Synthesis of activated carbon/bismuth oxide composite and its characterization for battery electrode

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Abstract. Synthesis of activated carbon/bismuth oxide composite and its electrical conductivity characterization have been undertaken. The purpose of this study was to synthesize activated carbon/bismuth oxide composite with several variations in the mass ratio of the composition of both precursors and to characterize the electrical property to determine the potential of this composite material as a battery electrode. Activated carbon from rice husk was mixed with bismuth nitrate pentahydrate with variations in the mass ratio activated carbon and bismuth nitrate pentahydrate 2:1, 1:1, and 1:2. The mixture was then put into a reactor and heated at 100°C for 5 hours. The next step was results of the hydrothermal process were then filtered and dried in an oven. LCR analysis demonstrated that the mass ratio of activated carbon and bismuth oxide 1:1 had the highest electrical conductivity value of 1.24 x 10⁻⁵ S.m⁻¹.

Keywords: activated carbon, bismuth oxide, battery, electrode

1. Introduction

Batteries are devices that can convert chemical energy into electrical energy through reduction and oxidation reactions [1]. We know there are two batteries that are rechargeable and non-rechargeable. For energy storage purposes, rechargeable batteries are more promising due to their high energy density. In addition, this type of battery is more environmentally friendly because of repeated use. Currently, the biggest challenge related to the development of rechargeable batteries lies on the manufacture of batteries which have high energy density, long durability and fast charging. Therefore, the constituent material of the battery component is a key solution to the performance of the battery. The main components of the battery consist of an anode (negative electrode), cathode (positive electrode), electrolyte and separator. In this study more focused on the development of negative battery electrodes.

One potential anode material is the use of carbon compounds, namely activated carbon. Activated carbon is amorphous carbon from flat plates arranged by C atoms covalently bonded in a flat hexagonal lattice with one C atom at each angle [2]. Activated carbon has the potential as an electrode because it has a specific capacity of 20 F/g [3] and volumetric capacity of 1770 mAh/cm [4]. In addition to activated carbon, another potential material as an anode is bismuth oxide because this material has a volumetric capacity of 3765 mAh/cm and a potential difference of 2.8 V [5]. Based on
the potential of both materials, this study combines these two materials as a composite. The combination of the two materials is expected to generate better composite electrical properties.

2. Experimental Methods

2.1. Materials
The materials used in this study were rice husk, H$_3$PO$_4$, distilled water, HNO$_3$, and Bi(NO$_3$)$_3$.5H$_2$O. All the reagents were analytical grade bought from Merck, Germany.

2.2. Activated Carbon Synthesis
The clean rice husk was treated by pyrolysis at a temperature of 300°C for 10 minutes. Then 4 gram of carbon was activated using 100 mL of 60% H$_3$PO$_4$ and heated for 1 hour at 420°C. The activated carbon was then washed with distilled water until the constant pH was achieved. After a constant pH, the activated carbon is heated at 110°C for 10 minutes. The activated carbon obtained was then grinded and sieved with a size of 100 mesh.

2.3. Production and Characterization of Activated Carbon/Bi$_2$O$_3$ Composite
Activated carbon (CA) was mixed with Bi(NO$_3$)$_3$ (Bi) with a mass ratio variation of 2:1, 1:1, and 1:2. Then the mixture was put into an autoclave and heated with a hydrothermal process at a temperature of 100°C for 5 hours. The results of the hydrothermal process were filtered and dried at a temperature of 110°C for 10 minutes. The resulting composite materials were then characterized using SEM-EDX to identify the morphology and the elements present in the samples, FTIR to analyse the presence of Bi-O functional group of the products, XRD to identify the crystal structure of the composite and LCR (inductance, capacitance, resistance) meter to measure the conductivity of the products. All the measurements were undertaken on the products in the powder form. The measurement of electrical conductivity of products using LCR meter was undertaken by 1000 Hz frequency. The data obtained was resistance value and it was converted into electrical conductivity.

