fig. 3 Effect of the pyrolysis on a of resorcinol-formaldehyde aerogel

(a) before pyrolysis (b) after pyrolysis

However, the conventional method is not suitable for commercial application because it involve a supercritical drying step which is very complicate, expensive and dangerous and use quite expensive raw material. Researchers have tried to produce carbon aerogels from cheap raw materials —cresol-formaldehyde [15], melamine-formaldehyde [16], and phenolic-furfural [17] — and safety synthesis method — freeze drying [18].

Structure and propreties of carbon aerogels

Carbon aerogels, which are highly porous materials consisting of a continuous rigid solid framework and an open, continuous network of pores, represent attractive properties such as:

- A high electrical conductivity (25-100 S/cm)
- Controllable pore structure
- Highly useable surface area (up to 1100 m^2/g)
- Biocompatibility
- Anti-corrosion by acid or base etc.

Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR), N_2 adsorption, Small-angle X-ray scattering (SAXS), Mechanical testing, Electrochemical testing etc. have been used to characterize organic and carbon aerogels especially, the analysis of mesoporous and microporous structures of the aerogels is very important for their application.

Fig. 4 Transmission Electronic Microscopie (TEM) of the carbon aerogel

Applications of carbon aerogel

Carbon aerogels can be used in many applications, especially electrochemical field such as electrical double-layer capacitor (EDLC) and supercapacitor (a unique electrical storage devices, which can store extremely high energy than conventional capacitors and offer much more power density than general batteries) because the carbon aerogels have capacitance values approaching 100–200 F/g. The capacitance density, rather than the specific capacitance, is most importance for potential device manufacturers. Unlike other materials e.g., activated carbon fiber cloths, the carbon aerogels combine high surface area with high bulk density to give large capacitance density values [19].

3. Experimental

3.1 Materials

All chemicals were used without further purification. Bisphenol-A
was purchased from Aldrich, Germany. Triethylenetetramine (TETA) was purchased from FACAI Group Limited, Thailand. Formaldehyde solution (37% by weight) and sulphuric acid (95-97% H_2SO_4 analytical grade) were purchased from Merck, Germany. *N*,*N*-Dimethlyformamide (DMF) was purchased from Labscan Asia Co., Ltd., Thailand.

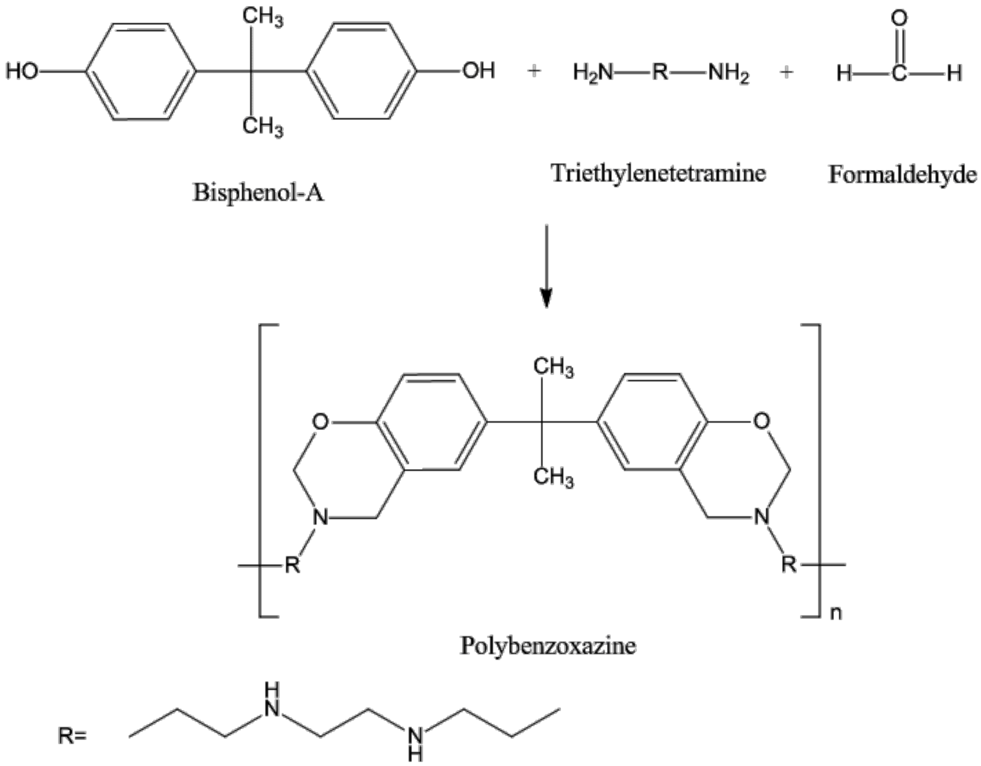
3.2 Measurements

Thermal behaviors of polybenzoxazine aerogel were determined with differential scanning calorimetry (DSC), Perkin Elmer DSC7; The sample was heated from ambient temperature to 300 °C at a heating rate of 10 °C/min under nitrogen flow rate of 10 ml/min. Thermogravimetric analysis was also conducted with Perkin Elmer Thermogravimetric/Differential Thermal Analyzer (TG-DTA) where the sample was heated from ambient temperature to 900 °C at a heating rate of 20 °C/min under nitrogen flow rate of 50 ml/min. FT-IR spectra of polybenzoxazine precursor and carbon aerogel were recorded on a Nicolet Nexus 670 FT-IR spectrometer using KBr pallet technique. The field emission scanning electron microscope (FE-SEM, HITACHI S4800) was used to study the microstructure of carbon aerogel, the samples were coated with platinum under vacuum prior to investigation. BET surface area and pore size distribution of all carbon aerogels were calculated from nitrogen adsorption isotherms at 77 K using a Quantachrome/Autosorb-1 Surface Area Analyzer based on the Brunauer–Emmett–Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively. For all electrochemical measurements, the electrochemical test cell consisted of graphite sheets as current collectors and two carbon aerogel electrodes separated by microporous polyethylene membrane. The carbon aerogel electrodes were soaked in 3M H_2SO_4 electrolyte for 24 hr before measurement to ensure complete filling of the porous electrodes [20]. The electrochemical properties were measured by a computer-controlled potentiotat/galvanostat (Autolab PG-STAT 30 with GPES software). Cyclic voltammograms were performed in the potential range of -1.0 V to 1.0 V with various scan rates. For galvanostatic charge/discharge measurement, the testing cell was charged with current density of 5 mA/cm^2 up to 1 V and discharged with 5 mA/cm^2 down to 0 V [5]. Electrochemical impedance spectroscopy measurements were carried out by Autolab PG-STAT 30 with FRA software in the frequency range of 10 kHz to 10 mHz with a sinusoidal signal of 10 mV. All of the electrochemical measurements were performed at room temperature.

3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine Aerogels

The synthesis of polybenzoxazine precursor was started by dissolving Bisphenol-A (2.3075 g) in *N,N,*-dimethylformamide (DMF) (15.00 g) and stirring continuously. Formaldehyde solution (3.2824 g) was then added into the bisphenol A solution. The solution was kept under low temperature by using ice bath. TETA (1.7388 g) was subsequently added dropwise into the mixture followed by continuous stirring for 1 hr until homogeneous yellow viscous liquid was obtained. The molar ratio of bisphenol-A:formaldehyde:TETA was 1:4:1. The synthetic reaction is shown in Scheme 5. Next, the precursor was filled in a vial with seal and placed in an oven at 80°C for 72 hr in a close system to generate benzoxazine ae-rogels. The benzoxazine aerogels were cut into disc shape and then dried at ambient temperature followed by placing in an oven at 160° and 180°C for 3 hr at each temperature and 200°C for 2 hr in order to polymerize benzoxazine aerogel.



Scheme 5 Preparation of polybenzoxazine precursor.

3.3.2 *Preparation of Carbon Aerogel Electrodes*

The benzoxazine aerogels were cut into a disc shape electrode and then pyrolyzed under a nitrogen flow rate of 600 cm^3/min. The heating profile was as follows: heating from room temperature to 250°C in 60 min, 250° to 600°C in 300 min, 600° to 800°C in 60 min, and holding at 800°C for 60 min and finally cool-ing down to room temperature. The carbon aerogel electrodes were heat treated at 300°C in air for 120 min to modify the electrode surface and to improve affinity with the electrolyte [20].

Activated carbon aerogel (ACA) was prepared by carbonization of carbon aerogel with carbon dioxide at 900°C for 180 min

3.3.3 Characterization of Polybenzoxazine Precursor and Carbon Aerogel Electrodes

The chemical structure of benzoxazine precursor was characterized by Fourier transform infrared (FT-IR) spectroscopy. The thermal behaviors were measured using DSC and TG-DTA.

The surface area of carbon aerogels and activated carbon aerogels were calculated from nitrogen adsorption isotherms at 77 K based on the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calcu-lated with the adsorption data based on the Barret-Joyner-Halenda method (BJH). The surface morphology was characterized using scanning electron microscope (SEM).

For electrochemical measurement, the galvanostatic charge/ discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were determined. All of the electrochemical measurements were performed at room temperature.

4. Results and discussion

4.1 Thermal Behaviors of Polybenzoxazine Precursors

The curing behaviors of polybenzoxazine were examined by DSC. The DSC thermogram shows the broad exotherm at 238 °C as shown in Figure 5 due to the ring opening polymerization of cyclic benzoxazine precursor. After the precursor was fully polymerized, the exotherm completely disappeared indicating that the ring opening of oxazine ring was completed. This result was similar to that reported by Takeichi and coworker [13].

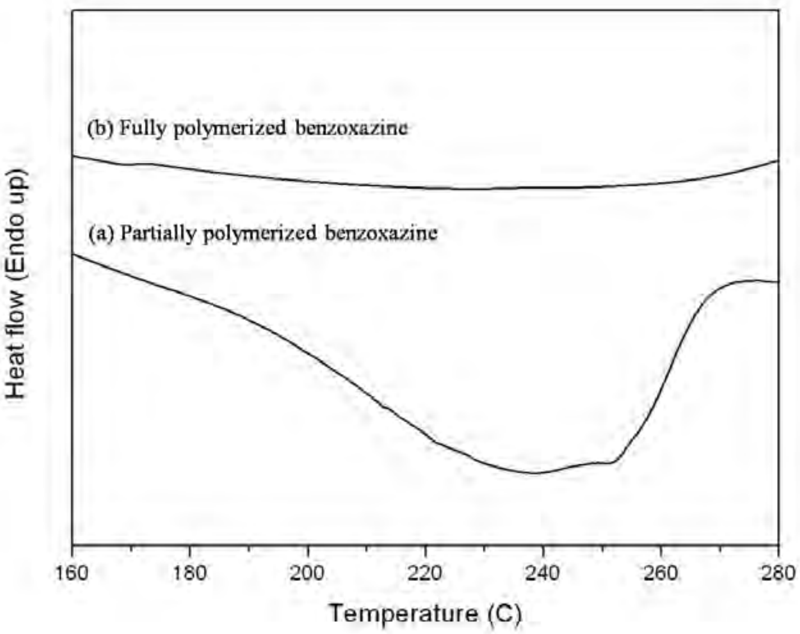


Figure 5 DSC thermograms of polybenzoxazine precursor.

