Electrical Properties of Electrochemically Exfoliated Graphite with Copper Addition

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Abstract. In this study, the electrical properties of exfoliated graphite (EG) with copper addition is reported. Firstly, EG samples were synthesized using electrochemical exfoliation of the pre-treated graphite sheet then combined with various copper concentrations. X-Ray Diffraction (XRD) characterization indicated that the composites of EG, Cu, and Cu\(_2\)O were formed. A higher Cu\(_2\)O amount obtained when the higher concentration of copper precursor was added in the EG. Scanning Electron Microscopy (SEM) images showed that more particles with larger sizes were anchored on the EG surface as higher copper concentration. The electrical properties of the samples were measured using the four-point probe method. The highest electrical conductivity of 37.86 S/cm was produced in the EG sample with 1 wt.% of copper addition. The result reveals that the optimum copper addition can increase the electrical properties of EG.

1. Introduction

Graphite is a carbonaceous material that has sp\(^2\)-hybridized carbon atoms forming the hexagonal lattice[1]. The sp\(^2\)-hybridized carbon atoms obtain free \(\pi\)-electron electron clouds responsible for its high electrical conductivity properties[2, 3]. The excellent electrical properties make this material suitable to realize the high power density of energy storage devices such as lithium-ion batteries and supercapacitors[4, 5]. However, due to the increasing demand for high capacity devices, especially for electrical vehicles, the capacity of graphite is not enough to fulfill this requirement. Therefore, the modification of graphite as the active material of electrodes is needed. Exfoliation of graphite has been one of the straightforward strategies to enhance the capacity of the graphite-based electrode by increasing the surface area of electrode material, which is used to store the ions or charges [6].

Currently, various methods to exfoliate the graphite have been introduced, such as micromechanical exfoliation[7], chemical exfoliation[8], direct liquid phase exfoliation[9], and electrochemical exfoliation[10]. Among them, electrochemical exfoliation has gained enormous
attention due to its easy-processability, high scalability, and tunability properties of the resulted product[11]. This process is conducted by applying voltage bias to the graphite electrode as a precursor and another inert electrode as the counter electrode which are submerged in an electrolyte. Based on the applied potential into graphite precursor, electrochemical exfoliation can be divided into cathodic exfoliation (negative bias is given into graphite precursor) and anodic exfoliation (positive bias is given into graphite precursor). Cathodic exfoliation is usually conducted in organic or ionic liquid electrolytes. By using these electrolytes, the defect of the resulted exfoliated graphite (EG) can be minimized because the oxidation process is not involved[12]. However, these electrolytes are expensive and cause pollution, making them not applicable to large scale production[13]. On the other hand, anodic exfoliation can be carried out in the water-based electrolytes, thus makes it cheaper and more eco-friendly[14]. However, the oxygen functionalities formation in the resulted EG synthesized using this method is inevitable since this route needs oxidation of graphite to open the graphite interlayer before the delamination process[15]. The oxygen functionalities can cause the loss of free π-electrons, thus the electrical conductivity of the resulted EG is decreased[3].

Previously, we reported that the addition of copper could enhance the electrical conductivity of reduced graphene oxide (rGO) in the optimum amount[16]. The addition of copper up to 1 wt. % could increase the electrical conductivity of rGO up to 44 %. This phenomenon happened because the metallic Cu could provide extra charge carriers for improving electrical conduction. When the copper amount was increased until 5 wt. %, the electrical conductivity of samples was decreased. The higher amount of Cu$_2$O produced in this samples was caused by incomplete reduction of Cu$^{2+}$ species as the precursor. The presence of Cu$_2$O could decrease the electrical conductivity due to less conductive properties of this species than Cu.

In this work, we study the electrical conductivity of the electrochemically exfoliated graphite with copper addition. Before the electrochemical exfoliation process, the graphite sheet precursor was pretreated in the H$_2$SO$_4$/H$_2$O$_2$ mixture solution. In our previous result, this pre-treatment could also improve the electrical conductivity of EG in the appropriate volume fraction[17]. By combining the addition of copper and pre-treatment of the graphite sheet, the electrical conductivity of the resulted EG is expected to be increased.

