Performance of graphite and graphene as electrodes in primary cell battery

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Abstract. Synthesis of graphene has been successfully done with the Hummers Method. This study aims to determine the characterization of graphite and graphene and the performance of graphite and graphene used as electrodes in primary cell batteries. The structural analysis on graphite with XRD resulted in the diffraction peak C(002) at 2θ = 26.369° with d-spacing 3.37721 Å with the result of graphene synthesis having decreased diffraction peak at 2θ = 23.98° with d-spacing 3.707 Å. The performance of graphite and graphene is 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 μScm⁻¹ respectively. This study proves that graphite and graphene are potentially used as electrodes in primary cell batteries.

1. Introduction

Primary batteries are 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 are 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 increases to two million units annually, so battery consumption will increase by more than two million units when combined with other companies year after year [2]. The quality and cost of battery production is determined by the constituent material, so the primary battery is relatively more affordable. The disadvantages of primary batteries can only be disposable and cannot be recharged then an alternative is required to produce electrodes on primary battery cells that have longer life time so that the life span is longer. In the usage and production of batteries shall meet the requirements of quality standards in accordance with the Regulation of the Ministry of Industry No.82/M-IND/PER/12/2016 concerning the enforcement of mandatory primary SNI batteries.

Graphene is 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 has 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 has several advantages as carbon material, including unique electronic properties, superior thermal properties, large touch surface area, mechanical resistance, high conductivity, the strongest material in the world, super conductors and can
be applied to fuel cells and capacitors [5]. Zhu, et al (2010) used graphene as an electrode material in Lithion batteries with a combination of manganese or coppers on that the battery can last a little longer than the commercial primary battery [6].

Manganese is used as a material for making dry-cell batteries. This is because manganese has sufficient electro positive properties and high electrical conductivity [7] that can be used as an electrode material with graphite alloys as well as manganese and graphene compounds have been used by Wang, etal., 2011 [8], and as an Mn/graphene cathode material having electrical conductivity of 579.5 μS/cm [9]. Graphene obtains electrical conductivity 0.00021 S/cm with 120 minutes of ultrasonication time and 12 hours hydro thermal time [10].

Copper is a p-type semiconductor material, which has been used for gas-sensors, solar energy conversion, and battery materials, with low energy and high catalytic activity, and non-toxic and affordable properties [11] but it is easy to experience electrode collapses and loss of inter particle contacts so that a matrix for the copper electrodes of graphene has been performed by Rai, et al., 2013 [12]. Therefore, the researcher is interested in conducting research on the study of the performance of graphite and graphene as electrodes in primary battery cells. In addition of graphene will increase the conductivity of the electrons and hence the ability of the battery cathode to conduct electricity will be better and the addition of metal can increase the quality of electronic interactions of graphene [13]. It is hoped that graphene can be a supporting material in the primary battery cathode cell.

2. Materials and Methods
2.1 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).

2.2 Synthesis of Graphene Oxide
Using the Hummers method, 5g of graphite was inserted into beaker glass, added 5g NaNO₃ and 375 ml H₂SO₄(l) and stirred for 5h ours in ice bath.25 grams of KMnO₄(s) are added step wise and stirred for 10 hours at 20°C. Then it was 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 a hour. Then, it was 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 5hours. Then, 50mL 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 and tested with conductometer.

2.3 Preparation of Electrodes in Primary Cell Battery
Preparation of electrodes in primary cell battery is 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, eacha dded 50 ml of ethanol and stirred for an hour. Then, graphite/ethanol solution and graphene/ethanol solution are mixed and stirred again for 2 hours. The solution is 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 is filtered and dried. The same procedure is 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.
2.4 Analysis of Results
X-ray diffraction analysis (XRD) is using X-Ray Rigaku Smartlab 3kW tool. Cu-Kα radiation used (1.540598Å) to observe samples from 5 to 70° with an intensity change curve of 20 (degree), scan speed 2° min-1, 44 kV, and 40 mA current. Conductivity analysis performed using AC 780-Conductivity Meteri-SOLV at room temperature.

