

2015 International Conference on Alternative Energy in Developing Countries and
Emerging Economies

Microporous Activated Carbon from KOH-Activation of Rubber Seed-Shells for Application in Capacitor Electrode

Thanchanok Pagketanang^a, Apichart Artnaseaw^a, Prasong Wongwicha^a,
Mallika Thabuot^{a,b*}

^aDepartment of Chemical Engineering, Faculty of Engineering, KhonKaen University, Thailand

^bCenter of Knowledge Development of Rubber Tree in Northeast group (KDRN), KhonKaen University, Thailand

Abstract

This study is to prepare the activated carbon from rubber seed-shells by KOH activation Activated Carbons (ACs) for the electrochemical double layer capacitors (EDLCs). Impregnation-Activation Method using 2%wt KOH solution as a chemical agent was used. The BET surface area, pore volume and pore size distribution of ACs were characterized using N₂ adsorption technique. The surface morphology was evaluated with SEM. Electrochemical properties of the prepared ACs electrodes have been studied using cyclic voltammetry (CV) in 30%wt of KOH as electrolyte. All prepared ACs had adsorption isotherm Type I indicating as the pore structure is mainly composed of micropores. Highest specific surface area (620 m²/g) with higher iodine number (639.73 mg/g) was obtained from the carbonization at 900°C. The specific capacitance of the microporous ACs sheet electrode reached 63.2 F/g at 1mV/s.

© 2015 Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE

Keywords: Chemical Activation; Rubber Seed Shells; Microporosity; Electrochemical Double Layer; Capacitors

1. Introduction

Electrochemical double layer capacitor (EDLC) is the interesting energy storage device because of its the dominant characteristics of environmentally friendly, longer lifecycle and high power supply in seconds, quickly rechargeable and faster energy transfer [1-4]. Porous carbon materials, activated carbons (ACs), carbon nanotubes (CNTs), carbon aerogels and ordered microporous carbon have been considered for the EDLC electrodes [8-14]. ACs are the most attractive materials due to their large specific surface area, unique pore structure, low cost, high electrical conductivity and electrochemical stability. ACs with

* Corresponding author. Tel.: +6643362240; fax: +6643362240.

E-mail address: tmallika@kku.ac.th.

high specific surface area are expected to give EDLCs with high electrochemical performance. However, surface morphology and pore structure of ACs depends on the precursors and selected activation. KOH activation was reported as a powerful method to develop and control the number of micropores with a very similar pore size distribution [5]. From the AC-based EDLC investigations, the KOH-activated starch AC presented higher BET surface area and larger pore volume than using ZnCl_2 as the activating agent [3]. This AC-electrode showed a high capacitance of 238 F/g in 30 wt% KOH aqueous electrolytes. Same method was used to produce the high specific surface area of AC presenting micro/meso-porous structure [1], the specific capacitance of their EDLCs reached 251.1 F/g at 2 mV/s scan rate. AC prepared from sunflower seed shell by impregnation-activation method with KOH had greater capacitive behavior than the AC made by carbonization-activation method because the former had more abundant macroscopic pores and less interior micro-porous surface [2]. KOH was used as the activating agent to produce the AC from rubber seed-shell with the majority structure of mesopores [6], and greater BET surface area than the physical activating method which presented before [7]. However, there has been no reported on its performance in supercapacitor electrode. In this study, we selected rubber seed-shell as the precursors to prepare activated carbon by KOH chemical activation followed by high temperature carbonization. As-prepared ACs electrode has been evaluated by cyclic voltammetry, the influences of pore structure on electrochemical properties were also discussed.

