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Synthesis of Graphene from Pencils Graphite Via Electrochemical Exfoliation Method as a Cu-Foil Coating on the Anode-Free Lithium-Ion Battery

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anode-free lithium-ion battery; electrochemical exfoliation method; graphene.

ABSTRACT. The Anode-free Li-ion Battery (AFLB) is an alternative to a new Li-ion battery model that offers high energy density at the same battery size as conventional models. Uncontrolled dendrite growth inactive the lithium deposition, resulting in decreased specific capacity, shortened lifecycle, and reduced coulombic efficiency. This work reported the utilization of graphene derived from pencil graphite for coating Cu foil as a current collector in AFLBs, to mitigate the formation of lithium dendrites and enhance battery capacity. The graphene-coated Cu foil exhibits a specific capacity of 143 mAh/g, representing a 20 mAh/g increase compared to batteries lacking a graphene coating. The coulombic efficiency of the battery with graphene coating in the charging and discharging process for three cycles is 84.53% in the 1st cycle, 101.44% in the 2nd cycle, and 98.58% in the 3rd cycle.

INTRODUCTION

The majority of electronic devices get their power from batteries, either primary (non-rechargeable) or secondary (rechargeable) batteries. Lithium-ion battery (LIB) is a common form of secondary battery found in energy storage systems (Liang *et al.*, 2014; Qian *et al.*, 2016). LIB with graphite anodes is considered to be among the most efficient energy storage technologies that can be used in a wide range of electronic devices and electric vehicles. LIB energy density is predicted to exceed 500 Wh/kg within the next ten years after recently surpassing 300 Wh/kg (Tong *et al.*, 2021). Lithium metal anode (Li-metal) becomes the suitable option for a battery.

On the other hand, because of irregular lithium deposition and an unstable Solid Electrolyte Interphase (SEI) formation, the usage of lithium metal-based anodes leads to the growth of lithium dendrites and a shortened lifecycle, which also causes a decrease in battery energy density (Hagos *et al.*, 2019). In addition, inappropriate utilization of lithium metal may result in other issues, including explosions and combustion (Tong *et al.*, 2021). Anode-free batteries are one promising solution. However, since the cathode is the only source of lithium, the ion will play a part in the SEI layer formation on the anode. In AFLB cells, lithium dendrites grow when lithium deposition becomes inactive, leading to an insufficient amount of lithium accessible to fully compensate for the loss of lithium ions from the cathode. (Wang *et al.*, 2021).

In comparison to other materials such as fullerene, graphite, and carbon nanotubes (CNTs), graphene indicates more advantageous characteristics consisting of high specific surface area (2630 m^2 g^{-1}), high electric charge mobility (230 000 cm^2/V s), and thermal conductivity (3000 – 5000 W/mK) (Mankge *et al.*, 2021). Several

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graphene synthesis methods have been developed involving electrochemical exfoliation. The electrochemical exfoliation method has been used to synthesize graphene in large quantities due to its affordable production costs and simple experimental preparation. Furthermore, this method is more environmentally safe and offers potential for industrial scale. Thus, this present study aims to synthesize graphene from pencil graphite using the electrochemical exfoliation method that will be further applied to anode-free lithium batteries to address the issue of lithium dendrites on anode-free lithium batteries.

RESEARCH METHODS

Preparation of Pencil Graphite Electrochemical Exfoliation

Approximately 6.6 g of ammonium sulfate $(NH_4)_2SO_4$ (Merck) was dissolved in 500 mL distilled water with a magnetic stirrer and sonicated for 10 min. The pencil graphite was immersed into the glass preparation with thermal insulation (6 cm long into the electrolyte) and exfoliated at 10 V for 10 min. The exfoliation results were divided into a bilayer and multiple layers, which were subsequently dispersed in alcohol for an hour for the washing process. The washing process took place three times, filtered, and stored in a bottle. Figure 1 shows a schematic of the exfoliation method.

