



BITE6453 by Suryadi Ismadji

From paper 2 (Hippo-hippo 02)

Processed on 2018年02月17日 19:11

WIB

ID: 917378184

Word Count: 5782

Similarity Index 16%	Similarity by Source Internet Sources: 7% Publications: 14% Student Papers: 7%
------------------------------------	--

sources:

1

2% match (student papers from 07-May-2014)

[Submitted to Monash University Sunway Campus Malaysia Sdn Bhd on 2014-05-07](#)

2

1% match (publications)

[Ma, Guofu, Haiping Wang, Kanjun Sun, Hui Peng, Yajuan Wu, and Ziqiang Lei. "A multi-level structure bio-carbon composite with polyaniline for high performance supercapacitors", RSC Advances, 2015.](#)

3

1% match (publications)

[Wu, F.C.. "Effects of pore structure and electrolyte on the capacitive characteristics of steam- and KOH-activated carbons for supercapacitors", Journal of Power Sources, 20050601](#)

4

1% match (publications)

[Palanichamy Kalyani .. "ON THE \(PSEUDO\) CAPACITIVE PERFORMANCE OF JACK FRUIT SEED CARBON", International Journal of Research in Engineering and Technology, 2014](#)

5

1% match (Internet from 04-Aug-2011)

http://www.q1.fcen.uba.ar/pdf/materias_qs_clases-2010-supercriticos.pdf

6

1% match (publications)

[Qian, Q.. "Textural and surface chemical characteristics of activated carbons prepared from cattle manure compost", Waste Management, 2008](#)

7

1% match (publications)

[Sulaiman, K. S., A. Mat, and A. K. Arof. "Activated carbon from coconut leaves for electrical double-layer capacitor", Ionics, 2015.](#)

8

1% match (publications)

[Ong, L.K., A. Kurniawan, A.C. Suwandi, C.X. Lin, X.S. Zhao, and S. Ismadji. "A facile and green preparation of durian shell-derived carbon electrodes for electrochemical double-layer capacitors", Progress in Natural Science Materials International, 2012.](#)

9

1% match (publications)

[J. C. Moreno-Piraján. "Study of Activated Carbons by Pyrolysis of Mangifera Indica Seed \(Mango\) in Presence of Sodium and Potassium Hydroxide", E-Journal of Chemistry, 2012](#)

10

1% match (Internet from 06-Jul-2014)

http://203.158.6.22:8080/sutir/bitstream/123456789/2542/2/Yuvarat_fulltext.pdf

11

1% match (publications)

[Guo, Zihan, Qingwen Zhou, Zhaojun Wu, Zhiguo Zhang, Wen Zhang, Yao Zhang, Lijun Li, Zhenzhu Cao, Hong Wang, and Yanfang Gao. "Nitrogen-doped carbon based on peptides of hair as electrode materials for supercapacitors", Electrochimica Acta, 2013.](#)

12

1% match (Internet from 03-Mar-2017)

<http://researchonline.jcu.edu.au/42312/1/42312-bainbridge-2015-thesis.pdf>

13

1% match (publications)

[Hisashi Tamai. "Mesoporous activated carbon as electrode for electric double layer capacitor", Journal of Materials Science, 07/2005](#)

14

1% match (publications)

[Yang, J.. "Carbon Electrode Material with High Densities of Energy and Power", Acta Physico-Chimica Sinica, 200801](#)

15

1% match (publications)

[Shaobo Ma, Bo Ren, Zhijun Diao, Yuwei Chen, Qinglian Qiao, Xuebo Liu. "Physicochemical properties and intestinal protective effect of ultra-micro ground insoluble dietary fibre from carrot pomace", Food & Function, 2016](#)

16

< 1% match (publications)

[Inal, I. Isil Gurten, Stuart M. Holmes, Anthony Banford, and Zeki Aktas. "The performance of supercapacitor electrodes developed from chemically activated carbon produced from waste tea", Applied Surface Science, 2015.](#)

17

< 1% match (student papers from 12-Nov-2016)

[Submitted to National Institute of Technology, Rourkela on 2016-11-12](#)

18

< 1% match (Internet from 17-Apr-2010)

http://doc.rero.ch/lm.php?url=1000,43,4,20080415091448-XC/Centeno_T.A._-_The_role_of_textural_characteristics_20080415.pdf

19

< 1% match (publications)

[Liliana Giraldo. "Synthesis of Activated Carbon Mesoporous from Coffee Waste and Its Application in Adsorption Zinc and Mercury Ions from Aqueous Solution", E-Journal of Chemistry, 2012](#)

< 1% match (publications)

20

[Zhong, Cheng, Yida Deng, Wenbin Hu, Daoming Sun, Xiaopeng Han, Jinli Qiao, and Jiujun Zhang. "Electrolytes for Electrochemical Supercapacitors", Electrochemical Energy Storage and Conversion, 2016.](#)