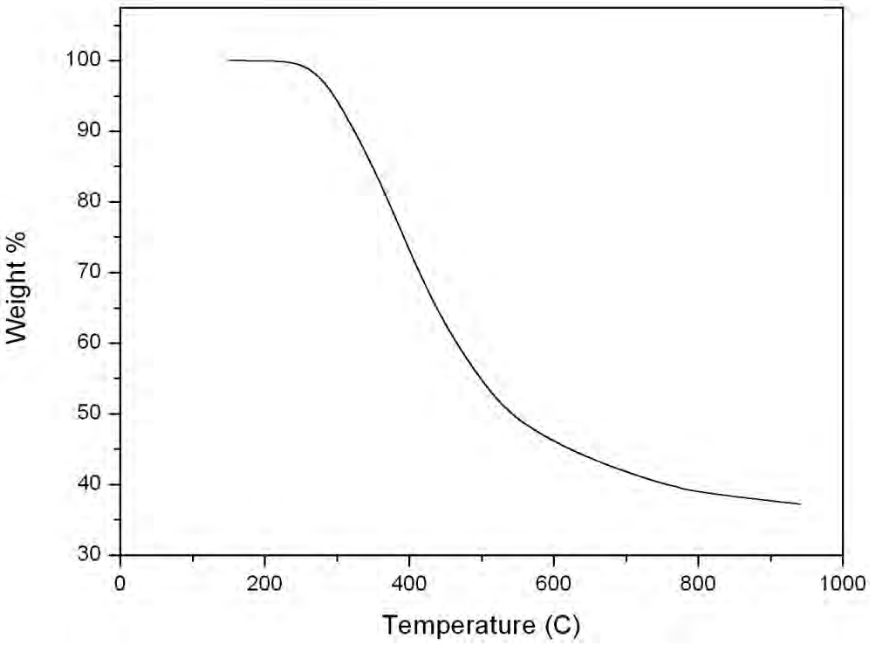


Figure 6 TGA thermogram of polybenzoxazine precursor.

In Figure 6, the TGA thermogram shows the thermal stability of polybenzoxazine. The decomposition temperature began at 260 °C with the maximum mass loss rate in the temperature range of 260-600 °C. The result was in accordance with our previous study [21].

4.2 The Chemical Structure of Polybenzoxazine Precursors

The chemical structure of benzoxazine precursor was examined by FTIR spectra as shown in Figure 7. The characteristic absorption bands at 1234-1238 cm^{-1} (asymmetric stretching of C-O-C of oxazine), 1187 cm^{-1} (asymmetric stretch of C-N-C) and 1334-1340 cm^{-1} (CH_2 wagging) were observed (Figure 7(a)). Additionally, the characteristic absorption assigned to the stretching of trisubstituted benzene ring at 1511 cm^{-1} and the out-of-plane bending vibrations of C-H at 943-949 cm^{-1} were detected, indicating the presence of the cyclic benzoxazine structure in the backbone of the precursor [22]. After polymerization at 200 °C, the intensity of those characteristic absorption bands decreased due to the ring opening polymerization was completed as shown in Figure 7(b) [13].

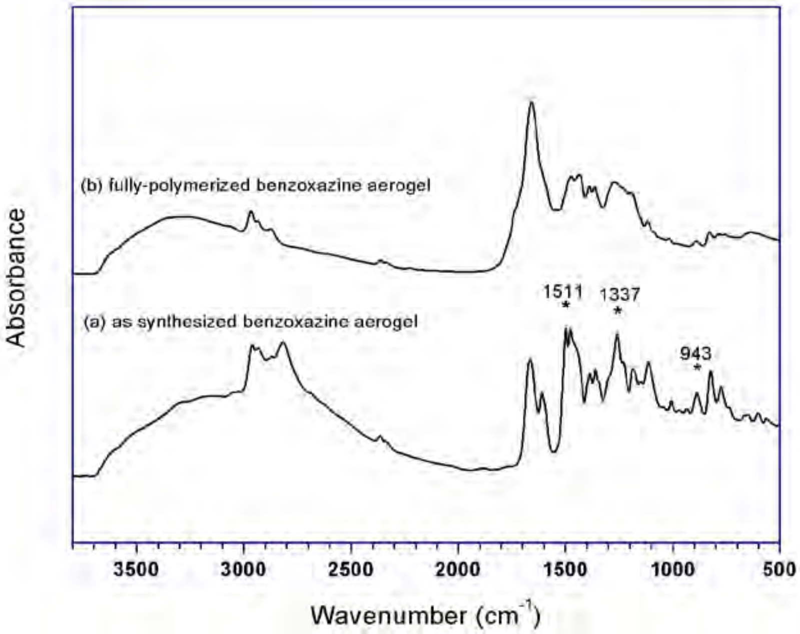


Figure 7 FTIR spectra of polybenzoxazine precursors.

4.3 Surface Characterization of Polybenzoxazine-Derived Carbon Aerogel

The surface area, pore volume and pore diameter of carbon aerogels are summarized in Table 1. It can be seen that the activated carbon aerogel had a high surface area with large amount of micropores whereas the non-activated sample had lower surface area, but larger pore size. The carbon aerogel had small amount of micropores. After the activation of carbon aerogel under carbon dioxide at 900 °C, the micropores had been introduced into the carbon aerogel, resulting in high surface area [23-26]. For the carbon aerogel with heat treatment in air at 300 °C, the surface area and porosity were similar [20]. Moreover, the pore diameter of all carbon aerogels prepared from polybenzoxazine precursor was in the range of 2-6 nm which was suitable for use as an electrode material in supercapacitors [20, 27].

Table 1 Surface area, pore volume and pore diameter of carbon aerogels prepared from benzoxazine precursor

Parameter	**CA**	**Heat-treated CA**	**Activated CA**
BET surface area (m^2/g)	360	372	910
Total pore volume (cm^2/g)	0.24	0.25	0.54
Average pore size (nm)	2.69	2.65	2.40
Micropore volume (cm^3/g)	0.14	0.16	0.40
Mesopore volume (cm^3/g)	0.13	0.11	0.17
*Mesoporosity (%)	54.2	44.0	31.5
*Microporosity (%)	58.3	64.0	74.1

*Mesoporosity = (mesopore volume/total pore volume) × 100

*Microporosity = (micropore volume/total pore volume) × 100

4.4 Morphology of Carbon Aerogels and Activated Carbon Aerogels

The SEM micrographs reveal the porous structure of the carbon aerogels prepared from polybenzoxazine via ambient drying as shown in Figure 8 (a)-(c). The structure of the carbon aerogel without heat treated at 300 °C in air composed of interconnected particles in three-dimension network containing continuous macropore, as shown in Figure 8(a) and (b), respectively. In case of the activation of carbon aerogels prepared by heat treated carbon aerogel with CO_2 at 900 °C, the micrograph also shows similar morphology compared with the unactivated one.

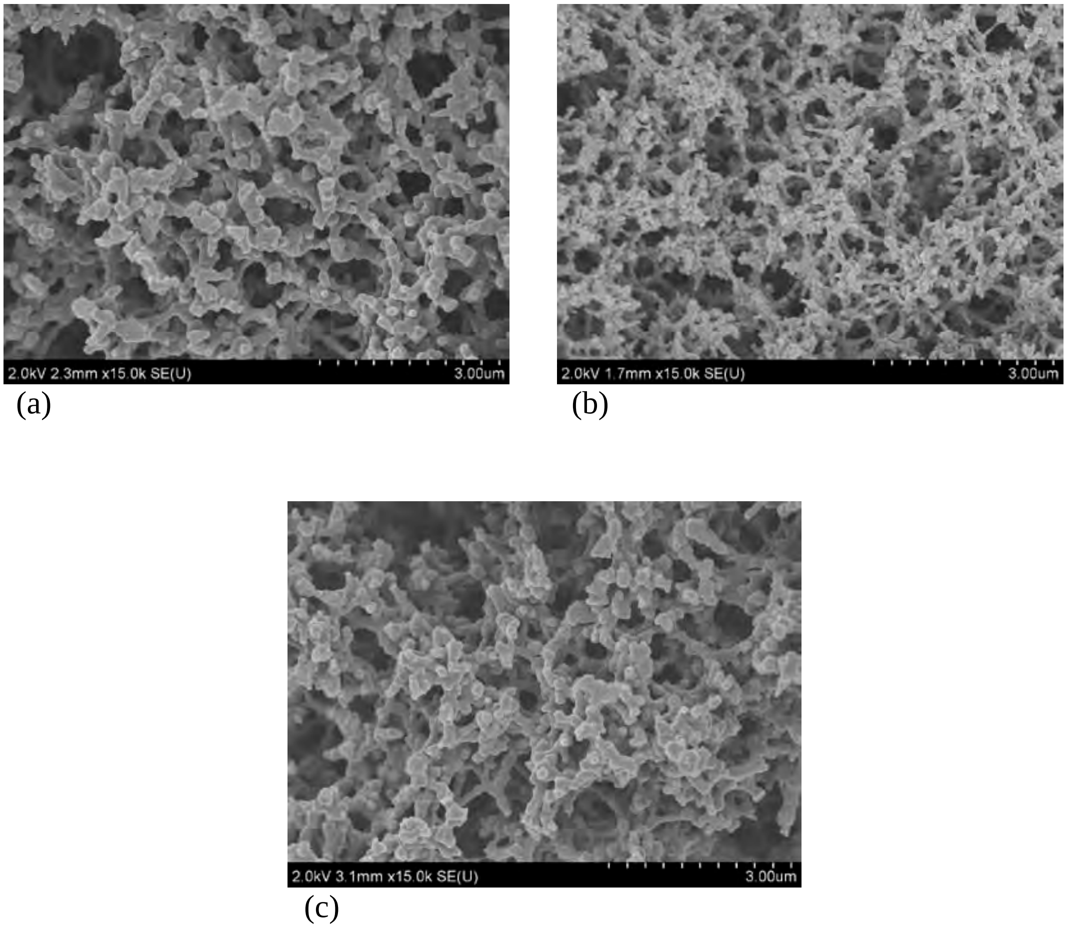
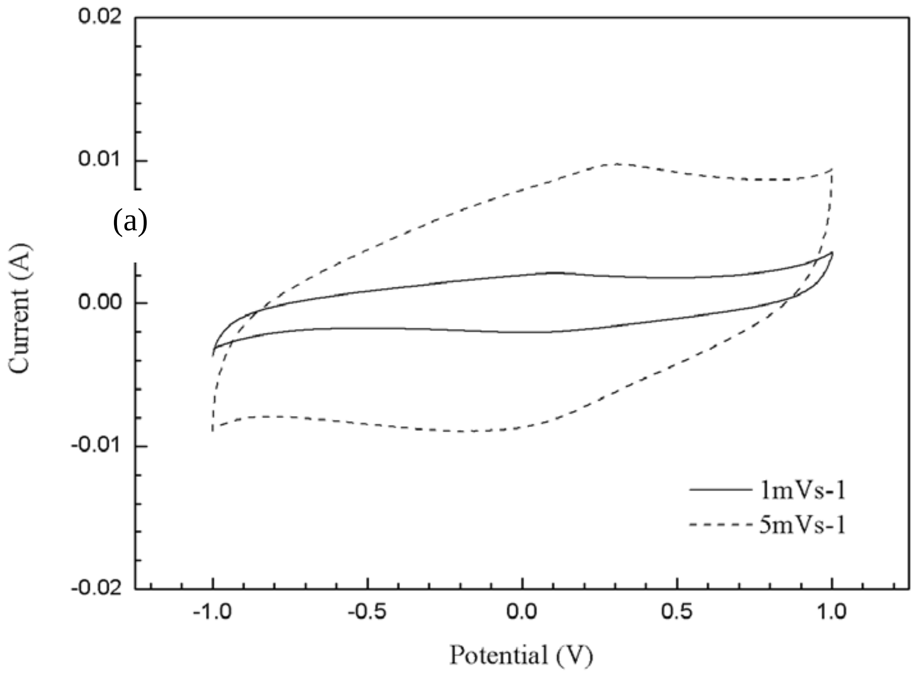