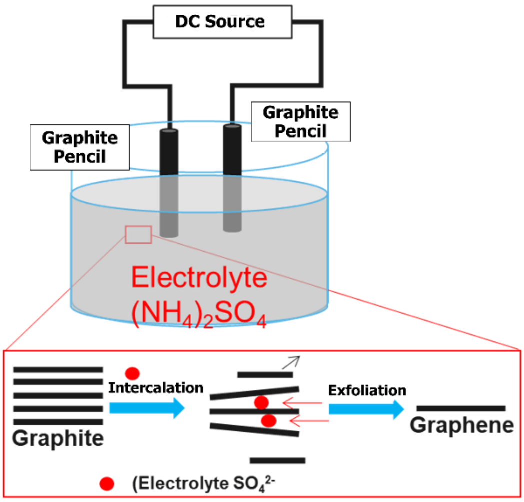

Figure 1. Schematic diagram of graphene synthesis through electrochemical exfoliation.

Precursor Preparation and Cu-foil Coating

The produced graphene 15.45 g, Carboxy Methyl Cellulose (CMC, Gelon, China) 0.5 g, and styrene butadiene rubber (SBR, Gelon, China) 0.3 g were stirred together via an over-head stirrer. CMC was added gradually until an appropriate slurry was formed. Water was added to the mixture until an appropriate thickness is achieved. The coating process was conducted using a doctor blade with a thickness of 50 μm. The slurry was gradually applied to the Cu-foil, and the doctor blade operated until the Cu-foil was completely coated with the slurry. Following the coating process, the Cu-foil was dried in an oven at 130 °C.

Battery Assembly

Nickel, Manganese, Cobalt 622 (NMC622) cathode sheets and graphene-coated Cu-foil electrodes were alternately pressed with a rolling press machine, sliced using a slitting machine, and assigned aluminum connectors at the end of the cathode and nickel at the end of the graphene-coated Cu-foil electrode by the welding process. A winding machine serves to wind the cathode sheet, separator, and Cu-foil with the shape of a jelly roll, which was examined afterward using a short circuit detector to ensure that there are no short circuits before placing the jelly roll into the cylinder. The assembled battery is placed in a vacuum oven to minimize the amount of water inside its package. Then, a dropper pipette from the glove box was utilized to add 1 M $LiPF_6$ electrolyte into the battery.

Characterization

The morphology and elemental analysis were conducted using Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX, JEOL Benchtop SEM JCM 7000). Meanwhile, the electrochemical properties of the battery were analyzed with a Neware 8-Channel battery analyzer. Charge-discharge testing on batteries was performed primarily to measure the specific capacity and calculate the coulombic efficiency (CE) value. The coulombic efficiency is calculated with Equation (1) (Agustin, 2017).

$$CE = \frac{Q\ discharge}{Q\ charge} x\ 100\% \tag{1}$$

Q *discharge* is denoted as discharge capacity (mAh) and Q *charge* is denoted as charge capacity (mAh).

RESULT AND DISCUSSION

Morphology and Chemical Composition of Graphene

The synthesis of graphene using electrochemical exfoliated graphite results in bilayer and multiple-layer graphene. When the exfoliation process was completed, sedimentation that scum on the colloid's surface formed bilayer graphene. Meanwhile, multiple layers of graphene were formed from the sludge of the exfoliated colloid. This result supports the previous study by Jamaluddin *et al.*, (2020). Figure 2 shows the morphological characterization of graphene obtained from the electrochemical exfoliation of pencil graphite in $(NH_4)_2SO_4$ electrolyte using Scanning Electron Microscopy (SEM) equipment, indicating bilayer and multiple-layer graphene, respectively.

Figures 2 (a and b) is *bilayer graphene*, whereas Figure 2 (c and d) is *multiple-layer graphene*. According to Wang *et al.* (2011) graphene morphology, graphene appears to have layers (flakes) in its structure. Wang's graphene manufacturing method (Wang *et al*., 2011) involves electrochemically broadening graphite as a cathode in a Li^+/propylene carbonate (PC) electrolyte at a high potential (-15+5V). The graphite is then sonicated for over 10 hours with an ultrasonic intensity of ~100 W/cm2 to completely exfoliate it. This results in 70% graphene with an average lateral dimension of 1-2 µm, with approximately 50% of the graphene sheet (Wang *et al*., 2011; Yu *et al.*, 2015). In the present study, the electrolyte utilized was $(NH_4)_2SO_4$, resulting in graphene with a width of around 6-7 µm.

