ISSN 1002-0071

Production and hosting by Elsevier

Progress in Natural Science
Materials International

Volume 22, issue 6 December 2012

Chinese Materials Research Society

International Union of Materials Research Societies

Progress in Natural Science: Materials International 2012;22(6):625–631

Chinese Materials Research Society

Progress in Natural Science: Materials International

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ORIGINAL RESEARCH

A facile and green preparation of durian shell-derived carbon electrodes for electrochemical double-layer capacitors

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Received 6 September 2012; accepted 7 October 2012
Available online 13 December 2012

KEYWORDS

Durian shell;
Activated carbon;
Ultrasonication;
Microwave irradiation;
EDLC

Abstract A facile and green preparation of high surface area activated carbons with mixed microporosity and mesoporosity from durian shell waste is reported in this work. The pore structure and surface chemistry of the parent carbon were modified by the combination of ultrasonication and microwave irradiation techniques. The effects of temperature and time in the ultrasonication treatment and power output and time in the microwave irradiation were studied. The electrochemical performance of carbon electrodes for supercapacitors was tested by cyclic voltammeter (CV) and galvanostatic charge–discharge. The results show that the capacitive energy storage of electrodes is critically dependent on the microporosity and surface chemistry of activated carbons. The highest electrode capacitance in this work was 103.6 F/g that prepared from activated carbon modified at an ultrasonication temperature of 323.15 K for 10 min and microwave power output of 900 W for 10 min.

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Peer review under responsibility of Chinese Materials Research Society.

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http://dx.doi.org/10.1016/j.pnsc.2012.11.001

1. Introduction

Supercapacitors, also known as electrochemical double-layer capacitors (EDLCs) are an energy storage device that can be used to store and release energy. Compared to commercial rechargeable batteries, EDLCs have a better delivery (charge–discharge) performance and longer cycle life [1–2]. The applications of EDLCs are mainly found as high power energy storage devices in the fields that need an ever-decreasing size such as electronic and military devices, space flight technology, automotive and public transports, and low-power equipment such as portable media players, game consoles, photographic flashs, and printers [3]. The disc-type EDLCs are fabricated by sandwiching a thin sheet or separator (e.g., polymers) with two round-shaped electrodes. For the roll-type EDLCs, the electrode foils and separators are rolled up together to make a roll—to—roll structure. Although the latter is more favorable for applications in devices, the disc-type EDLCs are actually more resistant to physical changes during capacitance measurement (e.g., swelling of the porous carbon layers) and more suitable for long term tests [4]. In addition, the disc-type is closer to the intended products (EDLCs) in terms of its design and structure.

While many materials have been developed as electrodes for EDLCs, such as graphene [5], carbon nanotubes (CNTs) [6], conducting polymers [7], metal oxides [8], carbon aerogels [9], and activated carbons [10–14], the activated carbon is the mostly used porous materials for EDLCs because of its benefits such as high surface area and chemical stability, wide availability, simpler and low cost preparation methods compared to other carbon-based materials such as carbon nanotubes, carbon aerogel, and graphene. Numerous studies have been conducted to explore the electrochemical performance of activated carbon-based electrodes for EDLCs [10–15]. It has been reported that the capacitance of electrode critically depends on the pore structure and surface chemistry of activated carbon [16–21]. To improve its electrochemical performance, activated carbons must be modified with proper activation methods. The most extensively used methods is through one-step or two-step chemical and/or physical (thermal) activations using various modifiers such as $ZnCl_2$, H_3PO_4, KOH, K_2CO_3, CO_2, or steam [15,18,19,22,23]. However, such conventional processes are energy-intensive in conjunction with high temperature carbonization process (mostly conducted at above 700 °C) and often cause environmental issues due to the generation of wastewater containing toxic chemicals.

Lately, microwave irradiation has become a fast emerging technique for surface modification of activated carbons. This technique has attracted many attentions because of reducing modification time and energy consumption compared to conventional methods [19,20]. It is known that microwave energy can vibrate polar molecules (e.g. water and some organic matters) in the carbon matrices and the generated heat triggers molecular evaporation of such molecules. Such phenomena lead to the tunneling and development of porosity in the carbon matrices. Microwave energy can also activate the surface carbon atoms to initiate the reactions with surrounding chemical(s), resulting in the modification of surface chemistry [21]. In addition, the burn loss of carbon in the process can be minimized.

