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SYNTHESIS OF EXPANDED VEIN GRAPHITE VIA ANODIC EXFOLIATION USING SULFURIC ACID AS AN ELECTROLYTE

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Abstract: The electrochemical exfoliation of graphite has been recognized as a costeffective eco-friendly method that consumes lower energy compared to mechanical, chemical, and thermal exfoliation. However. detailed electrochemical exfoliation of vein graphite which possesses higher crystallinity and purity is limited. Therefore, this study aimed to find out the possibility of synthesizing expanded graphite using vein graphite as a material via electrochemical raw exfoliation. The anodic exfoliation was carried out with the vein graphite rod and Pt as the working and reference rod electrodes, respectively with H₂SO₄ as an electrolyte under 1V for 30 minutes. Crystallographic and morphological analyses revealed an excessive volume increase in graphite layers caused by the electrochemical exfoliation process. Raman spectroscopy analysis showed that the oxidation of the graphite via electrochemical exfoliation had increased the defect density of the edge plane and basal plane in graphite layers. Further, FTIR analysis showed that the distinct peaks

appeared on electrochemically exfoliated graphite indicating that oxidation occurred during the anodic exfoliation process. Therefore, it suggests that this produced exfoliated graphite has a highly oxidized and defective nature. Overall, this study demonstrates the possibility of producing expanded vein graphite using the straightforward affordable and electrochemical exfoliation method using H_2SO_4 as the electrolyte.

Keywords: Expanded graphite, electrochemical exfoliation, sulfuric acid

I. INTRODUCTION

The significant characteristics of graphitebased materials, including their high thermal, electrical, mechanical, and permeability qualities, have made them one of the most researched materials in human history [1]. The majority of graphite-based materials are also used in a variety of electronic applications, including solar cells, rechargeable biosensors. batteries, aeronautics, and energy storage devices [2].

Naturally occurring graphite (NG), on the other hand, occurs as a non-functional material due to its hexagonal layered structure. Amorphous graphite, flake graphite, and vein graphite are the three types of NG. The only country in the world that can produce high-purity (about 95-99% of pure carbon), crystalline vein graphite on a commercially viable basis is Sri Lanka [3].

However, NG is not directly used for advanced applications. As a result, researchers have focused their efforts on modifying natural graphite through mechanical, thermal, or chemical structural modification methods [4]–[7].

Vein graphite is used to produce expanded graphite and improve its quality by using structural modification techniques. Previous studies demonstrated that the use of microwave irradiation technique can produce expanded graphite and it required higher energy for the exfoliation process [7]. Also, chemical intercalation using HNO₃, and exfoliated graphite preparation required a longer time to exfoliate process [6].

The electrochemical exfoliation technique has been recognized as a promising way for

structurally modifying the graphite to produce expanded graphite among the numerous methods [8]. Since it can be performed at room temperature in less time and with greater efficiency, it is a more costeffective and environmentally friendly method that uses less energy than mechanical, chemical, and thermal exfoliation methods [4].

Previous studies demonstrated that the exfoliation electrochemical of highly ordered pyrolytic graphite with 0.5 mol dm⁻ ³ H₂SO₄ as electrolyte under +3 V potential varied the duration of 5 s to 600 s can be produced exfoliated graphene oxide by a two-stage process [9]. Also, high-quality graphene flakes were prepared using graphite nanoplatelets with 0.1 mol dm⁻³ H₂SO₄ by supplying 10 V potential for 180 s [10]. These studies used flake and synthetic graphite, and higher voltages. There has been no research conducted to study the feasibility of employing electrochemical exfoliation to the natural vein graphite using sulfuric acid as an electrolyte, as well as lower voltages using sulfuric acid. Furthermore, limited investigations on electrochemical exfoliation of vein graphite carried out so far [11], [12].

Therefore, this research aimed to find out the feasibility of producing expanded graphite from Sri Lankan vein graphite via anodic electrochemical exfoliation with H_2SO_4 as an electrolyte.

II. METHODOLOGY AND EXPERIMENTAL DESIGN

A graphite rod (diameter 1 cm x length 10 cm) cut from vein graphite was obtained from the Kahatagaha graphite mine. Direct Current (DC) voltage supplier (EDU-LAB

power supply; 605-056) was obtained from Uva Wellassa University of Sri Lanka. Sulfuric acid (H₂SO₄) was purchased from Sigma Aldrich.