21

< 1% match (Internet from 01-Jun-2016)

<http://lup.lub.lu.se/luur/download?func=downloadFile&recordId=3990680&fileId=3990689>

22

< 1% match (Internet from 10-Jan-2014)

<http://ir.imr.ac.cn/bitstream/321006/30489/1/257.pdf>

paper text:

1 This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues. Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited. In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit: <http://www.elsevier.com/copyright> Bioresource Technology

101 (2010) 3534–3540

22 Contents lists available at ScienceDirect Bioresource Technology journal homepage: www.elsevier.com/locate/biortech Preparation of capacitor's electrode from

cassava peel waste Andrian Evan Ismanto, Steven Wang, Felycia Edi Soetaredjo,

5 Suryadi Ismadji * Department of Chemical Engineering, Widya Mandala Surabaya Catholic University Kalijudan 37, Surabaya 60114, Indonesia article info Article history: Received 10 October 2009 Received in revised form 12 December 2009 Accepted 16 December 2009 Available online 25 January 2010 Keywords:

Activated carbon Electric Double Layer Capacitor Cassava peel Surface modification Electrode material abstract Cassava peel was used as the precursor for activated carbon-based electrodes which were then prepared by a combination of

10 chemical and physical activation. The surface of the activated carbon

was treated with the oxidative chemical agents, 98 wt.% H₂SO₄, 65 wt.% HNO₃, and 30 wt.% H₂O₂ solutions. The surface modification had no significant effect on the specific surface area, but greatly influenced the surface chemistry of the carbons. The presence of oxygen-containing groups increased the polarity and hydrophilicity of activated carbon, and thus improved the performance of the activated carbon-based electrode. As a result, the specific capacitance of the HNO₃ modified AC-electrode reached 264.08 F/g, an increase of 72.6% compared to the original one. The results indicate that cassava peel waste can potentially be applied as a raw material

11 for the production of low cost -high performance activated carbon electrode materials for

Electric Double Layer Capacitors (EDLCs). Ó 2010 Elsevier Ltd. All rights reserved. 1. Introduction Electric Double Layer Capacitors (EDLCs), also known as supercapacitors, are a new breakthrough in energy storage device technology that have attracted considerable attention because of their high capacitance, power delivery performance and long life cycle (Tamai et al., 2005; Yansu et al., 2008). With all of these advantages, EDLCs have been widely used in the information technology industry, for electronic devices, electric vehicles, and military equipment where high power energy storage device with an ever-decreasing size is needed (Yafei et al., 2008). One of the most important components of a supercapacitor is the electrode. For EDLC electrodes, the most common used materials are metal oxides, polymers, and porous materials such as activated carbons and carbon aerogels. Furthermore, new carbon materials such as carbon nanotubes have been developed as electrode material, but complicated preparation and high cost led to difficulties in their practical application (Yafei et al., 2008). Activated carbon is a suitable material for the production of electrode

2 for supercapacitors, because of its high surface area, good thermal and electric conductivity, good

anti-causticity, high stability, low cost, and commercially available (Yafei et al., 2008). The application of activated carbons and other carbonaceous materials as the electrode of EDLCs has been studied by various research groups (Centeno and Stoeckli, 2006; Chmiola et al., 2006; Feng-Chin et al., 2006; Frackowiak and Beguin, 2001; Kim et al., 2006; Morishita *

5 Corresponding author. Tel.: +62 31 3891264; fax: +62 31 3891267. E-mail address: suryadiismadji@yahoo.com (S. Ismadji).

210960-8524/\$ - see front matter Ó 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2009.12. 123 et al.,

2006; Tamai et al., 2005; Tashima et al., 2007; Xu et al., 2008; Yafei et al., 2008; Yansu et al., 2008). Theoretically, the higher the surface area, the larger the capacitance; however, several studies reported that the specific capacitance was not proportional

6to the surface area of activated carbon,

because both

20pore structure and surface chemistry have influence on the capacitive behavior of

carbon materials (Qu and Shi, 1998; Yafei et al., 2008). Surface modifications to introduce and even increase the functional groups on the activated carbon surface have a significant influence on the performance of carbon electrodes (Tashima et al., 2007; Yafei et al., 2008; Yoshida et al., 1990). Yafei et al. (2008) reported that the specific capacitance of the carbon modified with 65% HNO₃ reached 250 F/g, 72.4% higher than that of the original carbon (Yafei et al., 2008). Cassava is known as one of the most important agricultural commodities in Indonesia (Sudaryanto et al., 2006). Cassava is used as raw material for the production of cassava starches and traditional foods and cakes. Its leaves can be utilized as vegetables or natural medicine since it contains high amounts protein and other bioactive compounds, and its wood is often used as firewood for cooking. Cassava starch processing

9produces a large amount of solid wastes (cassava peels), and direct discharge of these solid wastes causes environmental problems.