The objectives of this work are to prepare high surface area activated carbons from durian shell waste and develop high performance carbon electrodes for supercapacitors. The activated carbons were prepared by carbonization process, followed by surface modification via ultrasonication and microwave irradiation using water as the modifying agent. To date, there is no report on the preparation and modification processes of activated carbons by combination of such techniques using the green chemical (water). The effects of temperature and time in the ultrasonication treatment and power output and time in the microwave irradiation towards the pore structure and surface chemistry of the carbon were discussed. To this end, the capacitance and delivery performance of durian shell-derived carbon electrodes for supercapacitors was tested by cyclic voltammeter (CV) and galvanostatic charge–discharge.

2. Materials and methods

2.1. Materials

Analytical grade polyvinylidene difluoride (PVdF) was purchased from Sigma Aldrich, Singapore. Nickel foam substrate (30 cm in length × 8 cm in width × 0.008 cm in thickness, purity > 99.9%) was obtained from MTI Corp., China. Durian shell was obtained from a local supermarket in Surabaya, East Java, Indonesia. After the collection, the shell was cut into a size of 1 × 1 cm^2 and repeatedly washed with tap water to remove surface dirt and other insoluble materials. The shell was then dried in an oven at 373.15 K for 24 h and crushed with an IKA Labortechnick grinder to obtain particle size of 0.18–0.25 mm (60/80 mesh). Finally, the product was kept in the desiccators for further use.

The proximate analysis of durian shell was performed based on the ASTM E870-82 method and the results are given as follows: moisture content (MC) of 5.42%, volatile matters (VM) of 69.73%, ash of 2.21%, and fixed carbon (FC) of 22.64%. The compositions of durian shell, as determined by a Perkin–Elmer 2400 CHNS/O elemental analyzer, were found as follows: $C=60.48\%$, $H=3.11\%$, $N=8.53\%$, $S=0.1\%$ and $O=27.78\%$ (measured by difference). High carbon content in durian shell denotes the suitability of this biomass waste to be utilized as a precursor of activated carbon.

2.2. Preparation of activated carbons

The carbonization process of durian shell was performed in a batch pyrolysis reactor. The reactor was custom-made by a local manufacturer from 316 grade stainless steel with maximum working temperature of 1,273.15 K at atmospheric pressure. The reactor was connected to a gas cylinder containing nitrogen with purity of 99.9%. Prior to heating, nitrogen was flowed to the system to remove air. One hundred grams of durian shell was loaded into the reactor and heated at a rate of 10 K/min from room temperature (around 303.15 K) to 1,023.15 K. The process was conducted for 3 h under nitrogen flow at a flow rate of 2 L/min. After carbonization, the system was cooled down to room temperature under a flow of N_2. The resulted char was removed from the reactor and kept in the desiccators. Here, the char was designated as untreated carbon sample.

The surface modification of untreated char was described as follows: 10 g of char was mixed with distilled water at a mass/volume ratio of 1:2 in plastic wrapped test tubes. The mixture was then sonicated in a Wiseclean WUC-A03H ultrasonic water-bath at 40 KHz at various temperatures (303.15 K, 313.15 K, and 323.15 K) for 10 min, 20 min, and 30 min. The suspension was then placed in a microwave oven (Inextron WDS900DSL23-2) and irradiated at various power outputs (540 W, 720 W, and 900 W) for a certain period of time (5 min, 8 min, and 10 min). The modified carbons were then cooled to room temperature and dried in an oven at 373.15 K for 24 h. The resulted samples were labeled as follows: the first and the second terms refer to ultrasonication temperature and time, respectively while the third and the fourth refer to microwave power output and heating time, respectively. For example, activated carbon modified by ultrasonication at 323.15 K for 10 min and microwave irradiation at 900 W for 10 min was labeled as AC-323.15/10/900/10.

2.3. *Pore structure and surface morphology characterizations*

The pore structure of activated carbons was characterized by physical adsorption of nitrogen, in an automatic Micromeritics ASAP-2010 volumetric sorption analyzer at 77.15 K over a relative pressure (p/p^0) range from approximately 10^{-5}–0.995. The specific surface area (S_{BET}), micropore volume (V_{mic}), and micropore surface area (S_{mic}) of the samples were determined by means of Brunauer–Emmett–Teller (BET) and Dubinin–Asthakov (DA) methods. The pore size distributions (PSDs) of the samples were obtained from gas adsorption isotherm data by density functional theory (DFT) model available within the instrument with medium level of software regularization.

The surface morphology of untreated and modified activated carbons was visualized in a field emission scanning electron microscope JEOL JSM-6300F. Prior to analysis, the samples were coated with a thin layer of platinum to make them electronically conductive, using an Eiko IB-5 sputter–coater operated at 6 mA for 3 min in argon atmosphere. The coated samples were then placed in the SEM specimen chamber and scanned at an accelerating voltage of 10 kV, spot size of 8, aperture of 4, and working distance of 9 mm.

