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The conversion of biomass into carbon electrode material using FeCl₃ as an activating agent for battery application

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Abstract. Batteries and supercapacitors are one of the energy storage devices that had been used for a practical application most electronic devices such as mobile phone. The development of these energy storage devices is faced by the poor performance of (the) electrode. Electrode commonly used for batteries and supercapacitors is derived from nonrenewable carbon resources such as graphite. However, the availability of this material is becoming a long-term problem for the development of batteries and supercapacitors. Biomass from (the) waste plant as a green source for battery electrode is one of alternative carbon which has great potential, due to the low price, easy to process and has high stability. This paper reports the study of the biomass conversion into carbon electrode material having high electrical conductivity or low electrical resistivity using carbonization and pyrolysis process. The process involved FeCl₃ as an activating agent to reduce the electrical resistivity of the material as low as possible. The research was studying the effect of biomass sources and the processing method on the electrical resistivity of the electrode produced. The biomasses used in the study were corncob, water hyacinth, rice straw, and coconut husk. The material is the waste plant which is available in abundant. The morphological analysis of the carbon surface was conducted using Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). The lowest electrical resistivity was produced from corncob material through the carbonization process at 300ºC for 2 h, activated by 4 M FeCl₃ solution and followed by pyrolysis process at 800ºC for 6 h. The FeCl₃ is suspected responsible for the decreasing of the carbon resistivity or increasing the electrical conductivity produced, this correlates with the increase of the surface area of the material. The lowest electrical resistivity (highest electrical conductivity) produced from corncob has a value of 1 Ω with the surface area of 601 m²/g. This is considered better than graphite in term of electrical resistivity in which graphite has electrical resistivity between 10 - 30 Ω. The result of SEM images shows that the carbon surface activated by FeCl₃ has more pores compared to the carbon without activation.

1. Introduction

The battery is well known as an energy storage device and one of the most energy storage used for electronic devices application. However, preparing them cost-effective, safer and environmentally friendly is a challenge. In this respect, replacing non-renewable materials by introducing renewable derived biomass derivatives into the battery component is a challenging approach for the development of green materials for the new battery and supercapacitor. Different materials sources have been studied as electrode (anode) materials for batteries such as porous materials graphite, metal oxides and conducting polymers [1]. Graphite is the well-known material of anode in a battery application. A major drawback of graphite anode is their low capacity and non-renewable [2]. Therefore, attempts have been

made for developing other carbonaceous materials to obtain better performance and of course renewable. A novel biomass material which is suitable for battery anode must be developed as a substitute for graphite.

Biomass refers to plants or plant-derived materials which is abundant, renewable and low cost and can be exploited for various application. Biomass is often referred to as lignocellulose which is the most abundant natural polymers such as cellulose and lignin, derived from wood processing and other sources [3]. Here we report a method and the characterization of several types of biomass such as rice straw [4], water hyacinth [5-6], corncob [7] and coconut husk [8] as anode material for a battery application. Producing carbon from biomass to form an anode material is similar to the production of activated carbon (AC), however, the activating agent is used to increase the pores and electrical conductivity.

Usually, the preparation of carbon using biomass waste involves several processes such as washing and drying, carbonization and activation using chemical or physical, followed by thermal treatment in an inert atmosphere at high temperature. The thermal carbonization of dry biomass at a temperature between 200 and 300ºC with limited oxygen. The various chemical reaction during the carbonization converts biomass components such as cellulose, lignin, and hemicellulose into hard carbon. Further activation, carbon produced from the carbonization process by pyrolyzing the carbon at high-temperature 600-900ºC can increase the surface area and pore size [9].

The pyrolysis process, to produce high surface area and pore size can be affected by different starting materials, pyrolysis temperatures, duration of pyrolysis and catalyst used. The electrochemical properties of carbon anode depend on the specific surface area, pore size, surface chemistry and electrical conductivity of the carbon. Improving the graphitization of AC by introducing the iron chloride as activating agent simultaneously enhances the electric conductivity of the electrode and its surface wettability towards aqueous electrolytes, which can facilitate ion diffusion and electron transfer, thus improving the electrochemical performance [11].

In this research, carbonization and impregnation process followed by high-temperature pyrolysis method were applied to convert biomass to activated carbon material doped with iron for anode material. Different carbon sources from local plant and waste plant material were also utilized in the experiment. Iron chloride solution as a chemical activating agent was also used to increase the surface area and electrical conductivity of the carbon produced. The variation of iron chloride concentration was also applied to study the effect of the concentration whether correlating to the surface area and electrical property. The surface morphology and quantitative measurement to determine the iron present in the carbon were conducted using combination technique scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDAX).

