

Growth of Palladium Thin Film Deposited on Stainless Steel Current Electrodes by Wet Chemical Method for Activated Carbon Supercapacitor and Their Electrochemical Properties

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(Received 18 May 2019; revised manuscript received 21 October 2019; published online 25 October 2019)

To improve the performance of supercapacitors, a simple wet chemical method for the deposition of palladium (Pd) film on stainless steel (SS) as a current collector for an activated carbon (AC) electrode had been conducted. AC electrodes were produced using physical and chemical activation from oil palm empty fruit bunches (OPEFB) biomass material. The chemical activation comprised of KOH at concentrations of 0.3, 0.6, and 0.9 M. Physical activation involved CO₂ gas at a temperature of 700 °C with holding activation time for 2 hours. The synthesized Pd film was characterized using FESEM-EDAX, and cyclic voltammetry (CV) was performed to its electrochemical properties in a 0.5 M H₂SO₄ electrolyte solution. XRD, FESEM-EDAX have been used to investigate the structural and elemental AC electrodes. The microstructure of the AC electrode corresponds to (002) and (100) in a semi-crystalline form with diffraction peaks at 2θ of 24.92° and 45.12°. The result of EDAX showed that the AC electrode with KOH activation has an elemental carbon range 87.02 to 92.48 at. %. FESEM characterization indicated that the Pd film deposited onto a SS substrate consists mainly of microcrystallites coated with cauliflower-like structures in the size range 200-600 nm. Data from the EDAX analysis showed a palladium of 44.05 at. %. It was shown that the wet chemical method, which really affected the growth of Pd film on the SS surface, acts as a current collector electrode to improve the specific capacitance. CV charge-discharge value of modified supercapacitor electrode before (SS/AC) and after (SS/Pd/AC) Pd film coating increases the specific capacitance from 106 to 115 Fg⁻¹. The modified SS/Pd/AC electrode with AC/KOH ratio of 0.3 showed a good maximum specific capacitance at a scan rate 1 mVs⁻¹.

Keywords: Active carbon, Cauliflower-like, Pd film, Stainless steel electrode, Supercapacitor.

DOI: [10.21272/jnep.11\(5\).05006](https://doi.org/10.21272/jnep.11(5).05006)

PACS numbers: 81.16.Be, 87.85.jf

1. INTRODUCTION

Supercapacitor is currently a challenge for the application of energy storage devices. The electrode configuration for new construction supercapacitors is described in this article with a focus on preparation method, characterization, and electrochemical performance. This article presents a state-of-the-art SS/Pd-metal/biomass activated carbon (SS/Pd/AC) preparing process and reliability structure for supercapacitors. The supercapacitor using porous carbon electrode (CE) prepared from OPEFB waste fibers has already been reviewed [1]. OPEFB is an agricultural waste and was used as an eco-friendly and cheap biomass material in the present study to produce activated carbon which is meso-porous and has a high surface area. Chemical activation with KOH is a well-known method to activate high-surface carbon materials [2]. The activation is carried out by heating a carbon source material mixture of solid KOH and meso-porous carbon under N₂ at a temperature of 400 °C to 1000 °C [3, 4]. Generally, the percentage of KOH and the pre-carbonization activation process could affect the surface area and the structure of the pore [5, 6]. Various types have also been studied to enhance supercapacitor performance, such as current collector [7]. Taking into consideration the physical confinement of the carbon sphere to metal, it has been promising to introduce the small percentage of catalytic materials onto the carbon materials, which can significantly enhance supercapacitors performance. Transition metal or metal oxides are also one of the

most widely used current collector electrode materials in supercapacitor. Among them, platinum was proposed as a supercapacitor electrode material [8]. Pd nanoparticles-graphene nanosheet (GN) composite is reported as an efficient electrode material in supercapacitors [9] and sensors [10]. Many deposition methods have been developed to obtain the synthesis of metal films today. There is little research on the application of Pd for the supercapacitor to best of our knowledge so far. The strategy mainly includes designing an existing collector to effectively collect and transport charge carriers during the charge-discharge process [11, 12].