2. Methodology

The rubber seed-shell residue was separated from the extraction of Para rubber seeds, then it was dried at 60°C for 4 h before crushing and screening to get the particle sizes less than 1 mm. 150g of prepared rubber seed-shell residue was impregnated in 500 ml of 2wt.% KOH solution for 24 h. The sample was filtered and washed with distilled water for several times until the pH was neutral. It was dried at 110°C for 12 h before carbonization in a horizontal tube furnace under a flow of N_2 gas of 250 ml/min at a heating rate of 5°C/min. The final temperature was set at 700, 800 and 900°C with a holding time of 2 h. The cooled product was collected and dried in an air oven at 110°C for 24 h before property characterization. The proximate analysis of rubber seed-shell and prepared-ACs were measured using thermo gravimetric analyzer (TGA50, Shimadzu). The ultimate analysis was estimated using the equations provided in the other study [8]. Surface texture and pore properties of produced-ACs were characterized by N_2 adsorption at 77K using ASAP2010V5.03G surface analyzer (Micromeritics, USA). Scanning electron microscope SEM (Hitachi S-3000N) was used to examine surface morphology of rubber seed shell-based ACs at the accelerated voltage of 20 kV. Iodine number of prepared-ACs were also checked for the surface area covering pores which are larger than 1 nm. For the electrode fabrication, selected rubber seed shell-based ACs powders were well mixed with 20%wt. polyvinylidene difluoride (PVDF) binders for 1h with the helps of N-methyl-2-pyrrolidinone (NMP). Then, this paste was applied with the brush on the glass plates to form the thin layer before drying overnight at 110°C. Dried ACs layers were cut into sheet electrodes with the effective surface area of $1 \times 1 \text{ cm}^2$ and the thickness of 0.3 mm. The electrochemical measurements of each as-prepared electrode were performed on an electrochemical workstation (R600 Gamry Instrument, Germany) equipped to a three-electrode test cell in a 30 wt.% KOH electrolyte. A platinum sheet electrode and Ag/AgCl were used as the counter electrode and the reference electrode, respectively. The CV measurements were conducted in the voltage range -0.35 V to 0 V at different sweep rates ranging from 1, 5, 10 and 20 mV/s. All measurements were carried out at ambient temperature.

3. Results and discussion

Table 1 showed that rubber seed-shell has high carbon content with high potential to be the precursor of activated carbon production. The resultant ACs from carbonization at 700, 800 and 900°C are denoted as AC700, AC800 and AC900, respectively. During the carbonization, volatile matter was released from the carbon structure. Therefore, volatile content of produced activated carbon decreased with the higher carbonizing temperature. In comparison to AC700 and AC800, the AC900 had the lowest amount of ash at 1.17% with high percentage of fixed carbon at 89.67%. As shown in Table 2, the yield of activated carbon significantly decreased with the higher temperature of carbonization. The increase of carbonizing temperature (from 700 to 900°C) increased the specific surface area (from 429 to 620 m²/g) with the decrease of average pore diameter (from 2.165 to 0.950 nm). Differently from the previous report [8], ACs prepared here have the majority structure of micropores which caused by the stronger penetration of chemical ion into the material structure and it was assured by the improvement of iodine number. At higher carbonizing temperature, micropores had been developed because more heat dissipation into the charred surface even some pre-formed mesopores were corrupted. Therefore, pore volume and the N₂ adsorption capacity of activated were increased. Activated carbon has an increase of the microporosity (from 80.597 to 93.310 vol.%) and the decrease of average pore diameter (from 2.165 to 0.950 nm) when the carbonizing temperature increased (from 700 to 900°C). According to the classification of IUPAC, the isotherms of ACs prepared here exhibit type I isotherm curves suggesting the presence of a large number of micropores as illustrated in Fig. 1(a). Major N₂ adsorption occurs at the low relative pressures (< 0.15), while relatively horizontal adsorption plateau shows at higher P/P₀ values. The similar isotherms have also been reported for the activated carbon made from petroleum coke [9] and microporous carbon fibre by KOH activation [10]. In addition, the adsorbed amount of N₂ increases with an increase of carbonizing temperature, indicating that the micropores were developed resulting to higher specific surface area. From the calculation using BJH method, the mesopore size distribution (PSD) of ACs prepared in this work is presented as seen in Fig. 1(b). Each ACs had a similar distribution curve, and the proportion of mesopores is gradually decreased with the higher temperature of carbonization. The distribution was not completed near the lower pore size limit which indicates the existence of micropores (diameter < 2 nm). These PSDs confirm that the prepared ACs have both micropore and mesopore structure, and the AC700 shows biggest pore diameter and smallest total pore volume.

It is obviously seen in Fig. 2(a-c) that a lot of nano-holes were found on the surface in Fig. 2. Microscopic scale is formed already at the carbonization of 700°C, but AC700 has the rough surface of various pores. AC900 was comprised by a large number of pores with a clearly uniform size distribution and ordered pore structure. Highest proportion of micropores came with AC900 which caused by the higher temperature activated KOH ion to permeate deeply through the carbonized surface, so the smaller pores and more amounts of internal micropores were formed. All prepared ACs have mainly micropores fraction resulted from diluted KOH solution used in the impregnation step, so that low surface area and pore volume were obtained. Therefore, KOH activation under high temperature has influenced on the production of ACs with more microscopic structure.

