STRUCTURAL MODIFICATION OF SRI LANKAN VEIN GRAPHITE USING MICROWAVE IRRADIATION TECHNIQUE

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ABSTRACT

Sri Lanka possesses large fluid deposited vein graphite with high grade and highly crystalline nature. The aim of this study is to structural modification of Needle Platy Graphite (NPG) variety of Sri Lankan graphite by using rapid and efficient method for high tech applications. The microwave absorption property of graphite was used to carry out the structural modification of NPG by using HNO₃ and HClO₄ as intercalation agents and KMnO₄ as oxidation agents. Finely ground NPG was mixed with KMnO₄ in 1:1 ratio and similar fractions of the mixture were treated with HNO₃ and HClO₄, separately. The HNO₃ and KMnO₄ treated NPG showed the better performances than that of the HClO₄ treated sample. The particle size of the HNO₃ treated sample reduced with the smaller interlayer expansion. Therefore the prepared structurally modified graphite with HNO₃ and KMnO₄ may be a good candidate for the anode application in Li ion rechargeable batteries as well as other advanced technological applications.

Keywords: Vein graphite, Structural modification, Microwave irradiation, Oxidation

INTRODUCTION

Sri Lanka owns high pure, highly crystalline vein graphite and recent studies have proved its applicability as an anode material in rechargeable Li ion batteries (Balasooriya et al., 2007; Amaraweera et al., 2013; Hewathilake et al., 2016). There are four morphological varieties of Sri Lankan vein graphite already identified by considering their different physical and structural characteristics. They are shiny slippery fibrous (SSF), coarse flakes of radial (CFR), coarse striated flaky (CSF) and needle platy graphite (NPG) (Touzain et al., 2010). Almost all these varieties can be found with high initial purity of over 98 % of carbon content. A single vein contains two or more than one variety of graphite and the purity decreases from middle towards the wall rock. The NPG variety, which typically shows the highest purity, most of the time presents in the middle of the vein geologically (Touzain et al., 2010; Hewathilake et al., 2015). According to the geochemical data the main impurities found in the NPG are SiO₂, Fe₂O₃ and MnO and the CFR which owns the lowest purity contains SiO₂, Al₂O₃, Fe₂O₃, MnO, MgO and CaO. The SSF variety owns the second highest purity and it also find mostly in the middle of the vein. The SSF variety owns the like morphology and it forms fibrous perpendicular to the direction of vein propagation as well as the thick plates of the NPG. CFR and CSF are rarely found varieties which are located near to the wall rock and they posses lower purity than the SSF and NPG (Touzain et al., 2010; Amaraweera et al., 2013; Hewathilake et al., 2015).

Lithium ion rechargeable battery is getting more popular in current era due to the introduction of novel portable electrical/electronic devices including electrical vehicles, but the problem is the high cost and scarcity of Li metal. Reduction of high cost can be addressed up to a considerable level by introducing natural graphite instead of synthetic graphite to the anode material of Li ion batteries. Highly crystalline vein graphite is potential material for intercalation of Li ions by forming LiC_6 , with theoretical capacity of 372 mAhg⁻¹. Moreover, the increasing demand of Li metal can be overcome by switching to battery systems based on highly available Na and Mg ions. However, use of natural graphite for those Na and Mg batteries is not a simple task because the interlayer spacing of graphite is only suited for accommodating smaller ions such as Li. Therefore modification of graphite structure, by increasing the interlayer spacing is necessary to future rechargeable batteries. Also the expanded structure may better facilitate more Li ions intercalation hence increasing the capacity of Li ion batteries

From recent years the microwave irradiation of materials is widely popularized than the conventional heating. It is mainly due to its rapid and non-contact heating, energy transfer instead of heat transfer, selective material volumetric heating, heating, less time consuming, heating from the interior of the material body and higher level of safety and automation (Haque, 1999). Microwave irradiation is excellent only for selective electrical conducting materials such as carbon. Though graphite and highly graphitized carbon are electrical conductors due to the existence of vast delocalized π electrons within the carbon layers, they are good microwave absorbers. When adding microwaves to the graphite, the kinetic energy of some electrons increases enabling them to jump outside of the material by resulting ionization of the surrounding atmosphere. At the macroscopic level, it is observed as spark or electrical arc formation and at microscopic level it identified as plasma or microplasma formation.

Among the four morphological varieties of Sri Lankan vein graphite, the highest purity owns the NPG variety (Amaraweera et al., 2013; Hewathilaka et al., 2015) and hence the additional step of graphite purification can be neglected by using NPG as an initial material for the structural modification. It was performed by treating graphite with HNO₃ and HClO₄ acids as intercalating agents followed by treating with KMnO₄ as the oxidizing agent under the rapid and efficient microwave irradiation technique.