Utilization of cassava peels as precursor for

10activated carbon with a high surface area has already been

demonstrated (Sudaryanto et al., 2006). In this study, cassava peel was used as the raw material for the preparation of a capacitor's electrode. The cassava peel activated carbons were modified by surface treatment with HNO₃, H₂SO₄, and H₂O₂, to improve their surface chemistry. The

14influence of the surface modifications on the capacitance of

AC-electrode-based A.E. Ismanto et al. / Bioresource Technology 101 (2010) 3534–3540 3535 EDLCs was observed, and the relationships between the surface chemistry of modified ACs and capacitance of the corresponding AC-electrode-based supercapacitors was studied in order to obtain the highest capacitance.

2. Experimental 2.1. Materials Cassava peel was obtained from cassava starch industry located near Surabaya. Cassava peel is suitable as the precursor for activated carbon preparation because of its high carbon content (28.90%) (Sudaryanto et al., 2006). The cassava peel

It was repeatedly washed with distilled water to remove dust and other impurities, and then dried in oven for 24 h at 110 °C to reduce the moisture content.

Subsequently, dried cassava peel was crushed using a JAN- KE & KUNKEL micro hammer mill to obtain cassava peel powder with particle size of 80/100 mesh.

2.2. Activated carbon preparation The preparation of activated carbon was carried out using chemical followed by physical activation. Chemical activation

was performed by mixing the dried cassava peel with KOH solution at an impregnation ratio of 5:2 (mass KOH: mass cassava peel) and stirring at 323.15 K for 3 h. The resulting slurry was dried in an oven for at least 24 h at 383.15 K. The dried sample was placed in a pyrolysis reactor and heated at a carbonization temperature of

1023.15 K for 3 h. The carbonization and chemical activation was conducted under inert condition under nitrogen (flowrate of 3 dm³/min). The carbonization product was placed in a tubular furnace and heated to 1023.15 K. The physical activation was conducted for 1 h under CO₂ atmosphere (flowrate maintained at 2 dm³/min). The activated carbon products were washed sequentially with 0.5 N HCl to neutralize excess alkaline compounds. The samples were washed repeatedly with hot distilled water

until the pH of the washing solution reach 6.5 and then washed with cold distilled water twice or thrice. The

resulting activated carbon products were dried at 383.15 K for 24 h and stored in desiccators.

2.3. Surface modification Surface modification of activated carbon was conducted with the oxidative chemical agents, 98 wt.% H₂SO₄, 65 wt.% HNO₃, and 30 wt.% H₂O₂ solutions. The activated carbons were mixed with these chemical agents with mass ratio 1:1 (mass of chemical agent: mass of activated carbon), and then shaken under constant rate (130 oscillations per minute) for 4 h at 338.15 K. The resulting slurry was washed by distilled water repeatedly until the pH of washing solution reach 6.5, and then dried in oven for 24 h at 383.15 K.

2.4. Physical characterization The physical characterization of activated carbons was conducted by using Nitrogen sorption method and Scanning Electron Microscopy (SEM). Nitrogen sorption (Sudaryanto et al., 2006) was carried out to determine the pore structure of the carbons, and scanning electron microscopy (SEM) analysis was conducted to observe the surface morphology of activated carbon samples. The nitrogen adsorption/desorption isotherms were measured at 77.15 K (boiling point of nitrogen gas at

atmospheric pressure) by a QuadraSorb SI. Prior to gas adsorption measurements, the carbon was degassed at 473.15 K in a vacuum condition

15for a period at least 24 h. Nitrogen adsorption isotherms were measured over a relative pressure (P/P_0) range from approximately 0.05 to 0.995. The BET surface

area, pore volume and pore size distribution of the activated carbon were determined by using Brunauer–Emmett–Teller and Dubinin–Astakhov (DA) analysis software, which are available within the instrument, respectively. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range of 0.06–0.3. The total pore volume was calculated at a relative pressure of approximately 0.99 and at this relative pressure, all pores were completely filled with nitrogen gas. The DFT pore size distribution of all activated carbon samples were obtained based on nitrogen adsorption isotherms by using Quadrachrome Quadrawin software package with medium regularization. SEM images were recorded by using JEOL JSM-6300F field emission SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during FESEM imaging. The sputter coater

8(Eiko IB-5 Sputter Coater) was operated

in an argon atmosphere using a current of 6 mA for 3 min.

8The coated samples were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 5 kV, 8 spot size, 4 aperture, and 15 mm working distance.

