Potential of Sri Lankan Graphite as An Electrode Material for Water Treatment: A Review

A.G.M.P. Rajapaksha, R. Weerasooriya, T.N. Premachandra

Abstract: The structure of graphite consists of carbon atoms arranged in layers; a significant feature of this structure is the presence of delocalized electrons. As a result of these free electrons, graphite exhibits conductivity properties and therefore is commonly used for electrodes. High melting point, resistance to corrosion, high reversible capacity, and appropriate potential profile makes natural graphite more applicable as an electrode material. One of the main reasons scientists are interested in flake graphite as the electrode material is its high abundance. Sri Lankan graphite consists of Vein, Flake, and Amorphous types and has large reservoirs of vein graphite (Bogala and Kahatagaha) with high initial purity (95-98% carbon content) and high crystallinity. The high purity of this vein graphite eliminates the primary purification required for flake graphite. The main impurities in Sri Lankan graphite are Silica, $CaCO_3$, and pyrite. Hence, natural graphite should be upgraded to battery-grade electrode material for further applications. The required purity level of natural graphite is in the range of < 0.1% ash with the accepted level of heavy metals < 10 ppm. Graphite purification can be done through physical or chemical methods and Froth flotation is one of the commonly used physical methods. Most of the chemical techniques are based on acid treatment. Surface modification is also a crucial factor affecting the overall performance of the electrode. Currently, natural graphite is used as the electrode material for Lithium-ion batteries and this industry is dominated in China. The present review discusses the possibility of using Sri Lankan graphite as electrode material for EDR.

Keywords: Natural graphite; Sri Lankan graphite; Purification; Electrode material; EDR

1. Introduction

Carbon is a polymorphic substance consisting of three forms Diamond, Graphite, and Fullerenes. Graphite and Diamond are natural allotropes of carbon. The main difference between diamond and graphite is based on their bonding mechanism. Graphite is made out of sp^2 hybridization, and diamond is made out of sp^3 hybridization. Graphite consists of a carbon layer, and the layer structure of the graphite is arranged in a hexagonal pattern that makes the layer stack in the AB sequence. As well as, there is another form of graphite that consists of carbon layers stacked in the ABC sequence, making a rhombohedral structure. This one is less frequent than

__Mr. A.G.M.P.Rajapaksha__, B.Sc. (Material and Nanoscience tech) (Hons) (WUSL), Trainee, JRDC
Email: fot189107@kul.wyb.ac.lk
__Prof. R.Weerasooriya__, B.Sc. (Hons), PhD(Geology)(Peradeniya)/ Research professor ,NIFS
Email: rohan.we@nifs.ac.lk
__Dr. T. N. Premachandra__, B.Sc.(sp, Hons) (Peradeniya), PhD (SL)/Chemist, JRDC
Email: thejaninisa@gmail.com, ORCID ID: https://orcid.org/0000-0002-7797-9259

the Ab sequence. 2s, $2p_x$, and $2p_y$ electrons form of graphite lead to the formation of sp_2 hybridized orbitals directed 120° apart on a layer plane. Their orbitals lead to the formation of σ-bonding between carbon atoms on a layer plane. Other than that, $2p_z$ electron forms a delocalized orbital of π symmetry. The delocalized π electrons result from the high mobility that plays a major role in the electronic properties of graphite. Carbon layers of graphite bound with van der Waals forces that resulting graphite is anisotropic. (Chung, 2002) Graphite is an inert substance for most chemicals. It has a high melting point of 3550 °C, but the presence of oxygen will begin to oxidize at a temperature > 300 °C. Thermal conductivity of the graphite is anisotropic but it is very high in the direction parallel to the plane of the layer. The crystal density of graphite is 2.266 g/cm^3 and the specific gravity is between 2.20 – 2.30 depending on purity. Graphite is a soft material, Mohs, hardness of 1-2, greasy to feel, Flexible and sectile, but not elastic. The colour of the graphite is opaque black with metallic lustre but also can be dull and earthy. Graphite is classified as natural and synthetic graphite. (Keeling, 2017)

1.1 Synthetic graphite

Synthetic graphite is engineered or manufactured using carbon material such as calcined petroleum coke of suitable crystalline quality by human beings. It has specific specifications with high purity and predictable properties. As well as, it consists of some drawbacks. They are more expensive because of the manufacturing cost and are less conductive than natural graphite. Synthetic graphite can divide into three groups called powders (>600 ktpa), shapes (<900 ktpa), and carbon fibre (>35 ktpa). (Keeling, 2017) Mainly electrical performance of synthetic graphite is affected by its crystallinity. AlCl3 or BF3 is required as the catalyst for upgrading the crystallinity of synthetic graphite and needs to separate processes to remove the metals used in the catalyst process. (Kim et al., 2021) Synthetic graphite is mainly used for metal refining, graphite block and powders, carbon brushes and bearings, and graphite fibre reinforcement in polymer composites. (Keeling, 2017) The countries that produce synthetic graphite are China, India, Europe, and the USA. (Jara et al., 2019)