Table 1. Proximate and ultimate analyses (Note: *calculated by difference).

Samples	Proximate (wt.%)				Ultimate (wt.%)			
	Moisture	Volatile matter	Ash	Fixed carbon	C	H	O	N*
Rubber seed shell	10.54	67.83	0.58	21.05	44.27	5.30	38.69	11.74
AC700	4.26	12.45	1.15	82.14	57.99	5.04	30.90	6.07
AC800	2.94	8.65	1.18	87.23	59.50	5.07	30.64	4.79
AC900	2.18	6.98	1.17	89.67	60.30	5.10	30.58	4.03

Table 2. The pore structure parameters of activated carbon produced from rubber seed shell.

Sample	ACs Yield (%wt.)	BET area (m ² /g)	Total Pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Micropores (vol.%)	Average pore diameter (nm)	Iodine number (mg/g)
AC700	27.52	429	0.201	0.162	80.597	2.165	498.01
AC800	22.89	528	0.221	0.199	90.045	1.180	582.35
AC900	20.32	620	0.284	0.265	93.310	0.950	639.73

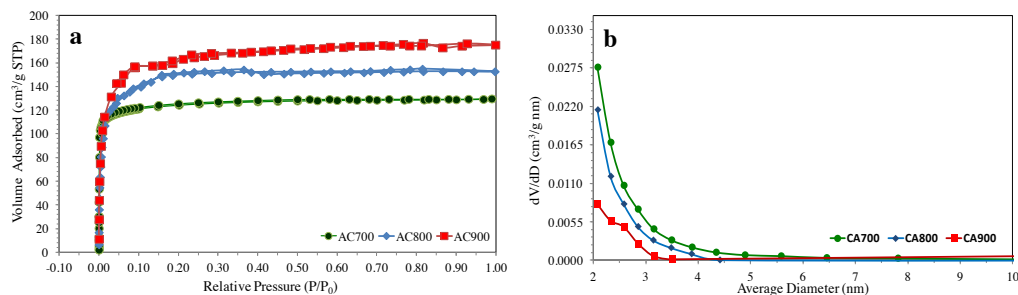
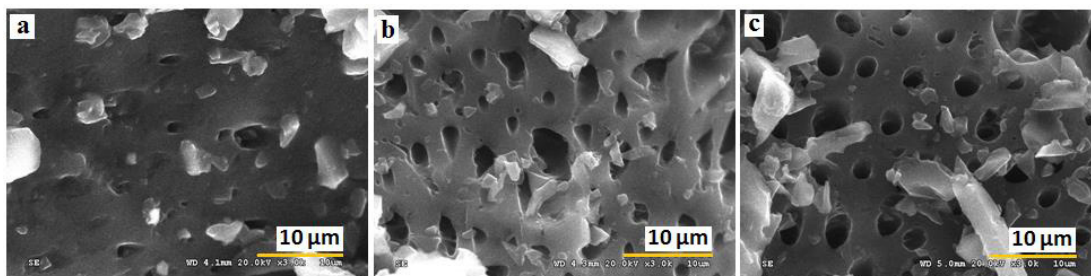
Fig. 1. (a) N₂ adsorption/desorption isotherms of activated carbons prepared from rubber seed shells under different temperatures of carbonization, and (b) pore size distribution of the activated carbon produced from rubber seed shell.

Fig. 2. SEM micrographs in different magnification of AC700 (a), AC800 (b) and AC900 (c).

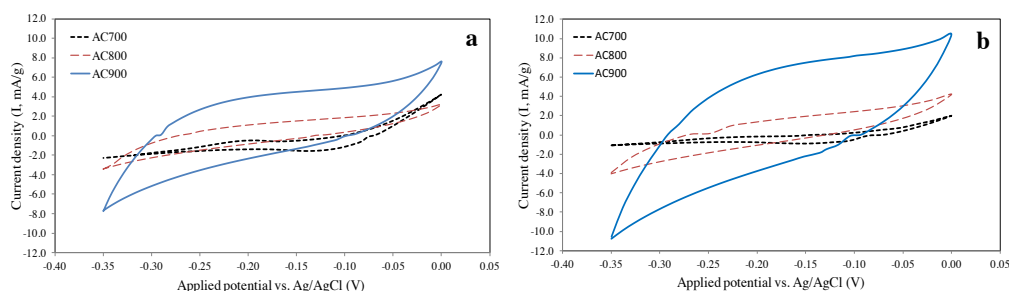


Fig. 3. Cyclic voltammograms of prepared activated carbon sheet electrodes recorded in 30%wt. KOH solution at the scan rates of (a) 10 mV/s and (b) 20 mV/s.