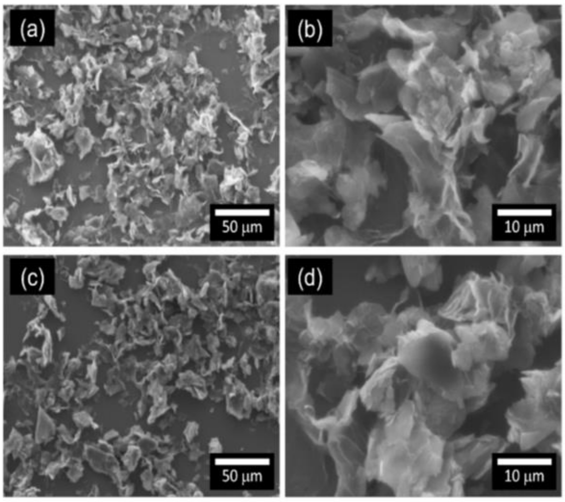

Figure 2. SEM images of graphene (a, b) bilayer and (c, d) multiple layers at 500x and 2500x magnification, respectively.

The produced graphene has the potential to generate contaminants, as confirmed by EDX tests (Figure 3, Table 1, and Table 2). The nitrogen and sulfur contaminate the graphite, as suggested by the electrolyte in both the bilayer and multiple layers, as confirmed by EDX results as shown in (Figure 4) and Table 3. Its insignificant mass enables Al and Fe to penetrate graphite cavities. Although impurities are less abundant than carbon, the contaminant can be removed by washing the sample with water. After washing the samples with water, neither N nor S elements were discovered in either bilayer graphene (Figure 3.b) or multiple-layer graphene (Figure 3.d), as confirmed by the EDX pattern.