Here we report on OPEFB's activated carbon supercapacitor performance investigated on SS current electrode deposited with Pd film. The structure of achieved CE samples and Pd film was investigated with X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). Finally, this work also studies the effect of Pd film deposition on the structure and morphology of the current collector electrode and its electrochemical properties in the H₂SO₄ electrolyte solution.

2. EXPERIMENTAL

2.1 AC Electrode Preparation

The method used in this study is the chemical and physical activation for producing activated carbon from OPEFB following the method mentioned in the literature [8]. First, CE from OPEFB fibers was pre-

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carbonized by the furnace at 200 °C for 3 hours, followed by milling (ball milling) and sieving through a 100 mm mesh to obtain a smaller particle of active carbon grains. The molar ratio of the active carbon grains to KOH carbonized OPEFB was varied from 1:0.3, 1:0.6 and 1:0.9 (labeled AC-0.3, AC-0.6, and AC-0.9) and converted to carbon pellets using a press with a pelleting hydraulic machine inside a 2 cm diameter mould. The pellet was heated up to 700 °C inside the furnace with holding activation temperature for 2 hours; the heating rate was 3 °C·min⁻¹ under N₂ gas flow (1.5 Lmin⁻¹) to obtain CE material. The CEs were then activated using CO₂ gas with a flow rate of 1.0 Lmin⁻¹ at a temperature of ~ 700 °C for 2 hours holding time. The CEs created were polished to 0.5 mm thick and washed with distilled water, and then dried with an oven at 100 °C for ± 24 hours.

2.2 Growth of Modified SS Electrodes

A wet chemical method has been described by Ref. [7] to synthesize large nano-/submicron Pd particles on the surface of the SS substrate. The SS (grade 316L) current collector was cleaned in an ultrasonic bath with acetone, ethanol and de-ionized water for 10 min in each solution. The solution for the growth of Pd films on the surface of a SS current collector was synthesized by mixing 0.5 mL of de-ionized water with a 0.01 M K₂PdCl₆ solution and 10 mL of 0.1 M ascorbic acid solution. Next, 18 mL of de-ionized water were mixed with 0.5 mL of 0.01 M K₂PdCl₆ solution, and then the SS was soaked in the 1 mL of ascorbic acid solution at 30 °C for 6 hours before washing with de-ionized water and then dried using a dryer (Fig. 1).

The growth is done by four repetitions of the above process. The formation of palladium films labeled with a white coloration of the solution became turbid.

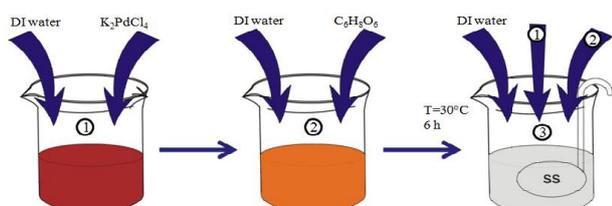


Fig. 1 – Schematic representation of a stepwise procedure to deposit submicron Pd particles on stainless steel: (1) 0.01 M K₂PdCl₄ solution, (2) 0.2 M ascorbic acid (C₆H₈O₆) solution, (3) 18 ml DI water + 1 ml 0.01 M K₂PdCl₄ solution + 0.5 ml 0.1 M ascorbic acid (C₆H₈O₆) solution + SS (4) after 1 hour, (5) after 2 hours, and (6) after 6 hours at $T = 30$ °C

3. RESULTS AND DISCUSSION

The structure of the CEs obtained at different KOH activation concentrations was presented. XRD in Fig. 2 shows that CEs have two dominant peaks at the diffraction peaks (002) and (100) at 2θ values of 24° and 44°, respectively. These peaks confirmed the carbon structure. In sample AC-0.9, there is a shifted peak in the diffraction pattern at about $2\theta = 24.92^\circ$ and peak (100) at $2\theta = 45.12^\circ$, which are diffraction peaks indicating that KOH ratio activating increase has a disorder crystallite layer parameter L_a and L_c . This is due to a shift in the distance between the carbon atom inter-

action of alkali with carbon phases via oxygen-containing surface functional groups. Previous studies have shown that the diffraction peaks corresponding to the (002) crystal plane are broader in the spectrum indicating the amorphous state diffraction angle which the presence the KOH activation [13].