The anodic exfoliation was carried out with the vein graphite rod as the working electrode and electrochemically treated for 30 minutes under 1V DC voltage using a Pt rod as a reference electrode with 500 ml of 1 mol dm⁻³ H₂SO₄ as an electrolyte. The exfoliated material in the solution was filtered and washed with distilled water until the solution pH become neutral (pH=7). This was assisted with vigorous stirring and vacuum filtering. When it became neutral, the sample was oven dried at 120 °C for 1 hour.

Natural vein graphite (RAW) and synthesized expanded graphite (EG) materials were characterized using the Xrav Diffractometer (XRD), Raman spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Particle Size Analyzer (PSA) and Scanning Electron Microscopy (SEM).

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffractograms of raw graphite (RAW) and vein the electrochemically treated expanded graphite (EG) sample for crystalline phase analysis and the calculated interlayer distance (d-space) of the materials. Figure 1 shows the characteristic Gr (002) peak and Gr (004) peak in the RAW sample, indicating the high crystallinity and high purity. The intensity of the 002 peak decreases significantly the electrochemically in treated EG sample than in the RAW sample. Moreover, Figure 1 shows that the primary (d₍₀₀₂₎) peak has broadened, affecting the

highly crystalline nature of this natural vein graphite after the electrochemical exfoliation. The interlayer distance was calculated related to the prominent peak (d (002)) using Bragg's law [13] and it revealed that the interlayer spacing of vein graphite had increased from 0.33859 nm to 0.33986 nm after the electrochemical exfoliation process. Based on the XRD results, the crystalline structure of the natural vein graphite may have been subjected to exfoliation and expansion due to the anodic electrochemical exfoliation.

After the anodic electrochemical exfoliation processes, powder RAW and



Figure 5. X-Ray diffractograms obtained for RAW and EG sample

electrochemically treated EG samples were characterized by Raman spectroscopy to explore the structural and chemical changes (Figure 2). The significant D peak at ~1350 cm⁻¹ which results from the breathing mode of the sp² carbon atoms is considered to be a sign of disorders due to edges, functional groups such as hydroxyl and epoxide groups, and the band is activated by the presence of the defects [14], [15]. The G band at ~1580 cm⁻¹ is also a characteristic peak of graphite and increases due to inplane stretching of sp² hybridized C atoms

[16]. The ratio of the intensity of the D peak and G peak (I_D/I_G) of Raman spectroscopy was used to estimate the average defect density on the graphite structure after the electrochemical exfoliation (Figure 2) [9]. The I_D/I_G ratio is related to structural defects and is known as a quality indicator of the produced material, which is having high value of the ratio related to the small-sized crystals or increased defect density [17]. The ratio of I_D/I_G of the edge plane of the graphite increased from 0.48 of RAW to 0.7 of EG after the anodic exfoliation. Similarly, the I_D/I_G of the basal plane of the graphite increased from 0.17 RAW to 0.46 of EG. This reveals that the average defect density on the graphite edge and basal surface after increased the electrochemical exfoliation (Figure 2). During the exfoliation process, the I_D/I_G value was increased due to the oxygen functional groups, which causes disorder at carbon edges [18]. According to Xia et. al 2020, the I_D/I_G value for the exfoliated graphite from highly ordered pyrolytic graphite was given 0.81 for 60 s, indicating that the cracks due to blistering were exposing fresh, less defective layers of the underlying bulk graphite. Hence, the present study shows that fewer defective layers with cracks. These observations are consistent with earlier research [19].

The number of graphene layers is determined using the 2D band of the Raman spectrum. However, the 2D band is too weak to determine the number of layers in exfoliated graphite because the stacking order of adjacent layers ruptured during electrochemical oxidation, vibrational signals from the edges of graphite, and introduced amorphized carbon atoms [9], [10]. The behavior of the Raman spectrum shows the that exfoliated graphite possesses a high defect density with a crystalline structure [19].



Figure 6. Raman spectra obtained for Edge (a) and Basal (b) planes of RAW and EG sample

The FT-IR spectrum of the RAW and electrochemically treated EG sample is shown in Figure 3. According to Figure 3, in the spectrum of RAW, there are no significant peaks relevant to any functional groups, however, there are noticeable differences in the EG spectrum with a number of distinct peaks appearing in the spectrum. The strong broad vibrational bands at 3200 cm⁻¹ - 3600 cm⁻¹ is responsible for stretching vibrations of the hydroxyl group, where the hydroxyl groups may be from absorbed water molecules or phenolic

OH⁻ or OH⁻ from carboxylic groups [20]. The doublet band at ~2356 cm⁻¹ corresponds to absorbed CO₂ molecules [20], and the sp² hybridization of the aromatic C=C bond was confirmed by a peak at ~1580 cm⁻¹ in the EG sample. EG sample has shown deformation vibration of C-OH, which can be identified at 1350 cm⁻¹ [21]. There isn't any information about sulfate-containing groups in spectra. It indicates that vacuum filtration and washing procedure have successfully removed the anions from the sample.