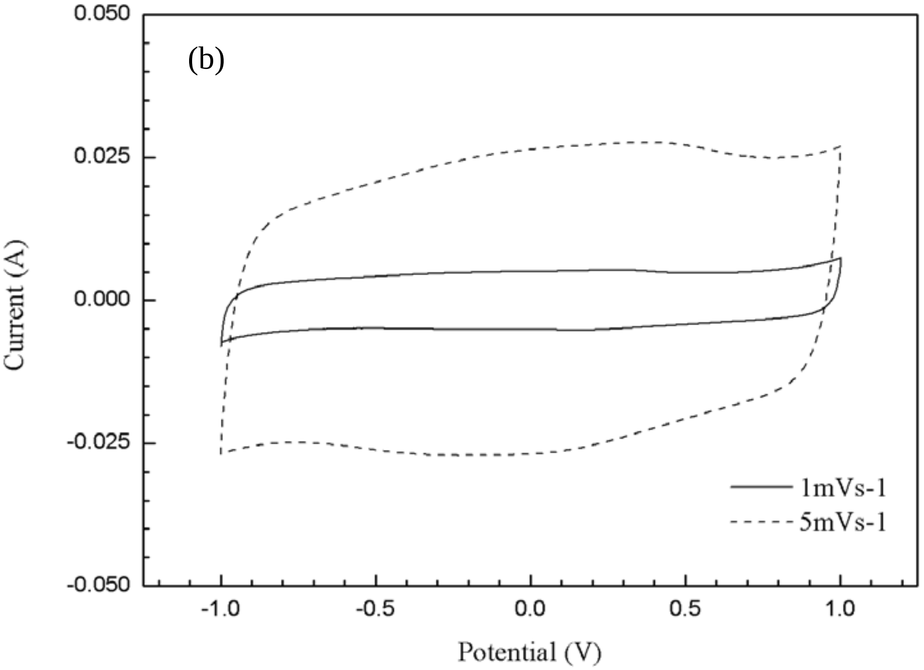
Figure 8 SEM micrographs of synthesized carbon aerogels: (a) no heat-treated, (b) heat treated at 300 °C in air, and (c) the activation.

4.5 Electrochemical Characterizations

4.5.1 Cyclic Voltammetry Behaviors

Figure 9 shows the cyclic voltammograms of the carbon aerogel electrodes obtained at a scan rate of 1 and 5 mV/s in 3M sulfuric acid. The figures show that the carbon aerogel electrodes particularly with heat-treatment at 300 °C in air and activated at 900 °C under carbon dioxide exhibited excellent electrochemical performances confirmed by a rectangular-like shapes of cyclic voltammograms, as shown in Figure 9 (b) and (c), suggesting that ions occupied some pores within the electrode for the electrochemical double layer formation [28]. In addition, they also imply that the charge/discharge processes of the electric double layer were highly reversible [28, 29]. For no heat-treated carbon aerogels, however, a small redox peak could be seen in the potential range of 0.1-0.4 V (Figure 9 (a)), which resulted from surface functional group. The pyrolysis temperature of 800 °C might not be enough to remove impurities completely from carbon network structure [20, 30]. As the scan rate increased, the rectangular shape became gradually depressed, because it was more difficult for the ions to transport into pores at high scan rate [31, 32].





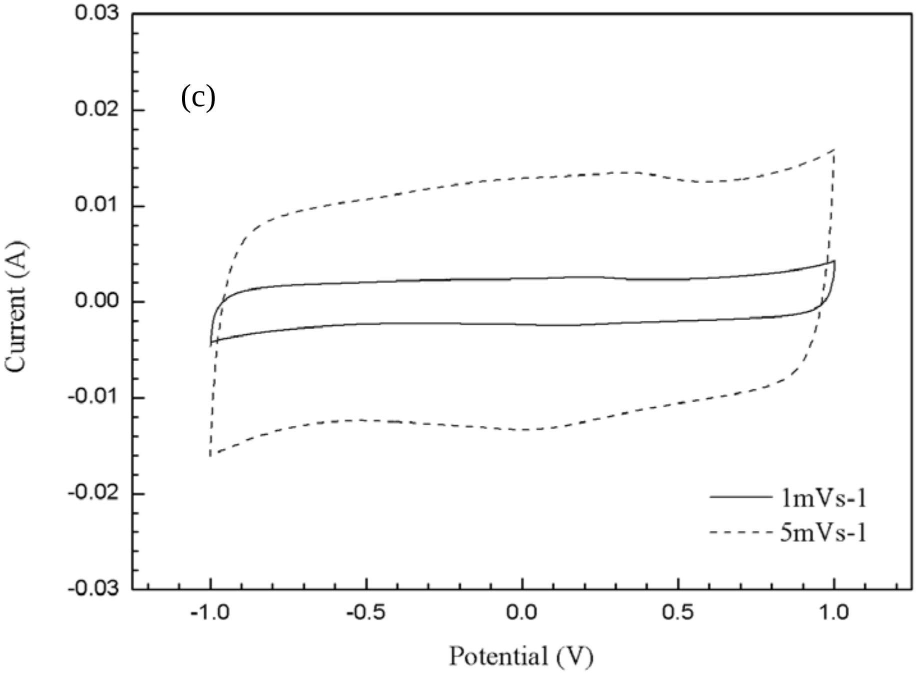
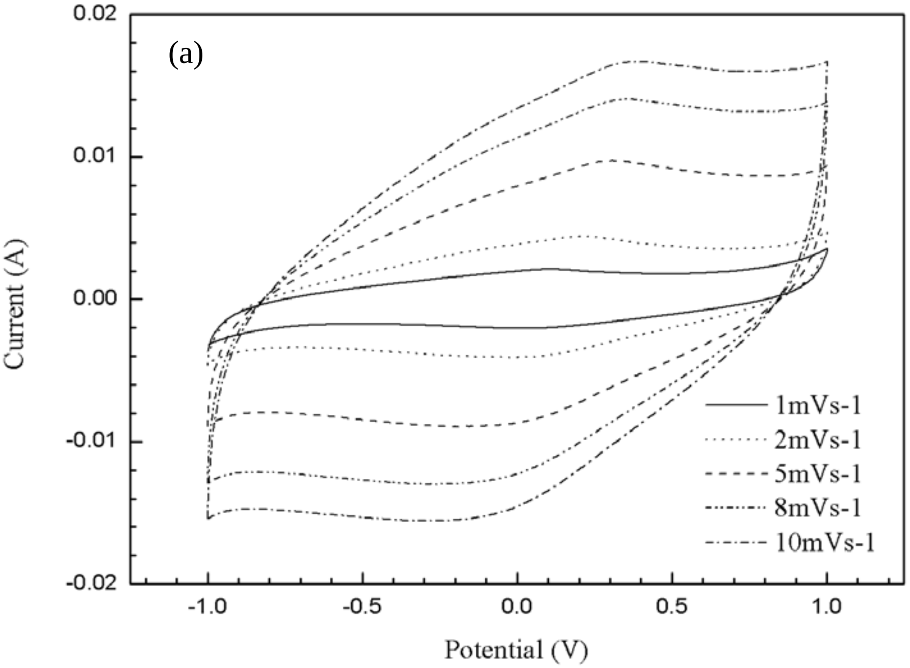
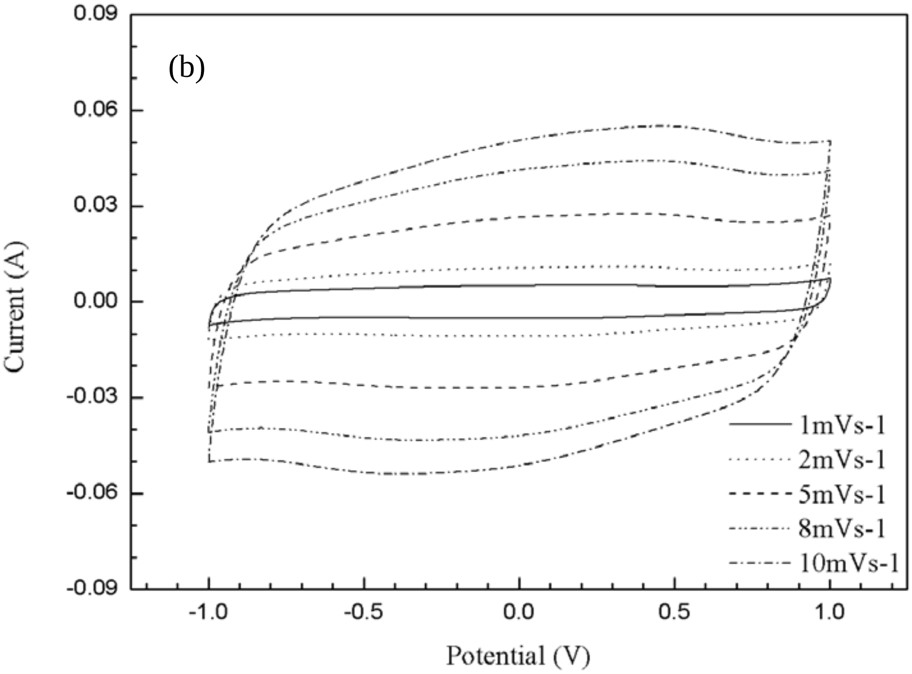


Figure 9 Cyclic voltammograms of carbon aerogel electrodes at a scan rate of 1 and 5 mV/s: (a) no heat treated, (b) heat-treated at 300 °C in air, and (c) activated at 900 °C under CO_2.


