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Synthesis of nanostructured silver particles incorporated vein graphite for the anode material application in rechargeable lithium-ion batteries

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ABSTRACT

Rechargeable lithium-ion batteries have emerged as the dominant energy storage source due to its higher capacity, energy density and excellent cyclability. Graphitic materials are commonly utilized as the anode material for lithium-ion batteries. Silver nanoparticles incorporated vein graphite (SVG) materials was prepared for Li Ion Battery (LIB) applications. The graphite sample was purified by acid leaching, followed by modifying the surface with HNO_3 . The silver graphite composite material was synthesized using $AgNO_3$ as the precursor and trisodium citrate as the reducing agent. Phase analysis revealed that the silver nanoparticles have been successfully incorporated into the surface of the modified graphite after chemical reduction and mechanical agitation. Half-cell testing was carried out using CR 2032 coin cells with silver vein graphite composite as the active material and 1 M $LiPF_6$ (EC: DMC; vol. 1:1) as the electrolyte at the National Center for Advanced Battery Research in NIFS. Galvanostatic charge-discharge study of the cell with silver vein graphite composite showed an initial charge-discharge Coulombic efficiency 88.3% and a promising discharge capacity of 373 mA h g^{-1} in the voltage range of 0.002 - 1.5V at C/10 rate. Overall, the electrochemical performance of our developed nanostructured silver particles incorporated vein graphite anode shows a noticeable improvement of the reversible capacity, Coulombic efficiency and cycling behaviour.

Keywords: Vein Graphite, Silver Nano Particles, Anode Material, Li-Ion Rechargeable Batteries

1. INTRODUCTION

Rechargeable Lithium-ion batteries (LIBs) are attracting much attention in recent decades owing to their high energy density, compactness, long-lasting life for service and low cost [1]. They have been widely used in portable consumer electronics and electric vehicles. However, there are still notable challenges in the improvements in the cycle life, power density and energy density of LIBs. Expensive electrode materials used in LIB lead to higher unit costs that hinders the development of LIB as a low-cost portable power source [2].

Graphite has been used as an anode material in state-of-the-art rechargeable Li-ion ion battery due to its high specific capacity, low working potential close to that of lithium metal and superior cycling behavior of its lithium intercalation compounds (Li_xC_6 , $x = 1$) [3]. Formation of a stable and protecting Solid Electrolyte Interface (SEI) during the first cycle of lithium intercalation is an important process affecting the overall electrochemical performance [4,5]. Expensive porous carbon materials and synthetic graphite are the most commonly used anode materials in commercial LIB. In this contest, natural graphite has been identified as an effective anode material for LIBs due to its high abundance. However, natural graphite can not be directly used for the anode material due to its poor electrochemical performance [6]. The poor electrochemical performance resulted due to electrolyte decomposition, solvent co-intercalation and movement of the graphene planes along the a-axis direction during the intercalation and de-intercalation [6].

The chemistry and morphology of the edge plane of graphite play a major role in electrochemical reactivity, the formation of SEI and lithium intercalation and de-intercalation [4,7]. The basal plane surface has only minor or no influence on those reactions. Therefore, many approaches have been investigated to obtain an effective SEI and to improve the performance of the whole battery system, either by designing the electrolyte components or by modifying the graphite electrode. Recent research on the modification of the surface structure of carbon materials mainly includes mild oxidation, deposition of metal and metal oxides, coating with polymers, coating with other kinds of carbon and coating with alkali carbonates [8].

These structural and textural features should be thoroughly addressed before moving into high tech applications. Many studies have been carried out to modify natural graphite as anode material for lithium ion rechargeable batteries. Mild oxidation is a successful method for modifying the graphite surface. Mild oxidation involves effective removal of active defects together with formation of a new dense surface film consisting of oxides, hence improving the graphite stability while introducing more nanochannels/micropores [9,10,11]. Deposition of metals and metal oxides on the surface of graphite particles gives rise to several advantages essential for an anode material of LIBs [8,12,13,14,15,16]. Firstly, metal or metal oxides coating covers the surface of graphite particles hence effectively blocking the edge surface. Secondly, the coating prevents the solvent co-intercalation and the exfoliation of graphite [17]. Thirdly, coating with good conductors decreases the charge-transfer resistance and the surface film resistance.