2.5. Surface chemistry characterization The surface chemistry characterization of activated carbon was performed with the Boehm titration method (Prahas et al., 2006) and Fourier Transform Infra Red (FTIR) spectroscopy. The Boehm titration method can be described as follows: 0.5 g of activated carbon were placed to a series of flask which contain 50 ml of 0.05 N sodium bicarbonate, sodium carbonate, sodium hydroxide, and hydrochloric acid. The flasks were sealed and shaken for 24 h. After 24 h, the solutions were filtered, and then 10 ml of each solution was pipetted to a flask and was titrated with 0.05 N sodium hydroxide or hydrochloric acid, depending on the original solution used. The amounts of acidic groups on the activated carbon

6were calculated under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 , carboxylic and lactonic; NaHCO_3 , only carboxylic group. The numbers of surface basic sites were calculated from the amount of HCl that reacted with the carbon. The

reaction between the reagents and the acidic oxygenated-

3functional groups on the surface is based on the

difference in acid/ base strength. The strength of acidic groups is as follow: carboxyl > lactone > phenol. A qualitative analysis of activated carbon was conducted by obtaining FTIR transmission spectra of carbon samples with the KBr technique (Prahas et al., 2006). The technique was conducted by placing the KBr powder grinded with an agate mortar in the sample cup and then the powder surface evened by using the attached sample pressing bar. The powder is then mounted to the instrument to make a background measurement. The activated carbon sample was diluted with the KBr powder with the ratio of 10% and grinded with the agate mortar until it becomes fine particles to mix the both kinds. The mixed powder was placed in the sample cup and the powder surface also evened using the sample pressing bar. The mixed powder was mounted to the instrument to make a sample measurement in the transmittance% T mode. The analysis was carried out by Shimadzu 8400S FTIR instrument in wavenumbers range of 4000–500 cm⁻¹.

2.6.

3Electrode preparation Activated carbon powders were mixed with distilled water, 20 wt.%

polyvinylidene difluoride (PVdF) as the binder, and N- methyl-2-pyrrolidone (NMP) as the solvent. The resulting slurry was molded into a tube shape and dried at 373.15 K for 24 h. The 3536 A.E. Ismanto et al. / Bioresource Technology 101 (2010) 3534–3540 dried tube shape-electrodes were insulated with a PTFE (polytetra- fluorene ethylene) sheet as the separator to prevent electric current bridging between electrodes in storage condition. 2.7. Capacitance measurement The electrochemical measurements were investigated by galvanostatic charge–discharge using a battery-test apparatus (1284 Potentiostat/Galvanostat), and the stability and reversibility of capacitor were tested by cyclic voltammetry (GAT 4000 polarographic/voltammetric). One type of electrochemical cell used is the 3-electrode cell. This cell consists of working electrode, reference electrode and counter electrode. In this research, Ag/AgCl electrode (Argenthal)

3was used as reference electrode **and a** piece of **platinum** gauze **with an exposed area equal to 4 cm² as the counter electrode. A Luggin capillary was used to minimize errors due** to the iR **drop in the electrolytes.**

0.5 M H₂SO₄ was used as electrolyte solution in the electrochemical cell and degassing was done

3with purified nitrogen gas for 25 min **before measurements**

(Feng-Chin et al., 2006). The gravimetric specific capacitance was calculated by using the following formula (Yafei et al., 2008): $C = \frac{I_d \cdot \Delta t}{m \cdot \Delta U}$ where I_d is discharge current (Ampere), Δt is discharge time (s), ΔU is difference of voltage in the time of Δt during discharge (Volt),

14m is Total mass of the two electrodes (gram) and w is mass fraction of activated carbon in the electrode.

Volume Adsorbed (cm³/gram) NT H₂SO₄ H₂O₂ HNO₃ 0.0 0.2 0.4 0.6 0.8 1.0 Relative Pressure (P/P₀) Fig. 1. Nitrogen adsorption isotherms of modified activated carbons derived from cassava peel. combination between micropore and mesopore, with dominant micropore (61.5%). This evidence also supported by the pore distribution of activated carbons obtained by using DFT method with medium regularization as shown in Fig. 2. In chemical activation using KOH as activated agent, at temperature higher than 673.15 K, the reaction between KOH and carbon occurs (Ganan et al., 2004; Sudaryanto et al., 2006) according to the following reaction: $3C + 6KOH \rightarrow 3H_2 + 2K_2CO_3$. 3. Results and discussion 3.1. Raw materials analysis 6KOH p C \$ 2K p 3H₂ p 2K₂CO₃ 0.2p The proximate analysis of cassava peel indicated that this raw material contains 28.7% of fixed carbon, 58.8% of volatile matter, 12.1% of moisture content, and 0.4% ash. The proximate analysis result shows that cassava peel has high carbon and low ash content, indicating that this precursor is a suitable raw material for the preparation of activated carbon. As the comparison, the fixed carbon content of several raw materials for activated carbon production is as follows: bamboo (16.60%) (Choy et al., 2005),

10coconut shell (18.60%) (Daud and Ali, 2004), palm shell

(18.70%) (Daud and Ali, 2004), durian shell (23.36%) (Chandra et al., 2006), and rubber wood sawdust (23.38%) (Srinivasakannan and Bakar, 2004). The