The results of EDX analyses confirm that all AC electrodes have an elemental carbon range 87.02–92.48 at. % and the other elements are oxygen, silicon, and calcium, respectively, and are in agreement with the XRD results shown in Fig. 2.

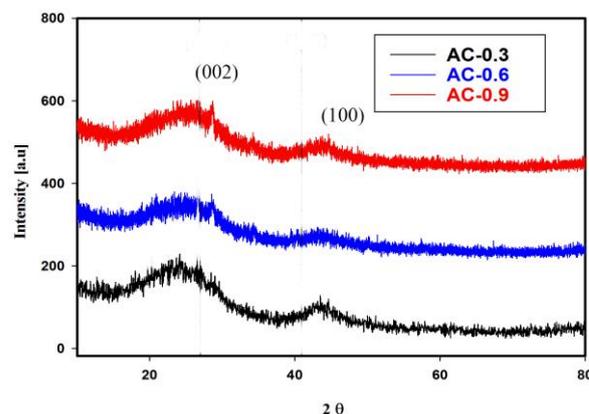


Fig. 2 – XRD pattern of AC electrode samples

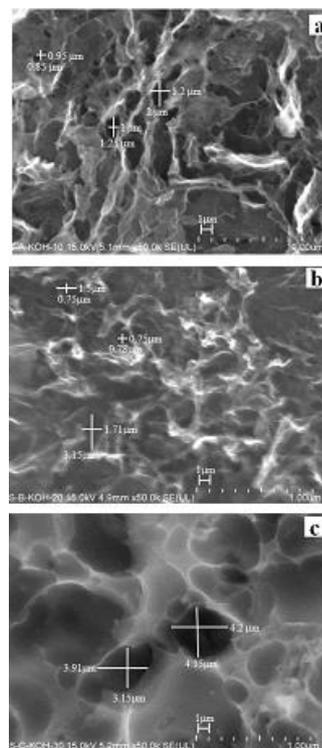


Fig. 3 – SEM micrographs of AC-0.3 (a), AC-0.6 (b), AC-0.9 (c) electrode samples derived from OPEFB in magnification of 50,000

Fig. 3 shows FE-SEM micrographs of the activated carbon electrode samples with variations in the concentration of KOH. FE-SEM image sample AC-0.3 indicates the presence of pores with a longitudinal structure and more pore distribution produced on the electrode surface is presented in Fig. 3a. Fig. 3b shows that

the pore distribution of carbon produced in sample AC-0.6 is less than in the sample AC-0.3, this is due to impurities in the sample. As seen from Fig. 3c with FE-SEM image of sample AC-0.9, there are large impurities which show less pore distribution because the addition of high KOH ratio produces macropores with a larger size.

Fig. 4a shows FE-SEM micrographs of the SS substrate without Pd films. The Pd film has been grown on the SS surface. FE-SEM images of the SS surface after Pd film deposition are presented. Fig. 4b indicates that less agglomerated Pd particles are not homogeneously distributed which can be attributed to the formation of palladium microcrystallites. High magnification images show that their grain size and the shapes of Pd film have dimensions of approximately in the size range 200-600 nm in diameter.

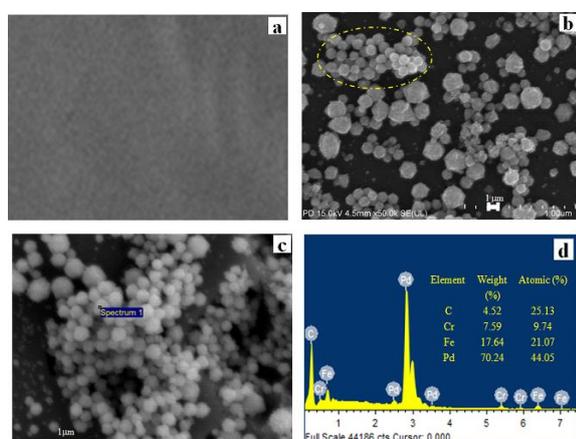


Fig. 4 – FE-SEM images of SS surface (a), after Pd film deposition on SS surface at magnification 50,000x (b), zoom from figure b (c) and EDS spectrum analysis of Pd film (d)