1.2 Natural graphite

Natural graphite can be found in metamorphic rocks as a result of metamorphism. It also occurs in igneous rocks. There are two methods of mining natural graphite. They are surface mining and underground mining. Commonly, Quartz, calcite, micas, and schist are the minerals combined with the ground's graphite. As well as metamorphic minerals including feldspar, muscovite, chlorite, garnet, orthopyroxene, and sillimanite are also associated with natural graphite. Only some of the mine in Sri Lanka has a lesser impurity level and the carbon content of the graphite is around 99 %. The main concern of natural graphite is the ash composition for final applications as well as the purification behaviour. To achieve the high purity level needed for the application, several chemical and thermal purification methods are required. (Handl, 2021) Natural graphite can be classified as flake, vein, and amorphous graphite regarding of their different physical properties, appearance, chemical composition, and impurities. (Keeling, 2017) As mentioned before, there are several minerals contained in natural graphite. That will directly affect the quality and performance of the industrial applications. All-natural graphite verities need purification regarding their impurity level. Several methods use for the purification of natural graphite. They are Hydrometallurgical purification, Pyro metallurgy purification, Comminution, Froth flotation, Reverse flotation separation, Air elutriation, Gravity separation, Magnetic separation, Microwave irradiation, Electrostatic separation, acid leaching, Film flotation, and Flushing process.

1.3 Sri Lankan available graphite verities

Sri Lanka is the only place that can find high-purity and high- crystallinity vein graphite in the world. Vein graphite exists in the Precambrian granulite rocks in the Wanni complex area. Wanni complex consists of supracrustal rocks, granitic gneisses, charnockitic gneisses, and migmatites of probable Proterozoic age. Metasedimentary rocks are available in the eastern part of the complex. The Bogala and Kahatagaha – kolongaha mines are situated north – northwest of Kandy in the Wanni complex. In bogala, the vein traverse succession of charnockite, quartzite, calc-gneisses, garnet gneisses and biotite gneisses. The metasedimentary units at Kahatagaha–Kolongaha are mainly quartzite, quartzofeldspathic gneisses, garnet–cordierite–biotite- and sillimanite-bearing gneisses and calc-gneisses. Pyrite, chalcopyrite, calcite, quartz, apatite, and biotite are the impurities consisting of graphite. Based on the shape analysis, there are 6 major types of graphite verities were identified in Kehelpannala; fibrous, flake-like, spherulitic, semispherulitic, finely crystalline, and recrystallized fine-grained graphite. On basis of this classification and the structural and physical characteristics, there are 4 common morphological verities were identified in Bogala and Kahatagaha – Kolongaha mines;

- Coarse flakes of radial graphite (CFR)
- Coarse striated-flaky graphite (CSF)
- Needle-platy graphite (NPG)
- Shiny-slippery-fibrous graphite (SSF)

Bogala and Kahatagaha – Kolongaha mine contains high-purity vein graphite at 98% carbon content. The main impurities found on this mine's graphite are silica, calcium carbonate, and pyrite.(Touzain et al., 2010) Purification and surface modification is essential for graphite preparation as the anode material. Raw graphite is containing more impurities and exhibits lots of well-needed graphite properties. Theoretically battery grade anode should contain $< 0.1\%$ ash with the accepted level of heavy metals < 10 ppm. Literature explained there are several physical and chemical experiments were done to get the higher purification rate as much as possible.

1.3.1 Cost-effective Purification methods of Sri Lankan graphite

1.3.1.1 Acid digestion method

The data on the acid digestion method carried out with HF, HNO_3, and H_2SO_4 (Table 01, Table 02) (Hewathilake et al., 2015) (Wickramaarachchi et al., 2016)

1.3.1.2 Froth flotation and Alkali roasting methods

All the vein graphite samples were collected from the Kahatagaha Kolongaha mine and Flake graphite samples were collected from two abandoned mines in the Pasyala area (Kaluaggala and Wawehena)(Table 03) to identify the most effective technique to purify graphite. (Balasooriya et al., 2015)

1.3.2 Surface modification

Surface modification of graphite is a crucial factor affecting graphite as the electrode material. Surface modification is carried out in several methods including coating with various kinds of pyrolytic carbons, dipping in the polymer solution, and formation of a dense oxide layer by oxidation with air, oxygen, and carbon dioxide. The surface modification reduces the presence of active sites on the graphite surface and some defective sites. (Wu et al., n.d.)

