Physicochemical characteristics and electrical conductivity of bismuth oxide/activated carbon composite

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Abstract. Bismuth oxide/activated carbon composite was prepared from precursors of bismuth nitrate pentahydrate and activated carbon. At first, the Bi(NO₃)₃ solution was mixed with activated carbon. The activated carbon used varies, namely commercial activated carbon and activated carbon derived from rice husk. The resulting mixtures were then heated into a hydrothermal reactor at a temperature of 110°C for 5 hours. The results obtained were then characterized using FTIR, XRD and LCR meter. The results showed that Bi-O and Bi-O-Bi functional groups and α-Bi₂O₃ had appeared in both products indicating bismuth oxide had been formed. Meanwhile, the results of electrical conductivity characterization for bismuth oxide/rice husk activated carbon composite is higher than bismuth oxide/commercial activated carbon composites. In the future, bismuth oxide/activated carbon composites can be applied as materials for producing battery electrodes; however, further research must be undertaken.

1. Introduction

Battery is a device that functions as an electronic charger and works by converting chemical energy in the active materials contained into electrical energy through electrochemical reactions that encompass reduction and oxidation that occur at the electrodes [1]. There are two types of batteries, namely primary (non-rechargeable) and secondary (rechargeable) batteries. Secondary (rechargeable) batteries hold more promising outlook as they can be used for a long time, have a high energy density, and are reusable, thus, environmentally friendly. The main components of a battery include electrodes (anode and cathode), electrolyte, and separator. This research will focus on the anode, the negative electrode of the battery.

Anodes in batteries are generally made out of graphite, known for being a good conductor. Still, its theoretical capacity is considered low at 372 mAh.g⁻¹ [2]. Developments to increase this capacity can be done through using metal oxides as the electrode materials for the battery. One of the metal oxides that has the potential to be used as an anode is bismuth oxide as it has good electrochemical stability, good electrochemical reversibility, and high capacity [3]. Additionally, bismuth oxide has a volumetric capacity value of 3765 mAh.cm⁻³, a potential difference of 2.8 V, is non-toxic, and relatively low in cost [4]. However, the nature of bismuth oxide as a semiconductor causes its ability to conduct charges to be considerably low. To overcome this problem, additional material modifications can be made to help increase the conductivity of bismuth oxide. Most notably, activated
carbon, which can also be used as an anode material as it has a volumetric capacity of 1770 mAh.cm-1 and a potential difference of 0.2 V [5].

The combination of bismuth oxide and activated carbon into a composite can be done using the hydrothermal method. The hydrothermal method involves heterogeneous reactions in a water media carried out at high temperature and pressure (temperature > 100°C and pressure > 1 atm) in a closed system [6]. The hydrothermal process is carried out by heating a solution or mixture later reacted in an autoclave under vacuum. The hydrothermal method has advantages of requiring relatively low temperatures, providing a safe reaction process without the use of reducing agents [7].

2. Experimental Methods

2.1. Materials

The materials used in this study were crystal Bi(NO$_3$)$_3$.5H$_2$O from Sigma-Aldrich, 65% HNO$_3$ solution from Merck, distilled water, activated carbon synthesized from rice husks, and commercial activated carbon (coconut shell) from Brataco.

2.2. Procedures

2.2.1. Synthesis of Bismuth Oxide/Activated Carbon Composite

The synthesis of bismuth oxide/activated carbon composite (denoted as Bi/AC) was carried out using the hydrothermal method [8] with slight modifications. The modification of the composite synthesis was done by the varying the activated carbon used, namely commercial activated carbon and activated carbon from rice husks. The synthesis of commercial bismuth oxide/activated carbon composites began with the preparation of a solution of 0.5 M Bi(NO$_3$)$_3$ from 2.4253 grams of Bi(NO$_3$)$_3$.5H$_2$O crystal added with 10 ml of 0.04 M HNO$_3$ stirred until homogeneous. The Bi(NO$_3$)$_3$ solution was then mixed with 0.5 grams of commercial activated carbon. The resulting mixture was then heated in a hydrothermal reactor (as shown in Figure 1) at a temperature of 110°C for 5 hours.

![Figure 1. Hydrothermal reactor scheme.](image)

The product from the hydrothermal process were filtered and dried using an oven (Fischer Scientific Isotemp Model 630 F) at 110°C for 10 minutes. Later, it was sieved with a size of 100 mesh. The same procedure was also carried out for the synthesis of bismuth oxide/activated carbon (rice husks) composite.

