Turnitin Originality Report

Journal of the Taiwan Institute of Chemical
Engineers 47 (2015) 197–201 by Suryadi
Ismadji

From paper 2 (Hippo-hippo 02)

Similarity Index	Similarity by Source	
12%	Internet Sources:	7%
	Publications:	10%
	Student Papers:	7%

Processed on 16-Feb-2018 14:34 WIB
ID: 916899603
Word Count: 3338

sources:

1 2% match (Internet from 03-Jul-2017)
http://hadinur.com/paper/hadi_jtice2014.pdf

2 1% match (Internet from 22-Jun-2017)
http://ifrj.upm.edu.my/23%20%2805%29%202016/%2841%29.pdf

3 1% match (publications)
Hakan Demiral. "Surface properties of activated carbon prepared from wastes", Surface and
Interface Analysis, 03/2008

4 1% match (publications)
"Announcement", Journal of the Taiwan Institute of Chemical Engineers, 2015.

5 1% match (Internet from 21-Dec-2017)

http://repository.its.ac.id/44003/1/A%20new%20approach%20in%20maximizing%20and%20direct%20utilization%20of%20whole%20jatropha

6 1% match (publications)
Haoqing Hou, Andreas K. Schaper, Frank Weller, Andreas Greiner. "Carbon Nanotubes and
Spheres Produced by Modified Ferrocene Pyrolysis", Chemistry of Materials, 2002

7 1% match (publications)
Zhou, H.. "Preparation, structure and electrochemical performances of nanosized cathode
active material Ni(OH)"2", Solid State Ionics, 200507

8 1% match (Internet from 11-Oct-2010)
http://www.eng.wima.ac.id/kimia/staff/aning.pdf

9 1% match (publications)
SpringerBriefs in Molecular Science, 2015.

10 1% match (student papers from 26-Jun-2015)
Submitted to Higher Education Commission Pakistan on 2015-06-26

11 1% match (publications)
Rios, R.V.R.A.. "Liquid phase removal of propanethiol by activated carbon: Effect of porosity
and functionality", Colloids and Surfaces A: Physicochemical and Engineering Aspects,
20070601

12 1% match (publications)
Li, J.I.. "Electrochemical characterization of MnO"2 as the cathode material for a high voltage
hybrid capacitor", International Journal of Minerals, Metallurgy and Materials, 200910

13 1% match (student papers from 23-Feb-2015)
Submitted to Universidad Nacional de Colombia on 2015-02-23

paper text:

4**Journal of the Taiwan Institute of Chemical Engineers 47 (2015)** 197–201

Contents lists available at ScienceDirect Journal of the Taiwan Institute of

Chemical Engineers journal homepage: www.elsevier.com/locate/jtice

Short communication

6 **Carbon microsphere from water hyacinth for supercapacitor electrode Fredi Kurniawan** a,1, **Michael Wongso** a,1, **Aning Ayucitra** a,*, **Felycia Edi Soetaredjo** a, **Artik Elisa Angkawijaya** b, **Yi-Hsu Ju** b,*, **Suryadi Ismadji**

a,* a

Carbon microsphere Subcritical water hydrolysis Subcritical water carbonization Microwave activation ABSTRACT In this study, water hyacinth was hydrolyzed to sugars with dilute sulphuric acid (0.25 M) under subcritical water conditions (P = 20 bar, T = 130 8C) for 2 h. The sugar solution was then carbonized under subcritical conditions to produce carbon microsphere. The subcritical water carbonization was conducted at 40 bar and various temperatures (160–200 8C) and times (6–10 h). The highest yield of carbon microspheres was 0.1019 g/g dry water hyacinth at the temperature of 200 8C for 10 h. The carbon microsphere was activated using

9 **a combination of chemical** (KOH solution) **and physical**

(microwave) treatments

9 **to increase the specific surface area and** porosity **of**

carbon microsphere. Electrocapacitive study of carbon microspheres showed that the carbon microsphere activated at impregnation ratio of 1:1 and microwave power of 630 W has the highest specific capacitance and excellent electrochemical stability.

