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STUDY OF THERMAL BEHAVIOR OF VEIN GRAPHITE FOR ADVANCE TECHNOLOGICAL APPLICATIONS

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ABSTRACT

Thermal behavior of graphite is very important in relation to modification of graphite surface and particularly when subjecting them to high temperature treatments. Therefore, the knowledge of the oxidative reactivity of graphite is very essential. This study is conducted on the thermal behavior of Sri Lankan vein graphite leading to the development of anode applications incorporated in rechargeable Li-ion batteries. Thermogravimetric analysis of Sri Lankan vein graphite varieties, having different structures was stable within 500-600 °C under normal atmospheric conditions. Further, the thermal behavior of vein graphite was observed to be dependent on the amount of active site in the edge plane, the type and the amount of impurities present in graphite. Mild thermal oxidation could result the formation of oxidizing species and elimination of structural imperfections within vein graphite surface. Electrochemical investigations indicated better electrochemical performance in graphite with low initial irreversible capacity, due to thermal oxidation. In addition, this study shows the potentiality of thermally oxidized vein graphite as a low-cost anode material for Li-ion batteries.

Key words: Vein Graphite, Thermal Behavior, Thermal Oxidation, Anode

INTRODUCTION

Sri Lanka is well known for high quality vein graphite consisting about 95-99 % of pure carbon. This vein graphite is unique because of its high purity, high crystallinity, large reserves and mode of occurrence (Herath, 1995). Vein graphite in Sri Lanka have been categorized into four common structurally distinct morphological graphite varieties, shiny-slippery-fibrous graphite (SSF), needle-platy graphite (NPG), coarse striated-flaky graphite (CSF) and coarse flakes of radial graphite (CFR) (Touzain et al., 2010). Shiny-slippery-fibrous graphite (SSF) consists of very fine fibers varying in length from 1 mm to 5 cm and may also contain continuous flakes. The needle-platy graphite (NPG) is characterized by short (<1 cm) needle-shaped fibrous grains. CFR has a radial structure and coarse flakes were found around the nuclei, which are often calcite and quartz (Touzain et al., 2010). The coarse striated-flaky (CSF) graphite is formed by the aggregation of striated coarse flaky grains, which indicate a movement of the graphite within the host rock. Traditionally, Sri Lankan vein graphite is used for crucibles, carbon brushes in electric motors, lubricant etc.. However, in the recent vears. а number of research investigations have been initiated to develop Sri Lankan vein graphite for advanced technological applications. Use of vein graphite for the anode of lithium ion rechargeable battery, polymergraphite composites, synthesized graphene oxides and their nano carbon composites are some of the products (Amaraweera, et al., 2014, Balasooriya, et al., 2013, Kumarasinghe, et al., 2013).

Thermal behavior of graphite can provide information of the anisotropy of the surfaces parallel and perpendicular to the basal plane (Badenhorsd and Focke, 2013, Zaghib *et al.*, 2014, Jiang, 2000). Recently, graphite has also been identified as a very important industrial mineral that could be utilized in thermal and high-friction applications, which require good thermal and electrical conductivity. Furthermore, graphite is widely used in the metallurgy, aeronautical and nuclear industry due to high heat conduction, high corrosion stability, in many media and the high thermal stability (Nightingale, 2013). However, graphite exhibits a very poor oxidation resistance in air at high temperature, which limits its applications in many environments (Xiaowei, 2004). Oxidation behavior of graphite depends on the porosity of graphite, active surface area, oxidizing temperature, particle size, relative fraction of edge and basal plane sites (Chen et al., 2012, Zaghib et al., 2001, Jiang et al., 2000). Thermally oxidized natural graphite was identified as a promising anode material for Lithium ion rechargeable batteries (Shim and Striebel 2007, Kumar, et al., 2001). Study of oxidation behavior can make prediction for weight loss and is of the greatest importance for practical applications (Chen et al., 2012, Kumar, et al., 2001). Therefore, this paper is based on studying the thermal behavior of Sri Lankan vein graphite varieties, having different structures. The work was carried out by thermally oxidizing the vein graphite surface, developing those as an anode material for lithium ion rechargeable batteries.

METHODS OF STUDY

Different structural types of vein graphite from Sri Lanka (Touzain et al., 2010) with particle size < 53 µm and carbon content 95-99%, were used for this study. Identification of different structural varieties was carried out by visual inspection. Small chips from each variety were crushed in a vibratory disk mill for three to four minutes to form fine powders. Particle size fraction of < 53 µm separated by mechanical sieving, was used for the analysis. Carbon percentages of the graphite samples were determined according to ASTM-C 561. Thermogravimetric analyses were carried out for graphite powder (0.5 mg) by heating up to 800 °C in a platinum pan at a heating rate of 10°C min⁻¹, under nitrogen atmosphere (Perkin-Elmer TGS-2, Thermogravimetric System).