2.4. *Surface chemistry characterizations*

The surface chemistry of untreated and modified activated carbons was characterized by the Boehm titration method [24]. FTIR analysis was also performed to identify the presence of carbon–oxygen surface groups and probe their alterations before and after modifications. The analysis was conducted in a Shimadzu FTIR-8400S spectrophotometer based on the KBr disk procedure with cumulative scans of 200. The spectra data of the samples were recorded in a wavenumber range from 4000 cm^{-1} to 500 cm^{-1}.

2.5. *Preparation of carbon electrodes*

The carbon electrodes were prepared by mixing activated carbon with PVdF as a binder and ethanol as a solvent with mass ratio of 8:1:1. The mixture was then pressed into a circular nickel foam substrate (1.3 cm i.d.) at 20 MPa and dried in a Lab-Line Duo-Vac oven at 353.15 K. The disc-type EDLCs were fabricated by placing a thin polypropylene film between the electrodes and pressed in a stainless steel cell at 100 MPa.

2.6. *Electrochemical measurements*

The electrochemical performance of the electrodes was tested by cyclic voltammetry (CV) in a potential range from +0 V to +1 V at a scan rate of 30 mV/s and galvanostatic charge–discharge using an electrochemical workstation (Model 660D, CH Instruments Inc.). The electrolyte solution used in the electrochemical cell was 1 M H_2SO_4. The gravimetric specific capacitance of the electrodes was calculated by following equation [16]:

$$C = 4\frac{I_{\mathrm{d}}\,\Delta t}{m\,\Delta U} \tag{1}$$

where I_d is the discharge current (A), Δt is the discharge time (s), ΔU is the potential difference of the electrodes during discharge (V), m is the total mass of activated carbon in both electrodes (g), and C is the specific capacitance of the electrodes (F/g).

3. Results and discussion

3.1. *Pore structure of activated carbons*

Generally speaking about materials science specifically activated carbon, the pore structure is the main aspect featuring various properties of carbon-based materials such as electrochemical, adsorptive, catalytic, etc. With regard to electrochemical properties, activated carbons with a tunable micropore/mesopore ratio are desirable for the fabrication of high performance supercapacitors in wide range of uses from low to high current density [1,25,26]. Fig. 1 depicts the nitrogen adsorption–desorption isotherms of untreated and modified carbons at 77.15 K. It can be seen that both untreated and modified carbons exhibit Type-II isotherm shape according to IUPAC classifications. Such isotherm was characterized by an inflection in the p/p^0 region above 0.1 after micropores filling, followed by gradual and then a rapid increase in the adsorption extents near saturation point, i.e. at p/p^0 above 0.9. This may reveal an adsorption phenomenon of gas onto solids with mixed microporosity and mesoporosity. It was also noted that the gradient of N_2 adsorption–desorption curves in the p/p^0 region from 0.1 to 0.9 for AC-313.15/20/720/8 and AC-323.15/10/900/10 carbons was steeper than untreated carbon. This may denote that more pores (typically mesopores) were evolved on the carbon surface after modification process, resulting in higher adsorption capacity of N_2. The specific surface area (S_{BET}), total pore volume (V_T), and micropore volume (V_{mic}) of untreated and modified carbon samples are listed in Table 1. The mixed characteristic of microporosity and mesoporosity on the carbon surface also proved from the DFT results (Fig. 2). Several narrow peaks were appeared at pore size range from 10 Å to 20 Å, which is the micropore zone and broad peaks at pore size range from 50 Å to 450 Å, which is the mesopore zone. The SEM micrographs of untreated and modified carbons at two magnifications of 5000 × and 10,000 × are displayed in Fig. 3. It was found that the surface of modified carbons (Fig. 3B and C) was uneven with significant amount of aggregated particles, which did not exist on the untreated sample (Fig. 3A). This observation indicates that the ultrasonic and microwave treatment lead to the aggregation of carbon particles that create higher surface area and pore volume as supported by the N_2 sorption analysis listed in Table 1.