The presence of OH bonds in the EG sample may responsible for the oxidation of natural vein graphite (RAW) via the electrochemical exfoliation process (Figure 3). Moreover, the oxidation may be the reason for an increment of the interlayer distance of graphene layers and an increment of I_D/I_G ratio along with defect density and structural disorder in RAW graphite structure [19].



Figure 3. Fourier Transform Infrared Spectroscopy (FTIR) spectra obtained for RAW and EG sample

Figure 4 shows the scanning electron microscopic (SEM) images of RAW and EG samples. Natural vein graphite has thin platy appearance with ideal layer structure characteristics to highly crystalline graphite (Figure 4. a). SEM image of EG (Figure 4. b) revealed an ideal layer-by-layer structure with increased interlayer spacing. Further, an analogous long-range-ordered layered microstructure composed of many translucent wrinkled and paper-like graphene sheets with fluffy morphology of edges can be clearly identified in the SEM of EG (Figure 4. b).

Particle size analysis of expanded graphite was calculated by using the laser diffraction method. A median particle size of 1260.6 nm and a polydispersity index value of 0.878, indicating the broad size distribution of particles, were reported for the EG sample (Figure 5).

In summary, the possibility of synthesizing expanded graphite using Sri Lankan vein graphite as a raw material via the electrochemical exfoliation method has been investigated. Crystallographic and morphological analyses revealed an excessive volume increase in graphite layers caused by the electrochemical exfoliation process.



Figure 4. Scanning electron microscopic images obtained for RAW (a) and EG (b) sample

Raman spectroscopic results revealed that the defect density of the edge plane and basal plane in graphite layers had increased due to the oxidation of the graphite via electrochemical exfoliation. FTIR and SEM analysis revealed that the oxidation occurred during the anodic electrochemical exfoliation process and showed the defective nature of expanded graphite. Therefore, it suggests that this produced exfoliated graphite has a highly oxidized and defective nature. Furthermore, this study shows that the expanded graphite has a higher crystallinity with fewer defects when compared with previous research [9], [10].



Figure 5. Particle size distribution graphs of RAW (a) and EG sample (b)

IV. CONCLUSION AND RECOMMENDATION

Overall, this study demonstrates the possibility of producing expanded vein graphite using the straightforward and affordable electrochemical exfoliation method using H_2SO_4 as the electrolyte. Additionally, the electrochemical exfoliation process makes it challenging to generate single graphene EG layers due to the inadequate intercalation of HSO₄-anions in acid. Material characterization and optimization of parameters such as electrolyte concentration and DC voltage, undergoing are currently to obtain expanded graphite for the investigations in intended rechargeable battery applications and obtained single-layer graphene.

REFERENCES

- Ibrahim, A. Klopocinska, K. Horvat, and Z. A. Hamid, "Graphene-based nanocomposites: Synthesis, mechanical properties, and characterizations," *Polymers*, vol. 13, no. 17. MDPI AG, Sep. 01, 2021.
- [2] Jiříčková, O. Jankovský, Z. Sofer, and D. Sedmidubský, "Synthesis and Applications of Graphene Oxide," *Materials*, vol. 15, no. 3. MDPI, Feb. 01, 2022.
- [3] N. W. B. Balasooriya, H. P. T. S. Hewathilake, R. M. U. M. Somarathna, H. W. M. A. C. Wijayasinghe, L. P. S. Rohitha, and H. M. T. G. A. Pitawala, "Physical and Chemical Purification of Sri Lankan Flake Graphite and Vein Graphite," 5th International Symposium 2015 – IntSym, SEUSL PHYSICAL, no. January, pp. 163-166, 2015.
- [4] M. Cai, J. M. Chem, D. Thorpe, H. Adamson, and H. C. Schniepp, "Methods of graphite exfoliation," pp. 24992–25002, 2012.
- [5] T. C. Senevirathna, H. P. T. S. Hewathilake, H. W. M. A. C. Wijayasinghe, N. W. B. Balasooriya, and H. M. T. G. A. Pitawala, "Structural Modification of Sri Lankan Vein Graphite Using Microwave Irradiation Technique," vol. 19, pp. 11–16, 2018.
- [6] N. W. B. Balasooriya and P. W. S. K. Bandaranayake, "Preparation of Exfoliated Graphite Using Natural Graphite of Sri Lanka," Journal of Geological Society of Sri Lanka, vol. 15, no. December, pp. 19–29, 2013.
- [7] T. C. Senevirathna, H. P. T. S. Hewathilake, and H. W. M. A. C.