Needle-platy graphite was thermally oxidized at 500 °C in air for six hours to study the oxidation behavior of vein graphite. The raw and thermally oxidized graphite was structurally characterized by X-ray diffraction (Siemens D5000 diffractometer). The rhombohedral phase content was calculated using $((101)_R/(101)_H)$ intensity ratio. The morphology of graphite was observed by field emission Scanning Electron Microscope (SEM, FEI Quanta 200 FEG-ESEM). The Fourier Transform Infrared (FT-IR) technique was used to identify the formation of acidic groups or an oxide layer on the graphite surface (Nicolet 6700 FTIR spectrophotometer).

Coin Cell (CR 2032) was assembled in an argon-filled glove-box (< 1 ppm O_2 and H_2O) with the prepared circular disks of purified and thermally oxidized NPG as anode electrode, Lifoil (Sigma Aldrich) as the reference and counter electrodes with а porous polypropylene separator (Cellgard 2400) in an non-aqueous electrolyte of 1M LiPF6 in ethylene carbonate, diethyl carbonate and dimethyl carbonate in 1:1:1 in weight ratio (LP71, BASF, USA). Finally, the charge discharge study of assembled cells were carried out at C/5 rate (1C = 372 mAg^{-1}) with a cut-off voltage of 0.002 - 1.5 V at room temperature using Metrohm Auto lab (PGSTAT302N) controlled by Nova 1.1 program.

RESULTS AND DISCUSSION

Thermal Behavior of Vein Graphite, having Different Structural Types

Figure 1 shows the X-ray diffractograms (XRD) obtained on SSF, NPG, CSF and CRF graphite varieties. In this figure, the diffraction pattern of the powdered sample exhibits welldefined peaks, which indicate that the graphite powders possess high crystallinity. X-ray diffractograms of raw SSF with 98.65 % carbon content shows the diffraction peaks corresponding to secondary phase of pyrite and chlorite. However, the diffractograms of NPG, CSF and CRF varieties show the existence of trace amounts of pyrite phase only.



Fig. 1 X-ray diffractograms obtained on SSF, NPG, CSF and CRF graphite verities



Fig. 2 Thermogravimetric plots of (1) raw SSF, (2) raw NPG, (3) raw CFR and (4) CFR, graphite varieties.

Thermogravimetric analysis (TGA) was used to investigate the thermal stability and oxidation behavior of vein graphite. Figure 2 shows the results of TGA analysis conducted on different structural varieties of vein graphite. TGA curves show an initial gradual change in weight, followed by a precipitous drop as the temperature increases.

The thermogravimetric plot of raw SSF graphite, which has higher impurity content as evident by XRD data, shows a three stage weight loss. The first weight loss occurs between 200 °C and 400 °C, resulting a weight loss of 0.29 %. The second weight loss occurs between 450 °C and 550 °C, which amount to 0.88 %. The final step of weight loss started at 592 °C and occurs rapidly. Similarly, the raw NPG with low impurity content also shows three stages of weight losses in thermogravimetric plot. The first weight loss occurs between 50 °C and 100 °C with a 0.01% of weight loss. The second weight loss.

 $^{\rm o}$ C and 350 $^{\rm o}$ C is related to 0.04 %. The final step of weight loss started at 614 $^{\rm o}$ C and completes rapidly. Moreover, the CSF graphite shows weight loss of 0.05 % between 150 $^{\rm o}$ C and 200 $^{\rm o}$ C and another weight loss of 0.04 % between 280 $^{\rm o}$ C and 310 $^{\rm o}$ C. Final rapid weight loss of CSF graphite sample started between 580 $^{\rm o}$ C and 590 $^{\rm o}$ C. Finally, the CFR graphite shows weight loss of 0.03 % between 280 $^{\rm o}$ C and 310 $^{\rm o}$ C and another rapid weight loss in between 580 $^{\rm o}$ C and 590 $^{\rm o}$ C.

TGA data of purified and raw graphite suggests that the thermal behavior of raw and purified graphite depends on the nature of each structural type and impurity content. Thermal behavior of SSF graphite with higher pyrite content shows a more complex thermal behavior and weight loss. This may be resulted due to the combination of following two factors. Firstly, of graphite oxidation behavior at low temperature is sensitive to the inhomogeneous distribution of impurities and some impurities 23

have elements that catalyze carbon-oxygen reactions (Badenhorsd and Focke, 2013). These elements include Na, K, Ca, Cu, Ti, Fe, Mo, Cr, Co, Ni and V (Badenhorsd and Focke, 2013). Therefore, it is evident that different thermal behavior in raw vein graphite with different impurity content, at temperatures below 500 °C. Secondly, the thermal decomposition of pyrite occurs in the temperature range of 350 °C to 780 °C in an inert atmosphere, depending on the size and morphology of pyrite crystals (Hu et. al., 2006, Boyabat *et al.*, 2003).