Based on the experimental results (Table 1), it can be seen that the combination of ultrasonication and microwave treatments can significantly increase the carbon surface area. The BET surface area of untreated carbon increases almost 2-fold from 352.41 m^2/g to 648.64 m^2/g after ultrasonication treatment at 303.15 K for 20 min and microwave irradiation at 720 W for 8 min. It was found that the effects of temperature and time in ultrasonication treatment may not be significant in increasing the BET surface area of the carbon. For example, the BET surface area between AC-313.15/20/720/8 and AC-323.15/20/720/8 was slightly different (645.39 m^2/g vs. 651.82 m^2/g) by ultrasonicating carbon at 313.15 K and 323.15 K (other conditions were unchanged). However, increasing ultrasonication temperature would enhance the diffusion rate of water into the carbon matrices thus more amounts of water were entrapped. During microwave irradiation, the entrapped waters were evaporated, leading to the tunneling and development of porosity that increase the surface area and total pore volume of the carbon. In contrast, extending ultrasonication time would decrease the surface area and total pore volume of the carbon due to partial blockades of internal pore accesses as a result of breakdown of carbon internal structure by ultrasound vibration, started from macropore and then smaller pores i.e. mesopore and micropore [27].

The effect of microwave power output may relevant to the energy input that used to evaporate entrapped water molecules in the carbon matrices and activate the molecular reaction that modified the carbon surface chemistry. As denoted in Table 1, increasing microwave power output from 540 W to 720 W would largely increase the BET surface area of activated carbons treated at the same ultrasonication time and temperature, for example from 578.32 m^2/g of AC-313.15/20/540/8 to 645.39 m^2/g of AC-313.15/20/720/8. However, the microporosity degree of the carbons i.e. S_{mic}/S_{BET} and V_{mic}/V_T decreases with increasing microwave power output, from 74.23% and 71.16% to 72.22% and 68.63% respectively. This is likely due to partial widening of micropores that caused by microwave energy whereas the effect was greater at higher power output. Extending microwave heating time also gives a positive effect on the surface area and total pore volume of the carbon, which can be explained from the basis of relation between time and the amount of energy transferred to the system.

3.2. Surface chemistry of activated carbons

The electrochemical performance of carbon-based electrode materials also strongly depends on the carbon surface chemistry, associated with the carbon–oxygen surface groups.

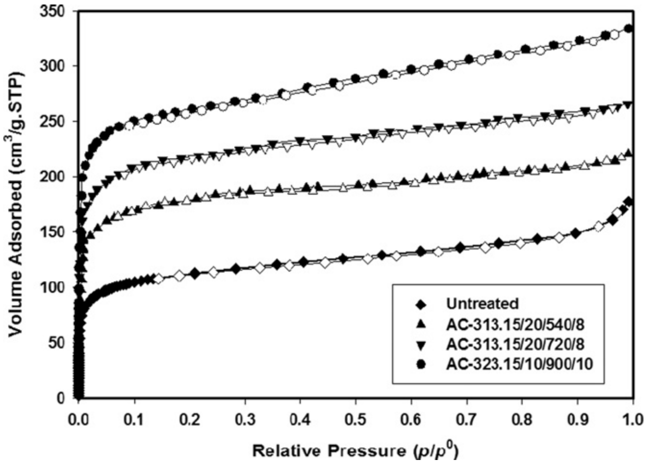

Fig. 1 Nitrogen adsorption–desorption isotherms for untreated and modified carbons (solid symbols—adsorption isotherm; hollow symbols—desorption isotherm).

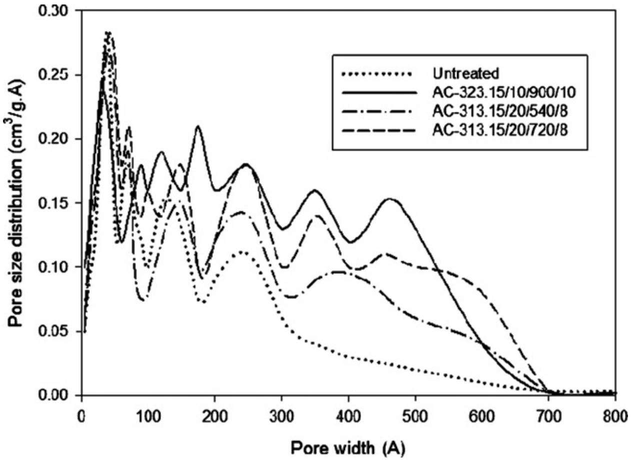

Fig. 2 Pore size distributions of untreated and modified carbons with medium level of software regularization.

Table 1 Pore characteristics of untreated and modified activated carbons.