Activated carbon has been widely in used as the electrode for supercapacitors due to its high surface area, excellent mechanical as well as chemical properties, tunable pore structure, and the most beneficial for industrial application are low cost and ready availability [1]. Different studies on the use of different kinds of carbons as the electrode of supercapacitors have been conducted in order to explore the electrochemical performance of the materials [2–7]. Their results indicate that the pore

11 **structure and surface chemistry of the activated carbons**

plays a crucial role on the electrochemical and capacitance performance of the carbon electrode. The pore

11 **structure and surface chemistry of activated carbon** depend on **the** methods **of** preparation **and the**

type of precursors. In this study, we employed a low cost biomass water hyacinth as the precursor for the preparation of carbon microsphere. The conversion of cellulose and hemicellulose content in water hyacinth into sugars was conducted using subcritical water hydrolysis process in the presence of dilute acid as catalyst. The * Corresponding authors at:

8 **Widya Mandala Surabaya Catholic University,** Chemical Engineering, **Kalijudan 37, Surabaya 60114, East Java, Indonesia.** Tel.: **+62 31 389 1264; fax: +62 31**

5E-mail addresses: aayucitra @yahoo.com (A. Ayucitra),

yhju@mail.ntust.edu.tw (Y.-H. Ju),

suryadiismadji@yahoo.com, alfin_kur@yahoo.com (S. Ismadji). 1 These authors contributed equally to this work. advantages of using subcritical water process for hydrolysis are the absence of concentrate acid as a catalyst and high yield of sugars. The dehydration and carbonization the resulting sugars were also carried out in subcritical water condition. Subcritical water acts as the dehydrating agent to convert glucose into carbon in the carbonization process. The carbonization using subcritical water process is known as environmental friendly process compared to those other carbon manufacturing process like pyrolysis [8], template [9], reduction [10], and chemical vapor deposition [11]. The carbon obtained from carbonization using subcritical process was then activated using KOH solution and microwave irradiation process to increase the specific area and porosity of carbon. The resulting activated carbon then was used as the raw material for electrode of supercapacitor. The novelty of the current study is the use of subcritical water process to produce carbon microsphere from water hyacinth. To the best of our knowledge, there is no literature discuss the production of carbon microsphere from biomass using subcritical water for carbonization. 2. Materials and methods 2.1. Materials Water hyacinth as the raw material for this study was obtained from swamp area in Surabaya, East Java, Indonesia. Analytical- grade PTFE (polytetrafluoroethylene) latex (60 wt% dispersion in

197–201 H2O) and potassium hydroxide (KOH) were supplied by Sigma Aldrich, Singapore. Nickel foam substrate (99.9%, 30 cm in length 3 cm in width 80 mm in thickness) was purchased from MTI Corp. Vulcan XC-72 carbon black was purchased from Cabot Corp. 2.2. Raw material preparation The fresh water hyacinth was cleaned using tap water to remove the mud and other dirt, and subsequently sun dried until its moisture content around 10%. The dried water hyacinth then was pulverized using grinder. The water hyacinth powders were added to 15 wt% of KOH solution for 24 h to remove the lignin content. After delignification process has completed, the processed water hyacinth powders were separated from the solution using centrifugation and filtration. The water hyacinth powders

3were repeatedly washed with distilled water until the pH of the washing solution was in the range of 6–7, and subsequently in the

oven at 100 8C for 24 h. 2.3. Hydrolysis process Twenty five grams of water hyacinth powder was loaded into the subcritical water reactor, and then 250 mL of sulfuric acid solution (0.25 M) were

5added into the reactor. The reactor was sealed and

purge with nitrogen in order to remove the air from the system.

5Prior to heating, the reactor was pressurized using nitrogen

until the pressure reached 20 bar. In order to make the powder mixed well with sulfuric acid solution, the system was equipped with external magnetic stirrer. The reactor was heated until the temperature reached the operating temperature of hydrolysis process (130 8C). The hydrolysis process was carried out for 2 h. After the hydrolysis process had finished, the reactor was cooled to room temperature. The cooled reaction mixture was filtered to separate the spent solid from filtrate. The filtrate was analyzed for its sugars content. 2.4. Synthesis of carbon microsphere The filtrate from the hydrolysis process was subsequently carbonized under subcritical water condition at various tempera- tures (160, 180, and 200 8C) and times (6, 8, and 10 h). Prior to heating, the nitrogen gas was introduced to the reactor to remove the air from the system. Subsequently the reactor was pressurized using nitrogen gas until its pressure reached 40 bar. After the reaction had completed, the solid carbon was separated from the solution, and repeatedly washed using distilled water and dried in the oven at 100 8C for 24 h. 2.5. Activation of the carbon microsphere Combination of chemical and microwave assisted activation was employed to activate the carbon microsphere. The ratio between the KOH and carbon were 1:2, 1:1, and 3:2. The impregnation of carbon in KOH solution was conducted for 24 h under constant stirring. The microwave irradiation process was

conducted in home appliance microwave oven InexTron. The microwave power was set at 630 W, and the radiation time was 10 min. After the activation process, the resulting activated carbon was repeatedly washed to remove excess KOH using