As shown in Fig. 3, the CV of AC700 exhibits clearly deformed asymmetric rectangular shape, which could be described to its small surface area, big average pore size with low microporosity structure (Table 2). Therefore, less ionic diffusion from bulk electrolyte can access to inner micropore surface when current changes its direction. The CVs plot of AC800 and AC900 are observed as the nearly symmetric

rectangular in the potential range of investigation indicating of acceptable capacitive behavior. These shape characteristics caused by the slower reorganization of the double layer as the slower ionic motions in the micropores. It has been reported that the pores in the range of 0.5-3.5 nm provided mainly specific surface area in forming double layer capacitance [1]. Therefore, AC900 shows the better EDLC performance whether the scan rate of 10 or 20 mV/s was applied (Fig. 3). Under various scan rates of measurements (Fig. 4), as the scan rate decreased the CV profile gradually became more rectangular indicating of the reversible charge-discharge responses of EDLC. Also, the voltammograms became distorted dramatically with the increase of scan rate, indicates that activated carbons are not suitable for quick charge-discharge operation. It can be discussed that the electrolyte ions had enough time to transport into micropores more easily at a low scan rate than at a high scan rate.

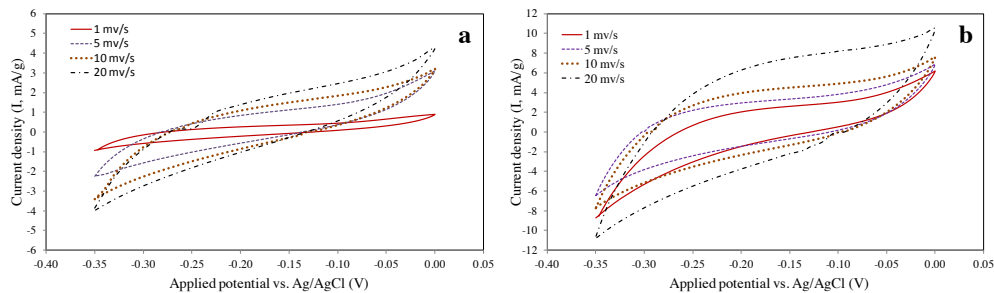


Fig. 4. Cyclic voltammograms at various scan rates of sheet electrodes in 30%wt. KOH solution of the activated carbon prepared at (a) 800°C and (b) 900°C.

Table 3. Specific capacitance versus voltage sweep rate for all activated carbons prepared in this study.

Samples	Specific capacitance (F/g)				
	1 mV/s	5 mV/s	10 mV/s	20 mV/s	50 mV/s
AC700	17.54	8.50	6.77	2.21	1.27
AC800	35.67	16.17	8.01	5.49	1.98
AC900	63.20	20.67	10.99	7.63	2.34

The specific capacitance values of the as-prepared ACs sheet electrode have been calculated from the respective CVs curves and presented (Table 3). Since the charge accumulation at the electrode/electrolyte surface has been not effected by whole pores, the specific capacitance of the resulted electrode was not directly depended to the surface area. This study showed ACs electrode sheet with higher micropore fraction gave the larger capacitance. It has been mentioned that ultramicropores (<0.5 nm) are too narrow for ion penetration, and mesopores (>2 nm) provide a limited capacitance contribution [10]. Herein, AC700, AC800 and AC900 have the pores with size between 0.9-1.2 nm which could produce optimum specific capacitance in aqueous electrolyte. As the pore structure of prepared ACs was the combination of scattered microporous surface and bottle-necked shape which contains of micropores inside the mesopore reservoir, the ions have enough time to diffuse into the micropore surface of activated carbon at low scan rate. AC900 has the higher specific capacitance due to its largest surface area and highest microscopic structure. Less electrochemically active surface area of pores being utilized at the higher scan rate resulted to the decrease of specific capacitance values for all three ACs investigated (Table 3). It gave the highest capacitance of 63.2 F/g at the scan rate of 1 mV/s. As the capacitance values depend on the type of biomass precursor, the surface area of its activated carbon, and the applied electrolyte. Even the AC-based EDLC electrode obtained in this work has the lower value of capacitance than the other reports [1-3, 11-14], it has proved that rubber seed shell is the potential precursor to be investigated.