After the surface modification by mild oxidation, the surface of vein graphite comprises with various functional groups such as hydroxyl, phenol, ether, ester, and carbonyl groups. These oxygen-containing functional groups can provide ideal nucleation sites for silver particles forming silver vein graphite composite. However, when utilized for the anode application of LIB, some problems such as low specific capacity, largely irreversible capacity loss due to the formation of solid electrolyte interface (SEI) layers and poor cyclability may persist [18].

Compared to other intercalated type anode materials, natural graphite possesses some attractive benefits such as low cost and abundance. It is a known fact of having many structural imperfections such as anisotropic surface conditions, surface active sites, sp^3 -hybridized carbon atoms, edge carbon atoms and carbon chains in natural graphite due to its incomplete graphitization during the natural formation process [19].

Sri Lanka processes high purity (>98%) vein graphite deposits in many underground mines namely; Kahatagaha, Kolongaha, Ragedara and Bogala. Recent investigations of the National Institute of Fundamental Studies (NIFS) and other research groups in Sri Lanka, have revealed the potentiality of vein graphite as a low-cost anode material for LIBs [9,10]. However, in order to make vein graphite more feasible for LIB application the properties its associated properties should be enhanced. One of the ways to enhance electrochemical performance is the deposition of metals and metal oxides, such as silver, copper and its oxides, aluminum and nickel, on the surface of natural graphite [20,21].

The objective of this work was to fabricate the natural vein graphite of Sri Lankan origin into silver vein graphite (SVG) composite as an anode of LIBs.

2. MATERIALS AND METHODS

Firstly, vein graphite was purified by employing the acid leaching method [22]. Then, the surface of the graphite was modified by subjecting to mild oxidation technique [9]. Silver-vein graphite (SVG) composite material was synthesized using $AgNO_3$ as a precursor and trisodium citrate as a reducing agent.

2.1 Materials

Vein graphite was collected from the Kahatagaha mine in Sri Lanka. The samples were powdered by using a laboratory crusher. The particle size fraction of < 53 μm was separated and collected by mechanical sieving.

2.2 Purification and surface modification of graphite

Purification was done by using the acid leaching, in this method, raw graphite was treated with 10 vol % HCl acid at 65 °C for 75 minutes [22] while the surface was modified by mild oxidation with 69% HNO_3 solution [9].

2.3 Preparation of Silver Vein Graphite (SVG) Composite

SVG composites were fabricated with $AgNO_3$ as a precursor. 150 ml of 0.00025 M $AgNO_3$ solution was heated until boiling on a magnetic stirring hot plate and 5.0 g of modified graphite powder was added to the solution. Then the mixture was heated for another six minutes and 15 ml of 1% trisodium citrate was added to the mixture as a reducing agent of Ag^+ . The mixture was vigorously stirred for five minutes and cooled down to room temperature. Finally, the solution was filtered and the sample was dried at atmospheric conditions to obtain the composite.

2.4 Material Characterization

X-ray diffraction (Ultima IV X-ray Diffractometer) with a step size 0.02° and Cu-K α 1 radiation was used to characterize the crystalline structure, impurity phases, the formation of silver vein graphite composite and the effect of surface modification. Bruker ALPHA Fourier-transform infrared spectroscopy (FT-IR) in the 400–4000 cm^{-1} region, was used to analyze the functional groups of purified, surface-modified graphite and prepared silver vein graphite composites. Surface analysis of raw, purified and modified graphite samples and silver vein graphite composites characterized by Scanning Electron Microscopy imaging by using “EVO/LS 15 ZEISS”.

2.5 Electrochemical analysis

The SVG composite electrode was prepared by casting a mixture of 85% of active material (silver vein graphite composite), 10% of PVDF (Sigma Aldrich) binder, and 5% of acetylene carbon black (Sigma Aldrich) together with N-Methyl-2-pyrrolidone (NMP/Sigma Aldrich) solvent, on a copper current collector. The tape cast electrodes were then dried at 120 °C for 24 h in a vacuum oven.