Many quasi-spherical shapes of Pd microcrystallites are observed with big sizes and shapes. Our method shows that their size distribution and the shapes are not controlled. It is known from the literature that the morphology of Pd nanoparticles depends on the reductant [14]. Morphology of Pd nanoparticles observed was octahedral, tetrahedral, cubical, and some other minor shapes are spherical and other minor quasi-spherical shapes. Fig. 4c shows that Pd films exhibited a small spherical shape covered with a cauliflower-like structure on the SS; well-defined spherical small microcrystallites adhered like chains were observed. Our morphology result similar to nanostructured Pd film was fabricated by applying electrodeposition [10], one double-potential step method [15] and DC magnetron co-sputtering technique [16]. The Pd film growth involves the formation of the K_2PdCl_6 solution from pure Pd and its electro-reduction to Pd atoms. The deposition method plays an important role in the amount of film deposited. The EDS results show that the SS surface film comprises about 44.05 at. % Pd, 25.13 at. % C, 21.07 at. % Fe, and 9.74 at. % Cr, respectively (Fig. 4d). It should also be noted that the Pd content in the films is much higher than C, Fe, and Cr content. In the literature has been described the EDS elemental analysis of SS before metal deposition revealed the presence of Fe, Cr, Ni, and Mo [7]. The obtained results prove that the

Pd film can be grown onto the surface of SS by wet chemical method.

The electrochemical properties of the all CV measurements were performed in a 0.5 M H_2SO_4 electrolyte solutions.

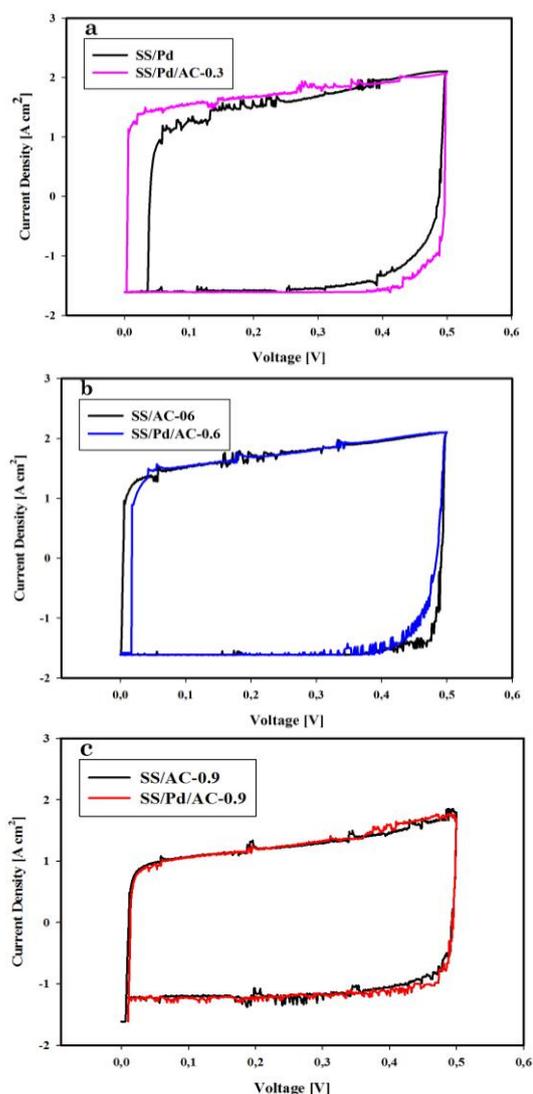


Fig. 5 – CV curves of the SS/AC-0.3 and SS/Pd/AC-0.3 (a), SS/AC-0.6 and SS/Pd/AC-0.6 (b), SS/AC-0.9 and SS/Pd/AC-0.9 (c) in 0.5 M H_2SO_4 electrolyte solution at a scan rate of 1 mVs⁻¹