The oxidation behavior of graphite in air is strongly dependent on crystallographic structure and surface area (Zaghib et al., 2014, Placke et al., 2012, Jiang, 2000). The crystallographic structure of carbon consists of distinct surface sites, i.e. basal plane and edge sites. The oxidation rate of graphite depends on the active surface area available for the reaction especially in edge site (Badenhorst and Focke, 2013). The study showed that the emergence of (1 1 0) peak at $2\Theta = 43^{\circ}$ in the XRD spectra is a strong indication of decrease in the concentration of active sites (Jiang, 2000). Graphite having highest fraction of edge site has low ignition temperature and once ignition occurs, the graphite samples with a higher fraction of edge sites oxidize more rapidly as the temperature increases due to enhanced heat that is generated by the exothermic oxidation reaction (Badenhorst and Focke, 2013).

The X-ray diffractograms obtained on NPG further indicates that the relatively intense peak at $2\Theta = 43^{\circ}$ relative to SSF, CSF and CRF graphite (Figure 1 (b). Peak at $2\Theta = 43^{\circ}$ in the XRD spectra indicate the decrease in the concentration of active sites (Jiang, 2000). NPG shows highest ignition temperature (614 °C) and low rate of oxidation. This may be related to the low concentration of active sites as indicated by the XRD of NPG. SSF, CSF and CRF varieties or morphologies with low intense peak at 2Θ = 43°, relative to the NPG show lower ignition temperature and rapid oxidation. These imply that the vein graphite is stable up to a temperature of 500 °C to 600 °C, depending on amount of active site in edge plan and impurity content.

Thermal Oxidation of Vein Graphite

NPG graphite purified to 99.98 % of carbon (Amaraweera *et al.*, 2014) were thermally oxidized (550 $^{\circ}$ C for six hours in air) to study the

oxidation behavior and to develop the anode material for lithium ion rechargeable batteries.

XRD analyses were used to study the effect of the crystal structure during the process of thermal oxidation. The XRD pattern indicates that the thermal oxidation of the graphite power does not affect the crystallographic structure of NPG graphite (Figure 3 (a)). The rhombohedral phase content, $((101)_R/(101)_H$ intensity ratio (%) also remains almost constant after the thermal oxidation (Figure 3 (b)). Furthermore, the XRD patterns clearly indicate that the thermal oxidation does not involve the formation of any intermediate graphite intercalation compound or any other secondary phase.

The SEM micrograph of raw NPG and thermally oxidized NPG sample are shown in Figure 4. The SEM image of raw NPG sample implies that the graphite particles consists of inhomogeneous or rough surfaces (Figure 4). SEM images of NPG sample after thermal oxidation indicates a significant reduction of surface roughness and heterogeneity.

The FT-IR spectra of the purified NPG and mild oxidized NPG (purified) by thermal oxidation in air are shown in Figure 5. In the FT-IR spectra, the broadband between 3500 and 3100 cm⁻¹ is attributed to the bending mode of the molecular water. The band at 2330 cm⁻¹ can be assigned to CO_2 in the gas phase, physically adsorbed on the material surface. The FT-IR spectrum of purified NPG showed weak absorption band owing to $v_{C=C}$ stretching at 1645 cm⁻¹ and doublet band between 2921 and 2850 cm⁻¹ corresponding to the presence of aliphatic C-H bonds (Kumar et al., 2001, Peckett et al., 2000). In contrast, mild oxidized NPG (purified) by thermal oxidation shows the evidence for formation of carboxylic acid group on the surface of graphite (Figure 5). Vibrational bands correspond to $v_{C=O}$ stretching between 1720 and 1680 cm⁻¹, v_{O-H} stretching at 1360 cm⁻¹ and v_{O-O} stretching between 1260 and 1100 cm⁻¹ imply the formation of carbonyl groups, alcoholic phenolic groups and single C-O groups respectively (Kumar et al., 2001, Peckett et al., 2000). Further, wide, weak band corresponding to $v_{(C-O-C)}$ presents around 1000 cm⁻¹. These bands are in agreement with those published in several other works (Kumar et al., 2001, Peckett et al., 2000).

Figure 6 shows the results of TGA study on NPG and mild oxidized NPG by thermal oxidation (in air). At first, the weight decreased slowly because of thermal decomposition of



Fig. 3 (a) The X-ray diffractograms of NPG and mild oxidized NPG by thermal oxidation (in air) and (b) Variation of the rhombohedral phase content in each NPG powder sample.

some oxides and slight oxidation under air including the removal of a small amount of absorbed water. Later, when the temperature reached at about 500 °C, combustion began. TGA results suggest that the temperature at which combustion began increased after thermal oxidation. The more reactive component in the carbon mixture will oxidize at lower ignition temperature (Badenhorst and Focke, 2013)]. Therefore, structural defects are rapidly oxidized and it initiates the combustion reaction of NPG at a lower temperature.

