Study on Graphite and Graphene Performance as Electrode in Primary Cell Batteries

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Abstract

Synthesis of graphene were carried out with the Hummers Method. This study aimed to determine the characterization of graphite and graphene and the performance of graphite and graphene used as electrode in primary cell batteries. The structural analysis on graphite with XRD resulted in the diffraction peak C (002) at 20 = 26.36° with d-spacing 3.7721 Å with the result of graphene synthesis having decreased diffraction peak at 20 = 23.98° with d-spacing 3.707 Å. Morphological analysis on graphene with SEM image shows that there was a smaller pore size and wrinkled surface. The performance of graphite and graphene was measured by the results of conductivity test of graphene, Mn/Graphene and Cu/Graphene with 939 μS cm⁻¹, 551.4 μS cm⁻¹ and 481.1 μS cm⁻¹ respectively. This study proved that graphite and graphene were potentially used as electrode in primary cell batteries.

Keywords: graphene, Hummers method, Mn/graphene, Cu/graphene, XRD, SEM, conductivity

I. INTRODUCTION

Primary batteries were widely used in electronic devices that have low power requirements due to the construction of simple primary battery components. The main components of the primary battery was the carbon rods as cathode, zinc (Zn) as anode and mixed pastes MnO₂, carbon powder and NH₄Cl as electrolyte [1]. The production capacity of Mn-based dry batteries increased to two million units annually, so that the battery consumption would increase by more than two million units when combined with other companies every year [2]. The quality and cost of battery production was determined by the constituent material, so the primary battery is relatively more affordable. The disadvantages of primary batteries could be disposable and could not be recharged then an alternative was required to produce electrodes on primary battery cells that had longer lifetime so that the lifespan was longer. In the use and production of batteries should meet the requirements of quality standards in accordance with the Regulation of the Minister of Industry No.82/M-IND/PER/12/2016 was concerning the enforcement of mandatory primary SNI batteries.

Graphene was a layer of transparent material made of carbon-shaped graphite, thin layer plates with hexagonally arranged sp² bonds [3]. Since it was reported in 2004, graphene had attracted great interest because of its unique electron, thermal, and mechanical properties arising from a two-dimensional structure and how its potential technical applications [4]. Graphene had several advantages as carbon material, including unique electronic properties [5-10], mechanical resistance, superior thermal conductivity (~5000 W m⁻¹ K⁻¹) [11], high specific surface area (2600 m²/g) [12], high electrical conductivity (1250 S/m) [13], mechanical resistance [13-17], mobility of charge carriers (200000 cm² V⁻¹ s⁻¹) [18], the strongest material in the world and extraordinary electronic transport properties [19, 20] and also with low manufacturing cost [21]. Graphene had applications in many technological fields such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors and hydrogen storage [22, 23] fuel cells and capacitors [22]. Graphene was used as an electrode material in Li-ion batteries with a combination of manganese or copper so that the battery can last a little longer than the commercial primary battery [24].

Manganese was used as a material for making dry-cell batteries because it had sufficient electropositive properties and high electrical conductivity [25] that could be used as an electrode material with graphite alloys as well as manganese and graphene compounds had been used [26] and as an Mn/graphene cathode material having electrical conductivity of 579.5 μS/cm [27]. Graphene obtained electrical conductivity 0.00021 S/cm with 120 minutes of ultrasonication and 12 hours of hydrothermal time [28]. Copper was a p-type semiconductor material, which had been used for gas-sensors, solar energy conversion, and battery materials, with low energy and high catalytic activity, and non-toxic and affordable properties [29] but it was easy to experience electrode collapses and loss of interparticle contacts so that a matrix for the copper electrodes of graphene [30].

This study presented of the performance of graphite and graphene as electrodes in primary battery cells. The addition of graphene would increase the conductivity of the electrons and hence the ability of the battery cathode to conduct electricity better and the addition of metal could increase the quality of electronic interactions of graphene [31] and could be used as a supporting material as electrode in primary battery cell.
II. MATERIALS AND METHODS

A. Materials

Materials used in this study such as graphite, H₂SO₄, NaNO₃, KMnO₄, H₂O₂, NH₃, MnSO₄, CuSO₄, ethanol derived from merck sigma Aldrich with pure analysis (pa).

B. Synthesis of Graphene

Using the Hummers method [32], 5 g of graphite was inserted into beaker glass, added 5 g NaNO₃ and 375 ml H₂SO₄(l) and stirred for 5 hours in ice bath. 25 grams of KMnO₄(s) were added stepwise and stirred for 10 hours at 20 °C. Then moved from ice bath and stirred for 5 days at 35°C. Then 200 mL of 5% H₂SO₄ and 10 mL H₂O₂ 30% were added and stirred for 1 hour. Then centrifuged at 3000 rpm for 100 minutes to separate between the supernatant and the precipitate. Then 120 ml was added to the solution to remove the oxidizing agent and then added 500 ml of aquadest and ultrasonication on 50/60 Hz for 5 hours. Then 50 mL of NH₃ 10 M was added and stirred for 48 hours, filtered and dried at 80°C for 24 hours to obtain graphene powder. The graphene powder was characterized by XRD, SEM and tested with the Conductometer.