1.3.2.1 Mild oxidation method

1.3.2.1.1 Mild oxidation using $(NH_4)_2S_2O_8$

Mild oxidation method that carried out with five different samples at different temperatures (Table 04)(Fig 01) (Wu et al., n.d.)

1.3.2.1.2 Using $(NH_4)_2S_2O_3$ (NS method) vs HNO_3 (NO method)

Comparison data between the above two methods which are physical and electrochemically (Table 05) (Fig 02) (Amaraweera et al., 2018)

1.3.2.2 Modification of vein graphite with alkali chloride

(A and B) are the SEM analysis of the NPG treated with LiCl and (C and D) are the NPG morphological varieties. The microphotographs of C and D have shown closely packed thin plates of graphite, which is identical to the NPG morphology (Fig 03). (Wickramaarachchi et al., 2016) The graphite sheets are formed by very fine fibrous material. (Jara et al., 2019) Growth of long, thin-bladed veins course in the form of needle-like microstructures. The needle could be cleaved due to the fibrous nature of its arrangement. Long, fibrous needles of graphite were well crystallized, and short fibrous needle shows an equigranular pattern that is evenly distributed and compacted.(Sasanka Hewathilake et al., 2015) The microphotographs of A and B have exhibited partly destroyed hexagonal sheets after surface modification.

Table 01: Carbon percentage in raw and purified four varieties of vein graphite obtain from Kahatagaha – Kolongaha mines

Variety	Carbon content %	
	Raw	Purified
NPG	99.93	99.99
SSF	99.65	99.98
CSF	99.08	99.98
CFR	98.66	99.99

Table 02: Carbon content of raw and purified graphite sample

Sample name	Carbon content %	
	Raw	Purified
NPG	98.90	99.99
F-SSF	97.46	99.00
SSF	97.50	99.50

Table 03: C % of raw and purified vein graphite samples by froth flotation and alkali roasting

Sample	Initial Purity	
NPG (1)	99.60 %	
SSF (2)	97.31 %	
	After froth flotation	After alkali roasting
NPG (1)	99.67 %	99.95 %
SSF (2)	97.32 %	99.89 %

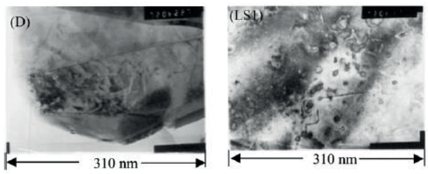

Fig 01: HREM micrographs of natural graphite before (D) and after (LS1) oxidation treatment

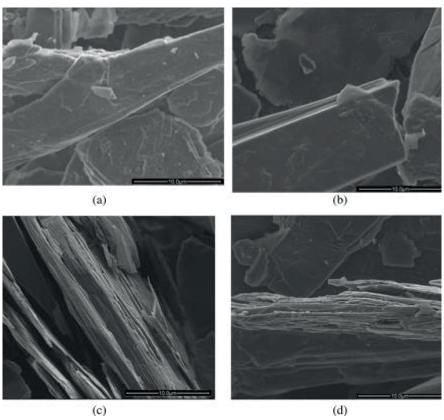

Fig 02: SEM image of the NPG (a) before purification and (b) after acid leaching purification, (c) after chemical oxidation in $(NH_4)_2S_2O_8$, (d) after chemical oxidation in HNO_3

2. Conclusion

Natural graphite has been used for many applications in several industries. Graphite can be converted into another form of a carbon variety to change the characteristics suitable for the needed industrial application. Graphene oxide and thermally expanded graphite are examples of graphite that are used in water purification applications. Natural graphite is also a good electrode material after purification and surface modification processes. Vein graphite is the highest purified form of the graphite verity and it can be found only in Sri Lanka. Furthermore, it doesn't require much more complex purification and surface modification processes because of the high purity. There are several research that has been conducted to identify the effectiveness of the Sri Lankan vein graphite as an electrode material for Li-ion batteries. Those researchers have given positive analysis results that vein graphite can be used as the electrode material. Electro-dialysis reversal (EDR) is one of the widely used purification techniques in the water purification industry that uses electrodes (anode and cathode) for water purification. The present EDR electrode system is very costly because of the materials (Iridium, Platinum) that are used for the fabrication process. Since graphite shows good results as an electrode material, there is a potential for using graphite for the EDR electrode system as an alternative to the existing EDR electrode system.