2.2.2. Characterization of Bismuth Oxide/Activated Carbon Composites

The synthesized bismuth oxide/activated carbon (Bi/AC) composites were then characterized using FTIR (Shimadzu Prestige 21), XRD (Shimadzu 7000), and EIS analysis using LCR meter (Hioki...
Characterization using FTIR ( Fourier Transform Infrared Spectrometer) was carried out in the wavenumber range of 400 cm$^{-1}$ - 4000 cm$^{-1}$. FTIR analysis was done determine the functional groups of the resulting composite products. XRD (X-Ray Diffraction) characterization was carried out using an X-ray source originating from the Cu anode with the test parameters at the angles of 25° to 90°. Analysis using XRD served to identify the crystalline structure of bismuth oxide in the synthesized composites by comparing the diffractogram of the sample with the diffractogram from the JCPDS database (Joint Committee on Powder Diffraction Standards). EIS (Electrochemical Impedance Spectrometry) analysis using an LCR meter was carried out to determine the conductivity value of the resulting composite material. In this particular analysis, sample preparation stage was first carried out to transform the powders produced into pellets with a diameter of 1.5 cm and a thickness of 2 - 5 mm.

3. Results and Discussion

3.1. Synthesis of Bismuth Oxide/Activated Carbon Composite

In the synthesis of bismuth oxide/activated carbon composites, the Bi(NO$_3$)$_3$.5H$_2$O was first converted into Bi$_2$O$_3$. This was carried out by dissolving Bi(NO$_3$)$_3$.5H$_2$O into 0.04 M HNO$_3$ so that 0.5 M Bi(NO$_3$)$_3$ was formed. The preparation was intended to facilitate the interaction between Bi(NO$_3$)$_3$ and activated carbon. HNO$_3$ concentrated acid was used as bismuth dissolves well in concentrated acid and it allowed the formation of a solution containing Bi (III). The composites were made by mixing Bi(NO$_3$)$_3$ and activated carbon. The method used in making these composites was the hydrothermal method. During the hydrothermal process, bismuth oxide would form because NO$_3$ from Bi(NO$_3$)$_3$ would have experienced evaporation when it was heated, leaving Bi to form Bi$_2$O$_3$. The compressive power and temperature influence of water during the hydrothermal process caused the bismuth oxide formed to bind with the activated carbon and form a composite. The bonds that make up the composite were formed as a result of the van der waals forces between the surfaces of bismuth oxide and activated carbon. The bismuth oxide composites with both commercial activated carbon and rice husk activated carbon are shown in Figure 2.

![Figure 2](image)

*Figure 2. Composite synthesis products: (a) bismuth oxide/commercial activated carbon; (b) bismuth oxide/activated carbon from rice husk.*

As can be seen from the above figure, the bismuth oxide/commercial activated carbon composite and bismuth oxide/rice husk activated carbon composite emerged as blackish gray powder. The color of the resulting composites originates from the mixture of bismuth oxide, which is yellow [9], and activated carbon, which is black. This indicated the presence of activated carbon as the material functioned to increase the conductivity value of the composite.

3.2. Characterization of Bismuth Oxide/Activated Carbon Composites

Composites of bismuth oxide with commercial activated carbon and synthesized rice husks activated carbon were then characterized using FTIR, XRD, and an LCR meter.
3.2.1. Fourier Transform Infrared (FTIR) Characterization

Characterization using FTIR was aimed to determine the presence of functional groups present in the composite samples. This analysis was carried out by comparing the peaks of the samples spectra with the absorption area of a particular functional group. The FTIR spectra for the bismuth oxide/activated carbon composites and their comparison with the Bi$_2$O$_3$ and activated carbon spectra are shown in Figure 3.

The Bi/Commercial AC spectra presents the absorption areas of Bi-O and Bi-O-Bi groups at wavenumbers 1306.66 cm$^{-1}$ [10], 806.60 cm$^{-1}$ and 719.03 cm$^{-1}$ [11]. The FTIR spectra of Bi/Rice Husk AC also shows the presence of Bi-O and Bi-O-Bi groups at wave numbers 1358 cm$^{-1}$ [10] and 809 cm$^{-1}$ [12]. Some of these absorption areas correspond to the absorption areas of the pure Bi$_2$O$_3$ spectra, namely the Bi-O group at wavenumbers 1400 cm$^{-1}$ - 1300 cm$^{-1}$ and Bi-O-Bi at wavenumbers 900 cm$^{-1}$ - 700 cm$^{-1}$. This highly indicates that there was a bismuth oxide content in the Bi/Commercial AC and Bi/Rice Husk AC composite materials.