(a)
Current (A)
0.02
0.01
0.00
-0.01
-0.02
-1.0
-0.5
0.0
0.5
1.0
Potential (V)
1mVs-1
2mVs-1
5mVs-1
8mVs-1
10mVs-1


(b)
Current (A)
0.09
0.06
0.03
0.00
-0.03
-0.06
-0.09
-1.0
-0.5
0.0
0.5
1.0
Potential (V)
1mVs-1
2mVs-1
5mVs-1
8mVs-1
10mVs-1

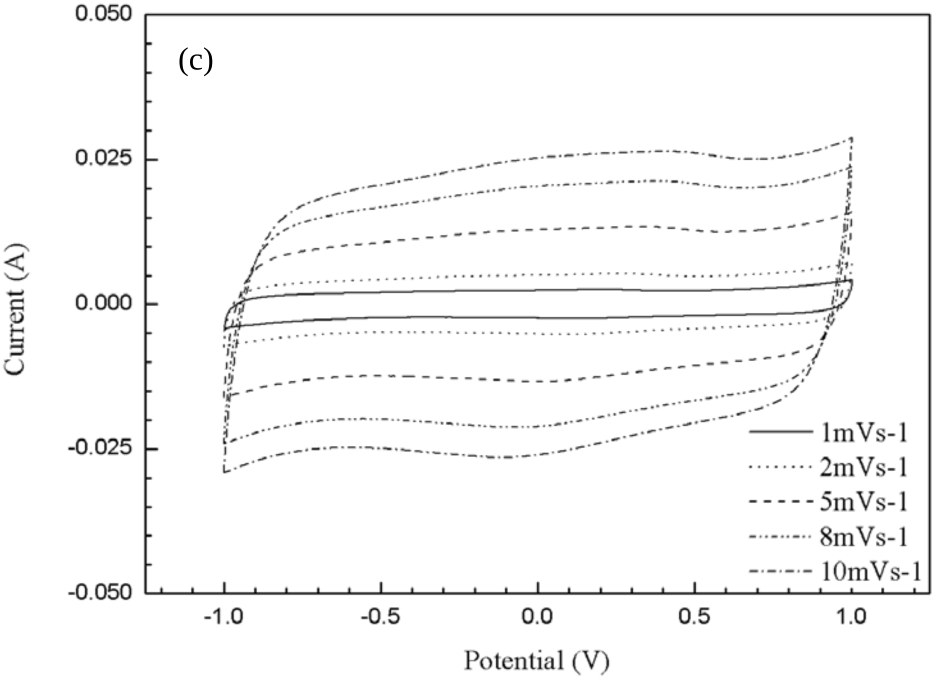


Figure 10 Cyclic voltammograms of carbon aerogel electrodes at a scan rate of 1, 2, 5, 8, and 10 mV/s: (a) no heat treated, (b) heat-treated at 300 °C in air, and (c) activated at 900 °C under CO_2.

4.5.2 Charge-Discharge Behaviors

The specific capacitance (C) of the carbon aerogel electrodes was calculated from the charge/discharge curve using the following equation [20, 21]:

$$C = \frac{i\Delta t}{m\Delta V} \qquad (1)$$

where C is the specific capacitance (F/g), I is the constant current (A), t is time period (s), ΔV is the potential difference (V) ,and m is the mass of carbon aerogel electrode (g).

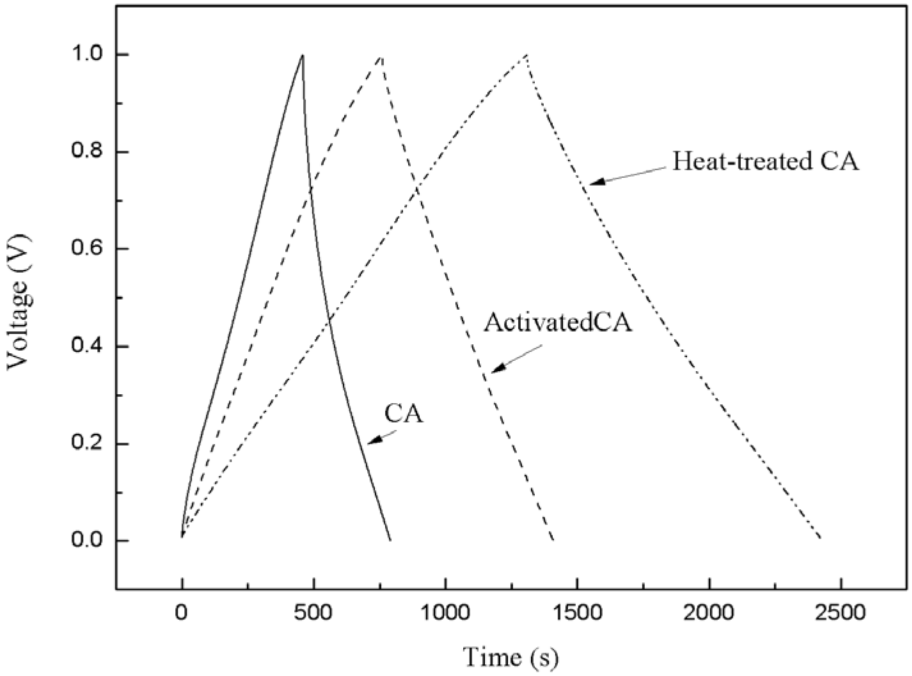


Figure 11 Charge/discharge curves of the carbon aerogel electrodes measured at 5 mA/cm^2.

Table 2 Specific capacitance of carbon aerogel electrodes calculated from discharge curves

Electrode	Specific capacitance (F/g)
Carbon aerogel	30
Heat-treated carbon aerogel	109
Activated carbon aerogel	78

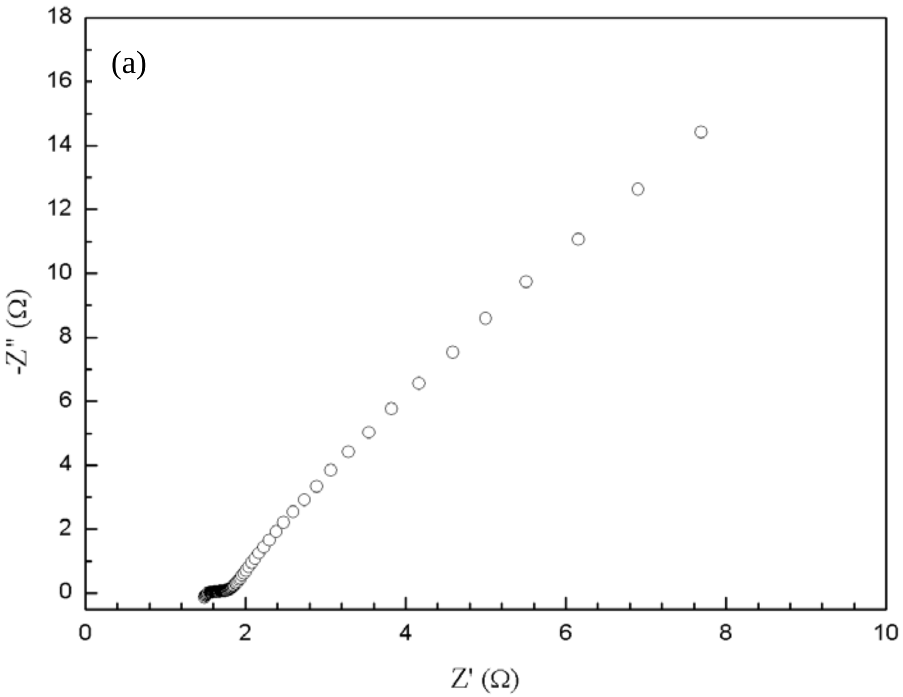
It can be seen from Table 2 and Figure 11 that the activated carbon aerogel had large amount of micropores along with high surface area, resulting in higher specific capacitance than that of non-activated sample. The reason is that the polybenzoxazine derived carbon aerogel activated at 900 °C under carbon dioxide had the average pore diameter approximately of 2.40 nm, which large enough for aqueous electrolyte to transport into pores to form the electrical double layer [25-27]. However, the heat-treated carbon aerogel at 300 °C in air yield the highest specific capacitance due to its low micropore fraction, suitable pore size for electrical double layer formation and its pseudocapacitive behavior originated from surface functional group on carbon aerogel surface, which built up during the heat treatment at 300°C in air. Generally, the higher the specific surface area of the activated carbon, the higher the ability for charge accumulation; resulting in the higher the specific capacitance of the carbon electrodes [28, 30]. However, it is rather difficult to make a conclusive summary on the parameters that effect the charge accumulation since the nature and the porosity of the precursor also play important roles [28, 33].

4.5.3 Electrochemical Impedance Characteristics

An electrochemical impedance measurement was carried out in the frequency range of 10 kHz to 10 mHz and the voltage between two electrodes was kept at 0 V during the measurement. Nyquist plots for these electrodes are presented in Figure 13. At high frequency, the intercept of the semicircle on the left of the real axis (Z') indicates the solution resistance, R_s and the intercept on the right of the real axis indicates the sum of the polarization resistance or charge transfer resistance, R_{ct}, and the solution resistance, R_s. The diameter of the semicircle is therefore equal to the charge transfer resistance, R_{ct} [31] which corresponds to the charge transfer process at the electrode-electrolyte interface [32].