2. Material and Preparation

2.1. Materials
Biomass used in this research was coconut husk, rice straw, and corncob and water hyacinth as shown in Figure 1. Those materials were collected from local sources. Iron chloride ($FeCl_3.6\ H_2O$) and methylene blue were purchased from Sigma Aldrich.
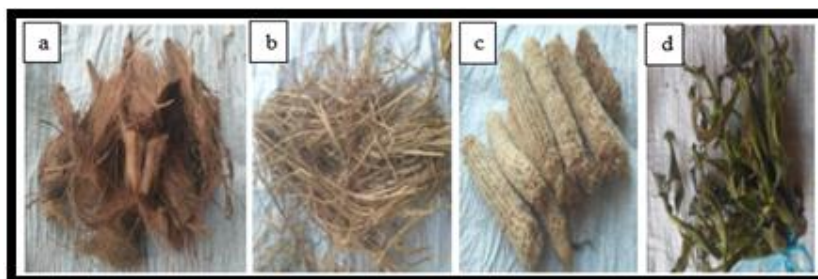

Figure 1. Biomass sources (a) coconut husk (b) rice straw (c) corncob (d) water hyacinth.

2.2. Methods

2.2.1. Procedures. The process of converting biomass to carbon anode through several processes such as drying, impregnating, activation and pyrolysis. Biomass was firstly dried to 100 °C for 24 h. The dried material is then grounded by grinding machine to a particle size of less than 60 mesh. This article was impregnated into iron chloride solution with the concentration of 1, 2, 3 and 4 M for 24 h in a closed container. The impregnated biomass was dried in the oven for 1 h at 100°C. The next step is the carbonization and activation process. The dried biomass impregnated by an iron solution is then placed in a stainless steel reactor for further heated at 300°C for 2 h and continued heated to 800°C for 6 h. The finished carbon anode produced was then grounded and screened to an obtained particle size of 60 mesh.

2.2.2. Sample characterization and analysis. The sample morphology of the carbon sample was characterized using SEM and EDAXS to see the pore size and surface characteristics. The surface area was measured using the methylene blue adsorption method. The electrical conductivity was measured as the resistivity of the material and it was carried out by direct simple measurement using ohm-meter.

3. Results and Discussions

3.1. The effect of treatment conditions on electrical resistivity
Different treatment conditions were applied to all carbon precursors. The result shows a different performance to the carbon produced. This is illustrated in Figure 2 below.
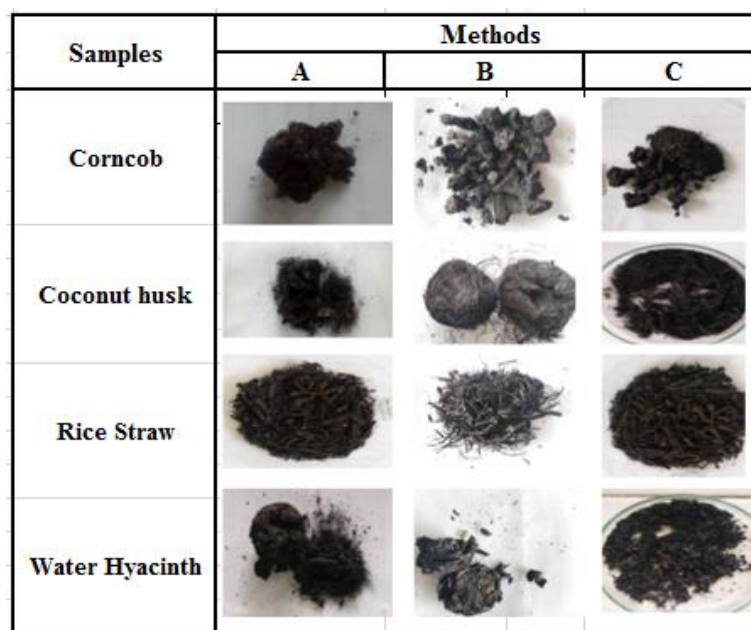

Figure 2. Different result on biomass types and processes (A= Carbonization-Pyrolysis; B = Activation-Carbonization-Pyrolysis; C= Carbonization-Activation-Pyrolysis).

