Development of Sri Lankan Vein Graphite for Lithium-Ion Rechargeable Battery Anodes by Chemical Oxidation

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Introduction

Graphite has been used as an anode material in state-of-the art Li-ion batteries due to high capacity (337 mAh/g) and low potential (0.1 – 0.3 V vs. Li^+/LI) of its lithium intercalation compound (Li_xC_6, X=1) (Kurzweil and Brandt, et al., 2009). Reversible intercalation and deintercalation of Li^+ ions with graphite are attributed to successful formation of a stable and protecting solid electrolyte interface (SEI) on the graphite surface, which is known to complete in initially few cycles. Previous studies have shown that formation of the SEI is greatly affected by electrolyte composition, morphology and surface chemistry of graphite (Fu et al., 2006). For this reason, only a limited number of graphite has been found to be suitable for the anode of Li-ion batteries. To use natural graphite that is inexpensive and abundant, many researchers have currently focused on the surface modification of natural graphite (Fu et al., 2006). The graphite surface can be modified by mild oxidation in air and using solution of strong oxidant (Balasooriya, et al., 2006,2007). Mild oxidation induce acidic group on the graphite surface, which act as surface film to produce SEI resulting high reversible capacity. However, in gas-solid inter-phase oxidation reaction, control of the homogeneity of the product is difficult to maintain. Consequently, a liquid-solid interface oxidation reaction has been introduced as the use of chemical oxidant. Nitric acid is well known as a strong oxidant and its standard potential is > 1.5V (Wu et al., 2003).

Sri Lanka is well known for high quality vein graphite, containing 95-99% of pure carbon (Herath, 1995). They were categorized into four structural types, namely, coarse flakes of radial (CFR) graphite, coarse striated-flaky (CSF) graphite, needle-platy (NPG) graphite and shiny-slippery-fibrous (SSF) graphite, based on the structural and physical characteristics (Touzain, et al., 2010). Recent investigation pointed out that vein graphite from Bogala mine have sufficient electrical conductivity to be used as potential candidate for Lithium ion rechargeable batteries (Geethika, et al., 2010) and chemical oxidation in $(NH_4)_2$ S_2O_8 increase the reversible capacity (Balasooriya, et al., 2006,2007). The present study aims to chemical oxidation of natural vein graphite in nitric acid in order to upgrade the quality of vein graphite as anode material for lithium ion rechargeable batteries.

Materials and Methodology

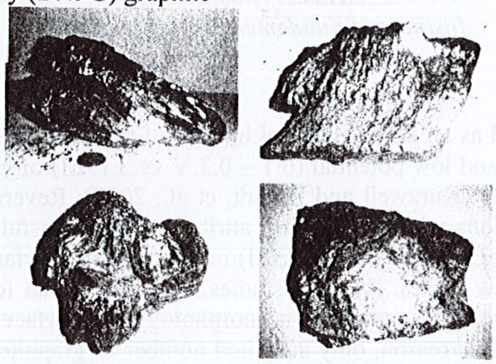
Natural Sri Lankan vein graphite from Bogala mine was obtained for this study. Identification of different structural varieties was done by visual inspections. Samples were categorized into the four structurally distinct graphite varieties (Touzain, et al., 2010), namely, shiny-slippery-fibrous graphite (BSSF), coarse striated-flaky graphite (BCSF), coarse flakes of radial graphite (BCFR) and needle-platy graphite (BNPG) (Figure 1).

Different structural varieties of vein graphite powder < 63 μm were dipped in concentrated nitric acid solutions (40-70 %) and kept under stirring at 60^0C, separately, for 15 minutes. Then samples were subsequently washed with water until neutral and dried. The modification of graphite matrix during oxidation was characterized by Nicolet 6700 FTIR spectrophotometer in 500- 4000 cm^{-1} region. Dense graphite pellets of 12 mm diameter and thickness of 8.5 mm were prepared using cold uniaxial pressing at 100 MPa. Electrical characterization was performed on the pellets by four-probe d.c. conductivity method at room temperature.

Figure 1: Structural types of vein (a) Bogala Coarse Striated Flaky (BCSF), (b) Bogala Shiny-Slippery Fibrous (BSSF), (c) Bogala Coarse Flakes of Radial (BCFR) graphite and (d) Bogala Needle-Platy (BNPG) graphite

(a) (b)

(c) (d)



Results and Discussion

Table 1: Electrical conductivity of different structural verities of Bogala graphite

Structural Type	Electrical Conductivity (σ) of Raw Sample at 25°C ($S\ Cm^{-1}$)	HNO_3 concentration	Electrical Conductivity of Chemically Oxidized Graphite at 25^{0}C ($S\ Cm^{-1}$)
BSSF(Bogala Shiny- Slippery-Fibrous graphite)	1.7	40%	1.8
		50%	2.2
		60%	6.6
		70%	4.7
BNPG(Bogala Needle-Platy graphite)	3.9	40%	1.8
		50%	3.4
		60%	4.0
		70%	1.0
BCFR(Bogala Coarse fakes of Radial Graphite)	2.4	40%	1.1
		50%	4.5
		60%	5.2
		70%	3.5
BCSF(Bogala Coarse Striated Flaky graphite)	3.2	40%	1.6
		50%	2.5
		60%	2.8
		70%	1.7

The d.c. electrical conductivity details of these structural varieties are given in Table 1. As seen in the table all these structural varieties of Bogala graphite possess the electrical conductivity around 1.7 to 3.9 Scm^{-1} at room temperature. The d.c electrical conductivity of graphite after oxidation with 60% and 70% HNO_3 has increased slightly. This suggests of having sufficient electrical conductivity in, vein graphite from Bogala and they are potential candidate for active anode materials in rechargeable lithium-ion batteries.