It was found from Figure 12 (a)-(c) that the values read from the intercept on the left of the real axis of the electrochemical impedance spectrum were similar, indicating that all carbon electrodes had similar solution resistance. Although the heat-treated carbon aerogel had the highest capacitance, the diameter of the semicircles was less for the activated carbon aerogel than for the heat-treated carbon aerogel, indicating that the activated carbon had lower charge transfer resistance than heat-treated carbon aerogel. This could be explained for the heat-treated carbon aerogel that the imparted polarity might impede the ion mobility. Hsieh and Teng reported that the specific capacitance of carbon fabric increased significantly with the extent of oxidation, however, the inner resistance also found to be increased with the extent of oxidation due to the local changes of charge density and the increase in redox activity [33].

The straight line with a slope of 45° at a low frequency (Figure 12(a)), caused by diffusion of electrolyte ions within pores of the electrode [31, 34]. At low frequency, the imaginary part of the impedance of all carbon aerogel electrodes increased, showing the capacitive behavior of the supercapacitor [31, 33]. The slope also related to dispersed resistance, R and capacitance, C, originated from various pore structures in carbon aerogels. This interpretation was called a “transmission line model”, reported by De Livie (Figure 13) [23, 35, 37]. At a low frequency, the activated carbon aerogels exhibited a vertical line (90°) to the real axis, indicating an ideal capacitor behavior (Figure 12(c)). In contrast to the unactivated one, which had a high slope, indicating that the activated carbon aerogels had smaller diffusion resistance of electrolyte ions in the pore than the unactivated one, resulting in high specific capacitance as agree with the cyclic voltammograms and the charge/discharge curves [28, 31, 36].



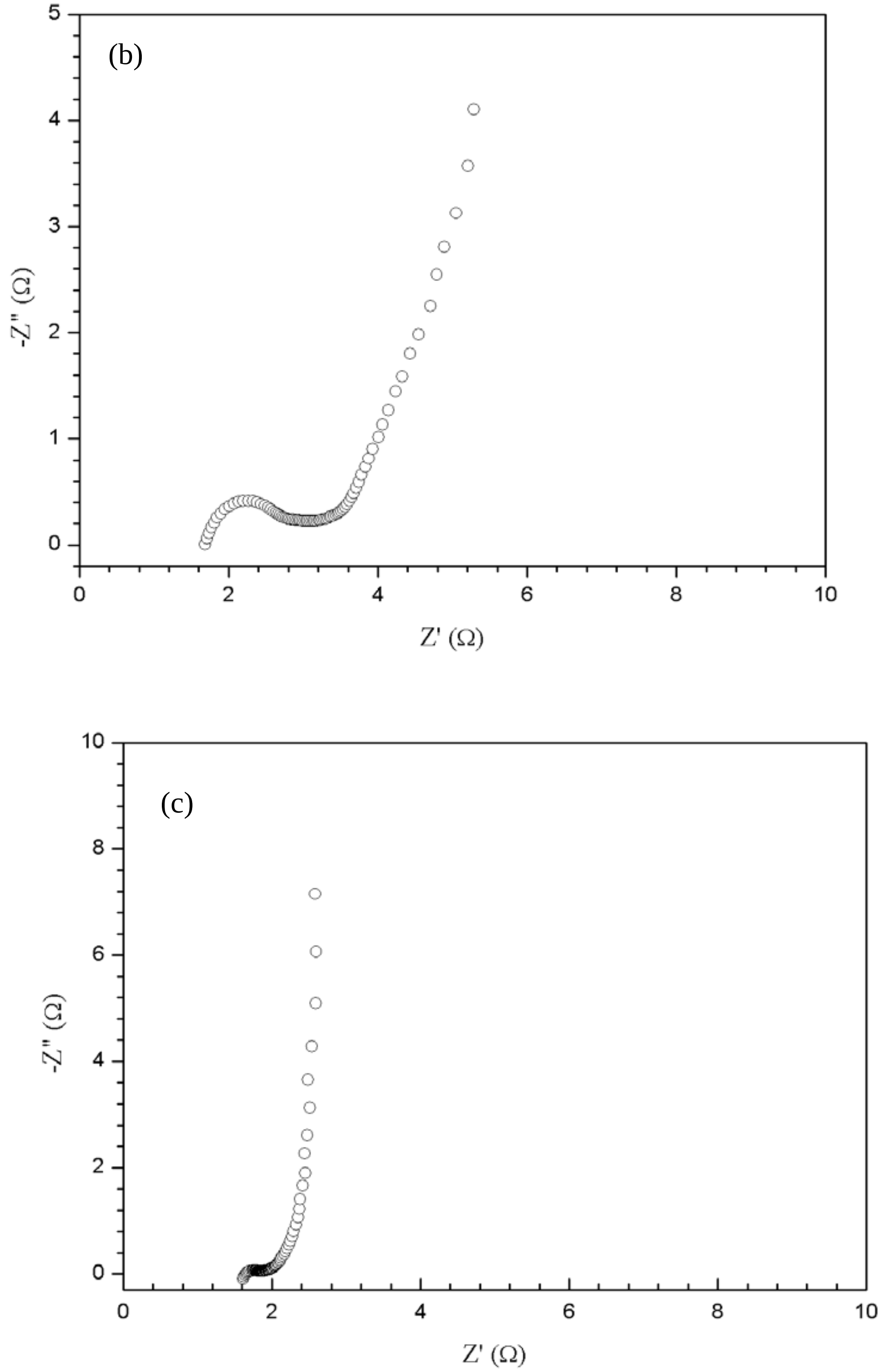


Figure 12 Nyquist plots for carbon aerogel electrodes: (a) no heat-treated, (b) heat-treated at 300 °C in air, and (c) activated at 900 °C under CO_2.

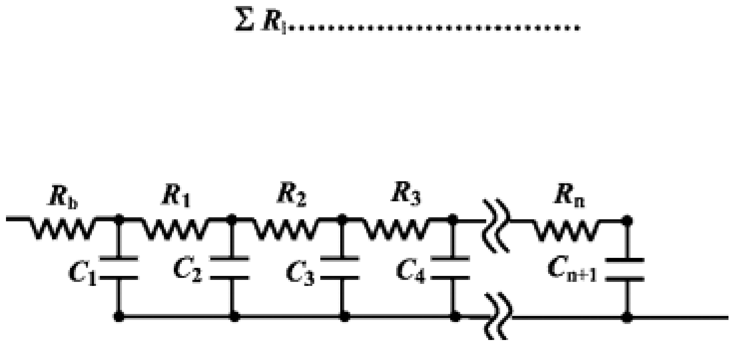


Figure 13 The equivalent circuit of carbon aerogel electrodes [37].

5. Conclusion

Carbon aerogel was successfully synthesized via ambient drying by using polybenzoxazine as a precursor. All carbon aerogel electrodes showed good electro-chemical performances. The specific capacitance of the electrode fabricated from activated carbon aerogel was higher than that derived from the non-activated one due to its high useable surface area for electrical double layer formation. However, the heat-treated carbon aerogel electrode showed the best specific capacitance due to its pseudocapacitive behaviors.

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Novel polybenzoxazine-based carbon aerogel electrode for supercapacitors

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ABSTRACT

In this study, polybenzoxazine, a new high performance thermosetting resin, was used to prepare carbon aerogels used as an electrode for supercapacitors. Two types of polybenzoxazines, derived from two different amines, aniline and triethylenetetramine, and denoted as BA-a and BA-teta, respectively, were chosen as the reactants for the organic precursor preparation. The surface area of carbon aerogels from both BA-a and BA-teta was 391 and 368 m^2/g, respectively. The pore size of each carbon aerogel was in the range of 2–5 nm, which is a suitable pore size for use as electrodes in electrochemical applications. The electrochemical properties of the obtained carbon aerogels showed good performance for supercapacitor applications with a specific capacitance of 55.78 and 20.53 F/g for BA-teta and BA-a, respectively. At low voltage scanning, 1 and 5 mV/s, the cyclic voltammogram of the carbon aerogel derived from BA-teta gave a better rectangular shape than that of the other carbon aerogel. The impedance spectra of both carbon aerogels confirmed the results of the capacitance and the cyclic voltammogram analyses.

1. Introduction

Supercapacitors, a new kind of electrical energy storage devices, can store much more energy than conventional capacitors and they offer much higher power density than batteries. They are based on carbon materials (activated carbon, carbon black, aerogel particulates, carbon cloth, etc.) and have been attracting much attention because of their high performance, low cost, and environmental friendliness [1].

Carbon aerogels are unique porous materials, comprising a continuous rigid solid framework, and an opened, continuous network of pores. Due to their attractive properties – such high electrical conductivity (25–100 S/cm), controllable pore structure, high porosity (80–98%), and highly useable surface area (up to 1100 m^2/g) – carbon aerogels are a promising candidate for application as supercapacitors [2–8]. Although carbon aerogels have excellent properties, they are cost intensive because of their preparation method, which involves a supercritical drying process. Traditionally, carbon aerogel is prepared through the polycondensation of resorcinol and formaldehyde, using acid or base as a catalyst.

Polybenzoxazine, an innovative high performance thermosetting resin, exhibits numerous excellent properties, including low water absorption, low shrinkage upon polymerization, no catalyst requirement, and high dimensional stability [9–11]. Due to its molecular design flexibility, the properties of polybenzoxazine can be tailored to accommodate any desired applications. The purpose of this work was thus to reduce the production cost of carbon aerogels by using an ambient drying process, to prepare carbon aerogels from benzoxazine precursors, and to investigate the electrochemical properties of electrodes prepared from the benzoxazine-derived carbon aerogels.

2. Experimental

2.1. Materials

All chemicals were used without further purification. Triethylenetetramine, TETA, was purchased from FACAI Group Limited, Thailand. Aniline (99%) was purchased from Panreac Quimica SA Company. The formaldehyde solution (37% by weight) and the sulfuric acid (95–97% H_2SO_4 analytical grade) were purchased from Merck, Germany. Paraformaldehyde (95%) was purchased from BDH Laboratory Supplies. Bisphenol-A (commercial grade) was kindly supported by Bayer Thai Co., Ltd. Xylene (98%) was obtained from Carlo Erba Reagenti and the 1,4-dioxane (reagent grade) was purchased from Labscan Asia Co., Ltd., Thailand.