The intrinsic electrical conductivity of carbon produced is an important parameter when it comes to the selection and application of electrode material. Different treatment conditions to the carbon precursors were applied to obtain carbon with low electrical resistance or high electrical conductivity. Serial processes of carbonization, activation, and pyrolysis and variation of those three methods were used. As shown in Figure 2, method A is a combination of carbonization and pyrolysis process. Method

B is a combination of activation, carbonization and pyrolysis process. And the method C is a combination of carbonization, activation, and pyrolysis. Carbonization is a method to convert biomass into carbon at a temperature of 300°C for 2 h. The activation is a method of impregnation of a material precursor using a chemical solution, in this case, iron (III) chloride solution is used at a certain time period. The pyrolysis is the process to decompose volatile organic matter and at the same time producing pores at a temperature of 600 to 800°C. Figure 2 illustrates the different treatment condition results in different particle size and color. Method A and C show blackish carbon and powdery, contrary to the method B the carbon produced has the brownish color and forming aggregate. This explains that method B shows that the oxidation was not completed. However, further pyrolysis process gives a different result. In this case, this explains that electrical conductivity is not fully affected by the carbonization process. It depends on the carbon precursor and the process. This argument can be supported by Figure 3, where there is a relation between different treatments conditions to the electrical conductivity of the carbon produced. Method B, the activation of the precursors was conducted before running the carbonization process and yield in high electrical conductivity compared to method A and C, especially for the water hyacinth and rice straw. This is supported by the data described in Figure 3 whereas the rice straw and water hyacinth precursor show high electrical conductivity when treated by method B. The value of electrical conductivity was measured to the carbon and it shows 15 and 14.6-ohm-cm respectively for the method B and 25.9 and 23.2-ohm-cm for the method C.
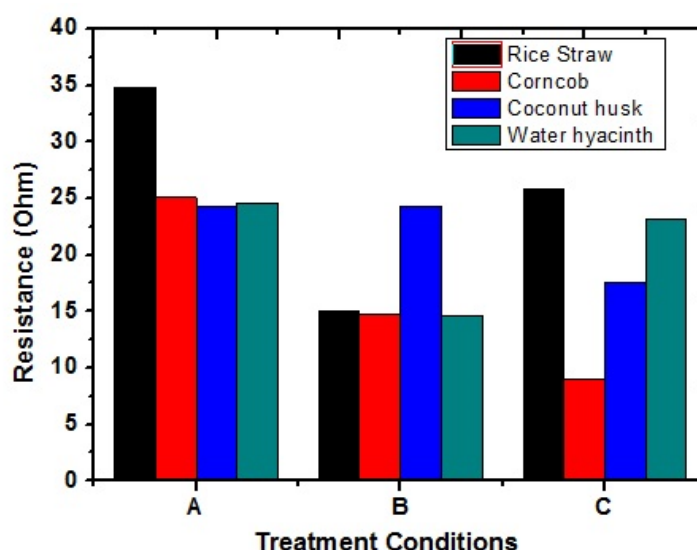

Figure 3. The effect of treatment conditions on the electrical resistance of carbon precursors.

3.2. The effect of surface area to electrical conductivity
The effect of treatment conditions on the surface area of carbon produced was also studied. The results are shown in Figure 4. It is expected that the high electrical conductivity is related to the higher surface area. The treated corncob using method C has the highest electrical conductivity, however, the surface area of this material is the lowest. This seems that the surface area of those materials has no contribution to the electrical conductivity for different treatment conditions. The random relation between electrical conductivity and the surface area can be clearly seen in Figure 4 for corncob.
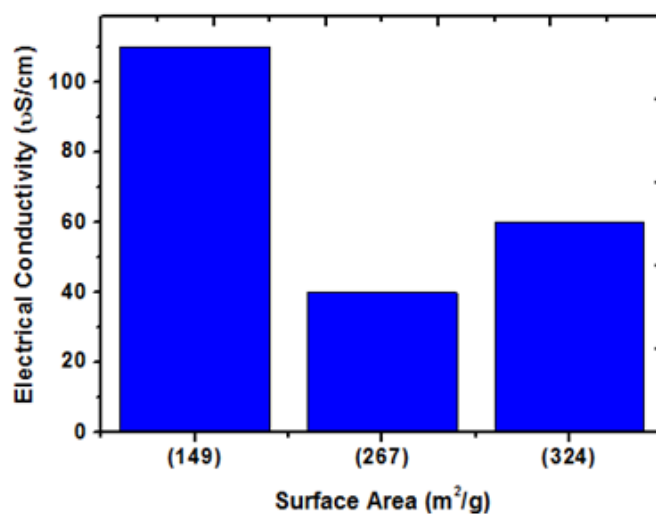
Figure 4. The relation of surface area and electrical conductivity.