Carbon samples	S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_T (cm^3/g)	V_{mic} (cm^3/g)
Untreated	352	272	0.12	0.08
AC-303.15/20/720/8	649	468	0.19	0.13
AC-313.15/10/720/8	635	466	0.19	0.13
AC-323.15/20/720/8	652	477	0.20	0.14
AC-313.15/20/720/8	645	466	0.19	0.13
AC-313.15/30/720/8	630	457	0.18	0.12
AC-313.15/20/540/8	578	430	0.17	0.12
AC-313.15/20/900/8	716	501	0.20	0.13
AC-313.15/20/720/5	621	447	0.18	0.12
AC-313.15/20/720/10	684	481	0.20	0.13
AC-323.15/10/900/10	768	525	0.21	0.13

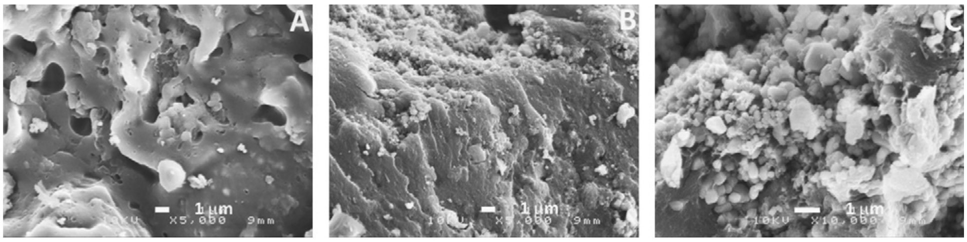

Fig. 3 SEM images of untreated (A) and modified activated carbons (B and C).

Table 2 Surface acidity and basicity of untreated and modified activated carbons.

Carbon samples	Carbon–Oxygen surface groups (meq/g)				
	Acidic Groups				
	Carboxylic	Lactone	Phenolic	Total	Basic groups
Untreated	0.05	0.18	0.10	0.33	0.16
AC-303.15/20/720/8	0.08	0.28	0.18	0.54	0.22
AC-313.15/10/720/8	0.08	0.29	0.18	0.55	0.22
AC-323.15/20/720/8	0.08	0.30	0.18	0.56	0.22
AC-313.15/20/720/8	0.08	0.28	0.17	0.53	0.21
AC-313.15/30/720/8	0.08	0.28	0.17	0.53	0.22
AC-313.15/20/540/8	0.06	0.26	0.16	0.48	0.19
AC-313.15/20/900/8	0.08	0.31	0.19	0.58	0.24
AC-313.15/20/720/5	0.08	0.28	0.18	0.54	0.22
AC-313.15/20/720/10	0.08	0.30	0.19	0.57	0.24
AC-323.15/10/900/10	0.10	0.32	0.21	0.63	0.26

It was known that carbon–oxygen surface groups either acid or basic such as carboxylic, lactone, phenolic, and quinone pose strong affinity towards electrolyte ions [28]. Therefore, activated carbon surface with highly exposed sites of these groups would be suitable for the binding of electrolyte ions into the external and internal structures of the carbon. To assess whether surface modification process by the combination of ultrasonication and microwave irradiation can enhance the surface polarity, the Boehm titration results of untreated and modified carbons are given in Table 2.

In Table 2, it can be seen that surface acidity and basicity of untreated carbon significantly increased after modification process. It was noted that the effect of temperature and time in the ultrasonication treatment was not significant to increase the surface polarity of the carbon. For example, the acidity on untreated carbon surface slightly increases from 0.3472 to 0.5661, 0.5768, and 0.5901 meq/g after ultrasonicated at 303.15 K, 313.15 K, and 323.15 K, respectively. Similar results were observed for activated carbons modified at a different ultrasonication time at the same temperature, for example AC-313.15/10/720/8 and AC-313.15/20/720/8. This can be explained by considering that ultrasonication treatment only causes structural changes i.e. the breakdown of carbon internal structure and entrapment of water molecules in the solid matrices. Therefore, it is expected that microwave irradiation plays an important role in modifying the carbon surface chemistry. It was known that microwave energy can trigger partial oxidation reactions on the surface carbon atoms by limited air and the surrounding chemicals in the system (e.g. water) to form various surface oxygenated complexes [21]. These reactions were expected to become more prominent at higher power outputs (also mean greater microwave energy) and longer heating time.

FTIR results (the spectra not shown here) also denote the increase of peak energy (in the unit of absorbance) of the symmetrical and assymmetrical bands at wavenumber ranges of 1100–1200 cm^{-1}, 1400–1680 cm^{-1}, 1700–1800 cm^{-1}, 2900–3200 cm^{-1}, and 3500–3600 cm^{-1} for carbons modified at different microwave power outputs and heating time. These bands may correspond to C–O stretch of carboxylic groups, C=O stretch of lactone groups, and O–H stretch of phenolic groups, respectively. The results above are in conformance with the Boehm titration results that show higher levels of acidity and basicity on the carbon surface after modification process.