3. Results and Discussion

3.1. Characteristics of the functional groups determined by FTIR

![FTIR spectra of activated carbon and three composite samples](image)

**Figure 1.** FTIR spectra of activated carbon and three composite samples
Characterization of the composite materials was undertaken using FTIR instrument in the wavenumber range of 600-4000 cm\(^{-1}\). The purpose of this characterization was to determine the presence of functional groups in the samples.

FTIR spectra in Figure 1 show that the vibration mode is located in the vibration area of 3752 cm\(^{-1}\) and 3470 cm\(^{-1}\) corresponding to the absorption of –OH group [6]. The vibration mode around at 1622 cm\(^{-1}\) indicates the presence of C=C group [7]. In addition, there is also a silica content indicated by the absorption band at 1175 cm\(^{-1}\) and 810 cm\(^{-1}\) which are attributed to Si-O-Si and Si-OH groups, respectively [8]. The vibration mode observed at 1175 cm\(^{-1}\) is associated with the P=OOH group which may be the remaining of H\(_3\)PO\(_4\) activating agent [7]. Meanwhile, the three activated carbon/Bi\(_2\)O\(_3\) composite samples show a similar spectrum where the wave number of about 3637 cm\(^{-1}\) and 1613 cm\(^{-1}\) are assigned to the vibration peak of –OH and C=C groups, respectively [6]. Peak observed at 2980 cm\(^{-1}\) and 2892 cm\(^{-1}\) are attributed to aliphatic C-H group [6]. There is also a silica content in the form of Si-O-Si group observed at 1085 cm\(^{-1}\) and Si-OH at 962 cm\(^{-1}\) [8]. However, there are striking differences between activated carbon and activated carbon/Bi\(_2\)O\(_3\) composites in which there is a Bi-O-Bi vibration mode observed at 615 cm\(^{-1}\) and 779 cm\(^{-1}\) [9]. Moreover, peak at 1380 cm\(^{-1}\) indicates the presence of vibration mode of Bi-O stretching [10]. These results confirm the presence of these two materials, namely bismuth oxide and activated carbon, in the composite. A summary of the peaks in the FTIR spectra of the activated carbon and three composite is presented in Table 1.

| Functional groups | Samples | Activated carbon | CA:Bi 2:1 | CA:Bi 1:1 | CA:Bi 1:2 |
|-------------------|---------|------------------|-----------|-----------|-----------|
| -OH               | 3752; 3470 | 3663             | 3637      | 3635      |           |
| C=C               | 1622    | 1624             | 1613      | 1618      |           |
| C-H               | -       | 2982; 2902       | 2980; 2892| 2982; 2904|           |
| Si-O-Si           | 1175    | 1091             | 1085      | 1084      |           |
| Si-OH             | 810     | 962              | 962       | 961       |           |
| P=OOH             | 1175    | 1135             | 1136      | 1134      |           |
| Bi-O-Bi           | -       | 792; 604         | 779; 615  | 784; 602  |           |

3.2. The value of electrical conductivity determined by LCR meter

Table 2 shows the electrical conductivity values for all three composites and pure bismuth oxide. The value of electrical conductivity was determined by looking at a value of electrical conductivity which is stable to changes in frequency.

| Samples        | Electrical conductivity |
|----------------|-------------------------|
| Ca:Bi 2:1      | 0.59×10\(^{-5}\) S.m\(^{-1}\) |
| Ca:Bi 1:1      | 1.24×10\(^{-5}\) S.m\(^{-1}\) |
| Ca:Bi 1:2      | 0.51×10\(^{-5}\) S.m\(^{-1}\) |
| Pure Bi\(_2\)O\(_3\) | 1.56×10\(^{-7}\) S.m\(^{-1}\) |
Table 2 shows that the highest electrical conductivity value is found in composite composed of activated carbon and bismuth nitrate pentahydrate (Ca:Bi) with a ratio of 1:1 that is $1.24 \times 10^{-5}$ S.m$^{-1}$. Meanwhile, composites composed of activated carbon and bismuth nitrate pentahydrate with a ratio of 2:1 and 1:2 show almost the same electrical conductivity values that are $0.59 \times 10^{-5}$ S.m$^{-1}$ and $0.51 \times 10^{-5}$ S.m$^{-1}$, respectively. Furthermore, the values of the electrical conductivity of the three samples were much better than those of pure bismuth oxide purchased from Sigma Aldrich, Singapore. This electrical conductivity value is close to the ideal value for battery electrode candidate ($>1 \times 10^{-4}$ S.m$^{-1}$); however, another treatment need to conduct to enhance the electrical conductivity of the composite.