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2.2. Characterization

The FT-IR spectra of the polybenzoxazine precursor and the carbon aerogel were obtained with a Nicolet Nexus 670 FT-IR spectrometer. The KBr pellet technique was used in the preparation of powder samples. The TG–DTA curve was collected on a Mettler Toledo TGA/SDTA 851e instrument, where the sample was loaded on a platinum pan and heated from ambient temperature to 900 °C at a heating rate of 20 °C/min under N_2 atmosphere with a flow rate of 50 ml/min. A scanning electron microscope (SEM, JEOL/JSM model 5200) was used to observe the surface morphology of the polybenzoxazine aerogel and the carbon aerogel. The specimens were coated with gold under vacuum before observation. Nuclear magnetic resonance was used to characterize the chemical structure of polybenzoxazine. ^{1}H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as a solvent. DSC analyses were carried out using a PerkinElmer DSC 7 instrument. The samples were heated from ambient temperature to 300°C at a heating rate of 10 °C/min under N_2 atmosphere with a flow rate of 10 ml/min. The nitrogen adsorption–desorption isotherms were obtained at 250 °C on a Quantachrome Autosorb-1. Samples were degassed at 250 °C for 12 h in a vacuum furnace prior to analysis. The surface area was calculated using the BET equation. The testing cell for the electrochemical measurements consisted of graphite sheets as current collectors, two carbon aerogel electrodes separated by a microporous polyethylene membrane, and 3 M H_2SO_4 as the electrolyte solution. Before the measurements, the carbon aerogel electrodes were placed in 3 M H_2SO_4 for 24 h to diffuse the electrolyte into the pores of the carbon aerogel electrodes [12,13]. Electrochemical characterization was done using a computer-controlled potentiostat/galvanostat (Autolab PG-STAT 30 with GPES software). Cyclic voltammetry (CV) was performed between −1 and 1 V with scanning rates of 1, 5, 20, and 50 mV s^{-1}. For the galvanostatic charge/discharge measurement, the testing cell was charged with a current density of 5 mA cm^{-2} up to 1 V and discharged with 5 mA cm^{-2} down to 0 V [13]. Electrochemical impedance spectra (EIS) were obtained using an impedance analyzer (Autolab PG-STAT 30, with FRA software) over a frequency of 10 kHz down to 10 mHz with a sinusoidal signal of 10 mV. All of the electrochemical measurements were performed at room temperature.

2.3. Synthesis of polybenzoxazine-based carbon aerogel

In this research, we used two types of polybenzoxazine precursors for the carbon aerogel preparation. The precursors were synthesized using two different amines (aniline and triethylenetetramine) as the reactant.

The synthesis of the benzoxazine precursor (abbreviated as BA-teta) (Scheme 1) from bisphenol-A, formaldehyde, and TETA was carried out using a “quasi-solventless method” adopted from the solventless method reported by Ishida et al. [9]. Compared with the conventional method, which took about 6 h to complete the reaction [11], benzoxazine precursors could be obtained within an hour via the quasi-solventless method. Dioxane was used only to help the mixing of all reactants. The molar ratio of all reactants used was 1:4:1. The synthesis was started by first dissolving bisphenol-A (4.52 g) in dioxane (20 ml) in a glass bottle and stirring until a clear solution was obtained. A formaldehyde solution (6.48 g) was then added to the bisphenol-A solution. The temperature was kept under 10 °C by using an ice bath. TETA was then added dropwise into the mixture and stirred continuously for approximately 1 h until a transparent yellow viscous liquid precursor was obtained. The precursor was placed in an oven at 80 °C for 72 h in a closed system, yielding benzoxazine aerogel. Finally, the benzoxazine aerogel was cut into a disk shape and placed in an oven for step-curing at 160 and 180 °C for 3 h at each temperature, and 200 °C for 2 h. The structural characteristics of the BA-teta-based aerogel were investigated by using FTIR and ^{1}H NMR, the thermal properties were measured using DSC and TG/DTA, and the morphology was observed by SEM.

Another benzoxazine precursor used in this study, denoted as BA-a, was followed our previous work via the solventless process [9]. Bisphenol-A (22.8 g), aniline (18.6 g), and paraformaldehyde (12 g), with a molar ratio of 1:2:4, were mixed together and heated at 110 °C for an hour until a transparent light-yellow viscous liquid was obtained.

The BA-a-based organic aerogel was prepared following the method previously reported. The Benzoxazine monomer was dissolved by using xylene as the solvent. The monomer concentration was 40 wt%. After that, the solution was poured into vials and sealed. The temperature was gradually raised to 130 °C for 96 h in an oven. The attained products were partially cured benzoxazine hydrogels. The hydrogels were dried at ambient temperature for 2 days to remove the xylene from their matrixes, yielding organic aerogels, which were then subjected to step-curing in an oven at 160 and 180 °C for an hour at each temperature, and 200 °C for 2 h. The detailed characterizations of BA-a precursor, BA-a derived organic and carbon aerogels were reported in our previous work [14].

2.4. Preparation of carbon aerogel electrodes

The fully cured organic aerogels of BA-teta and BA-a were cut into a disk shape by using a diamond saw and were then pyrolyzed under a nitrogen flow rate of 500 cm^3/min using the following ramp cycle: 30–250 °C in 60 min, 250–600 °C in 300 min, 600–800 °C in 60 min, and holding at 800 °C for 60 min. Carbon aerogel electrodes were then obtained.

2.5. Characterization of the carbon aerogel electrodes

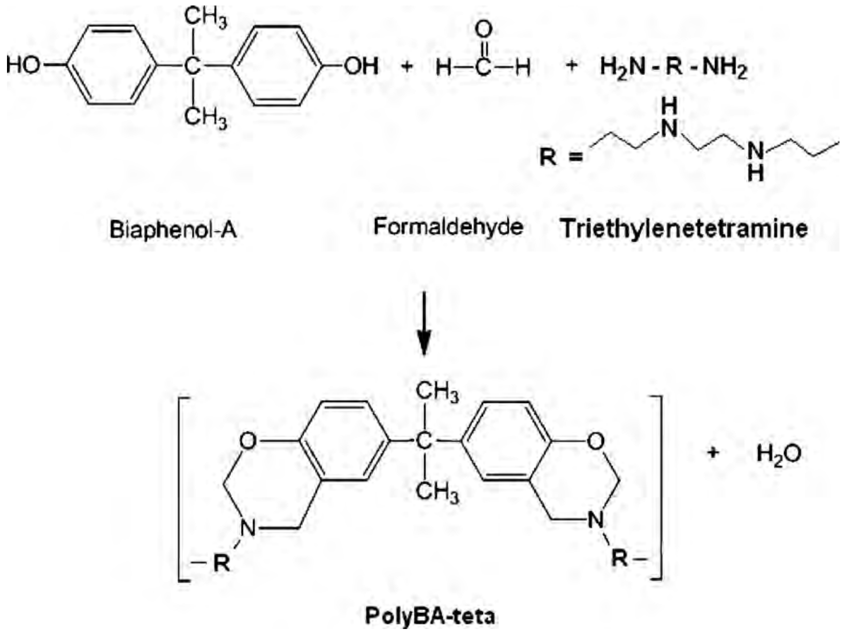
The surface areas of the carbon aerogel electrodes were calculated from the nitrogen adsorption isotherm at −196 °C (77 K). Galvanostatic charge/discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were used to determine the electrical properties.

3. Results and discussion

3.1. Chemical structure of polybenzoxazine precursors

The chemical structure of the BA-teta precursor was confirmed by ^{1}H NMR and FT-IR (Figs. 1 and 2). The aromatic protons appeared at 6.62–6.96 ppm. The peaks at 4.76 (O–CH_2–N) and 3.89 (Ar–CH_2–N) ppm were assigned to the methylene bridge of the oxazine ring. The methylene group of the opened oxazine ring was observed at 3.68 ppm. The methyl groups of bisphenol A appeared at 1.53 ppm and the proton of aliphatic amine was observed at around 2.51–2.71 ppm. The ^{1}H NMR spectrum indicates that the precursor was in a partially cured state, which means that the precursor contained both ring-opened and ring-closed benzoxazine functional groups in the structure, similar to the one prepared by conventional method reported by Takeichi et al. [11].

The BA-teta precursor was analyzed by FT-IR to confirm the chemical structure. The asymmetric stretching bands of C–O–C (1230 cm^{-1}), C–N–C (1185 cm^{-1}), and CH_2 wagging of oxazine



Scheme 1. Preparation of polyBA-teta.

(1325–1328 cm^{-1}) were detected [11]. The progress of polymerization and derivation from the precursor to the carbon aerogel was monitored by using the bands of 936 and 1498 cm^{-1}, which are attributed to the CH– out-of-plane bending of the oxazine ring and the trisubstituted benzene ring, respectively. After polymerization, the intensity of these peaks was decreased due to the ring-opening of the oxazine ring. These results are in agreement with Takeichi et al. [11]. Furthermore, all of the peaks of polybenzoxazine disappeared after pyrolysis, indicating that all organic residues were removed.

3.2. Thermal properties of polybenzoxazine precursor

The thermal properties of the BA-teta polybenzoxazine were observed by DSC and TGA, as shown in Figs. 3 and 4, respectively. The DSC thermogram (a) shows a broad exothermal peak centered at 245 °C, representing the ring-opening polymerization of the precursor. The onset of the polymerization was observed at around 180 °C, implying that the benzoxazine precursor was partially cured. In the fully cured stage (b), the exothermal peak disappears, suggesting that the benzoxazine precursor was com-

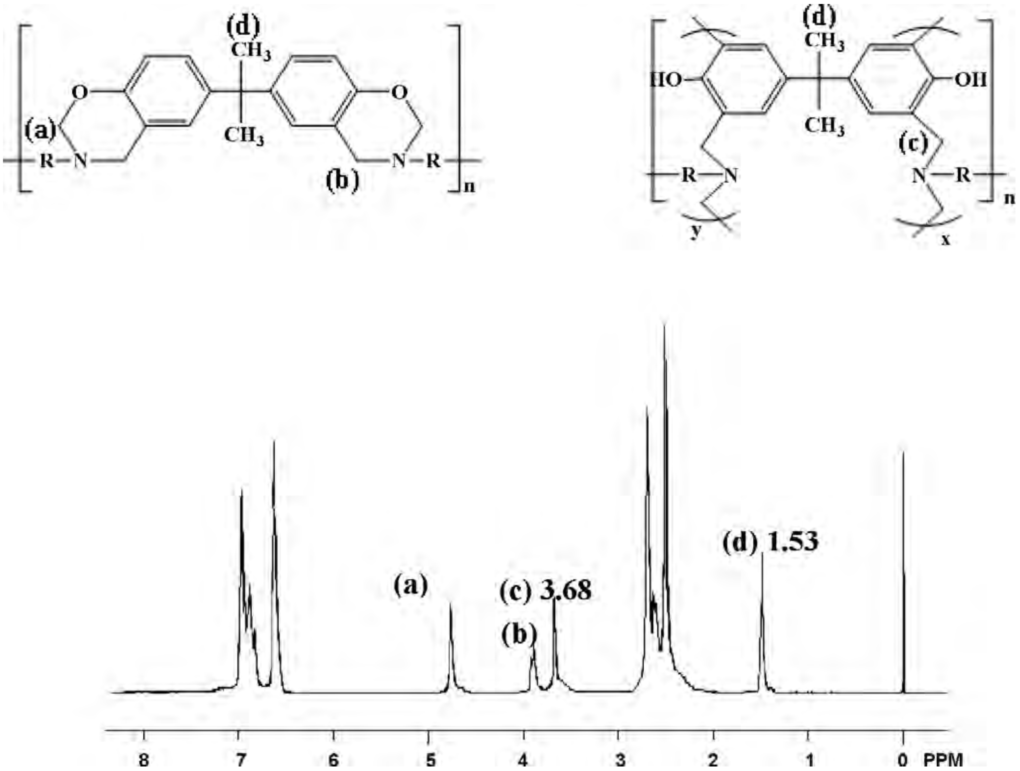


Fig. 1. ^1H NMR spectrum of BA-teta precursor.