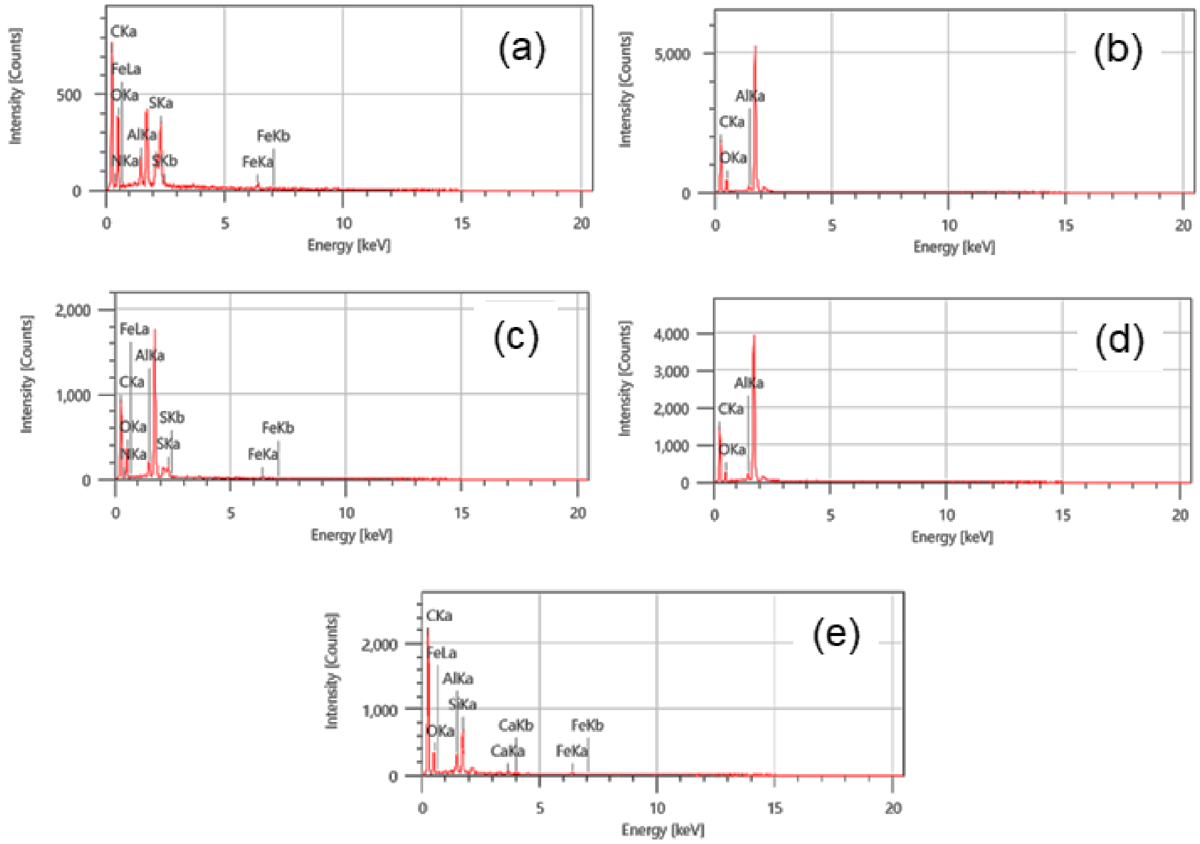

Figure 3. EDX spectrum of bilayer graphene, before washing (a) and after washing (b), and multiple layer graphene before washing (c) and after washing (d).

Table 1. Comparison of the chemical composition of bilayer graphene before and after washing.

No	**Element**	**Mass Weight Percent (%)**	
		Before washing	**Before washing**
1	C	45.16 ± 0.99	55.91 ± 1.01
2	O	35.18 ± 1.78	35.96 ± 1.89
3	Al	2.04 ± 0.22	3.95 ± 0.33
4	N	9.18 + 1.56	-
5	S	5.15 ± 0.33	-
6	Fe	3.29 ± 0.60	4.17 ± 0.75

Table 2. Comparison of the chemical composition of multiple-layer graphene before and after washing.

No	**Element**	**Mass Weight Percent (%)**	
		Before washing	**After washing**
1	C	49.84 ± 1.00	60.22 ± 1.02
2	O	36.08 ± 1.91	32.84 ± 1.88
3	Al	2.96 ± 0.28	3.43 ± 0.31
4	N	6.10 ± 1.44	-
5	S	2.12 ± 0.61	-
6	Fe	2.91 ± 0.61	3.50 ± 0.69

Table 3. Chemical composition of pencil graphite from testing using EDX.

No	Element	Mass Weight Percent (%)
1	C	67.33 ± 0.87
2	O	21.59 ± 1.19
3	Al	2.44 ± 0.18
4	Si	5.52 ± 0.27
5	Ca	0.59 ± 0.12
6	Fe	2.53 ± 0.42

Overall, SEM-EDX analysis indicates that, in a sample containing more than 60% carbon, the graphene generated contains approximately 30% oxygen. The presence of oxygen affects the morphology of graphene, leading to a non-homogeneous shape. The oxygen content is most likely derived from the distilled water used to store graphene after the washing process, due to the graphene characterized by SEM-EDX has not been dried and is not in sol-gel form, but rather in the form of a heterogeneous solution in distilled water. However, the oxygen content makes graphene more easily modified. SEM-EDX characterization demonstrates that the research was successful in producing graphene from graphite pencils.

Battery Performance Analysis

Battery performance was tested using an anode-free Lithium type 18650 cylindrical battery. The test was conducted to determine the battery capacity during charging and discharging. The capacity of AFLB with graphene coating on Cu-foil anode was compared to anode-free batteries without graphene coating to determine how successful the graphene material is in enhancing the capacity of anode-free batteries, even with a thickness of 4.5 μm. Figure 5 is a charge-discharge graph for both types of batteries at 0.1 C.