The dried electrode sheets were transferred into an argon-filled glove box and kept under controlled atmospheric conditions (water and oxygen level < 0.1 ppm) for 24 hours. Then 15.0 mm diameter electrodes were cut by using an electrode cutter and weighed to calculate the active materials in each 15.0 mm diameter electrodes. The electrochemical performance of the electrodes was examined after assembling into CR2032 coin cells. All coin Cells were assembled in an argon-filled glovebox (Mbraun) by controlling the O₂ and water levels at less than 1 ppm-level. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate and dimethyl carbonate (EC: DMC vol. 1:1 / Sigma Aldrich). The lithium foil of 15.0 mm in diameter (99.9% and 0.25 mm thickness / Gelone LIB) was used as a standard counter and reference electrode for all test cells. 18.0 mm of Celgard 2400 microporous membranes were used as the separator. The coin cells assembled were tested for their electrochemical behavior through cyclic charge-discharge measurements. All the measurements were performed at C/5 rate in a cutoff voltage window of 0.002-1.50 V vs. Li/Li⁺ at room temperature (25 °C). All the analysis was conducted by using Landat CT2001A battery testing system.

3. RESULTS AND DISCUSSION

3.1 Material characterization

The XRD patterns of raw graphite, purified graphite, modified graphite and the silver vein graphite composite sample are shown in Figure 1. The major crystallographic peaks of graphite, corresponding to (002) and (004) appear prominently in this diffractogram (JCPDS # 75-1621). The diffraction patterns of the samples exhibit well-developed peaks, indicating the high crystallinity of graphite. Furthermore, the diffractograms clearly indicate that the mild chemical oxidation does not affect the crystallographic structure of graphite and do not involve the formation of an intermediary graphite intercalation compound or any other secondary phases [9].

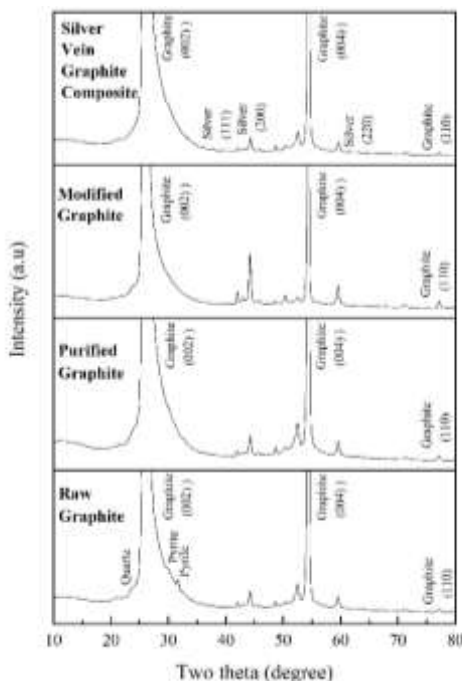


Fig. 1: X-ray diffractograms of raw graphite, purified graphite, surface modified graphite and silver vein graphite (SVG) composite.

In Figure 1, typical individual diffraction peaks of both graphite and silver can be observed separately, although the intensity of the typical diffraction peak of silver has been greatly weakened due to its very low content present in the composite. The prominent peaks of AgNPs, as well as silver vein graphite composite can be observed at 2θ values of 38.1°, 44.0° and 64.5°, respectively. These peaks are corresponding to the (111), (200), and (220) planes, respectively, of face-centered AgNPs (JCPDS # 87-0597), indicating that metallic silver has been successfully formed without formation of any secondary phase. The corresponding d-spacing values of the formed AgNPs are 2.36, 2.04 and 1.44, respectively. These are comparable and matching with those reported for AgNPs previously [23].

The FTIR measurements were carried out to identify the functional group present in the synthesized materials. The FTIR spectra of the raw graphite, purified graphite, modified graphite and the silver vein graphite composite are shown in Figure 2. A doublet band at 2921 and 2850 cm^{-1} appear in all samples and it evidences for the presence of aliphatic C-H bonds. Vibrational bands corresponding to $\nu\text{C}=\text{O}$ stretching at 1720-1620 cm^{-1} , $\nu\text{O}-\text{H}$ stretching at 1360 cm^{-1} , and $\nu\text{C}-\text{O}$ stretching at 1250-1100 cm^{-1} are present on the modified graphite surface. The mild oxidation could have introduced the carboxylic, phenolic and ether functional groups, on to the surface of vein graphite [9,10].