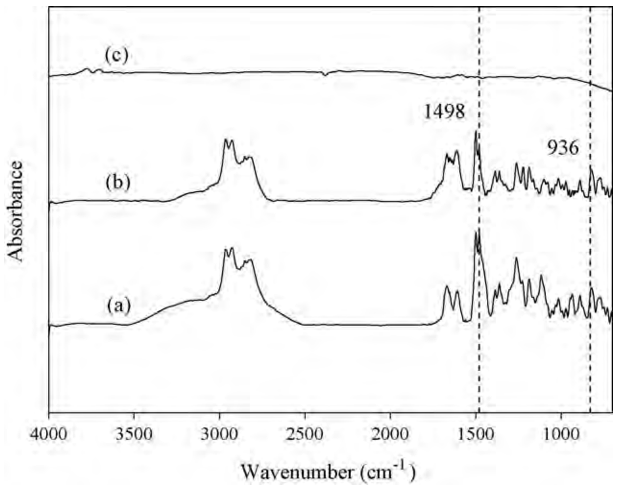


Fig. 2. FT-IR spectra of BA-teta (a), polymerized BA-teta at 200 °C (b), and pyrolyzed BA-teta at 800 °C (c).

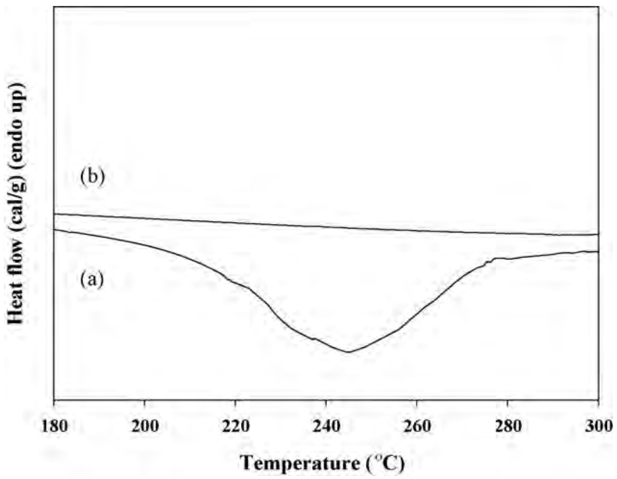


Fig. 3. DSC thermograms of BA-teta benzoxazine precursor (a) and polybenzoxazine in fully cured stage (b).

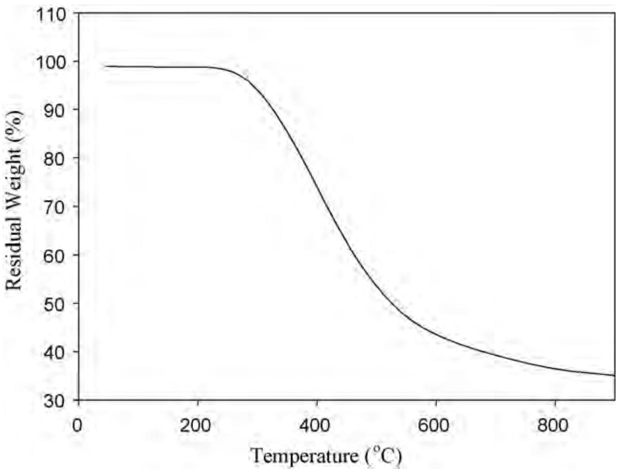


Fig. 4. TGA thermogram of BA-teta benzoxazine precursor.

Table 2
Texture characteristics of carbon aerogel electrodes derived from BA-teta (CA(BA-teta)) and BA-a (CA(BA-a)) polybenzoxazine precursor.

Parameter	CA(BA-teta)	CA(BA-a) [14]
BET surface area (m^2/g)	368	391
Total pore volume (cm^2/g)	0.34	0.21
Average pore size (nm)	3.67	2.20
Micropore volume (cm^3/g)	0.13	0.17
Mesopore volume (cm^3/g)	0.21	0.05
Mesoporosity (%)[a]	62	23

[a] Mesoporosity (%) = (mesopore volume/total pore volume) × 100.

pletely polymerized. This DSC result is in agreement with the study of Takeichi et al. [11], who showed the polymerization progress of the polybenzoxazine precursor from bisphenol-A, paraformaldehyde, and methylenedianiline (B-mda). The exotherm decreased with increasing temperature and the exotherm peak disappeared after 240 °C, indicating that the polymerization was completed.

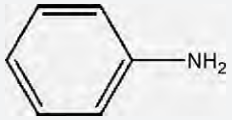
Fig. 4 shows that the BA-teta started to decompose at around 250 °C. The weight was rapidly decreased in the range of 250–600 °C. After 800 °C, the weight of the BA-teta approached steady state. Hemvichian et al. [15] also identified the decomposition of polybenzoxazines through the TGA–GC–MS technique, and they found that the decomposed compounds were from the degradation of polybenzoxazine or from the recombination of evaluated compounds during degradation.

Table 1 shows the 5% weight loss temperatures and the char yields of BA-a and BA-teta. The BA-a has a higher thermal stability than the BA-teta because of the presence of aromatic groups. However, the char yield of the BA-teta is higher, which might be because of the higher crosslink density due to the H-bonding of the secondary amines in the chain.

3.3. Surface characteristics and morphological study of polybenzoxazine-based carbon aerogel electrodes

The physical properties BA-teta and BA-a derived of polybenzoxazine-based carbon aerogel electrodes using the BET method are summarized in Table 2. The data from the pore volume and the surface area can be used to estimate the specific capacitance of the carbon aerogel electrodes [16]. In general, the micropores are required for the charge storage processes, however, the mesopores are also necessary in order for the fast accessability of the electrolyte ions into the electrodes. The porous carbon material containing mesopores can deliver high energy at a higher scanning rate [17,18].

Table 1
Thermal properties of polybenzoxazine precursors.

Precursor	Type of amine	$T_{-5\%}$ (°C)	Char yield (%)
PolyBA-a [14]		330	25
PolyBA-teta		293	37

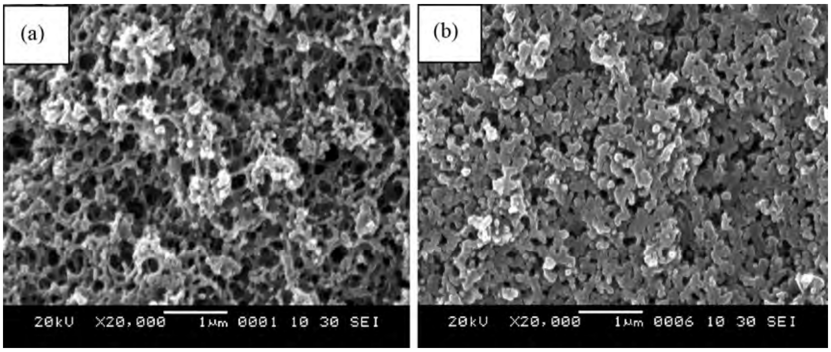


Fig. 5. SEM micrograph of organic aerogel (a) and carbon aerogel (b).

As summarized in Table 2, carbon aerogels derived from BA-teta and BA-a consisted of both mesopores and micropores, where the average pore size was 3.67 and 2.20 nm, respectively. However, BA-teta based carbon aerogel contained more of mesopores than micropores.

SEM micrographs of the BA-teta derived organic aerogel and the carbon aerogel are shown in Fig. 5. The porous structure was obtained from the removal of the solvent. In the structure of the organic aerogel, the solid phase presents a smooth continuous polymer network incorporated with open macropores. However, in the case of the carbon aerogel, a denser, porous structured three-dimensional carbon network containing continuous open macropores was obtained. Kim et al. [19] reported that the pore distribution of a resorcinol/formaldehyde resin aerogel was broadly spread, with pore diameters ranging from the nanoporous to the macroporous. In our case, the TEM observation indicates that BA-teta DERIVED carbon aerogels have a three-dimensional nano-network, and the pore size was less than 10 nm, as shown in Fig. 6.

3.4. Electrochemical characterization

Cyclic voltammograms (CV) of the two carbon aerogel electrodes at lower scan rates of 1 and 5 mV/s are shown in Fig. 7. The observed rectangular shaped profile of CA(BA-teta) showed good capacitor performance. The integrated areas of CV curves of CA(BA-teta) are higher than those derived from CA(BA-a) electrode [20]. The slope (*E*/*I*) derived from CV curves which represent the equivalent series resistances (ESR) are also lower for CA(BA-teta) electrode. The electrical double layer capacitor performance is related to the pore size in the electrode material and the movement of ions in the pores. CA(BA-teta) aerogel, having more mesopores (Table 2), provided better ions transport throughout the pores of the carbon aerogel layer. At higher scan rates up to 50 mV/s, the ESR obtained from CVs of both electrodes were lower and become more pronounced for CA(BA-teta) electrode, as shown in Fig. 8. However, the shape of the CV deviated from the rectangular shape when a fast scan rate was applied, which may be due to the increased difficulty of the ions being able to be transported into the pores at a shorter time [21].

