Investigation on Structural Modification of Sri Lankan Vein Graphite for Ion Intercalation

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Introduction

Rechargeable batteries have become the main energy source for the portable electronic devices. Synthetic graphite have been used as anode electrode material in rechargeable batteries. Presently these rechargeable batteries are expensive mainly due to high cost of materials, such as synthetic graphite and metal oxides, used in their electrodes. It is suggested that the cost of these batteries can be reduce by introducing cheaper natural graphite for their anode electrode. Sri Lankan natural vein graphite can be classified into four distinct structural verities. They are Shiny-Slippery-Fibrous Graphite (SSF), Needle-Platy Graphite (NPG), Coarse Striated-Flaky Graphite (CSF) and Coarse Flakes of Radial Graphite (CFR). Development of Sri Lankan natural vein graphite to the anode of Li-ion rechargeable batteries, through purification and surface modification have been investigated recently. Furthermore, natural graphite has to be structurally modified by expanding interlayer distance to facilitate the intercalation of larger Na^+ ions for the application in rechargeable Sodium Ion Batteries (SIB) (Wei, 2011). The present study investigated the possibility of expanding the interlayer distance of Sri Lankan natural vein graphite for accommodating Na-ion intercalation by converting into Graphite Oxide (GO).

Materials and methods

Purified samples from all four structural varieties of Sri Lankan vein graphite, were used in this study. Raw graphite samples were oxidized to Graphite Oxide (GO) by using improved hummers method (Madusanka Y.N., Amareweera T.H.N.G.,Wijayasinghe H.W.M.A.C., 2013). In this method 96% H_2SO_4 (Sigma-Aldrich) and 85% H_3PO_4 (Sigma-Aldrich) were added to purified vein graphite. Then $KMnO_4$ (Belgolabo) was added little by little to the mixture with in two hours and stirred. Sample was allowed to cool until room temperature. Solution was poured into 30% H_2O_2 in an ice bath and the sample was vacuum filtered using Fisher brand filter papers using distilled water.

The d.c. electrical conductivity of raw graphite and prepared GO samples were measured using the standard four probe method. Fourier Transform Infrared (FTIR) spectra of raw graphite and GO samples were employed to study the structural modification. Further the X-ray diffractometry was used to confirm the formation of GO.For the Na-ion intercalation study, the modified graphite oxide was tape casted by the doctor blade method to fabricate electrodes. GO was the active material, carbon black was selected as the conductive additive and the binder was polyvinylidene fluoride (PVDF). All the materials were weighed using a chemical balance and placed in a small beaker. Then excessive amount of acetone and dimethylformamide (1:1 ratio) were added to the beaker, covered with an aluminum foil and stirred for 12 hours. Mixture was poured on to a copper foil pasted on a glass to form a very thin layer. It was allowed to dry. The electrodes were fabricated by cutting the copper foil to required shape. A half-cell was assembled using the fabricated GO anode with a gel electrolyte and sodium metal as the reference electrode. Assembling and testing of the cell was conducted inside a N_2 filled glove box. Discharging current of the half-cell under 0.5 kΩ load over time was measured and it was recorded using a computer interfaced program.

Results and Discussion

As shown in Figure 1, the FTIR spectra confirmed the presence of functional groups of alcohols, carboxylic, carbonyls and phenol. These functional groups are present in GO, which are not in raw graphite, indicate a successful conversion of graphite into GO. FTIR spectra also confirm the presence of non-oxidized carbon rings in the GO.