Table 04: Experimental data of the natural graphite before (D) and after (LS1, LS2, LS3, LS4) oxidation with a solution of $(NH_4)_2S_2O_8$

Sample	Treatment temperature °C	Weight loss %	The atomic ratio of O at the surface %	The atomic ratio of C at the surface %
D	-	-	4.11	95.89
LS1	20	2.64	4.70	95.30
LS2	60	2.07	6.03	93.97
LS3	100	1.83	5.95	94.05
LS4	120	1.67	5.33	94.67

Table 05: Results of the first cycle charge-discharge study conducted using the NPG at a 0.2 C rate between 0.002 V and 1.5 V

	Discharge capacity ($mAhg^{-1}$)	Charge capacity ($mAhg^{-1}$)	Efficiency (%)	Irreversible capacity ($mAhg^{-1}$)
NPG	317.6	267.8	84.3	49.8
Purified NPG	327.6	287.5	87.8	39.7
NPG NS	345.4	326.1	94.4	19.2
NPG NO	341.4	313.5	91.8	27.9

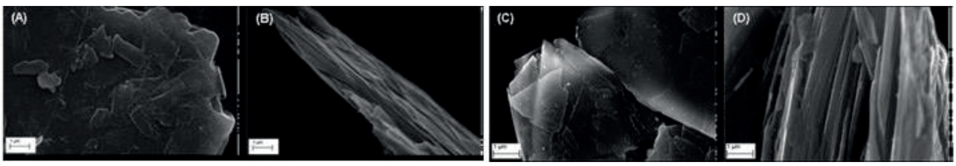

Fig 03: SEM images of the NPG treated with LiCl (A and B) and NPG morphological varieties taken from Ragedara Mine (C and D), performed with JSM 6400 and Gemini Zeiss ultra-scanning electron microscopes-back scattered and secondary electron mode

References

Amaraweera, T. H. N. G., Balasooriya, N. W. B., Wijayasinghe, H. W. M. A. C., Attanayake, A. N. B., Mellander, B. E., & Dissanayake, M. A. K. L. (2018). Surface modification of natural vein graphite for the anode application in Li-ion rechargeable batteries. *Ionics*.

Balasooriya, N. W. B., Hewathilake, H. P. T. S., Somarathna, R. M. U. M., Wijayasinghe, H. W. M. A. C., Rohitha, L. P. S., & Pitawala, H. M. T. G. A. (2015). *PHYSICAL AND CHEMICAL PURIFICATION OF SRI LANKAN FLAKE GRAPHITE AND VEIN GRAPHITE*.

Chung, D. D. L. (2002). Review: Graphite. In *Journal of Materials Science* (Vol. 37, Issue 8, pp. 1475–1489). https://doi.org/10.1023/A:1014915307738

Handl, W. (2021). *6.1.4 Natural Graphite* 6.1.4.1 Occurrence and Classification*.

Jara, A. D., Betemariam, A., Woldetinsae, G., & Kim, J. Y. (2019). Purification, application and current market trend of natural graphite: A review. In *International Journal of Mining Science and Technology* (Vol. 29, Issue 5, pp. 671–689). China University of Mining and Technology. https://doi.org/10.1016/j.ijmst.2019.04.003

Keeling, J. L. (2017). Graphite: properties, uses and South Australian resources. *MESA*, *3*, 84.

Kim, M. Il, Cho, J. H., Hwang, J. U., Bai, B. C., & Im, J. S. (2021). Preparation of high-crystallinity synthetic graphite from hard carbon-based carbon black. *Applied Physics A: Materials Science and Processing*, *127*(2). https://doi.org/10.1007/s00339-021-04300-7

Sasanka Hewathilake, H. P. T. S., Karunarathne, R. I. C. N., Balasooriya, N. W. B., Wijayasinghe, H. W. M. A. C., & Pitawala, H. M. T. G. A. (2015). *AMELIORATION OF SRI LANKAN VEIN GRAPHITE AS AN ADVANCE ELECTRODE MATERIAL FOR THE ANODE APPLICATION IN LI-ION RECHARGEABLE BATTERIES*.

Touzain, P., Balasooriya, N., Bandaranayake, K., & Descolas-Gros, C. (2010). Vein graphite from the bogala and kahatagaha-kolongaha mines, Sri Lanka: A possible origin. *Canadian Mineralogist*, *48*(6), 1373–1384. https://doi.org/10.3749/canmin.48.5.1373

Wickramaarachchi, M., Sasanka Hewathilake, H. P. T., & Balasooriya, N. W. B. (2016). *A NEW CHEMICAL METHOD FOR PURIFICATION AND SURFACE MODIFICATION OF SRI LANKAN VEIN GRAPHITE*. https://www.researchgate.net/publication/317604932

Wu, Y. P., Jiang, C., Wan, C., & Holze, R. (n.d.). *Anode materials for lithium ion batteries from mild oxidation of natural graphite*.