As seen from Fig. 5, the charge-discharge increases from 0 to 0.5 V and then decreases continuously until 0.4 V. However, the CV of SS/AC and SS/Pd/AC cells are good rectangular shapes. These results are similar to other reports for the same Pd metal synthesized on WO_3 current collector by hydrothermal method [17]. The specific capacitance (C_{sp}) for SS/AC-0.3, SS/AC-0.6 and SS/AC-0.9 is 106, 96 and 80 Fg⁻¹, respectively (without Pd films). The C_{sp} of SS electrode deposited Pd films was 115 Fg⁻¹ for SS/Pd/AC-0.3 (Fig. 5a), 105 Fg⁻¹ for SS/Pd/AC-0.6 (Fig. 5b) and 88 Fg⁻¹ for SS/Pd/AC-0.9 (Fig. 5c), respectively. This can be explained by an increased surface area electrode created by the Pd film on the surface of SS accessible to the electrolyte. However, when ratio of KOH activation on the active carbon grains is higher than 0.6 and 0.9 was prepared, the cur-

rent density of different electrodes decreased significantly, probably due to the decreasing surface area of the electrode. As the ratio of KOH/AC decreases, C_{sp} increases. It is remarkable that SS/Pd/AC-0.9 electrode showed extremely low C_{sp} due to the very poor energy conversion over SS/Pd/AC-0.9 compared to those of SS/Pd/AC-0.3 and SS/Pd/AC-0.6 electrodes. According to Fig. 5b, c, it can be seen that C_{sp} has a small limitation in term of improving both voltage window and current densities due to their narrow rectangular shape. This is the reason why their specific capacitance is decreased, and the surface area of Pd film on the surface of SS by creating micropores is small enough for ion diffusion in these electrodes [18, 19].

The influence of Pd film on the specific capacitance of electrode with different modified Pd films on the SS current collector was investigated from 88 to 115 Fg^{-1} (Table 1). From the obtained results it can be concluded that the modification of the SS current collector with Pd metal increased the C_{sp} . The highest C_{sp} is observed for the SS/Pd/AC-03.

Table 1 – Specific capacitance (C_{sp}) values evaluated from CV data for different cells

without Pd	C_{sp}, Fg^{-1}	with Pd	C_{sp}, Fg^{-1}
SS/AC-03	106	SS/Pd/AC-0.3	115
SS/AC-06	96	SS/Pd/AC-0.6	105
SS/AC-09	80	SS/Pd/AC-0.9	88

Poor specific capacitance due to the relative AC/KOH activation ratio increases the AC pore size, and pore volume distribution of carbon electrodes might be the reason for such a low energy conversion. From this point of view, the highest C_{sp} and H_2SO_4 electrolyte solution selectivity over SS/Pd/AC-0.3 electrodes seem reasonable. The highest C_{sp} is found in the SS/Pd/AC-0.3 electrode, which can attribute to the effected growth of Pd films on SS current collector.

The Pd metal deposition on Pd/SS/AC electrode showed the maximum C_{sp} of 115 Fg^{-1} . This indicates that the Pd metal is reasonably deposited on the SS surface. One research group has been developed strategy to prepare Pd doped on WO_3 (Pd- WO_3) current collector as supercapacitor electrode [17]. This was synthesized by hydrothermal method. Pd- WO_3 shows that specific capacitance from GDC is 33.34 Fg^{-1} at 0.5 Ag^{-1} . According to [18, 19], the presence of Pd films is stable as a catalyst so that it can change the ability of electrolyte ion to enter the pores of the activated carbon electrode during the discharge/charge process.

In SS/Pd/AC electrodes, an activated carbon support mainly plays the following roles for this enhancement: (1) An activated carbon support to favor the dispersion of metallic particles on the SS surface. The highly dispersed Pd particles can contribute to a strong interaction between Pd particles and the surface of carbon that would increase capacitance. (2) Probably, the morphology of the Pd can be distributed around grain boundaries

of SS surface such as small spherical shape covered with a cauliflower-like [17]. (3) Most of the Pd particles can facilitate the transfer of ions and electrons to the electrode surface that influences the capacitive behavior.