3.3. *Electrochemical performance of carbon electrodes*

The cyclic voltammogram and galvanostatic charge–discharge of several carbon electrodes are depicted in Figs. 4 and 5. Fig. 4 indicates that the current density of untreated and modified carbon electrodes in H_2SO_4 solution are fairly stable at potential ranging from +0 V to +1 V. The symmetrical rectangular shape of combined curves at positive and negative sweep rates was observed and reveals the current stability of the electrodes during charge and discharge [16]. The voltammogram curve areas for AC-323.15/10/900/10 and AC-313.15/20/900/8 electrodes were broader than the untreated sample, which may be ascribed to higher capacitance of these electrodes. The profiles of cyclic galvanostatic charge–discharge (Fig. 5) support the stability performance of electrodes over

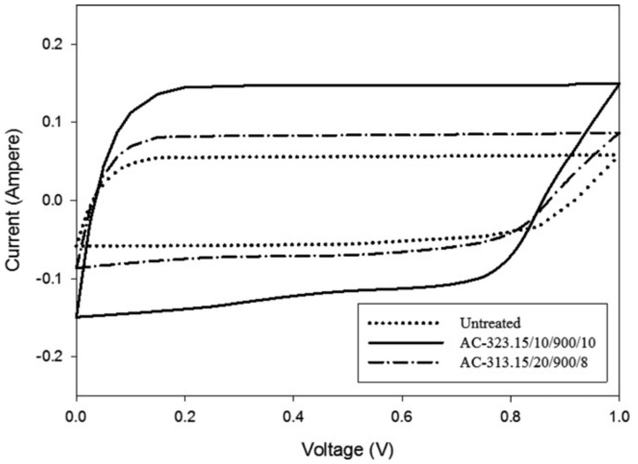

Fig. 4 Cyclic voltammograms of untreated and modified carbon electrodes.

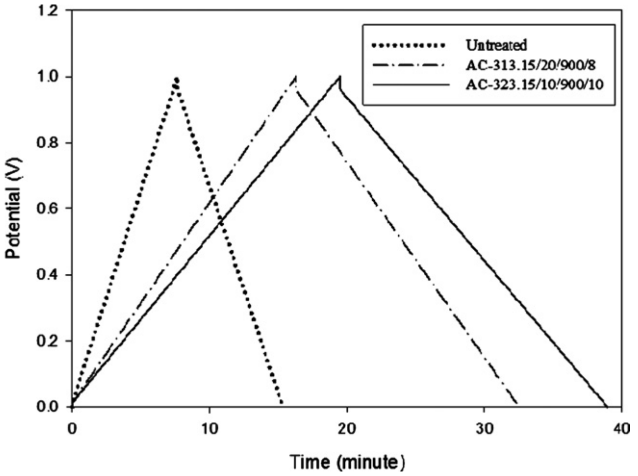

Fig. 5 Galvanostatic charge–discharge curves of untreated and modified carbon electrodes.

potential range studied. In this figure, an isosceles triangle shape was shown in all charge–discharge curves which denote high efficiency electrodes with low internal resistance and potential drop [16].

Table 3 The specific capacitance untreated and modified activated carbon electrodes.

Carbon samples	C (F/g)
Untreated	60.8
AC-303.15/20/720/8	94.8
AC-313.15/10/720/8	95.8
AC-323.15/20/720/8	99.7
AC-313.15/20/720/8	94.7
AC-313.15/30/720/8	90.9
AC-313.15/20/540/8	87.3
AC-313.15/20/900/8	98.9
AC-313.15/20/720/5	91.5
AC-313.15/20/720/10	96.6
AC-323.15/10/900/10	103.6

