

AMELIORATION OF SRI LANKAN VEIN GRAPHITE AS AN ADVANCE ELECTRODE MATERIAL FOR THE ANODE APPLICATION IN LI-ION RECHARGEABLE BATTERIES

H.P.T.S. Hewathilake¹, R.I.C.N. Karunaratne¹, N.W.B. Balasooriya²,
H.W.M.A.C. Wijayasinghe¹ and H.M.T.G.A. Pitawala³

¹ National Institute of Fundamental Studies, Kandy, Sri Lanka

² Faculty of Applied Sciences, South Eastern University, Sammanthurai, Sri Lanka

³ Department of Geology, University of Peradeniya, Peradeniya, Sri Lanka
tharindu.tsh@gmail.com, niroshan_ka@yahoo.com

ABSTRACT

Sri Lanka has large reserves of vein graphite with high initial purity and high crystallinity. The application of natural graphite as an anode material for lithium-ion rechargeable batteries was able to provide better performance with high reversible capacity, appropriate potential profile, and low cost. For this study, natural graphite samples were obtained from Kahatagaha-Kolongaha mines of Sri Lanka. Initially the samples were categorized into the four structurally distinct graphite varieties, by visual observation. Half-cell testing was confirmed that purified Sri Lankan vein graphite can achieve highest capacity than the theoretical capacity of Li-ion rechargeable battery. Therefore the purified and surface modified Sri Lankan vein graphite by acid digestion method can be successfully utilized as an anode material for the Li-ion rechargeable batteries.

Keywords: Vein Graphite; Crystallinity; Lithium-Ion Rechargeable Batteries

INTRODUCTION

Graphitic materials most commonly utilized as the anode component for the Lithium-Ion rechargeable Batteries (LIB). However problems associated with graphitic anodes forced to look forward for the application of synthetic anode materials for the rechargeable lithium ion battery anode [3]. High cost, lower discharge capacity and large capacity losses are still remain as major limitations. The application of natural graphite as an anode material for lithium-ion rechargeable batteries was able to provide better performance with high reversible capacity, appropriate potential profile, and low cost. The natural state gangue minerals and other impurity contaminations and the anisotropic conditions on the graphite surface highly affected for the large irreversible capacity loss and the poor cycleability. [1-3]. Therefore natural graphite should be upgraded up to battery grade electrode material.

Sri Lanka has large reserves of vein graphite with high initial purity and high crystallinity. They have been categorized into structurally distinct four morphological varieties, shiny-slippery-fibrous graphite (SSF), needle-platy graphite (NPG), coarse striated-flaky graphite (CSF) and coarse flakes of radial graphite (CFR) [4]. Recent studies on anodic application proved that Sri Lankan vein graphite has a good potential as its raw form. However chemical purification, mechanical and chemical modification show that the effectiveness of the anodic performances can be further upgraded. The purification methods such as HCl acid leaching and alkali roasting evidenced that the purity of Sri Lankan vein graphite can be upgraded over 99% of carbon content. [5, 6]. Mild oxidation is a well-known surface modification method that introduces acidic group on the graphite surface by thermal and chemical treatments. However, the oxidation procedures have a bulk usage of strong chemicals, high temperature treatments and time consuming procedures [7-9]. Since the purification showed a profound effect on surface modification of natural graphite, previously the purification and the surface modification done as separate steps.

Therefore this study focused on acid digestion method with three strong acids to achieve ultra-high purity modified graphite for the electrode applications via minimizing the utilization of chemicals and treatment time.

METHODOLOGY

For this study, natural graphite samples were obtained from Kahatagaha-Kolongaha mines of Sri Lanka. Initially the samples were categorized into the four structurally distinct graphite varieties, by visual observation. For the acid digestion method each variety of vein graphite powder samples (particle size <math><53\ \mu\text{m}</math>) 10.0 g were treated with a mixture of acids HF, HNO₃ and H₂SO₄ acids until the evaporation of the mixture. After complete evaporation, 25.0 ml of distilled water was added to each container and stirred for one hour at room temperature. The mixture was filtered and residue was washed to neutral and vacuum dried at 120 °C for 12 hours [5]. Both raw and treated samples were characterized by ASTM - 561 method for carbon content, X-ray Diffraction techniques (XRD) and Fourier Transform infrared (FTIR) spectroscopy.

Anodic performances evaluated with CR 2032 coin cells composed with graphite anode and a counter electrode (lithium metal) that were separated by a glass fiber film. The anode was prepared by a mixture of treated graphite, PVDF, acetylene black together with N-Methyl-2-pyrrolidone solvent, on a copper current collector. 1M LiPF₆ in EC: DMC vol. 1:1 was used as an electrolyte.

RESULTS AND DISCUSSION

Table. 1 summarizes the carbon content analysis of the treated and untreated vein graphite samples. It is clearly noted that the applied digestion procedure was able to enhance the carbon content comparable with the initial values. All four morphological varieties were upgraded over 99.98%.