3**distilled water until the pH of** the washing **solution** was in the **range of 6–7.**

2.6. Supercapacitor preparation The electrodes of the supercapacitor were made from 80% activated carbon, 10% PTFE, and 10% carbon black. The well mixed slurry was painted on a nickel foam strip, pressed at 150 MPa, and vacuum dried at 110 8C. The electrodes were separated by polypropylene membrane and 30 wt% KOH solution as the electrolyte fluid. 2.7. Characterization of carbon microsphere and activated carbon The characterization pore structure and surface morphology of carbon microsphere and activated carbons were conducted by SEM and nitrogen sorption methods. The SEM analysis were conducted on a JEOL JSM-6390 field emission scanning electron microscope equipped with a backscattered electron (BSE) detector

9**at an accelerating voltage of** 20 **kV** and working distance **of**

12 mm. The characterization using nitrogen sorptions were conducted at boiling point of nitrogen gas using an automated Micromeritics ASAP 2010 sorption analyzer. In the nitrogen sorption experi- ments, prior to analysis, the samples were vacuum-degassed at 573 K and 10 3 Torr for 3 days. 2.8. Electrochemical measurements The electrochemical performance of the electrodes was tested by using galvanostatic charge-discharge on a YHI 650 electrochem- ical workstation at room temperature. The measurements of cyclic voltammetry were carried out in a three-electrode cell. The electrochemical testing system consists of platinum sheet (1 cm2) as the counter electrode and Hg/HgO was employed as the reference electrode. The size of the electrode was 20 10 1 mm and contains of 120 mg of active material. The KOH solution with the concentration of 6 N

7**was used as the electrolyte** solution **in this** study. **3. Results and discussion 3.1. The** effect **of**

temperature and time of carbonization process to the yield of carbon microsphere The yield of carbons obtained from different carbonization temperatures and time is given in Table 1. The temperatures of carbonization process were 160 8C, 180 8C, and 200 8C while the processing times were 6, 8, and 10 h. The result of carbon yield is calculated using Eq. (1) with mc is the mass of carbon produced and mb is the dry mass of water hyacinth used. %Yield ¼ m c m 100% (1) b The increase of carbonization temperature and time increases the yield of carbon. By increasing both of those operation parameters, the heat available for a break down the hydrogen bond of water and the availability of H3O+ and OH ions also increased. The presence of excess H3O+ and OH ion concentra- tions in the solution accelerate the dehydration process of sugars in Table 1 The yield of carbon microsphere at different temperatures and processing time. No Temperature (8C) Time (h) mb (g) mc (g) Yield (%) 1 160 2 160 3 160 4 180 5 180 6 180 7 200 8 200 9 200 6 10.0091 8 10.0103 10 10.0023 6 10.0007 8 10.0319 10 10.0176 6 10.0011 8 10.0236 10 10.0021 0.8227 8.22 0.8739 8.73 0.9122 9.12 0.9051 9.05 0.9340 9.31 0.9737 9.72 0.9711 9.71 1.0034 10.01 1.0192 10.19 F. Kurniawan