19presence of metallic potassium will intercalate to the carbon matrix, resulting in widening of the spaces between carbon atomic layers and increasing the total pore volume (Ahmadpour and

Do, 1997; Sudaryanto et al., 2006). At temperatures higher than 923.15 K,

17the surface metal complex is responsible for further gasification, leading to the widening of micropore to

mesopore (Ganan et al., 2004; Sudaryanto et al., 2006). The physical activation using CO₂ gas was performed in order to maximizing the pore opening in the activated carbon and transforming some of the KOH-activated carbon's micropore into mesoporous (20 Å < d < 500 Å) structure (Feng-Chin et al., 2006). Therefore, by combining chemical activation and physical activation, a 3.2. Physical characterization 0.04 3.2.1. The effect of activation on the pore characteristic Details of pore characteristic of activated carbon samples are given in Table 1. Fig. 1 shows the nitrogen adsorption isotherms at H₂SO₄ 77.15 K of the cassava peel carbon and its modified forms. From 0.03 H₂O₂ the result, it can be seen that the BET surface area of activated carbon derived from cassava peel was 1352 m²/g, higher than commercial activated carbons available in Indonesia (500–700 m²/g). This result indicates that the KOH–CO₂ activation greatly enhanced 0.02 the pore development during the carbonization–activation process. Table 1 shows

that the activated carbons pore structure is a Pore size distribution ($\text{cm}^3/(\text{g}\cdot\text{\AA})$) 0.01 Table 1 Pore characteristic of activated carbons before and after modification. Sample SBET (m^2/g) S_{mic} (m^2/g) V_{tot} (cm^3/g) V_{mic} (cm^3/g) $V_{\text{mic}}/V_{\text{tot}}$ (%) 0.00 0 100 200 300 400 500 600 NT 1352 876 0.579 0.356 61.5 H₂O₂ 1276 828 0.543 0.337 62.1 Pore size (\AA) HNO₃ 1186 772 0.501 0.312 62.3 H₂SO₄ 1336 866 0.569 0.352 61.7 Fig. 2. Pore size distribution of modified activated carbons derived from cassava peel. A.E. Ismanto et al. / Bioresource Technology 101 (2010) 3534–3540 3537 combination between micropore–mesopore structures of activated carbon with certain percentage of micropore was obtained, which is desired for the electrode application. For electrode application, it is desirable to obtain activated carbon with a combination of micropore and mesopore, because it has different role at different level of

13 **current density. At low current density (<100 mA/cm²),**

micropores are dominant and enhance greater capacitance than mesopores. However, micropores are less stable than mesopores, the capacitance of micropores decreasing with the increase of

13 **discharge current density. At high discharge current**

(100–200 mA/cm²),

13 **rapid movement of electrolyte ions is capable only in mesopores, so** mesopores could **exhibit high**

capacitance (Tamai et al., 2005). 3.2.2. The effect of surface modification on the pore characteristic The effect of the surface modification on the surface area and pore development can be seen in Fig. 2 and Table 1. The surface modifications gave no

17 **significant effect, neither on the surface area and pore development of the** activated carbons. **The**

surface area of modified activated carbons changed only slightly after surface modifications were introduced. A decrease in surface area and pore volume due to the molecules or ions of modifying agents occupied some pores of activated carbon and produced some surface functional groups which reduced pore size or even partially blocked some pores (Yafei et al., 2008). Fig. 3 depicts the surface morphology of activated carbons before and after modification. It can be seen that similar surface morphology was observed for all activated carbons studied. 3.3. Surface chemistry characterization Oxygen-containing groups such as carbonyl, hydroxyl, carboxyl, and quinone are some of the functional groups which give positive

20 **effects on the performance of activated carbon-based**

electrodes (Centeno and Stoeckli, 2006; Wenzhong et al., 2007; Yafei et al., 2008). Table 2 shows the amount of acid and basic sites on activated carbons before and after modification. It was found

10that the amounts of acidic functional groups were increased significantly after

modification. The amount of carboxyl group before modification was 0.1925 meq/g whereas, after modification with HNO3 and H2SO4, the amount of this functional group was 0.5554 and 0.5104 meq/g, an increase by 188.5% and 165.1%, respectively. The number of other acidic functional groups, lactone and phenols, also increased. The FTIR analysis was performed to determine the other functional groups, especially the oxygen-containing groups. FTIR spectra revealed the specific surface functional groups on activated carbons surface qualitatively based on the characteristic of absorbed energy for each bonds in certain groups (Putra et al., 2009). The FTIR spectra of activated carbons before and after modification are shown in Fig. 4. Fig. 4 reveals the increase of symmetrical and asymmetrical stretching vibration at wavelength ranges of 1000–1300, 1550–1800, 2300–2450, and 3100–3700 cm⁻¹, for all modified activated carbon samples. Based on Table 3 for FTIR assignments of functional groups on carbon surfaces, these bands were assigned to C–O, C=O and –OH stretching vibration, respectively. The increase of these bands shows the increase of carbonyl, hydroxyl, carboxyl, quinone, and lactone groups on the surface of modified activated carbons, indicating that the surface modification with acidic and oxidative chemical agents developed the surface oxygen-containing groups on the activated carbons.