3. Results and Discussion
3.1 Crystal Analysis of Graphene with XRD
The graphene crystal structure was analyzed using X-ray diffractometer. Figure 1 shows graphite structure analysis having a sharp diffraction peak at 26.369° with C(002) having a d-spacing of 3.372Å showing high crystalline properties, as reported previously (Shao, 2012). However, after the oxidation process, the diffraction peak shifted to 9.535° with 9.628Å d-spacing indicating the formation of graphene oxide due to the introduction of oxygen into the interlayer space in graphite [14].

![Figure 1. Pattern of Graphite, Graphene Oxide and Graphene](image)

The presence of functional groups such as hydroxyl groups, epoxy groups, carboxyl groups, and carbonyl groups in graphene oxide can spread the distance between layers to facilitate the exfoliation process. This is seen in the increasingly wide d-spacing of 3.372 to 9.628 Å. In addition, the formation of a wider peak indicates the decreasing nature of crystalline because the entry of the functional group into the graphite structure will impair the regularity of the structure.

In the reduction process to graphene, the graphene structure analysis with XRD has a diffraction peak at 23.98° with C(002) with d-spacing 3.707Å as previously reported (Suwandana, 2015). The graphene peak has a very low intensity, decreasing compared to graphite indicating that the grains tend to have an amorphous crystal structure. This indicates there has been a reduction of some functional groups by ammonia reduction and the rearrangement of the structure of graphene. There are several other sharp peaks with diffraction peaks at 26.335° and 27.46° with d-spacing of 3.381 and 3.245Å, respectively. The peak C(002) in the sharp graphene shows that the formation of graphene has not been single layer [15].
3.2 Crystal Analysis of Electrode in Primary Cell Battery with XRD

The crystal structure of the electrode in primary cell battery is 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 was analyzed by using X-ray diffractometer. In Figure 2a the graphite/graphene ratio (0.1 : 0.1) has a sharp diffraction peak at 26.475° with d-spacing 3.36 Å and graphite : graphene (0.3 : 0.7) has 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 formation of graphene has not been single layer, it is seen from the peak that still sharp [16]. In Figure 2b the Mn/graphite ratio (0.1 : 0.1) has a sharp diffraction peak at d-spacing of 3.517 and 17.976° with d-spacing of 4.93 Å. In Mn/graphite (0.3 : 0.7) has 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 is a diffraction peak at 34.506° with d-spacing 2.596 Å and 34.277° with d-spacing 2.614 Å, respectively, this indicates the presence of manganese deposited in graphite and there is a shift towards adding larger amounts of graphite because manganese has chemical properties similar to graphite. The results of manganese and graphite analysis still have a sharp peak, but the intensity is low and the crystalline has been decreased [17].

![Figure 2](image-url)
In Figure 2c, the Mn/graphene (0.1 : 0.1) ratio has a sharp diffraction peak at 25.33° with d-spacing 3.513Å, and other diffraction peaks at 28.371° with d-spacing 3.143Å and at 26.51° with d-spacing 3.360Å. In Mn/Graphene (0.3 : 0.7) there is a sharp diffraction peak at 25.274° with d-spacing 3.521Å and another diffraction peak at 26.41° with d-spacing 3.373Å. The peak at 34.73° with 2.58 spaces d-spacing in both comparisons indicates that manganese has been deposited into graphene. In Figure 2d the ratio of Cu/graphite (0.1 : 0.1) and (0.3 : 0.7) has a sharp diffraction peak at 26.50° with d-spacing of 3.360 Å and at 26.20° with d-spacing 3.398. The absence of other diffraction peaks because copper is not deposited into graphite. This is 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) has a sharp diffraction peak at 26.455° with d-spacing of 3.362Å, and some other sharp diffraction peaks that is at 18.716° with d-spacing 4.737Å, at 23.921° with d-spacing 3.717Å. In Cu/graphene (0.3 : 0.7) has a sharp diffraction peak at 26.474° with d-spacing 3.364Å and some other diffraction peaks that is at 23.942° with d-spacing 3.713Å and 18.73° with d-spacing 4.733Å, indicating, the existence of diffraction peak at 32.465° with d-spacing 2.755Å. In Cu/graphene (0.1 : 0.1), it shows that Cu is deposited into graphene because graphene is carbon sp², which in bonds there is a π-bond, when it was bound to copper metal, forming a strong bond.