Moreover, the Bi/Commercial AC spectra illustrates the presence of C-O; C = C; and C-H groups at wavenumbers 1036.75 cm$^{-1}$, 1594.59 cm$^{-1}$; 2883.13 cm$^{-1}$ and 2979.52 cm$^{-1}$ [13]. The absorption areas are in accordance with the absorption areas possessed by commercial AC, which are C-O; C = C; and C-H groups at wavenumbers 1032.86 cm$^{-1}$; 1570.01 cm$^{-1}$; and 2883.30 cm$^{-1}$ and 2981.68 cm$^{-1}$. The FTIR spectra of the Bi/Rice Husk AC also shows absorption areas for the C = C; C-O; and Si-O groups at wavenumbers of about 1619 cm$^{-1}$ [14]; 1039.87 cm$^{-1}$; and 809.00 cm$^{-1}$. The vibration absorption areas are in accordance with the spectra shown by AC from rice husk, namely the wavenumbers 1032.86 cm$^{-1}$; 1570.01 cm$^{-1}$; and around 800 cm$^{-1}$ indicating the C-O; C = C; and Si-O groups. These absorption regions portray that activated was contained in the synthesized composites. The spectra regions of all samples (Bi/Commercial AC and Bi/Rice Husk AC), pure bismuth oxide [15], commercial AC, and AC from rice husk are summarized in Table 1.

![FTIR Spectra of Bismuth Oxide/Activated Carbon Composites, Bi$_2$O$_3$, and Activated Carbon](image)

**Figure 3.** FTIR spectra comparisons of Bi/Commercial AC and Bi/Rice Husk AC composites, pure Bi$_2$O$_3$, commercial AC, and rice husk AC.
Table 1. Functional groups data of FTIR spectra for Bi/Commercial AC, Bi/Rice Husk AC, bismuth oxide [15], commercial AC, and rice husk AC.

| Functional Group | Bi/AC (Commercial) | Bi/AC (Rice Husk) | Bismuth Oxide | Commercial AC | Rice Husk AC |
|------------------|---------------------|-------------------|--------------|---------------|--------------|
| Bi-O             | 1306.66 cm⁻¹        | 1358.72 cm⁻¹      | 1400 cm⁻¹    | -             | -            |
|                  | 1310.01 cm⁻¹        | 1300 cm⁻¹         |              |               |              |
| Bi-O-Bi          | 806.60 cm⁻¹         | 809.00 cm⁻¹       | 900 cm⁻¹     | -             | -            |
|                  | 719.03 cm⁻¹         | 722.92 cm⁻¹       | 700 cm⁻¹     |               |              |
| C-O              | 1036.75 cm⁻¹        | 1039.87 cm⁻¹      | -            | 1032.86 cm⁻¹  | 1032.86 cm⁻¹ |
| C=C              | 1594.59 cm⁻¹        | 1619.10 cm⁻¹      | -            | 1570.01 cm⁻¹  | 1570.01 cm⁻¹ |
| C-H              | 2883.13 cm⁻¹        | -                 | -            | 2883.30 cm⁻¹  | -            |
|                  | 2979.52 cm⁻¹        | 2981.68 cm⁻¹      | ± 800 cm⁻¹   |               |              |

Based on some of the group absorption areas, bismuth oxide and activated carbon as the building blocks of the composite have been successfully synthesized into composites.

3.2.2. X-Ray Diffraction (XRD) Characterization
Characterization using XRD was carried out to analyze the crystalline system of bismuth oxide contained in the composite. The diffractograms for bismuth oxide composites with both commercial and rice husk activated carbon and their comparison with the diffractogram of Bi₂O₃ are shown in Figure 4, meanwhile the 2θ value in Table 2.