3.4. Capacitance measurement The performance of the electrodes from modified activated carbons was investigated by using galvanostatic charge–discharge Fig. 3. Surface morphology of modified activated carbons from cassava peel. 3538 A.E. Ismanto et al. / Bioresource Technology 101 (2010) 3534–3540 Table 2 Surface functional groups determined by Boehm titration. Sample Functional groups on activated carbon (meq/g activated carbon) Acid group Basic group Carboxylic Lactonic Phenolic Total Non treatment HNO3 H2SO4 H2O2 0.1925 0.5618 0.5554 1.0805 0.5104 1.0364 0.3426 0.9769 0.4106 1.1649 0.6481 2.2840 0.6628 2.2096 0.5893 1.9088 0.5047 0.5156 0.4876 0.4974 50 100 95 45 90 85 80 %T 40 %T 75 70 35 65 60 55 30 0 0 0 8 0 0 0 2 0 0 0 0 0 0 0 0 0 0 0 3 4 0 3 3 2 8 0 2 6 0 2 4 0 2 2 2 0 0 0 0 0 0 0 0 0 50 4 3 3 6 0 1 8 0 1 6 0 1 4 0 1 2 0 1 0 0 4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 1 /cm 1/cm Non treatment HNO3 90 60 85 80 55 75 70 %T 65 %T 50 60 55 45 50 45 40 40 4 0 0 0 0 3 8 0 6 0 0 3 4 0 0 3 2 0 0 3 0 0 0 4 0 0 0 0 0 6 0 0 0 0 0 3 2 8 0 0 2 6 0 0 0 2 2 2 2 0 0 1 8 0 1 1 4 0 0 0 1 2 0 1 0 0 4 0 0 0 3 8 0 3 6 0 0 3 4 0 0 3 2 0 0 3 0 0 2 8 0 0 2 6 0 0 2 4 0 0 2 2 0 0 2 0 0 0 1 8 0 0 1 6 0 0 1 4 0 0 1 2 0 0 1 0 0 0 1/cm 1/cm H2O2 H2SO4 Fig. 4. The FTIR spectra of activated carbon before and after modification. Table 3 FTIR assignments of functional groups on carbon surfaces. Functional group Wavelength (cm⁻¹) 3700–2050 2050–1500 1500–1000 Hydroxyl Quinine Carbonyl Carboxyl Lactone 3650–3200 – – 3300–2500 – – 1680–1550 1780–1650 1760–1665 1790–1675 – – – 1200–1120 1370–1160 and cyclic voltammetry. The

16principle of this method is to investigate the time of current charge and discharge process performed by the measured electrode.

Fig. 5 shows the galvanostatic charge–discharge cycles of all activated carbon electrodes from 0 to 1 V in the acidic electrolyte (0.5 M H2SO4 solution). The result of each galvanostatic measurement was similar. All

curves extended

7the isosceles triangle shape with the discharge time close to that of charge, reflecting high charge–discharge efficiency for all AC -electrodes. The difference of charge and discharge time was the factor that influenced the symmetry of the isosceles triangle. The less the difference was, the more symmetric the

isosceles tri- angle-shape and the

4more symmetric the triangle- shape, the high- er the charge–discharge efficiency

(Yafei et al., 2008). The high charge–discharge efficiency of capacitors indicated that carbon electrodes

4contacted well with electrolyte solution, or in other words the electrodes had a high hydrophilicity of their surface. Although the

triangle shapes were similar, the details were different. The difference of each shape indicates the time needed for current charge and discharge during the measurement processes. The charge and discharge time of all modified AC-electrodes was longer than the unmodified AC-electrode, indicate that the modified AC- electrodes could

16be charged with more electrons or electrolyte ions than the

unmodified one. A.E. Ismanto et al. / Bioresource Technology 101 (2010) 3534–3540 3539 1200 1200 1000 1000 Potential (mV) 800 600 Potential (mV) 400 800 600 400 200 200 0 0 0 20 40 60 80 100 120 0 20 40 60 80 100 120 140 160 180 200 t (minute) t (minute) Non treatment HNO3 1200 1200 Potential (mV) 1000 800 600 400 1000 Potential (mV) 800 600 400 200 200 0 0 0 20 40 60 80 100 120 140 160 180 0 20 40 60 80 100 120 140 160 180 t (minute) t (minute) H2O2 H2SO4

8Fig. 5. Cyclic charge–discharge curves of activated carbon electrodes.