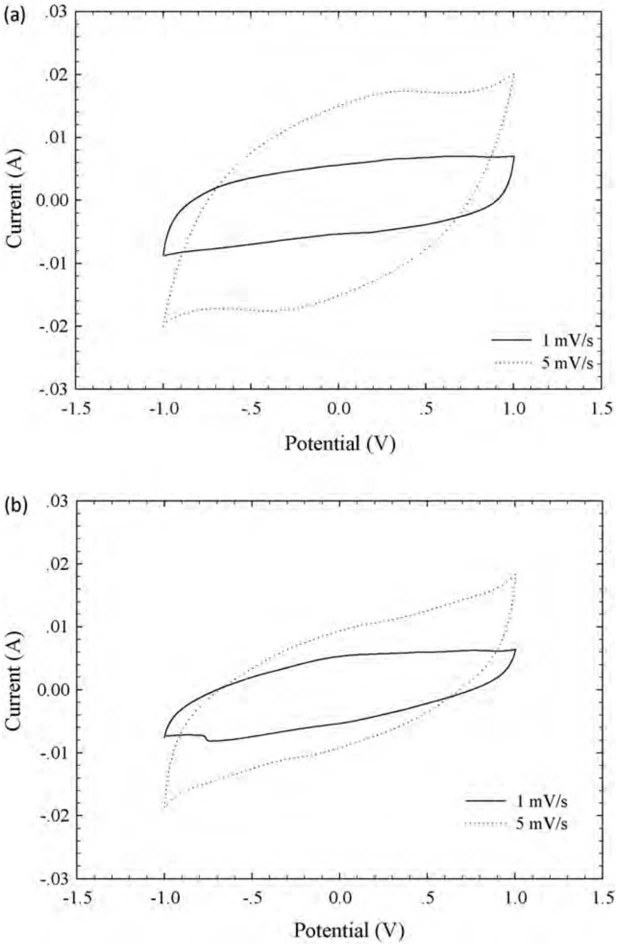


Fig. 7. Cyclic voltammograms of CA(BA-teta) (a) and CA(BA-a) (b) with scan rates of 1 and 5 mV/s.

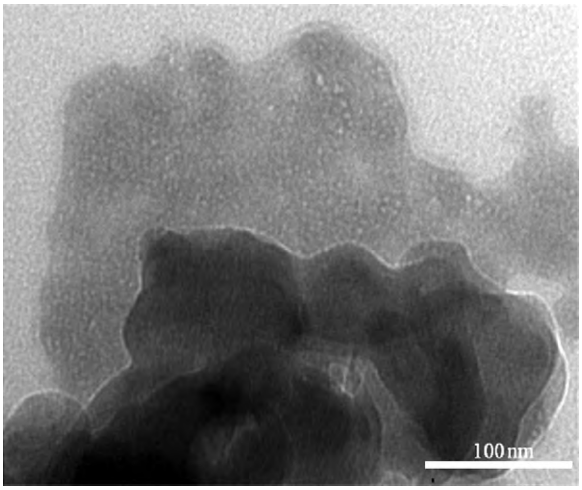


Fig. 6. TEM micrograph of the carbon aerogel.

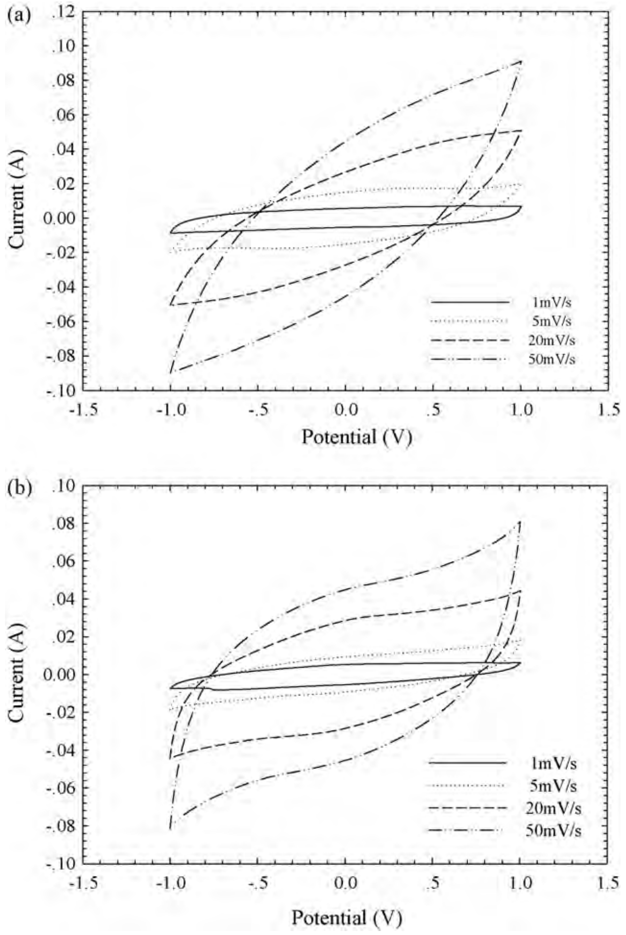


Fig. 8. Cyclic voltammograms of CA(BA-teta) (a) and CA(BA-a) (b) with scan rates of 1, 5, 25, and 50 mV/s.

The specific capacitance (C) of the carbon aerogels was calculated from the discharge curve (Fig. 9), using the following equation [22]:

$$C = \frac{it}{m\ \Delta V} \tag{1}$$

where i is the discharge current (A), t is the discharge time (s), m is the mass of the carbon aerogel electrode (g), and ΔV is the potential difference during the discharge (V).

The electrodes derived from the CA(BA-teta) showed better specific capacitance than those derived from CA(BA-a). As mentioned earlier the CA(BA-teta) has about twice the mesoporosity as the CA(BA-a); it can thus be concluded that the mesoporosity of the carbon aerogel electrodes indeed has an influence on the electrochemical properties of supercapacitors, as proposed by Lv et al. [18].

Electrochemical impedance measurements were made over the frequency range of 10 kHz to 10 mHz and the voltage between the two electrodes was kept at 0 V during the measurement. The Nyquist plots of the electrodes derived from both carbon aerogels are shown in Fig. 10. The semicircles at a high frequency can be correlated to the contact resistances at the interface of the carbon aerogel layer, the current collector and the internal resistance inside the electrode [20,23]. With the same electrolyte resistance (R_S), it was found that the diameter of the semicircle derived from CA(BA-teta) spectra was smaller than that of CA(BA-a), indicating a lower polarization resistance for CA(BA-teta) electrode. A straight lines along the imaginary axis (Z'') in the Nyquist plots showed slopes in the low frequency range of about 45° for CA(BA-teta) and >45° for CA(BA-a) which contributed to the diffusion resistances of the electrolyte ions into the pores [24]. The slope is also related to the dispersed capacitance C and the resistance R, derived from various pore structures of the carbon aerogels [25]. Mass transfer process involving the diffusion of the ions within the pores resulted in the Warburg impedance of CA(BA-teta) while the smaller pores of CA(BA-a) behaves as a transmission line of series resistances and capacitances as reported by Levie [26].

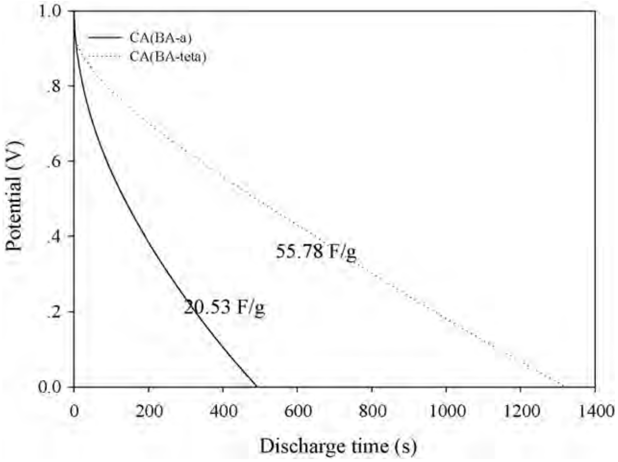


Fig. 9. Discharge curves of polybenzoxazine-based carbon aerogel electrode at current discharge (5 mA/cm^2).

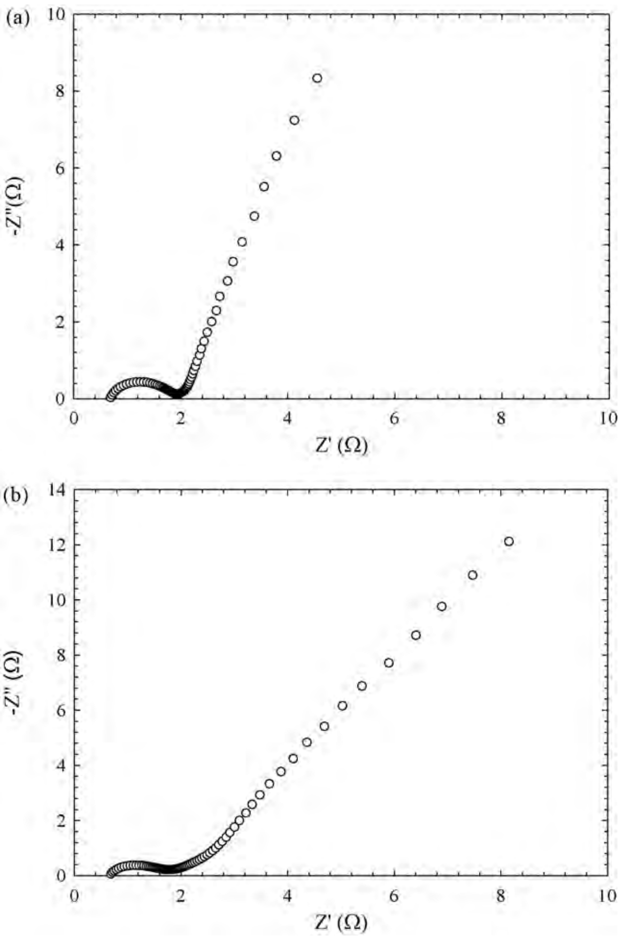


Fig. 10. Nyquist plots for CA(BA-a) (a) and CA(BA-teta) (b).

4. Conclusions

Polybenzoxazines were successfully used as organic precursors to prepare a carbon aerogel with a suitable pore size for electrodes in electrochemical applications. The carbon aerogel derived from bisphenol-A and teta showed higher specific capacitance than that derived from bisphenol-A and aniline due to a larger amount of mesopores.

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