Table 2. Comparison of XDR 2θ sample data with JCPDS database.

| Sample                  | Crystal            |
|-------------------------|--------------------|
| Bi/Commercial AC 2θ     | Bi/ Rice Husk AC 2θ |
| 27.771°                 | 27.771°            |
| 41.272°                 | 46.525°            |
| 52.578°                 | 52.508°            |

From the characterization with XRD, peaks are presented at 2θ 27.771°, 41.272°, and 52.578° for the Bi/Commercial CA composite and 27.771°, 46.525°, 52.508° for Bi/Rice Husk AC composite. The diffractogram data were then compared with the Joint Committee on Powder Diffraction Standards (JCPDS) database to determine the sample crystal system. The data obtained only show the presence of bismuth oxide in the samples as activated carbon is an amorphous material with low crystallinity and thus does not produce sharp peaks when characterized using XRD.
Figure 4. Comparison of XRD diffractograms of Bi/Commercial AC, Bi/Rice Husk AC with Bi$_2$O$_3$ (JCPDS).

The diffractogram peaks of the sample have similarities with the XRD diffractograms of the α-Bi$_2$O$_3$ crystal system, namely 27,377°, 46,305° and 52,273°. The results of these data indicate that the synthesized composite probably has a monoclinic crystal system or α-Bi$_2$O$_3$. Thus, bismuth oxide as the main material for composites has been successfully synthesized and has a good level of crystallinity.

3.2.3. Electrochemical Impedance Spectrometry (EIS) Characterization

EIS characterization was carried out using an LCR meter to determine the conductivity value of the bismuth oxide/activated carbon composite samples. The conductivity needs to be characterized in order to determine the ability of a material to conduct electric current. This is in association with the charge or ion conductivity of a material used as a battery electrode. The conductivities the composites, pure Bi$_2$O$_3$ and commercial activated carbon, and rice husk activated can be seen in Table 3.

Table 3. The conductivity values from the EIS test.

| Sample                        | Conductivity       |
|-------------------------------|--------------------|
| Bi/Commercial CA              | $0.905 \times 10^{-5}$ S.m$^{-1}$ |
| Bi/Rice Husk CA               | $2.59 \times 10^{-5}$ S.m$^{-1}$ |
| Commercial Activated Carbon   | $0.741 \times 10^{-5}$ S.m$^{-1}$ |
| Rice Husk Activated Carbon    | $8.17 \times 10^{-5}$ S.m$^{-1}$ |
| Pure Bi$_2$O$_3$              | $0.01555 \times 10^{-5}$ S.m$^{-1}$ [8] |
Table 3 presents that the conductivity value of bismuth oxide is smaller than that of activated carbon. The addition of activated carbon can increase the conductivity value of bismuth oxide as bismuth will have a lower crystallinity compared to pure bismuth oxide. A crystal arrangement that is not too dense and strong allows that ion/electron mobility to not be inhibited [16]. Additionally, the higher conductivity value of Bi/AC composites compared to pure Bi has been discussed in a research [17] regarding AC/Si$_2$O$_3$ composite as lithium ion battery anodes. In this study, it was explained that activated carbon (AC) acts as a matrix in the composite so that the Si distribution is more even and the conductivity value is higher. This finding is similar to that found in this study, where the presence of activated carbon (AC) as a matrix in the Bi/AC composite causes a more even distribution of Bi, meaning that the movement of Bi charges/ions is easier and thus increases the value of its conductivity. Furthermore, the measurement results from the EIS analysis show that the bismuth oxide and rice husk activated carbon composite had a higher conductivity value than the bismuth oxide and commercial activated carbon composite. This is because rice husks, which are agricultural waste, are a source of amorphous silica [18]. The synthesized amorphous silica produces high surface area, high porosity, high heat insulator value and very low dielectric constant that can be used in various applications, one of which is as a supercapacitor [19].

4. Conclusion
Functional groups of Bi-O and Bi-O-Bi and α-Bi$_2$O$_3$ observed in both products indicating bismuth oxide was formed in the composite. Meanwhile, the results of electrical conductivity characterization showed bismuth oxide/rice husk activated carbon composite is higher than bismuth oxide/commercial activated carbon composites. In the future, bismuth oxide/activated carbon composites can be applied as materials for producing battery electrodes; however, further research must be undertaken.

Acknowledgement
Authors would like to thank Faculty of Sciences and Mathematics also Ministry of Research and Technology/National Research and Innovation Agency, Indonesia for financial support in fiscal year 2020.

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