2. Method
The pre-treatment of the graphite sheet was carried out similar to the route reported in our previous work [17]. The pre-treatment of the graphite sheet was conducted in the H$_2$SO$_4$/H$_2$O$_2$ mixture solution with avolume fraction of 95:5 vol. % for 5 minutes. After that, the pre-treated graphite sheet was electrochemically exfoliated by applying a positive potential of 15 V in 0.1 M (NH$_4$)$_2$SO$_4$ electrolyte. In this process, Pt wire was acted as the counter electrode. The exfoliation process was conducted until the submerged part of the graphite was entirely dissociated. It was signed with a current of 0 A shown in the power supply display. The exfoliated product was then rinsed using DI water until pH ~ 7 and followed by ethanol washing. The washed sample was dried in the oven at 60 °C for 2 h.

The dried sample was then dispersed in ethylene glycol (1 mg/mL) by the sonication process for 30 minutes and followed by vacuum filtration to obtain the supernatant. The supernatant was mixed by Cu (NO$_3$)$_2$.2H$_2$O solution in ethylene glycol with the copper composition of 1 and 5 wt. % to produce EG/Cu$^{2+}$ suspension. The mixture was stirred using a magnetic stirrer for 15 minutes and homogenized using Ultra-turrax homogenizer for 40 minutes, subsequently. After that, EG/Cu$^{2+}$ suspension was reduced using hydrazine (1 mL for 1 g of EG) with microwave assistance in low mode for 20 minutes to obtain EG/Cu/Cu$_2$O composites. After the reduction process, the resulted sample was washed with DI water to remove the ethylene glycol by vacuum filtration. The washed sample was dried in the oven at 80 °C for 2 h to acquire the powder formed sample. The resulting samples were named based on the added of the Cu amount through EG/Cu$^{2+}$ mixtures i.e., EG/Cu/Cu$_2$O 1 wt. % and EG/Cu/Cu$_2$O 5 wt. %. As the control experiment, the EG sample without copper addition was also synthesized with the similar method above.
The samples were characterized using X-ray Diffractometer (XRD, Bruker D8 Advance, Bruker) with Cu-Kα radiation (λ=1.54056 Å) to study the formed crystalline structure in the samples. Besides, the morphology of the samples was also observed using Scanning Electron Microscope (SEM, SU3500, Hitachi). The electrical conductivity was measured using the four-point probe method. The four probes were connected to the current source (R6240A, Advantest) and multimeter (2100 Series: 6½-digit USB multimeter, Keithley). Before electrical conductivity measurement, the powder samples were pressed using press equipment to obtain the bulk pellet form.

3. Result and Discussion

Figure 1 shows the X-ray diffractogram of EG and EG with various amounts of copper addition. The peaks at 20 ~ 26° are originated from the (002) plane of graphitic structure[18]. The sharp peaks in these samples indicate good crystallinity of the resulted EG due to mildly oxidized samples during the electrochemical exfoliation process [19]. Meanwhile, the peaks at 20 ~ 42° and 54° (shown in the inset) are the characteristics of (101) and (004) plane of EG [20]. In the EG samples with copper addition (1 wt.% and 5 wt.%), peaks at 43°, 50°, and 74° are attributed to (111), (200), and (311) planes of Cu based on JCPDS-04-0836[21]. In the sample with copper addition of 1 wt.%, there are also peaks at 42.5° and 78°, which indicate the formation of (200) and (222) planes of Cu2O(JCPDS-05-0667). Whereas, in the sample with Cu addition of 5 wt.%, there are other peaks at 36° and 61.5°, which correspond to (111) and (220) plane of Cu2O, respectively[22].

![XRD patterns](image)

**Figure 1.** XRD patterns of EG, EG/Cu/Cu2O 1 wt.%, and EG/Cu/Cu2O 5 wt.%. The inset demonstrates the enlarged XRD patterns at the range of 2θ = 30° - 80°.
An incomplete reduction of Cu$^{2+}$ species into metallic Cu apparently causes the presence of Cu$^{+}$ species in the form of Cu$_2$O. The ratio of the total integrated area below Cu$_2$O and Cu peaks (A-Cu$_2$O/A-Cu) was used to analyze the amount of Cu$_2$O in the samples quantitatively. Based on this calculation, the A-Cu$_2$O/A-Cu of EG/Cu/Cu$_2$O 1 wt.% and EG/Cu/Cu$_2$O 5 wt.% are 0.6 and 1.5, respectively. These results indicate that the Cu$_2$O amount in the EG/Cu/Cu$_2$O 5 wt.% is larger than EG/Cu/Cu$_2$O 1 wt.%. It reveals that the formation of Cu$_2$O is preferable in a higher amount of copper addition. The incomplete reduction of Cu$^{2+}$ species is suggested due to less volume of the hydrazine used to reduce Cu$^{2+}$ since the volume of this substance was maintained same although the Cu$^{2+}$ amount in precursor was increased.