3.3. 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 using AC780-Conductivity Meteri-SOLV at room temperature can be seen in Table1. Based on the results of conductivity analysis of the above data graphene has the greatest conductivity value of 939 μScm⁻¹. In accordance with previous research with graphene conductivity analysisis 921 μS cm⁻¹ [9]. This is caused 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 are not many oxygen blocking functions. Graphene is flat structure with specific surface area of 2630 m²/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 [18].

In the variation ratio 0.3 : 0.7 in Mn/graphene and Cu/Graphene has a high conductivity value that is equal to 551.4 μScm⁻¹ and 481.1 μS cm⁻¹, this is due to graphene is a deep carbon sp² bond is a π-bond which, bonding with the metal is formed stable and strong covalent bond during its is used. Graphite/Graphene conductivity, Mn/Graphite and Cu/Graphite conductivity values in comparison variations were higher than the cathode on commercial batteries of 115 μScm⁻¹, because the commercial battery cathodes 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 is expected to be a supporting material on the primary battery cathode cell.
Table 1. Conductivity analysis on commercial battery cathode, 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.

| Sample          | Comparison | Measurement of Conductivity (μS/cm) |
|-----------------|------------|-----------------------------------|
| Commercial      | -          | M1  | M2  | M3  | Average |
| Battery Cathode |            | 115.00 | 115.05 | 115.05 | 115     |
| Graphite        |            | 101.10 | 101.10 | 101.10 | 101.1   |
| Graphene        |            | 939.05 | 939.03 | 939.01 | 939     |
| Graphite/Graphene| 0.1 : 0.1 | 161.15 | 161.15 | 161.16 | 161.2   |
|                | 0.3 : 0.7 | 333.61 | 333.59 | 333.60 | 333.6   |
| Mn/Graphite     | 0.1 : 0.1 | 224.22 | 224.23 | 224.22 | 224.2   |
|                | 0.3 : 0.7 | 317.38 | 317.37 | 317.37 | 313.4   |
| Mn/Graphene     | 0.1 : 0.1 | 411.49 | 411.49 | 411.48 | 411.5   |
|                | 0.3 : 0.7 | 551.35 | 551.35 | 551.35 | 551.4   |
| Cu/Graphite     | 0.1 : 0.1 | 112.21 | 112.21 | 112.23 | 112.2   |
|                | 0.3 : 0.7 | 234.14 | 234.13 | 234.13 | 234.1   |
| Cu/Graphene     | 0.1 : 0.1 | 339.05 | 339.03 | 339.03 | 339     |
|                | 0.3 : 0.7 | 481.14 | 481.14 | 481.14 | 481.1   |

4. Conclusion
Graphite and graphene’s performance can be measured by conductivity test resulting indicate that graphene’s conductivity has the greatest value among the others (939 μS/cm-1). In the variation ratio 0.3 : 0.7 in Mn/graphene and Cu/graphene has a high conductivity value that is equal to 551.4 μS cm-1 and 481.1 μS/cm-1. The value of cathode conductivity on commercial batteries of 115 μS/cm-1 is lower than that of graphite/graphene, Mn/graphite and Cu/graphite.

Acknowledgement
We would like to thankful for Rector of Universitas Sumatera Utara who supported financing of this research (TALENTA USU, 2018, No.2590/UN5.1.R/PPM/2018, 16 Maret 2018).

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