MATERIAL AND EXPERIMENTAL PROCEDURE

CHARACTERIZATIONS OF RAW MATERIALS

The carbon content of raw graphite was analyzed using ASTM-561 method. The morphology and microstructure of graphite powders were observed with scanning electron microscopy (SEM) (JSM 6400 and Gemini Zeiss ultra-scanning electron microscope) and X-ray diffraction (XRD) (Rigaku-ultimate IV X-ray diffractometer Cu K_{α} radiation, 1.54 A^{\circ}) was used for the phase analysis. The functional groups on the surface of graphite were analyzed transform infrared by Fourier (FTIR) spectroscopy (Nicolet 6700). The particle size distributions were obtained using particle analyzer (CILAS Nano DS Sn 110).

SAMPLE PREPARATION

The needle platy vein graphite (NPG) variety collected from deep underground operating mines in Sri Lanka was used for the study. The selected graphite sample was subjected to grind using laboratory disk mill and sieved to separate the fraction >75 microns. Powdered graphite and KMnO₄ were mixed in the weight ratio of 1:1 and two similar fractions of the mixture were treated with HNO₃ and HClO₄, separately. After that, the prepared samples were directly placed in a domestic microwave oven at 900 W for one minute. Finally both samples were washed with distilled water until neutral.

RESULTS AND DISCUSSION

CHARACTERIZATION OF RAW MATERIALS

The inspected veins in different levels of underground mine shows strongly zoned but comparably narrow veins. Upward insertion of the hydrothermal fluid through a narrow vein might have formed the NPG morphology at the central part of the vein during the crystallization. However, middle layers composed of mainly SSF and NPG morphologies (Fig. 1) (Hewathilake et al., 2015).



Figure. 1. Occurrence of NPG at the central part of the vein. (A) SEM image of the sample obtained from the vein.

NPG variety of Sri Lankan vein graphite typically contains higher C content and the measured C content of the raw sample was 99.20 %. The completeness of the microwave irradiation process within 1 min inside the microwave oven was verified by the ending of fuming and formation of gases. As seen in the Fig. 2 puffed like macro structure of modified graphite under microwave irradiation was clearly observed by the volume expansion in both HNO₃ and HClO₄ treated samples. In this process, the intercalation agents had migrated in between graphene layers. Under microwave radiation, those intercalate molecules vaporized by forming energy to overcome the vanderwaal forces between graphene layers (Falcao et al., 2007; Kim et al., 2014).



Figure 2. Optical photo of puffed like microstructure of the material with large expansion of volume during the microwave irradiation.

Graphite is a good microwave absorber and when it absorbs microwaves, the π electrons presents in graphite structure will start to oscillate by generating heat. But the heat generated by microwaves is not strong enough to break the existing interactions between graphite layers. Apparently the volume expansion of HClO₄ treated sample seems to be higher than that of HNO₃ treated sample. The exchange reaction path in graphite intercalation compounds with different Bronsted acids depend on the strength of the acid in the order of HClO₄>H₂SO₄>HNO₃>>H₃PO₄. HClO₄ is the strongest inorganic acid whose acidity is greater than that of HNO₃. KMnO₄ with HClO₄ shows extremely strong oxidizing capacity.



Figure 3. XRD graphs of raw NPG, HClO₄ treated and HNO₃ treated graphite.



Figure 4. SEM images of (a) raw NPG, (b) HNO₃ treated NPG and (c) HClO₄ treated NPG.

Therefore, graphite would be over oxidized in HClO₄ treated sample at the beginning. But this reaction consumes large amount of H⁺ ions and it causes to increase the pH value of the system by decreasing the oxidizing capacity of KMnO₄ (Ying et al., 2007). Since the oxidizing ability of HNO₃ is much lower than that of HClO₄, HNO₃ treated graphite is not over oxidized as HClO₄ treated one. Also HNO₃ not only act as an intercalation agent but it provides H⁺ ions by increasing the acidity of the system, which helps to promote the oxidation ability of KMnO₄. When the HNO₃ amount increases, it provides HNO₃ intercalates to accommodate in between graphene layers by increasing the expanded volume. However, excessive amount of intercalates will cause over oxidation and decrease the volume (Wei et al., 2008).