10**et al. / Journal of the Taiwan Institute of Chemical Engineers 47 (2015)**

197–201 199 the solution [1] leading to increase the yield of carbon microsphere. 3.2. Characterization of carbon microsphere and activated carbon 3.2.1. Carbon microsphere morphology Fig. 1 depicts the surface morphology of carbon microsphere produced from water hyacinth through hydrolysis and carboniza- tion using subcritical water process. This figure clearly shows that the carbons possess smooth surface and good sphericity. The diameters of the carbons are around 2 to 4 mm. The formation of spherical carbons occurred through several stages [4]. The first stage is dissociation and protonation of water into H3O+ and OH at subcritical condition, and the hydrogen bond among water molecules became very weak. The H3O+ (hydroxonium) represent the nature of the proton in aqueous solution. The next stage, the hydroxonium attack the sugars molecules through intermolecular condensation reaction which cause the loss of water clusters from sugars structure and the sugars partially dehydrated from solution. Any further dehydration of sugars causes the formation of nuclei- oligomer in the micelles to form small particles. The formation of spherical nano size particles occurred due to the further growing of nuclei-oligomer in the micelles. In the last stage, the nuclei polymerization occurred and the of spherical nano size particles growing further to micro-size particles. 3.2.2. Pore structure of activated carbon Determination of surface area (SBET) of the activated carbon was conducted using standard BET equation in the relative pressure (p/p0) between 0.05 and 0.35. Total pore volume was determined from the amount of nitrogen gas absorbed in activated carbon at the highest relative pressure (p/p0 = 0.995). The micropore volume of the carbons (Vmicro) and micropore surface area (Smicro) were obtained based on Dubinin–Radushkevich (DR) analysis. The pore characteristics of carbon microsphere and activated carbons prepared from water hyacinth are summarized

in Table 2. The carbon microsphere obtained in this study has low BET surface area and micropore volume. After activation treat- ment, the surface area of the carbons significantly increases as seen in Table 2. During the activation of carbon microsphere using KOH and assisted by microwave irradiation, the evolution and opening new pores within the carbon particles occurred due to the removal of volatiles, impregnated KOH and its derived compounds, such as K_2O and K_2CO_3 from the carbon walls. These volatiles are generated from complex reactions occurred during the impregna- tion and activation processes, these reactions include decomposi- tion, dehydration, and condensation of macromolecules [1]. The nitrogen adsorption isotherms on activated carbon microsphere (impregnation ratio 1:1) and the pristine carbon Table 2 The pore characteristic of activated carbons and carbon microsphere. Parameters Impregnation ratio (KOH:carbon) Carbon microsphere 1:2 1:1 3:2

3**SBET (m2/g) Smicro (m2/g) Vmicro (cm3/g)** VT **(cm3/g)**

131 761 32 660 0.07 0.36 0.12 0.48 1010 901 0.43 0.59 852 757 0.37 0.51 microsphere are given in Fig. 2. Type I isotherm is observed for the activated carbon microsphere, typical for microporous material,

13where micropore filling may take place by primary filling at very low relative pressure, p/po

(Fig. 2a). The pore size distributions of activated carbons were determined using density functional theory and the results confirm that the dominant structure on the surface of carbon are microporous structure (Fig. 2b) with pore width between 0.5 and 1.7 nm. 3.3. Electrocapacitive properties of activated carbon microsphere Electrocapacitive stability of the carbon electrode (impregna- tion ratio 1:1) was measured by galvanostatic charge and discharge. This technique is widely employed for evaluating the normalized capacitance and internal resistance of an electrochem- ical device [1]. Fig. 3 depicts the cycling stability performance curve of the carbon electrode (impregnation ratio 1:1) and commercial electrode (made from commercial activated carbon F-400 Calgon Carbon). From the analysis over 1000 cycles, the electrode of activated carbon and commercial electrode have capacitance decreased insignificantly. For activated carbon elec- trodes, the capacitance decreased from 179.6 F/g to 168.9 F/g, and for commercial electrode, the capacitance decreased from 182.2 F/g to 172.2 F/g. The analysis of the results showed that activated carbon electrode had a high electrochemical stability even after experiencing 1000 cycles.

12**Fig. 4 shows the** galvanostatic **charge and discharge** curves **of the** activated carbon **electrode at** loading **current density of 1 A/ g. The**