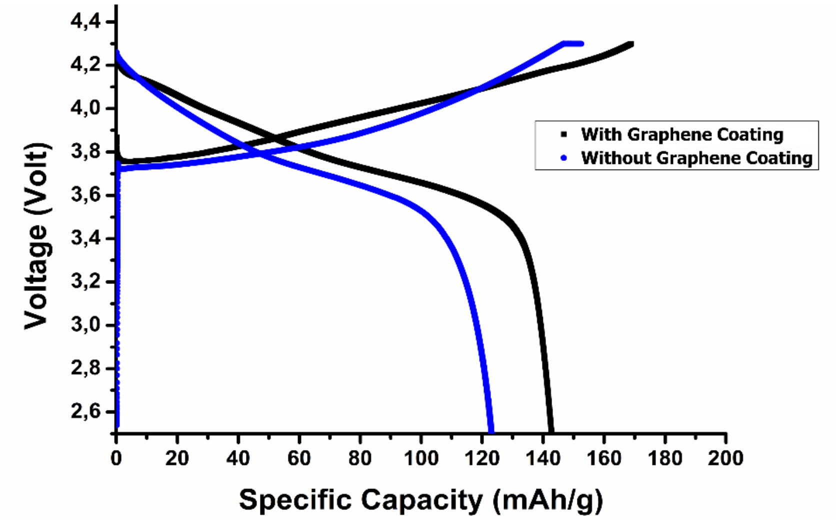

Figure 5. AFLB Charge-Discharge graph with graphene coating and without graphene coating.

Tests were conducted within a voltage range of 2.5–4.3 V for three cycles. Figure 5 shows a clear difference in specific capacity between AFLB with and without graphene coating. The specific capacity of batteries using a graphene-coated anode is 143 mAh/g, while batteries with an uncoated anode have a specific capacity of 123 mAh/g. AFLB with coating has a higher specific capacity than AFLB without coating, by 20 mAh/g. This difference indicates that the graphene coating on the Cu-foil anode affects the capacity of AFLB. This is because batteries with coatings contain graphene as an active agent, thus acting as the Li host, resulting in a larger battery cell volume than AFLB without coatings. Graphene coating over Cu-foil has been shown to facilitate the intercalation and deintercalation of Li ions in AFLB cells. Despite its thinness, the graphene layer is capable of receiving Li ions. More Li ions entering and exiting the cathode and anode can enhance the performance of anode-free batteries. The specific capacity number falls throughout the discharging process due to the lack of space that accommodates the Li-ion. As a result, the inactive layer on the formation was formed, interrupting the Li-ion flow mechanism.

Table 4. Coulombic Efficiency (CE) data on AFLB.

Battery Type	Cycle 1 (%)	Cycle 2 (%)	Cycle 3 (%)
Battery with graphene-coated anode	84,53	101,44	98,58
Battery with uncoated anode	80,73	96,78	96,84

Table 4 is the final result of Coulombic Efficiency (CE) measurements performed during the first three cycles. The results showed that AFLB with graphene coating exhibited a higher coulombic efficiency value than AFLB without graphene coating in the charging and discharging process for three cycles: 84.53% in cycle 1, 101.44% in cycle 2, and 98.58% in cycle 3. In the first three cycles, the battery with Cu-foil coated with graphene on the current collector exhibits a consistent CE value. Table 4 shows the magnitude of the coulombic efficiency in percentage form. This is because the battery's resistance consumes some electrical energy, resulting in total electrical energy discharged that is always less than the total electrical energy charged. When the discharge current is higher, the coulombic efficiency is lower, and the internal resistance increases because of the larger discharge current. The more strong the electrochemical reactions in the battery, the more substantial the internal resistance produced, leading to a greater amount of energy consumption of the battery (Wang *et al.*, 2021).

CONCLUSION

Graphene was efficiently synthesized from pencil graphite using the electrochemical exfoliation method using a 1 M $(NH_4)_2SO_4$ solution and a voltage of 10V. SEM-EDX analysis reveals the graphene morphology in the form of thin sheets (flakes). Charge-discharge tests indicate that the graphene coating on Cu-foil improves AFLB performance. The specific capacity of the battery with graphene coating is 143 mAh/g, which is 20 mAh/g higher than the battery without it. The graphene coating in AFLB acts as an active material on the anode side that serves as the Li host. AFLB with graphene coating have a greater coulombic efficiency value than those AFLB without graphene coating, showing 84.53%, 101.44%, and 98.58% during 1st, 2nd, and 3rd cycle, respectively.

CONFLICT OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

AUTHOR CONTRIBUTION

NNA: Investigation, Writing Original Draft, Data Collecting, Visualization; MI: Data Collection; AJ: Conceptualization, Methodology, Validation, Writing Original Draft, Review, and Editing; AN: Writing Review & Editing; ELS: Writing Review and Editing; and HW: Conceptualization, Methodology, Validation, Writing Original Draft, Review and Editing.

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