### 3.3. Composite components of CA: Bi 1: 1

Composite with the highest electrical conductivity value was then characterized using XRD to determine the constituent components. Based on the diffractogram shown in Figure 2 it can be seen that the composite composed of CA and Bi with a ratio of 1:1 indicates that the composite is composed of materials with a low crystallinity. However, there are also sharp peaks at 20 of 20.10, 22.10, and 25.20 indicating the presence of SiO$_2$ [11]. In addition, weak peaks at 20 of 27.30 and 33.00 indicate the existence of Bi$_2$O$_3$ [12]. Diffractogram peaks attributed to Bi$_2$O$_3$ planes are weak because the content of this material in the composite indicated by the concentration of Bi element is far less than Si and C and O elements which are the main components of activated carbon. However, the presence of weak diffractogram peaks attributed to bismuth oxide shows that bismuth oxide was successfully formed.

![Figure 2. X-ray diffractogram of CA: Bi 1: 1 composite](image)

Composite Figure 3 shows the SEM image and EDS spectrum of CA:Bi 1:1 composite. SEM images (Figure 3(a) and (b)) show that the composite is predominantly composed of carbon. This is also consistent with the EDS data in Figure 3(c). EDX data in Figure 3 (c) and Table 3 confirm that the largest element of CA:Bi 1:1 composite is carbon followed by oxygen and silicon with the atomic concentration values of 69.31%, 26.78%, and 2.67%, respectively. These three elements are the main components of activated carbon. Meanwhile, the content of the Bi element in the composite is very small, which is 0.20% atomic concentration. Therefore, it can be concluded that CA:Bi 1:1 composite consists of mainly activated carbon. Moreover, some elements: C, Si, Br, and P come from activated carbon.

### 3.4. The constituent elements of CA: Bi 1:1 Composite

Figure 3 shows the SEM image and EDS spectrum of CA:Bi 1:1 composite. SEM images (Figure 3(a) and (b)) show that the composite is predominantly composed of carbon. This is also consistent with the EDS data in Figure 3(c). EDX data in Figure 3 (c) and Table 3 confirm that the largest element of CA:Bi 1:1 composite is carbon followed by oxygen and silicon with the atomic concentration values of 69.31%, 26.78%, and 2.67%, respectively. These three elements are the main components of activated carbon. Meanwhile, the content of the Bi element in the composite is very small, which is 0.20% atomic concentration. Therefore, it can be concluded that CA:Bi 1:1 composite consists of mainly activated carbon. Moreover, some elements: C, Si, Br, and P come from activated carbon.
Figure 3. SEM image (a), mapping of elements distribution (b) and EDS spectrum (c) of CA:Bi 1:1 sample.

Table 3. Composite elements of CA: Bi 1: 1.

| Element Symbol | Element Name | Atomic Conc. | Weight Conc. |
|----------------|--------------|--------------|--------------|
| C              | Carbon       | 69.31        | 58.21        |
| O              | Oxygen       | 26.78        | 29.96        |
| Si             | Silicon      | 2.67         | 5.25         |
| Bi             | Bismuth      | 0.20         | 2.96         |
| Br             | Bromine      | 0.40         | 2.26         |
| P              | Phosphorus   | 0.63         | 1.37         |

4. Conclusion
Activated carbon/bismuth oxide composite was successfully synthesized through variations in the ratio of activated carbon and bismuth nitrate pentahydrate (CA:Bi) 1:1, 1:2 and 1:3 confirmed by FTIR and XRD analysis. The highest value of electrical conductivity is owned by composite produced using the CA:Bi with the ratio of 1:1 that is \(0.24 \times 10^{-5}\) S.m\(^{-1}\). This value is greater than the value of pure bismuth oxide electrical conductivity.
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