4. Conclusions

Microporous activated carbons were prepared from rubber seed-shell by impregnation in 2 wt.% KOH solution, followed by carbonization. As the carbonizing temperature increases, the specific surface area, total pore volume, microporosity proportion and iodine number value of prepared ACs increased. The smaller average pore size came with the increase of micropore volume. The specific capacitance increases with surface area and microporosity scale, reaching a maximum of 63.2 F/g for a surface area and microporosity proportion of 620 m²/g and 93.31%, respectively. However, the next work will be concentrated on the surface area improvement of microporous activated carbon derived from rubber seed shell, in order to obtain the higher capacitance of EDLC electrode.

Acknowledgements

This work was financially supported by Center of Knowledge Development of Rubber Tree in Northeast group (KDRN), KhonKaen University (Thailand).

References

- [1] Li X, Han C, Chen X, Shi C. Preparation and performance of straw based activated carbon for supercapacitor in non-aqueous electrolytes. *Microporous and Mesoporous Materials* 2010; **131(1)**: 303-309.
- [2] Li X, Xing W, Zhuo S, Zhou J, Li F, Qiao SZ., Lu GQ. Preparation of capacitor's electrode from sunflower seed shell. *Bioresource technology* 2011; **102(2)**: 1118-1123.
- [3] Wang H, Zhong Y, Li Q, Yang J, Dai Q. Cationic starch as a precursor to prepare porous activated carbon for application in supercapacitor electrodes. *Journal of Physics and Chemistry of Solids* 2008; **69(10)**: 2420-2425.
- [4] Wei L, Yushin G. Electrical double layer capacitors with activated sucrose-derived carbon electrodes. *Carbon* 2011; **49(14)**: 4830-4838.
- [5] Wu FC, Tseng RL, Hu CC. Comparisons of pore properties and adsorption performance of KOH-activated and steam-activated carbons. *Microporous and Mesoporous Materials* 2005; **80(1)**: 95-106.
- [6] Borhan A, Kamil AF. Preparation and Characterization of Activated Carbon from Rubber-seed Shell by Chemical Activation. *Journal of Applied Sciences* 2012; **12(11)**: 1124-1129.
- [7] Sun K, Chun Jiang J. Preparation and characterization of activated carbon from rubber-seed shell by physical activation with steam. *biomass and bioenergy* 2010; **34(4)**: 539-544.
- [8] Mythili R, Venkatachalam P. Briquetting of Agro-residues. *Carbon* 2013; **42(41.80)**: 42-08.
- [9] He XJ, Ting W, Qiu JS, Zhang XY, Wang XT, Zheng MD. (2011). Effect of microwave-treatment time on the properties of activated carbons for electrochemical capacitors. *New Carbon Materials* 2011; **26(4)**: 313-319.
- [10] Ma C, Song Y, Shi J, Zhang D, Zhai X, Zhong M, Liu L. Preparation and one-step activation of microporous carbon nanofibers for use as supercapacitor electrodes. *Carbon* 2013; **51**: 290-300.
- [11] Zhou PW, Li BH, Kand FY, Zeng YQ. The development of supercapacitors from coconut-shell activated carbon. *New Carbon Materials* 2006; **21(2)**: 125-131.
- [12] Kim YJ, Lee BJ, Suezaki H, Chino T, Abe Y, Yanagiura T, Endo M. Preparation and characterization of bamboo-based activated carbons as electrode materials for electric double layer capacitors. *Carbon* 2006; **44(8)**: 1592-1595.
- [13] Balathanigaimani MS, Shim WG, Lee MJ, Kim C, Lee JW, Moon H.. Highly porous electrodes from novel corn grains-based activated carbons for electrical double layer capacitors. *Electrochemistry Communications* 2008; **10(6)**: 868-871.
- [14] Peng C, Yan XB, Wang RT, Lang JW, Ou YJ, Xue QJ. Promising activated carbons derived from waste tea-leaves and their application in high performance supercapacitors electrodes. *Electrochimica Acta* 2013; **87**: 401-408.