However, an obvious change of the vibrational bands of the oxygenated functional groups is seen in the FTIR spectrum of the silver vein graphite composites with the peak at 1720 cm^{-1} –

1620 cm^{-1} corresponds to the C=O groups. This could be attributed to both the reduction due to the existence of the AgNPs on the surface of modified graphite [24].

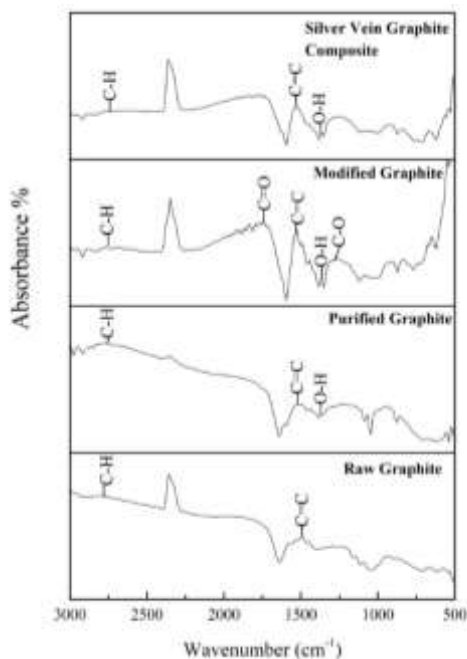


Fig. 2: FTIR spectra of the raw graphite, purified graphite, surface modified graphite and silver vein graphite (SVG) composite.

Scanning electron microscopy (SEM) was employed to observe the occurrence and spreading of AgNPs on modified graphite together with its morphology. The SEM images of the purified graphite, modified graphite and silver vein graphite composites are shown in Figure 3. The SEM morphology of our prepared composite as shown in Figure 3(c) clearly indicate that nano-scale silver particles are deposited and embedded on modified graphite during the composite formation. Further, the SEM images indicates the size of the particles to be around 100 nm.

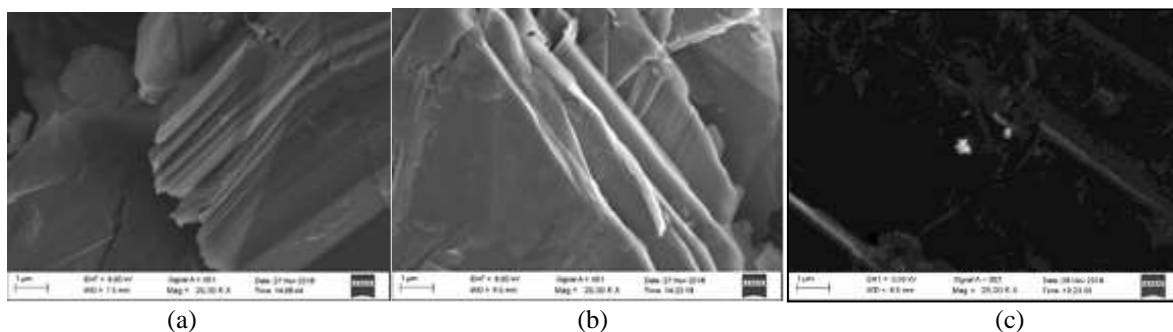


Fig. 3: SEM images of the (a) purified graphite, (b) surface modified graphite and (c) 0.00025 M AgNO₃ used SVG composite.

The chemical composition of the silver vein graphite composite was analyzed by EDS analysis (Figure 4). Only the peaks corresponding to C, O and Ag are appearing in the EDS spectrum indicating the presence of oxygen, carbon and silver elements only by confirming the purity of the composite.

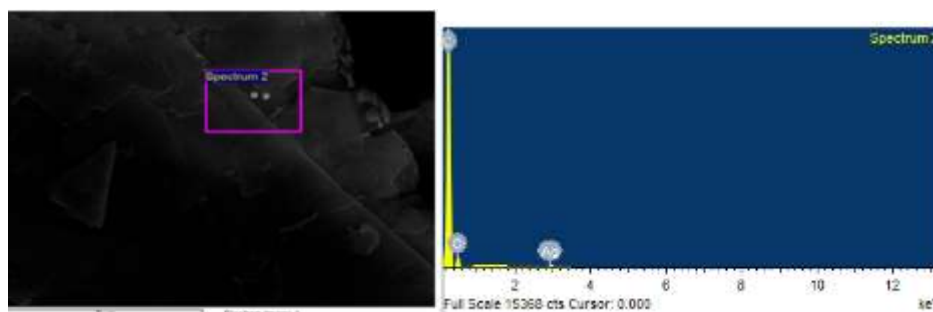


Fig. 4: EDS and its corresponding SEM image of silver vein graphite composite.