In this study, the specific capacitance of a Pd film grown on the SS as a current collector for activated carbon supercapacitor from OPEFB biomass increased from 88 to 115 Fg^{-1} as the AC/KOH ratio decreases from 0.9 to 0.3. The major advantage of Pd thin film on the SS surface can involve shorter ion transport path for the diffusion of protons and resistance to corrosion due to the H_2SO_4 electrolyte solution. Finally, noble metals such as palladium are attractive to research the electrode material of supercapacitors. Farma *et al.* [8] reported a supercapacitor based on SS/Pt film as a current collector showed an increase in specific capacitance of 10 % (from 106 to 115 Fg^{-1}) estimated from electrochemical impedance spectroscopy. However, due to the high cost of Pd material is considered one of the state-of-the-art to minimize their consumption for comparison the electrode materials without and with noble metal. For further study, all SS/Pd/AC electrode cells are very important to measure charge transfer resistance value by electrochemical impedance spectroscopy and galvanostatic charge-discharge for determining the performance of these electrode material modifications and cycle life.

4. CONCLUSIONS

The Pd film metal-based material deposited on SS as a current collector is examined to improve the electrode specific capacity. The supercapacitor cells activated carbon electrodes are prepared from OPEFB carbonized biomass material. The surface of SS current collectors was modified by depositing wet chemical grown with Pd films to be a contact between the activated carbon electrodes (SS/Pd/AC) of the supercapacitor. The activator KOH concentration influences the electrochemical properties of the electrode supercapacitor. The achievement of these supercapacitor cells is shown to have better performance specific capacity with a concentration of 0.3 M. Based on the electrochemical values evaluated from CV, it is concluded that the growth of the current SS collector after the Pd deposition showed significant improvement in the specific capacitance of the supercapacitor. The specific capacitance increases from 106 to 115 Fg^{-1} with the AC/KOH molar ratio being 0.3 M. The improved performance of the Pd film deposited on a SS current collector electrode essentially plays a very important role in the transfer of ions and electrons on the charge-transfer process between the SS and the AC surface.

ACKNOWLEDGEMENTS

The financial support by University of Riau for Excellent Research Grant through project number 126/UN.19.5.1.3/LT is greatly acknowledged.

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Зростання тонкої плівки паладію, нанесеної на струмові електроди з нержавіючої сталі вологим хімічним методом для суперконденсатора з активного вуглецю, та її електрохімічні властивості

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Для підвищення продуктивності суперконденсаторів було використано простий вологий хімічний метод осадження плівки паладію (Pd) на нержавіючу сталь (SS) як струмоприймача для електрода з активованим вугіллем (AC). Електроди з AC вироблялися за допомогою фізичної та хімічної активації з матеріалів біомаси OPEFB. Хімічна активація складається з KOH у концентраціях 0,3; 0,6 та 0,9 М. Фізична активація включала газ CO₂ при температурі 700 °C із затримкою часу активації протягом 2 годин. Синтезовану Pd плівку характеризували за допомогою FESEM-EDAX, а циклічну вольтаметрію (CV) застосовували до її електрохімічних властивостей у 0,5 М розчині електроліту H₂SO₄. XRD, FESEM-EDAX були використані для дослідження структурних та елементних електродів з AC. Мікроструктура електрода з AC відповідає (002) та (100) у напівкристалічній формі з піками дифракції при 24,92° та 45,12°. Результат EDAX показав, що електрод з AC з активацією KOH має елементний діапазон вуглецю з 87,02 до 92,48 ат. %. Характеристика FESEM вказує на те, що плівка Pd, нанесена на підкладку з SS, складається в основному з мікрочастин, покритих структурами купчастої форми з розмірами 200-600 нм. Дані, отримані з аналізу EDAX, показали, що паладій становив 44,05 ат. %. Було показано, що вологий хімічний метод, який дійсно вплинув на ріст плівки Pd на поверхні з SS, виконує функцію струмоприймача для поліпшення питомої ємності. CV значення заряду-розряду модифікованого електрода суперконденсатора до (SS/AC) та після (SS/Pd/AC) покриття плівкою Pd збільшує питому ємність з 106 до 115 Fg⁻¹. Модифікований електрод SS/Pd/AC зі співвідношенням AC/KOH 0.3 показав гарну максимальну питому ємність при швидкості сканування 1 мВс⁻¹.

Ключові слова: Активне вугілля, Купчаста форма, Pd плівка, Електрод з нержавіючої сталі, Суперконденсатор.