The Fourier Transform Infrared (FTIR) spectra of ground, untreated graphite and chemically oxidized BSSF graphite are shown in Figure 2. Weak absorption bands around 628-669 cm^{-1}, 1384.661 cm^{-1}, 1654.651 cm^{-1} and 2298-2360 cm^{-1} appeared at untreated graphite powder. The FTIR spectroscopic pattern of the chemically oxidized samples belonging to BSSF, BCSF and BCFR types showed absorption peaks corresponding to stretching vibration of aryl carbonyl groups around 1700-1680 cm^{-1} region (Aurbachet al., 1999, Kumar et al., 2001). The absence of such absorption peaks in untreated graphite reveals the formation of carbonyl group on periphery of hexagonal carbon basal plane.

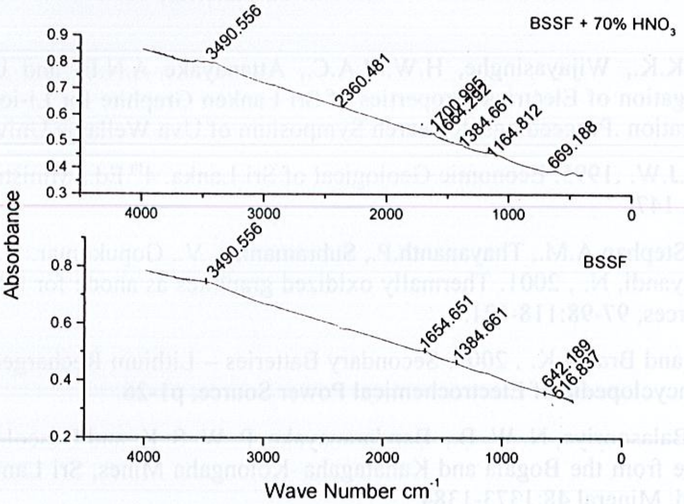


Figure 2: FTIR spectrum of Bogala shiny-slippery-fibrous (BSSF) before and after oxidation with 70% HNO_3at 60^0C for 15 minutes

Conclusions

Bogala graphite shows of having sufficient electrical conductivity. Chemical oxidation with HNO_3 slightly modify the graphite surface by forming acidic group which act as surface film to produce SEI resulting high reversible capacity of lithium ion rechargeable batteries. However, chemical oxidation with HNO_3 has not significantly change the d,c electrical conductivity

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References

Aurbach, D., Markovsky, B., Weissman, I., Levi, E. and Ein-Eli, Y., 1999. On the correlation between surface chemistry and performance of graphite negative electrodes for Li ion batteries,Electrochim. Acta, 45: 67-86.

Balasooriya, N.W.B., Touzain,Ph and Bandaranayake, P.W.S.K., 2006. Lithium electrochemical intercalation into mechanically and chemically treated Sri Lanka natural graphite, J. Phys. Chem.Solids, 67: 12-13.

Balasooriya, N.W.B., Touzain,Ph, Bandaranayake, P.W.S.K., 2007. Capacity improvement of mechanically and chemically treated Sri Lanka natural graphite as an anode material in Li-ion batteries,Ionics, 13:305-309.

Fu,L,J., Liu,H., Li,C., Wu,Y.P.,Rahm,E., Holze, R. and Wu,H.Q., 2006. Surface modifications of electrode materials for lithium ion batteries, Solid State Sciences, 8:113-128.

Geethika, A.K.K., Wijayasinghe, H.W.M.A.C., Attanayake A.N.B. and Udagedara, T., 2010. Investigation of Electrical Properties of Sri Lanken Graphite for Li-ion Rechargable Battry Application .Proceedings, Research Symposium of Uva Wellassa University, 139.

Herath, M.M.J.W. ,1995. Economic Geological of Sri Lanka. 4th Ed., Ministry of industrial development. 147.

Kumar,T.P., Stephan,A.M., Thayananth,P., Subramanian, V., Gopukumar, S., Renganathan, M. and Muniyandi, N. , 2001. Thermally oxidized graphites as anode for lithium-ion cells, J. Power Sources, 97-98:118-121.

Kurzweil, P. and Brandt,K. , 2009. Secondary Batteries – Lithium Rechargeable Systems - Overview, Encyclopedia of Electrochemical Power Source, p1-26.

Touzain, P., Balasooriya, N. W. B., Bandaranayake, P. W. S. K. and Descolas-Gros , 2010. Vein Graphite from the Bogala and Kahatagaha–Kolongaha Mines, Sri Lanka: A Possible Origin, Canad. Mineral.48:1373-1384.

Wu, Y.P., Jiang, C., Wan, C. and Holze, R. , 2003. Anode materials for lithium ion batteries by oxidative treatment of common natural graphite, Solid State Ionics, 156:283– 290.