Thermal oxidation leads to stabilize the graphite structure due to elimination of some reactive structural imperfections at graphite surface (Shim and Striebel 2007, Kumar, et al., 2001). Since the reactive structural imperfections are removed, temperature of started shifting combustion to higher temperatures, after the mild oxidation treatments. This is indicated by the shifting of temperature, at which combustion started in the TGA plot (Figure 6). Thermally oxidized NPG exhibits a lower weight loss of 0.5 to 1.7 wt. % compared to the NPG (purified) graphite (4.75 wt. %). The lowering of weight loss suggests a lower concentration of surface defects and impurities on the graphite surface (Placke et al., 2012). Relating to the previous results, it seems that a decreased amount of surface "defects" and possible removal of surface impurities by mild oxidation treatment by thermal pathways lead to a thermally more stable graphite surface structure (Shim and Striebel 2007, Kumar, 2001).

Figure 7 shows the d.c. electrical conductivity of NPG and thermally oxidized NPG

powders. The d.c. electrical conductivity measurements performed on the dense pellets prepared with the graphite powders, indicate a the semiconducting nature to these materials. Further, the thermal oxidation had not caused any adverse effect on the electrical conductivity of graphite.

Table 1 summarizes the charge-discharge data obtained with half cells assembled with purified and thermally oxidized graphite anodes. The first cycle discharge and charge capacity of purified NPG (99.98 % of C) are 327.5 mA h g⁻¹ and 287.5 mA hg⁻¹ respectively. Initial irreversible capacity of purified NPG is 40.1 mAhg⁻¹ with coulombic efficiency of 87.8 %. After the thermal oxidation, initial discharge capacity of NPG of C) increased to 369.52 mAhg⁻¹ while reducing the initial irreversible capacity to 35.7 mA h g⁻¹.

Morphology and chemistry of the graphite surface have significant influence on the formation of SEI (Solid Electrolyte Interface) laver and irreversible capacity of graphite anode (Placke et al., 2012, Kumar, 2001). In this study, the FT-IR, TGA and SEM analysis conducted on NPG graphite indicate the possible elimination of reactive structural imperfections from the graphite surface and formation of dense layer of oxides on the graphite surface as a result of thermal oxidation. The dense oxidized layer could give rise to a more stable SEI during the first lithium intercalation process as also reported previously (Kumar et al., 2001). Further, this layer could act as a passive film and block the solvent co-intercalation that leads to exfoliation of graphite (Kumar et al., 2001). Therefore, it is the reason behind the thermally



Fig. 4 SEM image of (a) NPG and (b) mild oxidized NPG by thermal oxidation (in air)



Fig. 5 FT-IR spectra of the NPG and mild oxidized NPG by thermal oxidation (in air)



Fig.6 TGA of purified NPG and mild oxidized NPG (purified) by thermal oxidation (in air)



Fig. 7. The d.c. electrical conductivity of NPG and thermally oxidized NPG.

 Table 1
 The first, second and tenth cycles charge - discharge data for the half cells assembled with raw and purified graphite electrodes.

Anode	Cycle No	Discharge Capacity mA h g ⁻¹	Charge Capacity mA h g ⁻¹	Columbic Efficiency %	Irreversible Capacity mA h g ⁻¹
NPG	1	327.6	287.5	87.8	40.1
	2	283.8	276.9	97.6	6.8
	10	227.8	224.6	98.6	3.1
Thermally Oxidized	1	369.52	333.6	90.2	35.7
NPG	2	342.24	334.8	97.8	7.4
	10	288.92	285.2	98.7	3.7

oxidized NPG to show a higher initial coulombic efficiency and low initial irreversible capacity compared to purified NPG, in this study.

CONCLUSIONS

Thermogravimetric analyses of different structural verities of the vein graphite indicate that the thermal behavior of vein graphite depends on the amount of active site in the edge plane and type and amount of impurities present. SSF graphite, which has higher impurity content, shows the more complex thermal behavior. NPG graphite is characterized by having lower level of active sites in edge plane and highest ignition temperature and low rate of oxidation. The stability of the Sri Lankan vein graphite lies within 550 to 600 °C, in air indicates its potentiality for high temperature applications. Thermal oxidation of NPG in air leads to formation of dense layer of oxides on the graphite surface and reduces surface roughness and heterogeneity. This oxidized layer does not leads to changes in the crystallographic structure and formation of an intermediate graphite intercalation compound or other secondary phase. Further the lithium ion half-cell assembled with thermally oxidized vein graphite shows promising electrochemical performance. This implies the suitability of thermally oxidized Sri Lankan vein graphite for the anode application of lithium ion rechargeable batteries.

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