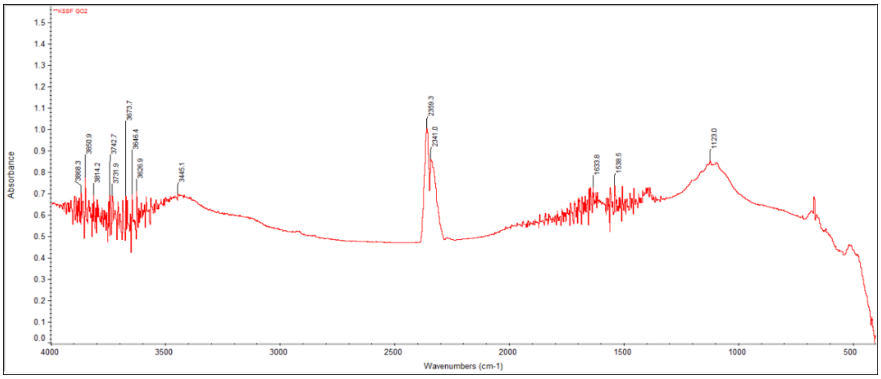

Figure 1: FTIR spectrum of GO prepared from SSF graphite

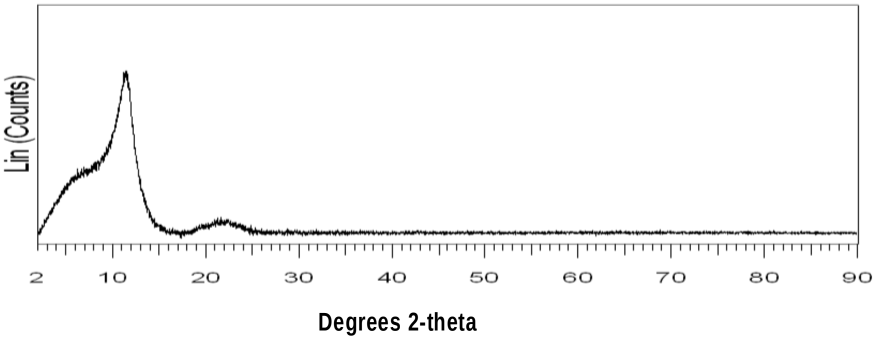

Figure 2: XRD spectrum of GO synthesized from CSF graphite

The XRD spectrum of graphite oxide which is shown in Figure.2 has two peaks at 22.50 and 11.00 degrees and these peaks are slightly shifted to the left side when compare to the XRD pattern of graphite (Madusanka Y.N., Amareweera T.H.N.G.,Wijayasinghe H.W.M.A.C., 2013).Graphite Oxide is showing a prominent broad peak at 11.00 degrees and analyzing these peaks can easily identify the oxidation and hydration level of the GO sample. This is a direct indication for the oxidation of graphite.

Conversion of natural graphite into GO has drastically decreased the electrical conductivity indicating the formation of low conducting oxide materials. Out of the four GO samples prepared in this study, the SSF shows the highest electrical conductivity of 1.6 x 10^{-5} S cm^{-1} while the CSF has the lowest conductivity of 3.2 x 10^{-6} S cm^{-1} at 25 ^{0}C.Figure 3 shows the discharge characteristics of the cell with configuration GO(developed) /GPE/ Na metal at room temperature for constant load of 0.5 kΩ. The open circuit voltage (O.C.V.) of the cell was about 2.9 V and the initial voltage drop was concluded due to the formation of electrode - electrolyte interface.

The discharge current-time characteristics of the cell exhibits a low stable current value due to the cell fabrication failures such as oxidation of the sodium metal caused by atmospheric exposure.

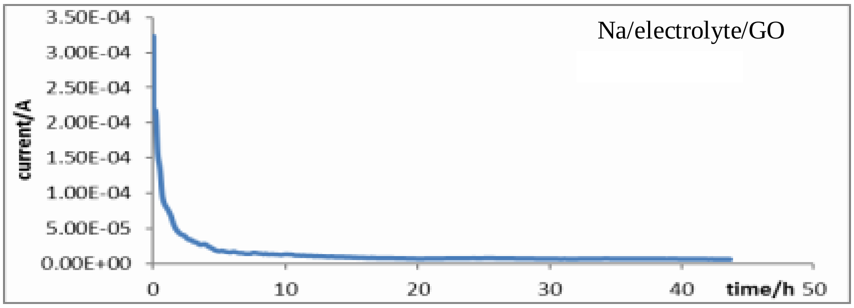

Figure 3: Current vs time curve of half-cell

Conclusions

This study revealed the possibility of structural modification of all four varieties of Sri Lankan natural vein graphite by oxidizing graphite into GO using improved Hummer's method. FTIR spectra gave the evidence for successful oxidation of graphite into GO and the XRD phase analysis further confirmed the transformation. In cell testing of the Na/electrolyte/GO half-cell gave a significant O.C.V. of 2.9 V. It is a clear evidence for the possibility of intercalating relatively larger but more abundant and low cost ions like Na^{+} ions to GO. Altogether, this study indicates the possibility of structurally modification of Sri Lankan natural vein graphite for the anode application of Na-ion battery.

Acknowledgement

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