near symmetrical triangular shape of V-t response indicates that the electrode has low ohmic resistance and potential drop. The activated carbon electrode also has good reversibility during charge and discharge process. The cyclic voltammograms (CV) of the activated carbon electrode and that produced from commercial activated carbon are depicted in Fig. 5. The CV of the activated carbon electrode (solid line) show rapid current response on the voltage reversal at the end of potential and near symmetrical rectangular shape of the Fig. 1. SEM images of carbon microsphere synthesized at temperature of 180 8C and 10 h. 200 F. Kurniawan et al. / Journal of the Taiwan Institute of Chemical Engineers 47 (2015) 197–201 (a) 1.0 400 KOH:Carbon = 1:1 Commercial 0.8 300 Vads, cm3/g STP 0.6 200 KOH:Carbon = 1:1 Before activation Potential (V vs. Hg/HgO) 0.4 100 0.2 0.0 0 0 50 100 150 300 350 400 450 200 250 0.0 0.2 0.4 0.6 0.8 1.0 Time (s) Relative pressure p/po Fig. 4. Galvanostatic charge and discharge of carbon electrode and commercial activated carbon electrode at a current density of 1 A/g. (b) 0.30 0.25 KOH:Carbon=1:2 Pore size distribution (cm3/g.nm) KOH:Carbon=1:1 KOH:Carbon=3:2 0.20 0.15 0.10 0.05 0.00 0 2 4 6 8 10 Pore width (nm) Fig. 2. Pore structure of the carbon microsphere and its activated forms (a) nitrogen adsorption isotherms and (b) DFT pore size distribution of activated carbons. Current Density (A/g) 6 4 2 0 -2 -4 -6 -8 0.0 0.2 0.4 0.6 0.8 1.0

7**Potential (V vs. Hg/HgO) Fig. 5. Cyclic voltammograms of**

activated carbon microsphere with impregnation ratio 1:1 (solid line) and commercial activated carbon electrode (dash line). 180 Specific Capacitance (F/g) 160 140 KOH:Carbon = 1:1 Commercial 120 0 200 400 600 800 1000 Cycle Numbers Fig. 3. Cycling stability performance curves for activated carbon microsphere with impregnation ratio 1:1 and commercial electrode. combined curves at positive and negative sweep rates. This evidence indicates that the activated carbon electrode possesses a near ideal double layer capacitance [1,7]. 4. Conclusions Carbon microspheres have been synthesized from water hyacinth using subcritical water hydrolysis and carbonization methods. Carbonization process which was performed at 200 8C, 40 bar and 10 h gave the highest yield of carbon microspheres (10.19%). The activation process with impregnation ratio of 1:1 and 630 W microwave power produced carbon with the highest specific area and high electrochemical stability.

—Research Grant (PKM-P). References [1] Kurniawan A, Effendi C, Ong LK, Kurniawan F, Lin CX, Angkawijaya AE, et al. Preparation of nanoporous carbon microspheres by subcritical water carboni- zation and electrocapacitive study. Electrochim Acta 2013;111:99–107. F. Kurniawan et al. / Journal of the Taiwan Institute of Chemical Engineers 47 (2015) 197–201 201 [2] Ong LK, Kurniawan A, Suwandi AC, Lin CX, Zhao XS. A facile and green preparation of durian shell-derived carbon electrodes for electrochemical double-layer capacitors. Prog Nat Sci Mater Int 2012;22:625–31. [3] Pandolfo AG, Hollenkamp AF. Carbon properties and their role in supercapa- citors. J Power Sources 2006;157:11–27. [4] Xia X, Shi L, Liu H, Yang L, He Y. A facile production of microporous carbon spheres and their electrochemical performance in EDLC. J Phys Chem Solids 2012;73:385–90. [5] Guo P, Gu Y, Lei Z, Cui Y, Zhao XS. Preparation of sucrose-based microporous carbons and their application as electrode materials for supercapacitors. Microporous Mesoporous Mater 2012;156:176–80. [6] Ma X, Liu M, Gan L, Zhao Y, Chen L. Synthesis of micro- and mesoporous carbon spheres for supercapacitor electrode. J Solid State Electrochem 2013;17:2293–301. [7] Xiong W, Liu M, Gan L, Lv L, Li Y, Yang L, et al. A novel synthesis of mesoporous carbon microspheres for supercapacitor electrodes. J Power Sources 2011;196:10461–64. [8] Hou H, Schaper AK, Weller F, Greiner A. Carbon nanotubes and spheres produced by modified ferrocene pyrolysis. Chem Mater 2002;14:3990–4. [9] Hu G, Ma D, Cheng M, Liu L, Bao X. Direct synthesis of uniform hollow carbon spheres by a self- assembly template approach. Chem Commun 2002;8: 1948–9. [10] Liu J, Shao M, Tang Q, Chen X, Liu Z, Qian Y. A medial-reduction route to hollow carbon spheres. Carbon 2003;41:1682–5. [11] Serp P, Feurer R, Kalck P, Kihn Y, Faria JL, Figueiredo JL. Chemical vapour deposition process for the production of carbon nanospheres. Carbon 2001;39:621–6.