The specific capacitances of AC-electrodes as a function of discharge current were calculated according to Eq. (1) and the results are summarized in Table 4. From Table 4, it could be

20found that the specific capacitance of the modified AC-electrodes increased

significantly compared with the unmodified one. The specific capacitance of unmodified AC-electrode was only 153 F/g, whereas the AC-electrodes modified by HNO₃ and H₂O₂ are 264.08 and 240.67 F/g, increased by 72.6% and 57.3%, respectively. It can be seen that the highest capacitance was reached by the HNO₃-modified AC-electrode (264.08 F/g), followed by the H₂O₂ (240.67 F/g) and H₂SO₄ (210.98 F/g) electrodes, respectively. This phenomenon showed that the modification with HNO₃ increased the amount of oxygen-containing groups more than the other chemical agents. Table 4 The specific capacitances of AC-electrodes.

Sample	Dt (min)	Specific capacitance (F/g)
Non treatment	12.40	153.00
HNO ₃	21.40	264.08
H ₂ O ₂	18.18	240.67
H ₂ SO ₄	18.93	210.98

This evidence is supported by the surface chemistry analysis (Section 3.3). This result was compared with the performance of activated carbon-based electrode made from the other raw materials. Kim et al. (2006) prepared electrodes from bamboo-based activated carbon for an electrochemical supercapacitor. The specific surface area of bamboo-based activated carbon without any modification was 1025 m²/g and its specific capacitance reached 60 F/g (Kim et al., 2006). Meanwhile, the specific capacitance of cassava peel-based activated carbon was higher by about 150%, it reached 153 F/g

3with a specific surface area of 1352 m²/g

for the unmodified one. This comparison showed that the activated carbon derived from cassava peel has a higher specific surface area and better surface functional groups than the bamboo-based activated carbon. Although the specific surface area of the modified was lower than that of unmodified activated carbon, a higher specific capacitance was achieved by electrodes made from modified activated carbons. This phenomenon showed that surface area was not the only factor that influenced specific capacitance, surface chemistry of activated carbon also played an important role in the performance of the activated carbon electrode. The reactivity of the oxygen-containing groups is primarily due to the difference in electronegativity between oxygen and carbon 3540 A.E. Ismanto et al. / Bioresource Technology 101 (2010) 3534–3540 Fig. 6. Cyclic voltammogram of activated carbon electrodes at 20 mV/s. or hydrogen atoms. Oxygen has the greater affinity for electrons that makes oxygen more electronegative than carbon atom (in carbonyl and quinine group) or hydrogen (in hydroxyl group). It acquires a partial negative charge, becoming electron-rich; meanwhile the other atoms become electron-deficient, acquiring a partial positive charge. The difference in electronegativity in the oxygen-containing groups increased their bond's polarity. Therefore, the presence of the oxygen-containing groups on the surface of activated carbon enhanced the polarity of activated carbon and makes it more hydrophilic. Water, one of the polar compounds,

18has a low affinity for pure carbon, but it interacts strongly with oxygen containing surface groups.

The

18strong affinity of water for the oxygen containing surface groups

4plays an important role for the performance of aqueous electrolyte capacitor,

such as Electric Double Layer Capacitor (EDLC) (Centeno and Stoeckli, 2006). Cyclic voltammetry was used to study the stability and reversibility of Electric Double Layer Capacitor. The cyclic voltammograms of the activated carbon electrodes at 20 mV/s potential sweep rate are shown in Fig. 6. The experimental data showed that all of the electrodes were stable in the H₂SO₄ solution. Fig. 6 indicates that all curves have similar and symmetric rectangular shape between positive and negative sweep rate, indicating the good reversibility characteristic and high stability of EDLC during charge and discharge process of carbon electrode materials. The reversible reduction and oxidation

4 reactions of functional groups introduced on the carbon surface might occur to generate pseudocapacitance during charge–discharge, so that the total capacitance

of capacitor was increased (Yafei et al., 2008). The cyclic voltammogram of modified AC-based electrodes which had a broader area compared with the original AC-electrode, indicates that the capacitance of modified activated carbons is higher than the original one. This evidence supports the result of galvanostatic charge–discharge experiment. The HNO₃ modified electrode had the broadest area, showing that this electrode had the highest capacitance, good reversibility and high stability. 4. Conclusion A high performance capacitor's electrode was prepared from the modified activated carbon derived from cassava peel. The activated carbon was prepared from cassava peel with KOH–CO₂ activation and modified by surface treatment, using nitric acid, sulfuric acid and hydrogen peroxide. It was found that the preparation of capacitor's electrode from cassava peel-based activated carbon with surface modification by acidic and oxidative chemical agents

11 is an effective process for the production of high performance and low cost activated carbon electrode materials for the