 $5C_n + MnO_4 + 8H^+ \iff 5C_n^+ + Mn^{2+} + 4H_2O \text{ (Ying et al, 2008)}$ $C_n^+ + ClO^- + xHClO_4 \iff C_n^+ ClO^- .xHClO_4 \text{ (Ying et al, 2008)}$ $nC + xHNO_3 \iff C_n^+ (HNO_3)_{x-1} NO_3^- + H^+ + e^- \text{ (Herold, 1978)}$ $HNO_3 + e^- + H^+ \iff NO_2 + H_2O \text{ (Balasooriya et al, 2013)}$

XRD results (Fig. 3) were used for the phase analysis and to calculate the cell parameters of the raw, HNO₃ and HClO₄ treated graphite. They exhibit some changes in the position of the G(002) major crystalline peak. Two theta values of raw NPG, HClO₄ and HNO₃ treated graphite are 26.55°, 26.49° and 25.44°, respectively. Hence the corresponding d_{002} values are 0.3353 nm, 0.3363 nm and 0.3498 nm. Microwave treatment of graphite with HClO₄ slightly had increased the inter-planar distance of graphite but without disturbing the crystalline structure. But in the case of HNO₃ treatment, interlayer space is higher than that of HClO₄ treated sample. Moreover, the major (d_{002}) peak has got broaden and hence affected the highly crystalline nature of this vein graphite.

According to the SEM images (Fig. 4), both HNO₃ and HClO₄ treated samples show a loosened and puffed structure. Further sharp edges of the raw graphite have become blunted in the treated samples. The over oxidation due to the strong oxidizing ability of HClO₄ acid with KMnO₄ can be clearly seen in the SEM image of HClO₄ treated NPG. But the HNO₃ treated sample show slightly oxidized behavior when compared with HClO₄ treated sample.

The functional groups attached to the graphite structure during the intercalation and oxidization processes were identified by the FTIR analysis (Fig. 5).



*Figure 5. FTIR spectra of NPG raw, HNO*₃ *treated and HClO*₄ *treated graphite.*



Figure 6. Particle size distribution of (a) Raw NPG, (b) HClO₄ treated and (c) HNO₃ treated samples.

The broad band between 3400- 3700 cm⁻¹ in all three graphs corresponds to O-H stretching mode while the peak at 1635 cm⁻¹ can be related to the C=C bond of unoxidized sp² groups. The sample treated with HNO₃ shows the high intensity of O-H stretching vibration.

The sharp peak at 1360 cm⁻¹ in HNO₃ treated sample corresponds to hydroxyl groups of carboxylic acid (Sasha, el al., 2006; Yoshiaki, et al., 2007). The vibrational mode of single C-O bonds present in both HNO₃ and HClO₄ treated samples at 1250 cm⁻¹ and 1100 cm⁻¹ respectively. The number of functional groups attached to surface is higher in HClO₄ treated sample than the HNO₃ treated sample due to the over oxidation of HClO₄ in the presence of KMnO₄ oxidizer. As well as the sharp peaks with high intensities in HNO₃ treated sample confirms the efficiency of oxidizing process.

Table 1.	Particle	size	distribution	of	`samples
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	Raw (µm)	HClO ₄ treated	HNO ₃
		(µm)	treated (µm)
D10	1.3186	1.4885	0.3305
D50	2.2169	2.5028	0.4204
D90	3.7142	4.1931	0.5327

As can be seen from Table 01 and Fig. 6, the particle size distribution of samples, the average particle size of the raw NPG, HClO₄ treated and HNO₃ treated are 2.2169 μ m, 2.5028 μ m and 0.4204 μ m, respectively. Particle size of the HNO₃ treated sample shows rapid decrement when comparing with HClO₄ treated sample. It is obvious that with the increasing of particle size, the surface area of the material increases. Therefore the HNO₃ treated graphite may provide larger surface area which aids to accomadate more Li ions, hence promoting the electrode performance.

CONCLUSIONS

The structurally modified graphite was synthesized within a very short time by a prompt and efficient method using microwave irradiation technique using NPG variety of Sri Lankan vein graphite. Although the HClO₄ is stronger acid than the HNO₃, over oxidation with the increasing of pH value decrease the oxidation ability of HClO₄. Therefore preparation of structurally modified graphite using HNO₃ as intercalation agent and KMnO₄ as oxidizer under microwave irradiation technique is more efficient. The sharp peaks in HNO₃ treated sample in FTIR spectrum also confirm successful oxidation of graphite. The surface area of the HNO₃ treated sample is higher than that of the raw graphite and HClO₄ treated graphite. Hence the prepared surface and structurally modified NPG variety with HNO3 and KMnO₄ can be a good candidate for advanced technological applications such as an anode material for Li ion rechargeable batteries.

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