![Figure 2](image1.png)

**Figure 2.** SEM images of a) graphite sheet, b) EG/Cu/Cu$_2$O 1 wt.%, and c) EG/Cu/Cu$_2$O 5 wt.%. SEM images of graphite sheet, EG/Cu/Cu$_2$O 1 wt.%, and EG/Cu/Cu$_2$O 5 wt.% were demonstrated in Figure 2. SEM image of the graphite sheet shows well-stacked layers with smooth morphology. After the exfoliation process, the graphite sheet layers were delaminated into thinner or disordered layers. In EG/Cu/Cu$_2$O 1 wt.% sample, the dot-like particles deposited on the EG layers were recognized as Cu or Cu$_2$O particles. Meanwhile, in EG/Cu/Cu$_2$O 5 wt.%, the Cu or Cu$_2$O particles were found more frequently with irregular shapes and larger sizes than the Cu or Cu$_2$O particles in EG/Cu/Cu$_2$O 1 wt.. This observation indicates that a larger amount of copper addition apparently increases the opportunity of Cu or Cu$_2$O particles to aggregate.

![Figure 3](image2.png)

**Figure 3.** The electrical conductivity results of EG with various copper concentration measured using four-point probe method. The inset shows the scheme of electrical conductivity measurement by four-point probe method.
The electrical conductivity measurements were exhibited in Figure 3. From this graphic, it can be seen that the electrical conductivity of EG increases when 1 wt.% copper is added. The highest electrical conductivity value is 37.86 S/cm. This improvement can be caused by several reasons. The first reason is that the metallic Cu (Cu$_{\text{metal}}$) could provide extra electron into EG thus the carrier concentration increases and lead to improvement of electrical conductivity[23]. The second reason is the role of Cu as the bridge for allowing electron conduction over vacancies or sp$^3$-hybridized carbon atoms resulting from the oxidation process during electrochemical exfoliation[16]. Whereas, when copper was added until 5 wt.%, the electrical conductivity decreases due to a larger amount of Cu$_2$O in this sample compared to EG/Cu/Cu$_2$O 1 wt.%. Cu$_2$O has a higher resistivity than Cu thus it can inhibit the electron mobility along the conduction path in the samples[24]. The results reveal that 1 wt.% of copper addition is an optimum concentration that can be added to enhance the electrical conductivity of EG. This modification of EG can provide insight to produce high-performance electrode materials for energy storage devices application.

4. Conclusion
The composites of EG/Cu/Cu$_2$O with various amounts of copper addition have been successfully synthesized. XRD characterization reveals that Cu$_2$O species has higher content at the composite with a higher concentration of Cu$^{2+}$ addition. An incomplete reduction of Cu$^{2+}$ probably causes the presence of Cu$_2$O as a result of insufficient volume of the added hydrazine as a reducing agent. SEM images of the resulted samples show that higher copper concentration leads to aggregation of Cu or Cu$_2$O particles. Four-point probe characterization results indicated that the addition of copper can improve the electrical conductivity of EG when 1 wt.% of Cu$^{2+}$ was added to EG dispersion. However, a larger amount of the added Cu$^{2+}$ causes the decreasing value of electrical conductivity due to more Cu$_2$O species are formed. The improved electrical properties of EG can offer new insight into the development of materials for energy storage devices, which requires high charge mobility of electrodes.

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**Acknowledgment**

This work was supported by The Ministry of Research and Technology/ National Agency for Research and Innovation through Master Thesis Research Program and The United States Agency for International Development (USAID) through Sustainable Higher Education Research Alliances (SHERA) Program – Center for Collaborative (CCR), National Center for Sustainable Transportation Technology (NCSTT).