C. Preparation of Electrodes in Primary Cell Battery

Preparation of electrodes in primary cell battery was performed on various variations in grams of 0.1:0.1 and 0.3:0.7 in graphite/graphene, Mn/graphite, Mn/graphene, Cu/graphite and Cu/graphene. In the comparison variation 0.1: 0.1 ie by weighing 0.1 grams of graphite and graphene, each added 50 ml of ethanol and stirred for an hour. Then graphite/ethanol solution and graphene/ethanol solution were mixed and stirred again for 2 hours. The solution was filtered and dried. In the comparison variation 0.3: 0.7 ie by weighing 0.3 grams of graphite and 0.7 grams of graphene, each added as much as 50 ml of ethanol and stirred for an hour. Then the solution of graphite/ethanol and graphene/ethanol solution were mixed and stirred again for 2 hours. The solution was filtered and dried. The same procedure was performed for variation in gram ratio of 0.1:0.1 and 0.3:0.7 in Mn/graphite, Mn/graphene, Cu/graphite and Cu/graphene. Then the results were characterized by XRD and tested conductivity with the Conductometer.

D. Analysis of Results

X-ray diffraction analysis (XRD) was using X-Ray Rigaku Smartlab 3 kW tool. Cu-Kα radiation used (1.540598 Å) to observe samples from 5 ° to 70 ° with an intensity change curve of 2ɵ (degree), scan speed 2o min⁻¹, 44 kV, and 40 mA current. SEM was using SEM type EM 30 COXEM with a voltage of 20,000 kV with enlargement 100-5000 times. Conductivity analysis performed by using AC780-Conductivity Meter i-SOLV at room temperature.

III. RESULTS AND DISCUSSION

A. Crystal Analysis of Graphene with XRD

The graphene crystal structure was analyzed using XRD. Figure 1 shows graphite structure analysis having a sharp diffraction peak at 26.36° with C (002) having a d-spacing of 3,372 Å showing high crystallinity properties, as reported previously [33]. However, after the oxidation process, the diffraction peak shifted to 9,535° with 9,628 Å d-spacing indicating the formation of graphene oxide due to the introduction of oxygen into the interlayer space in graphite [34].

![Graphene Analysis](image.png)

Fig. 1: Pattern of Graphite, Graphene Oxide dan Graphene
The presence of functional groups such as hydroxyl groups, epoxy groups, carboxyl groups, and carbonyl groups in graphene oxide could spread the distance between layers to facilitate the exfoliation process [35]. This was seen in the increasingly wide d-spacing of 3.372 Å to 9.628 Å. In addition, the formation of a wider peak indicated the decreasing nature of crystallinity because the entry of the functional group into the graphite structure would impair the regularity of the structure. In the reduction process to graphene, the graphene structure analysis with XRD had a diffraction peak at 23.98° with C (002) with d-spacing 3.707 Å as previously reported [36]. The graphene peak had a very low intensity, decreasing compared to graphite indicating that the grains tend to have an amorphous crystal structure. This indicated there had been a reduction of some functional groups by ammonia reduction and the rearrangement of the structure of graphene. There were several other sharp peaks with diffraction peaks at 26.335° and 27.46° with d-spacing of 3.381 Å and 3.245 Å respectively. The peak C (002) in the sharp graphene showed that the formed graphene had not been single layer [37].

B. Crystal Analysis of Electrode in Primary Cell Battery with XRD

The crystal structure of the electrode in a primary cell battery was performed on various variations in grams of 0.1:0.1 and 0.3:0.7 in graphite/graphene, Mn/graphite, Mn/graphene, Cu/graphite and Cu/graphene analyzed by using X-ray diffractometer. In Figure 2a the graphite/graphene ratio (0.1:0.1) had a sharp diffraction peak at 26.475° with d-spacing 3.364 Å and graphite:graphene (0.3:0.7) had a sharp diffraction peak at 26.53° with d-spacing 3.357 Å. The result of analysis with XRD showed that in the graphite/graphene mixture the ratio of 0.1:0.1 and 0.3:0.7 position 2θ shifted toward the addition of the number of graphene, but the formed graphene had not been single layered, it was seen from the peak that still sharp [38].
In Figure 2b the Mn/graphite ratio (0.1:0.1) had a sharp diffraction peak at d-spacing of 3.517 Å and at 17.976° with d-spacing of 4.93 Å. In Mn/graphite (0.3:0.7) had a sharp diffraction peak at 26.516° with d-spacing 3.358 Å and diffraction peak at 25.26° with d-spacing 3.522 Å. In the ratio of 0.1:0.1 and 0.3:0.7 there was a diffraction peak at 34.506° with d-spacing 2.596 Å and 34.277° with d-spacing 2.614 Å respectively, this indicated the presence of manganese deposited in graphite and there was a shift towards adding larger amounts of graphite because manganese had chemical properties similar to graphite. The results of manganese and graphite analysis still had a sharp peak, but the intensity was low and the crystallinity had decreased [39]. In Figure 2c the Mn/graphene (0.1:0.1) ratio had a sharp diffraction peak at 25.33° with d-spacing 3.513 Å, and other diffraction peaks at 28.371° with d-spacing 3.143 Å and at 26.51° with d-spacing 3.360 Å. In Mn/Graphene (0.3:0.7) had a sharp diffraction peak at 25.274° with d-spacing 3.521 Å and another diffraction peak at 26.41° with d-spacing 3.373 Å. The peak at 34.739 with 2.58 sp d-spacing in both comparisons indicated that manganese had been deposited into graphene.