The capacitance of electrodes prepared from different carbon samples is presented in Table 3. As expected, the capacitance of electrodes prepared from modified carbons was higher than the untreated carbon. In order to investigate the role of microporosity and surface chemistry of the carbon towards the electrode capacitance, we compare the capacitive energy storage of AC-313.15/20/720/8, AC-323.15/20/720/8, and AC-313.15/20/900/8 electrodes. These electrodes were selected as the model to study the importance of ultrasonication and microwave irradiation in conjunction with the aforesaid factors. It was found that the capacitance of electrodes was increased with increasing carbon microporosity, from 60.8 F/g of untreated ($S_{\mathrm{mic}} = 271.24\ \mathrm{m}^2/\mathrm{g}$) to 94.7 F/g AC-313.15/20/720/8 ($S_{\mathrm{mic}} = 466.10\ \mathrm{m}^2/\mathrm{g}$), 99.7 F/g of AC-323.15/20/720/8 ($S_{\mathrm{mic}} = 476.55\ \mathrm{m}^2/\mathrm{g}$), and 98.9 F/g of AC-313.15/20/900/8 ($S_{\mathrm{mic}} = 500.47\ \mathrm{m}^2/\mathrm{g}$). However, it should be noteworthy that the capacitance of electrode does not solely depends on the carbon microporosity. For example, the capacitance of AC-313.15/30/720/8 was lower than AC-313.15/20/720/5 (90.9 F/g vs. 91.5 F/g) although its micropore surface area was higher than the latter ($456.63\ \mathrm{m}^2/\mathrm{g}$ vs. $447.32\ \mathrm{m}^2/\mathrm{g}$). This result may confirm the synergistic effects between microporosity and carbon surface chemistry in improving the electrochemical performance of electrodes. Similar results were also found in several works [16,29,30]. The electrodes prepared from AC-313.15/20/900/8 and AC-323.15/10/900/10 carbons (Fig. 5) have longer charge–discharge time than untreated sample (32.5 min vs. 15.3 min and 39 min vs. 15.3 min). This is due to higher surface area and surface polarity in modified carbons that facilitate the interaction between carbon surface and the electrolyte solution, which are responsible for higher energy storage capacity and lower internal resistance for the electrolyte ion movement. The highest capacitance of carbon electrodes in this work was 103.6 F/g that was prepared from AC-323.15/10/900/10 carbon. This value was 70% higher than the capacitance of untreated carbon electrodes (60.8 F/g).

4. Conclusions

The preparation of high surface area activated carbons with mixed microporosity and mesoporosity from durian shell waste has been demonstrated in this work. The combination of ultrasonication and microwave irradiation techniques using water as the modifying agent was found to be an efficient and effective way to increase the surface area and surface polarity of activated carbons. The electrochemical performance of durian shell-derived carbon electrodes was tested by cyclic voltammeter and galvanostatic charge–discharge. The results show that both untreated and modified carbon electrodes show good current stability over potential range from +0 V to +1 V. The profiles of cyclic galvanostatic charge–discharge curves denote high efficiency and low potential drop electrodes with longer charge–discharge time for the electrodes prepared from modified carbons. The highest capacitance of carbon electrodes in this work was 103.6 F/g that prepared from AC-323.15/10/900/10, i.e. activated carbon modified at an ultrasonication temperature of 323.15 K for 10 min and microwave power output of 900 W for 10 min.

Acknowledgments

The Australian Research Council (ARC) is acknowledged for financial support under the ARC Future Fellow Program (FT100100879).

References

[1] H. Tamai, M. Kunihiro, M. Morita, H. Yasuda, Mesoporous activated carbon as electrode for electric double layer capacitor, Journal of Materials Science 40 (2005) 3703–3707.

[2] W. Yansu, W. Chengyang, G. Chunyu, S. Zhiqiang, Influence of carbon structure on performance of electrode material for electric double layer capacitor, Journal of Physics and Chemistry of Solids 69 (2008) 16–22.

[3] R.A. Huggins, Supercapacitors and electrochemical pulse sources, Solid State Ionics 134 (2000) 179–195.

[4] C. Hu, Fluid coke derived activated carbon as electrode material for electrochemical double layer capacitor - a thesis submitted for the degree of Master of Applied Science. Graduate Department of Chemical Engineering and Applied Chemistry, University of Toronto, 2008.

[5] M.D. Stoller, S. Park, Z. Yanwu, J. An, R.S. Ruoff, Graphene-based ultracapacitors, Nano Letters 8 (2008) 3498–3502.

[6] C. Niu, E.K. Sichel, R. Hoch, D. Moy, H. Tennent, High power electrochemical capacitors based on carbon nanotubes electrodes, Applied Physics Letters 70 (1997) 1480–1482.

[7] D. Tashima, E. Yamamoto, N. Kai, D. Fujikawa, G. Sakai, M. Otsubo, T. Kijima, Double layer capacitance of high surface area carbon nanospheres derived from resorcinol–formaldehyde polymers, Carbon 49 (2011) 4848–4857.

[8] J. Bai, X. Bo, C. Luhana, L. Guo, A novel material based on cupric(II) oxide/macroporous carbon and its enhanced electrochemical property, Electrochimica Acta 56 (2011) 7377–7384.

[9] C.Y. Kim, A.R. Jang, K.Y. Cho, Optimization of pore structures and supercapacitor properties of carbon aerogel electrodes, Asian Journal of Chemistry 24 (2012) 4205–4212.