Electric Double Layer Capacitor (EDLC). The surface modification gave significant effect on the performance of EDLC. References Ahmadpour, A., Do, D.D., 1997. The preparation of activated carbon from macadamia nutshell by chemical activation. *Carbon* 35, 1723–1732. Centeno, T.A., Stoeckli, F., 2006. The role of textural characteristics and oxygen-containing surface groups in the supercapacitor performances of activated carbons. *Electrochimica Acta* 52, 560–566. Chandra, T.C., Mirna, M.M., Sudaryanto, Y., Ismadji, S., 2006. Adsorption of basic dye onto activated carbon prepared from durian shell: studies of adsorption equilibrium and kinetics. *Chemical Engineering Journal* 127, 121–129. Chmiola, J., Yushin, G., Dash, R., Gogotsi, Y., 2006. Effect of pore size and surface area of carbide derived carbons on specific capacitance. *Journal of Power Sources* 158, 765–772. Choy, K.K.H., Barford, J.P., McKay, G., 2005. Production of activated carbon from bamboo scaffolding waste-process design, evaluation and sensitivity analysis. *Chemical Engineering Journal* 109, 147–165. Daud, W.M.A.W., Ali, W.S.W., 2004. Comparison on pore development of activated carbon produced from palm shell and coconut shell. *Bioresource Technology* 93, 63–69. Feng-Chin, W., Ru-Ling, T., Chi-Chang, H., Chen-Ching, W., 2006. The capacitive characteristics of activated carbons-comparisons of the activation methods on the pore structure and effects of the pore structure and electrolyte on the capacitive performance. *Journal of Power Sources* 159, 1532–1542. Frackowiak, E., Beguin, F., 2001. Carbon materials for the electrochemical storage of energy in capacitor. *Carbon* 39, 937–950. Ganan, J., Gonzalez-Garcia, C.M., Gonzalez, J.F., Sabio, E., Macias-Garcia, A., Diaz-Diez, M.A., 2004. Preparation

of activated carbon from bituminous coal pitches. *Applied Surface Science* 238, 347–354. Kim, C., Lee, J.-W., Kim, J.-H., Yang, K.-S., 2006. Feasibility of bamboo-based activated carbons for an electrochemical supercapacitor electrode. *Korean Journal of Chemical Engineering* 24, 592–594. Morishita, T., Soneda, Y., Tsumura, T., Inagaki, M., 2006. Preparation of porous carbons from thermoplastic precursors and their performance for electric double layer capacitors. *Carbon* 44, 2360–2367. Prahas, D., Kartika, Y., Indraswati, N., Ismadji, S., 2006. Activated carbon from jackfruit peel waste: preparation, characterization, and its application on methylene blue adsorption. *Journal of Environmental Protection Science* 2, 1–10. Putra, E.K., Pranowo, R., Sunarso, J., Indraswati, N., Ismadji, S., 2009. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: mechanisms, isotherms and kinetics. *Water Research* 43, 2419–2430. Qu, D., Shi, H., 1998. Studies of activated carbons used in double-layer capacitors. *Journal of Power Sources* 74, 99–107. Srinivasakannan, C., Bakar, M.Z.A., 2004. Production of activated carbon from rubber wood sawdust. *Biomass and Bioenergy* 27, 89–96. Sudaryanto, Y., Hartono, S.B., Irawaty, W., Hindarso, H., Ismadji, S., 2006. High surface area activated carbon prepared from cassava peel by chemical activation. *Bioresource Technology* 97, 734–739. Tamai, H., Kunihiro, M., Morita, M., Yasuda, H., 2005. Mesoporous activated carbon as electrode for electric double layer capacitor. *Journal of Materials Science* 40, 3703–3707. Tashima, D., Kurosawatsu, K., Sung, Y.-M., Otsubo, M., Honda, C., 2007. Surface modification of nanoporous materials for electric double layer capacitors application. *Material Chemistry and Physics* 103, 158–161. Wenzhong, S., Zhijie, L., Yihong, L., 2007. Surface chemical functional groups modification of porous carbon. *Recent Patent in Chemical Engineering* 1, 27–40. Xu, B., Wu, F., Chen, R., Chao, G., Chen, S., Zhou, Z., Yang, Y., 2008. Highly mesoporous and high surface area carbon: a high capacitance electrode material for EDLCs with various electrolytes. *Electrochemistry Communications* 10, 795–797. Yafei, L., Zhonghua, H., Kun, X., Xiangwei, Z., Qiang, G., 2008. Surface modification and performance of activated carbon electrode material. *Acta Physico-Chimica Sinica* 24, 1143–1148. Yansu, W., Chengyang, W., Chunyu, G., Zhiqiang, S., 2008. Influence of carbon structure on performance of electrode material for electric double layer capacitor. *Journal of Physics and Chemistry of Solid* 69, 16–22. Yoshida, A., Tanahashi, L., Nishino, A., 1990. Effect of concentration of surface acidic functional groups on electric double-layer properties of activated carbon fibers. *Carbon* 28, 611–615.

12 **Author's personal copy Author's personal copy Author's personal copy**
Author's personal copy Author's personal copy Author's personal copy
Author's personal copy