3.3. The effect of molar concentration on electrical conductivity

The optimization was carried out by adjusting the concentration of activator $FeCl_3$ with the same treatment condition to the corncob precursor. This experiment was set to see whether at the same treatment conditions give a good correlation between the surface area and the electrical conductivity of the carbon. And this will prove if the molar concentration of iron chloride affects the electrical conductivity of the material. A variation on concentration was done by varying iron chloride solution from 1 M, 2 M, 3 M and 4 M. Figure 5 illustrates the relation of the molar concentration of activator and the surface area and electrical conductivity. That figure shows that by increasing the molar concentration of iron chloride increases the surface area and the electrical conductivity.
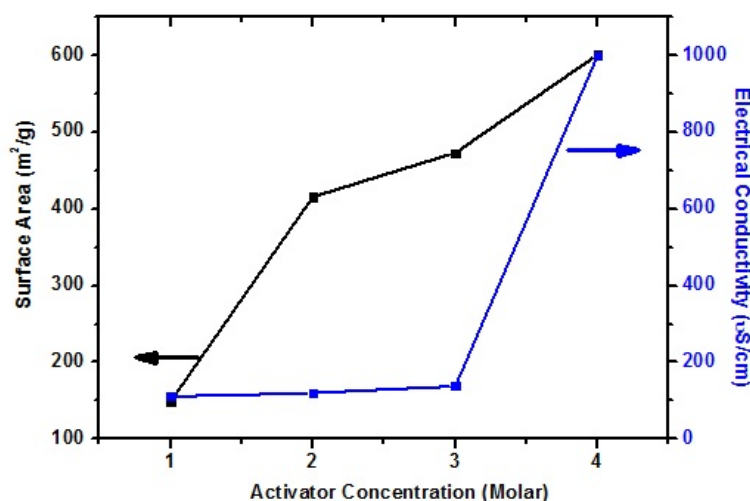

Figure 5. The effect of activator concentration on electrical conductivity and surface area.

The number of iron chloride concentration does affect the conductivity since the iron metal reduced during pyrolysis distributed and proportional in number with the concentration. Figure 5 demonstrates the effect of the concentration level of activator to surface area and electrical conductivity. And there is a positive correlation between surface area and conductivity if the precursors are treated with the same method (method C). Increasing the activator concentration of iron concentration, the larger the surface

area and the easy of the transport of electrons over the surface hence increasing the conductivity of the carbon.

The concentration of the iron chloride has also raised the distribution of the iron and its effects on the catalytic of graphitization of the carbon and also contributing to the increase the conductivity of the carbon. The graphitization is also speeding up at high-temperature environment.

3.4. Surface morphology of carbon

The surface morphology of carbon is compared between the untreated and treated precursor with $FeCl_3$. The surface morphology and the iron content was mapped with SEM and EDX. The same picture was scanned at difference enlargement that is 500, 1000, 2000 times and 5000 times. The picture of those materials is presented in Figure 6 and Figure 7 below.
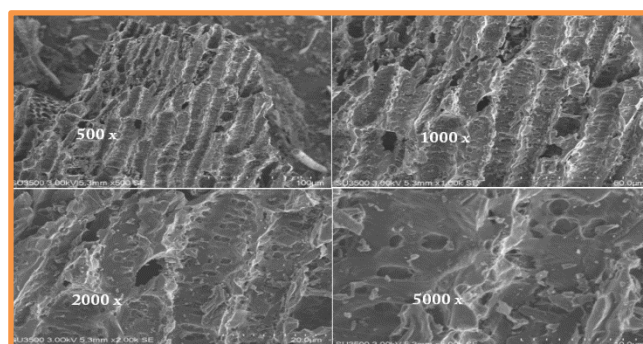

Figure 6. SEM images for the corncob precursor using method A (carbonization-pyrolysis).

Figure 6 shows that the surface of the carbon is only covered by several pores and most of them in large diameter. The pores are not produced for untreated carbon (method A). This explains that without the presence of iron chloride no oxidation on the surface takes place, hence no pores are created. The small portion pores present is due to decomposition an organic matter during heating the temperature at 300 and 800°C.In contrast, Figure 7 shows the graphitic carbon is easily observed, especially at the enlargement of 5000 times. Flower-like carbon produced so many pores. In this case, iron chloride has played roles in the opening closed surface through oxidation of the organic and volatile matter. The graphitic structure is also suspected to be the most responsible in the formation of large surface area and the present of iron chloride has also increased the electrical conductivity of the carbon surface.
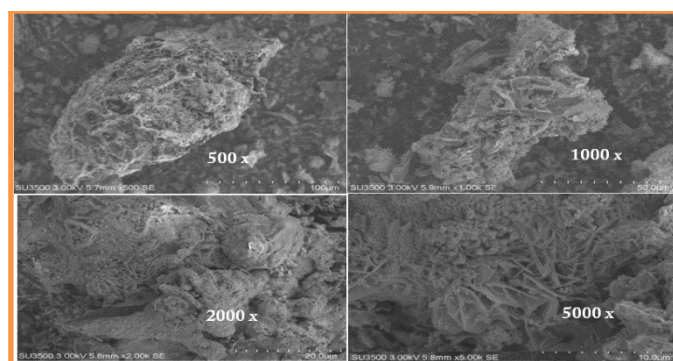

Figure 7. SEM images for the corncob precursor treated using method C (activation carbonization and pyrolysis).