[10] T. Morishita, Y. Soneda, T. Tsumura, M. Inagaki, Preparation of porous carbons from thermoplastic precursors and their performance for electric double layer capacitors, Carbon 44 (2006) 2360–2367.

[11] X. Xia, L. Shi, H. Liu, L. Yang, Y. He, A facile production of microporous carbon spheres and their electrochemical performance in EDLC, Journal of Physics and Chemistry of Solids (2013) 385–390.

[12] L. Wei, G. Yushin, Electric double layer capacitors with activated sucrose-derived carbon electrodes, Carbon 49 (2011) 4830–4838.

[13] W. Xing, X. Li, X. Gao, S. Zhuo, Highly porous carbon derived from sunflower seed shell for electrochemical capacitor, Advances in Materials Research 287–290 (2011) 1420–1423.

[14] S. Shiraishi, Heat-treatment and nitrogen-doping of activated carbons for high voltage operation of electric double layer capacitor, Key Engineering Materials 497 (2012) 80–86.

[15] S.L. Zhang, Y.H. Song, X.G. Li, W. Li, Study on the capacitance performance of activated carbon material for supercapacitor, Advances in Materials Research 239–242 (2011) 797–800.

[16] Y. Liu, Z. Hu, K. Xu, X. Zheng, Q. Gao, Surface modification and performance of activated carbon electrode material, Acta Physico–Chimica Sinica 24 (2008) 1143–1148.

[17] J. Li, X.D. Zhao, Preparation and electrochemical characterization of an activated carbon material of high surface area for supercapacitor, Advances in Materials Research 463–464 (2012) 410–414.

[18] K. Xia, Q. Gao, J. Jiang, J. Hu, Hierarchical porous carbons with controlled micropores and mesopores for supercapacitor electrode materials, Carbon 46 (2008) 1718–1726.

[19] X.J. He, Y.J. Geng, J.S. Qiu, M.D. Zheng, X.Y. Zhang, H.F. Shui, Influence of KOH/coke mass ratio on properties of activated carbons made by microwave-assisted activation for electric double-layer capacitors, Energy Fuel 24 (2010) 3603–3609.

[20] X. He, R. Li, J. Qiu, K. Xie, P. Ling, M. Yu, et al., Synthesis of mesoporous carbons for supercapacitors from coal tar pitch by coupling microwave-assisted KOH activation with a MgO template, Carbon 50 (2012) 4911–4921.

[21] J.A. Menendez, E.M. Menendez, M.J. Iglesias, A. Garcia, J.J. Pis, Modification of the surface chemistry of active carbons by means of microwave-induced treatments, Carbon 37 (1999) 1115–1121.

[22] J. Zhang, L. Gong, K. Sun, J. Jiang, X. Zhang, Preparation of activated carbon from waste *Camellia oleifera* shell for supercapacitor application, Journal of Solid State Electrochemistry 16 (2012) 2179–2186.

[23] H. Chen, F. Wang, S. Tong, S. Guo, X. Pan, Porous carbon with tailored pore size for electric double layer capacitors application, Applied Surface Science 258 (2012) 6097–6102.

[24] H.P. Boehm, Surface oxides on carbon and their analysis: a critical assesment, Carbon 40 (2002) 145–149.

[25] D. Qu, Studies of the activated carbons used in double-layer supercapacitors, Journal of Power Sources 109 (2002) 403–411.

[26] J. Mi, X.R. Wang, R.J. Fan, W.H. Qu, W.C. Li, Coconut-shell-based porous carbons with a tunable micro/mesopore ratio for high-performance supercapacitors, Energy Fuel 26 (2012) 5321–5329.

[27] T. Ohkubo, R. Hori, K. Tsuchiya, H. Sakai, M. Abe, Pore-size control of carbon nanospace with ultrasonic irradiation, NSTI-Nanotech 1 (2006) 162–165.

[28] T.A. Centeno, F. Stoeckli, The role of textural characteristics and oxygen-containing surface groups in the supercapacitor performances of activated carbons, Electrochimica Acta 52 (2006) 560–566.

[29] D. Tashima, K. Kurosawatsu, Y.M. Sung, M. Otsubo, C. Honda, Surface modification of nanoporous materials for electric double layer capacitors application, Materials Chemistry and Physics 103 (2007) 158–161.

[30] A. Yoshida, L. Tanahashi, A. Nishino, Effect of concentration of surface acidic functional groups on electric double layer properties of activated carbon fibers, Carbon 28 (1990) 611–615.