Wijayasinghe, "A Rapid Method to Prepare Exfoliated Graphite Using Sri Lankan Vein Graphite," 2016, pp. 304–309.

- [8] K. Parvez, Z. Wu, R. Li, X. Liu, R. Graf, and X. Feng, "Exfoliation of Graphite into Graphene in Aqueous Solutions of Inorganic Salts," *Journal of the American Chemical Society*, 136(16), 6083–6091.
- [9] Z. Xia, V. Bellani, J. Sun, and V. Palermo, "Electrochemical exfoliation of graphite in H₂SO₄, Li₂SO₄and NaClO₄solutions monitored: In situ by Raman microscopy and spectroscopy," *Faraday Discuss*, vol. 227, pp. 291– 305, 2021.
- [10]L. S. Lin, L. Li-Shang, A. Westwood, and R. Brydson, "Graphene Synthesis via Electrochemical Exfoliation of Graphite Nanoplatelets In Aqueous Sulfuric Acid," 2016.
- [11]S. M. T. D. Wimalasoma, H. M. H. D. K. Naranpanawa, T. H. N. G. Amaraweera, and H. W. M. A. C. Wijayasinghe, "Development of expanded graphite from vein graphite via electrochemical exfoliation with sodium sulfate as an electrolyte," in *Proc. IPRC*, 2022, p. 95.
- [12]S. M. T. D. Wimalasoma, H. M. H. D.
 K. Naranpanawa, T. H. N. G.
 Amaraweera, S. M. Young, and H.
 W. M. A. C. Wijayasinghe, "Anodic Electrochemical Exfoliation of Vein Graphite in Aqueous Magnesium Sulfate Electrolyte," in *Proc. GARI*, 2022, p. 50.

- [13] P. J. Wibawa, M. Nur, M. Asy'ari, and H. Nur, "SEM, XRD and FTIR analyses of both ultrasonic and heat generated activated carbon black microstructures," *Heliyon*, vol. 6, no. 3, p. e03546, 2020.
- [14]T. C. Achee *et al.*, "High-yield scalable graphene nanosheet production from compressed graphite using electrochemical exfoliation," *Sci Rep*, vol. 8, no. 1, pp. 1–9, 2018.
- [15]A. C. Ferrari *et al.*, "Raman spectrum of graphene and graphene layers," *Phys Rev Lett*, vol. 97, no. 18, 2006.
- [16]S. Bandi, S. Ravuri, D. R. Peshwe, and A. K. Srivastav, "Graphene from discharged dry cell battery electrodes," J Hazard Mater, vol. 366, pp. 358–369, 2019.
- [17]G. Konstantopoulos, E. Fotou, A. Ntziouni, K. Kordatos, and C. A. Charitidis, "A systematic study of electrolyte effect on exfoliation efficiency and green synthesis of graphene oxide," *Ceram Int*, vol. 47, no. 22, pp. 32276–32289, 2021.
- [18] P. Yu, S. E. Lowe, G. P. Simon, and Y. L. Zhong, "Electrochemical exfoliation of graphite and production of functional graphene," *Curr Opin Colloid Interface Sci*, vol. 20, no. 5–6, pp. 329–338, 2015.

- [19]W. W. Liu and A. Aziz, "Review on the Effects of Electrochemical Exfoliation Parameters on the Yield of Graphene Oxide," ACS Omega, vol. 7, no. 38. American Chemical Society, pp. 33719–33731, Sep. 27, 2022.
- [20]J. N. Kanagaratnam, T. H. N. G. Amaraweera, N. W. B. Balasooriya, and H. W. M. A. C. Wijayasinghe, "Chemical intercalation of graphite using chromium trioxide for the anode application in rechargeable sodium-ion batteries," *Ceylon Journal of Science*, vol. 51, no. 1, p. 21, 2022.
- [21]M. Ciszewski and A. Mianowski, "Survey of graphite oxidation methods using oxidizing mixtures in inorganic acids," *Chemik*, vol. 67, no. 4, pp. 267–274, 2013.