3.5. Element analysis

Table 1 shows the composition of carbon with and without activation. The carbon with no activation gives only carbon almost 97% and small trace iron 1.16 % is present.

Table 1. The element composition of corncob carbon with and without activation.

No.	Elements	Composition (%)	
		Without Activation (Method A)	With Activation (Method C)
1	Carbon (C)	96.84	53,38
2	Oxygen (O)	-	19.57
3	Silicon (Si)	-	0.74
4	Chloride (Cl)	-	4.48
5	Iron (Fe)	1.16	19.38

This argument is also supported by Figure 8 where no iron present was observed at EDX peak. The small amount of iron present is suspected due to iron leached out from the reactor since the reactor is made from mild steel. In contrast, the carbon with activation Figure 9, the amount of iron is clearly observed which is 19.38 %. The chloride ion is also present for about 4.48 %.

This is the result of the impregnation of the precursor in the iron chloride solution. The number observed carbon is reduced to 53.38 % and the oxygen content is almost 20%. The decrease of the carbon content is due to some part of the carbon surface covered by iron and other elements. The presence of iron as an activating agent speed up the oxidation proses and some hydroxyl group may present, this can confirm by the presence of oxygen in the same amount of iron.
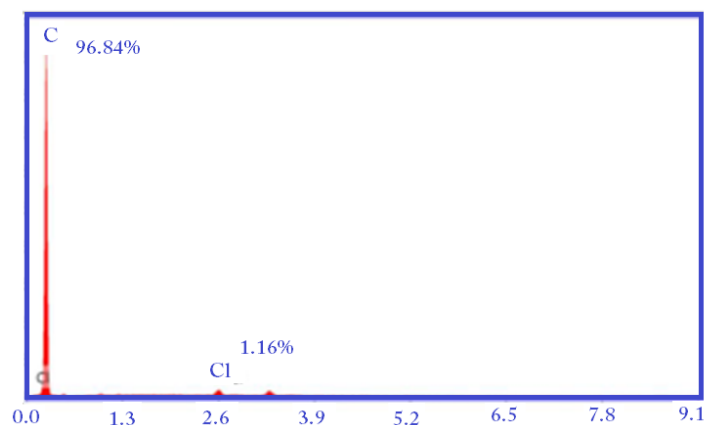

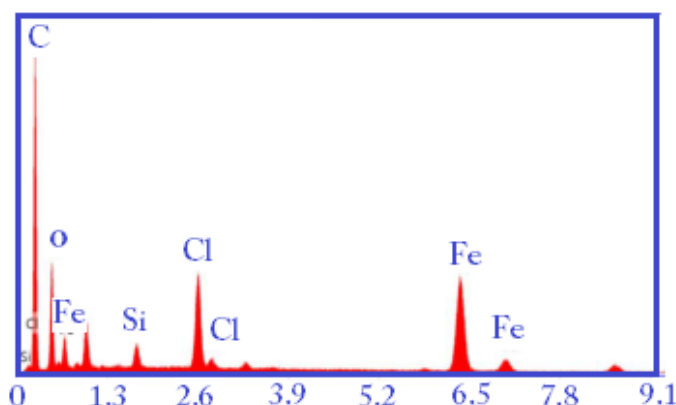**Figure 8.** EDX peak for carbon without activation (method A).

Figure 9. EDX peak for carbon with activation using FeCl$_3$ (method A).

4. Conclusions

The corncob yield the lowest electrical resistivity treated with activation using iron chloride solution compared to other biomass studied. There is no correlation between surface area and electrical conductivity for different carbon precursor and using different treatment condition. However, increasing the activating agent concentration has been increasing the surface area and proportionally increasing the electrical conductivity of the carbon material at the same treatment. The number of iron present in the surface gives the possible oxidation to take place and could open the pores of the surface. This large number of pores is possibly the one which is responsible for the increase of the electrical conductivity. The corncob precursor has the potential to be used as a starting material to produce graphitized carbon for the replacement of graphite as a battery electrode.

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