In Figure 2d the ratio of Cu/graphite (0.1:0.1) and (0.3:0.7) had a sharp diffraction peak at 26.50° with d-spacing of 3.360 Å and at 26.20° with d-spacing 3.398 respectively. The absence of other diffraction peaks because copper was not deposited into graphite. This was because the sp³ bonds on graphite form a weak sigma bond on the copper metal. In Figure 2e the ratio of Cu/graphene (0.1:0.1) had a sharp diffraction peak at 26.455° with d-spacing of 3,362 Å, and some other sharp diffraction peaks were at 18.716° with d-spacing 4,737 Å, at 23.921° with d-spacing 3.7170 Å. In Cu/graphene (0.3:0.7) had a sharp diffraction peak at 26.474° with d-spacing 3,364 Å and some other diffraction peaks were at 23.942° with d-spacing 3.71377 Å and 18.73° with d-spacing 4,733 Å. The existence of diffraction peak at 32.46° with d-spacing 2.7557 Å in Cu/graphene (0.1:0.1) showed that Cu was deposited into graphene because graphene was carbon sp², which in bonds there was a phi bond that formed a strong bond to copper metal.

C. Morphological Analysis of Graphene with SEM

Morphological analysis on graphene surface with enlargement 2000 and 5000 times were showed in Figure 3. In SEM image of A and B showed that graphene appear to be thin and the smaller pore size and wrinkled surface [40]. This was due to the imperfection of the reduction process with ammonia that had not been able to create a single-layered graphene structure [4] because of the presence of impurities atoms that were residual reducers and solvents attached to the graphene.

Fig. 3: Image of SEM on Graphene Surface with Enlargement (A) 2000 times and (B) 5000 times
D. Conductivity Analysis

Conductivity analysis on commercial battery, graphite and graphene cathodes and variations in grams of 0.1:0.1 and 0.3:0.7 in graphite/graphene, Mn/graphite, Mn/graphene, Cu/graphite and Cu/graphene by using Conductometer type AC780-Conductivity Meter i-SOLV at room temperature could be seen in Table 1. Based on the results of conductivity analysis of the data graphene had the greatest conductivity value of 939 μS cm\(^{-1}\). In accordance with previous research with graphene conductivity analysis was 921 μS cm\(^{-1}\) (Lodo, 2016). It was because graphene has a higher electron mobility than graphite and based on the SEM morphology results in graphene, the structure and spacing between layers in the small graphene causing the electrons to flow more smoothly because there were not many oxygen blocking functions. Graphene was flat structure with a specific surface area of 2630 m\(^2\)/g so that electrons can mobility to all surfaces and electrical conductivity either very potentially applicable to various electronic devices including solar cells, touch screens and Li-ion batteries [42].

In the variation ratio 0.3:0.7 in Mn/Graphene and Cu/Graphene had a high conductivity value that was 551.4 μS cm\(^{-1}\) and 481.1 μS cm\(^{-1}\), this was due to graphene was a carbon sp\(^2\) with π bond when bonded with the metal, formed a stable and strong covalent bond during its use. Graphite/graphene, Mn/graphite and Cu/graphite conductivity values in comparison variations were higher than the cathode on commercial batteries was 115 μS cm\(^{-1}\), because the commercial battery cathode were only slightly soluble in ethanol to obtain small conductivity measurements on a commercial battery cathode. Therefore, based on the magnitude of the conductivity value of graphene, graphene was expected to be a supporting material as an electrode on the primary cell batteries.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comparison</th>
<th>Measurement of Conductivity (μS/cm)</th>
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<tr>
<td></td>
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<tr>
<td>Commercial Battery Cathode</td>
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<tr>
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<td>Graphene</td>
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IV. CONCLUSION

The result of characterization of structural analysis on graphite and graphene with XRD indicated there had been a reduction of functional group and deposite of metals. The morphological analysis on graphite and graphene with SEM photographs showed that graphene didnot appear to be thin, but still indicated by the presence of graphene because of the smaller pore size and the wrinkled surface in both variations with the manganese and copper metals. Graphite and graphene performance could be measured by conductivity test that resulted graphene conductivity had the greatest value was 939 μS cm\(^{-1}\) because graphene had a higher electron mobility than graphite. In the variation ratio 0.3:0.7 in Mn/Graphene and Cu/Graphene had a high conductivity value were 551.4 μS cm\(^{-1}\) and 481.1 μS cm\(^{-1}\) respectively. Graphene was expected to be a supporting material as an electrode on the primary cell batteries.

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REFERENCES


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