Table 1.: Carbon percentage in raw and purified four varieties of vein graphite varieties

Variety	Carbon content (C%)	
	Raw form	After Purification
Needle Platy Graphite (NPG)	99.93	99.99
Shiny Slippery Fibrous graphite (SSF)	99.65	99.98
Coarse striated-flaky graphite (CSF)	99.08	99.98
Coarse Flakes of Radial graphite (CFR)	98.66	99.99

X-ray diffractograms for purified graphite were shown in figure 1. All the diffractograms for the four morphological varieties evidenced for a common phases appearance such as 002, 004, 101 hexagonal and 112 of graphite.

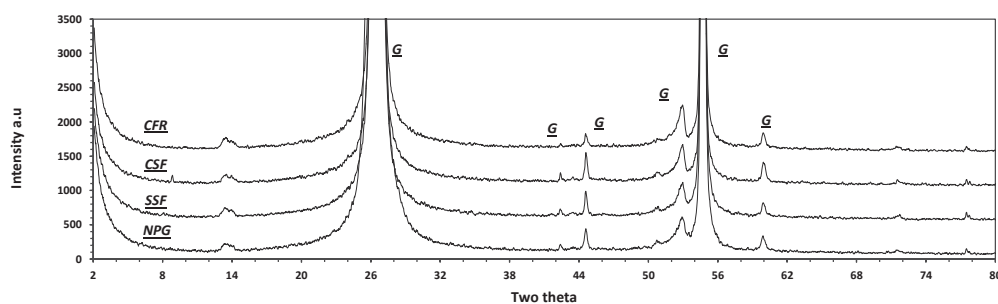


Figure 1.: XRD diagrams of each purified varieties of Sri Lankan vein graphite. The prefix “G” denote for the phases of graphite.

A detailed analysis of the XRD patterns shows that impurity phases, 101 rhombohedral, 100 and 102 phases were greatly suppressed. However the treatment able to preserve the structure of graphite without any major changes.

Figure 2 represents the three FTIR spectrum series of treated vein graphite varieties. After the purification treatment particular vibrational bands were introduced for all four varieties. Carbonyl group $\nu_{C=O}$ stretching at $1720-1680\text{ cm}^{-1}$, alkene group $\nu_{C=C}$ stretching at 1637 cm^{-1} and ν_{O-H} stretching at 1360 cm^{-1} were present with high absorption values. Further ν_{C-O} stretching at 1260 cm^{-1} given a broad band. Appearance of these peaks relevant proved that the applied acid digestion technique was able to modify the surface of all four morphological vein graphite simultaneously with purification.

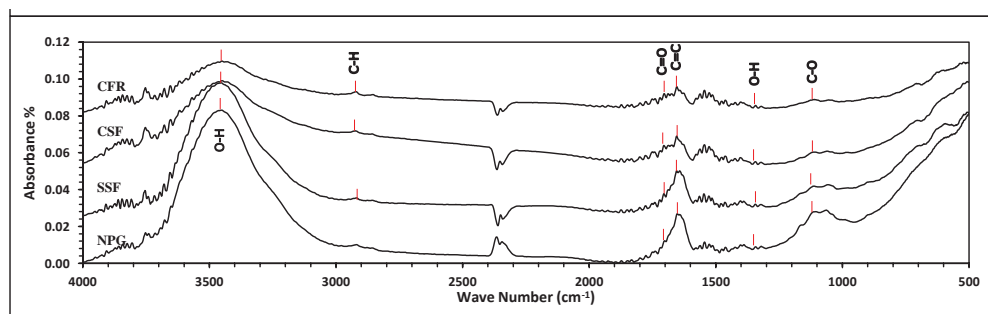


Figure 2.: FTIR spectra (KBr Pellets, Absorbance mode) for the purified four morphological varieties of Sri Lankan vein graphite.

The initial discharge-charge profiles for the assembled half-cell with purified NPG vein graphite variety at the current rate of $C/5$ has provide more interesting results. The discharge curves drop down smoothly to the 0.2 V point, where the first lithium intercalation initiates and clearly illustrate the next three steps of lithiation after that. Further, purified NPG vein graphite variety able to achieve high discharge capacity at around 430 m Ah/g at the first cycle discharge with very low irreversible capacity.

CONCLUSION

The acid digestion technique was successfully improved the purity of Sri Lankan vein graphite for all four varieties up to extra high purity level over 99.98% of carbon. Notably the same purification method was able to perform the surface modification of graphite as same as the traditional mild oxidation process, with the minimum usage chemicals and reaction time. Moreover half-cell testing was confirmed that purified Sri Lankan vein graphite can achieve highest capacity than the theoretical capacity of Li-ion rechargeable battery. Therefore the purified and surface modified Sri Lankan vein graphite by acid digestion method can be successfully utilized as an anode material for the Li-ion rechargeable batteries.

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