3.2 Electrochemical performance

Figure 5 shows the first cycle charge-discharge curves of silver vein graphite composite at the current rate of 0.2 V. The discharge curve drop down smoothly from OCV (1.23 V) to about 0.1 V, where the first lithium intercalation initiates. This indicates the absence of a strong passivation reaction. Moreover, a slight plateau appears in about 0.8-0.9 V, provides evidence for the formation of the SEI layer.

Galvanostatic charge-discharge study of the cell with silver vein graphite composite showed an initial charge-discharge Coulombic efficiency 88.3% and a promising discharge capacity of 373 mA h g⁻¹ in the voltage range of 0.002 - 1.5 V at C/10 rate. The cycling behavior of silver vein graphite composite is shown in Figure 6. The discharge capacity of silver vein graphite composite faded from 373 mA h g⁻¹ to 249 mA h g⁻¹ over 10 cycles.

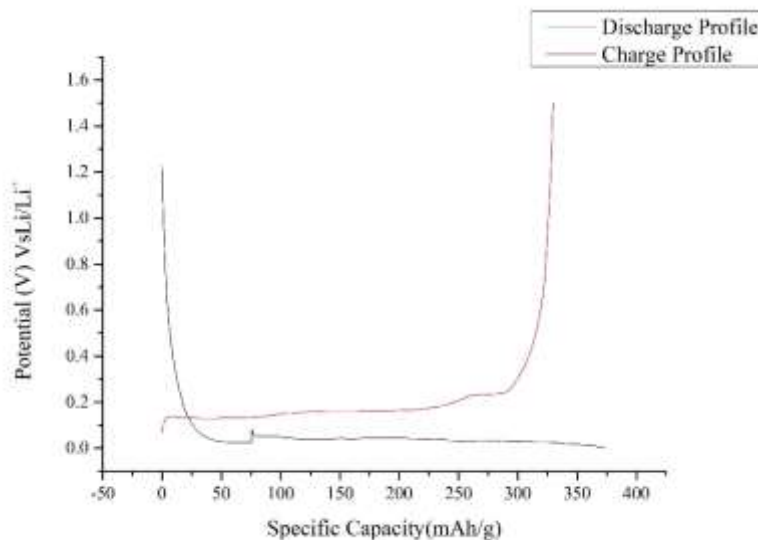


Fig.5: Discharge and charge profiles in the first cycle of silver vein graphite composite.

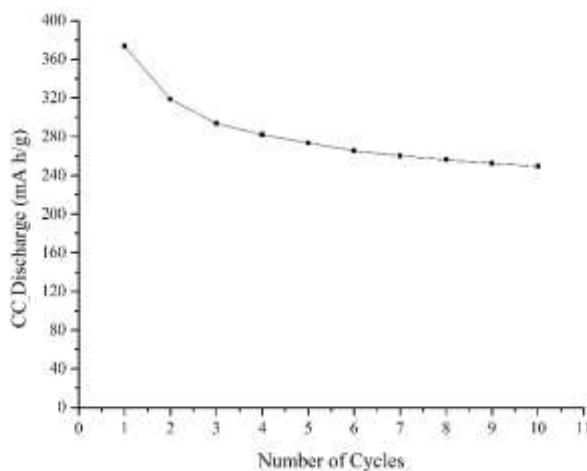


Fig. 6: Cycle profiles of silver vein graphite composite anode at the charge-discharge rate of 0.2 C.

4. CONCLUSION

In conclusion, silver-graphite composites could successfully be synthesized using Sri Lankan vein graphite. Mild chemical oxidation purification process could remove anisotropic surface conditions, surface active sites, sp³-hybridized carbon atoms, edge carbon atoms and carbon chains in natural graphite to form a new dense film consisting of oxides while improving the stability of the material. Interestingly, the conversion of vein graphite into silver-vein graphite composite could decrease the charge-transfer resistance and surface film resistance. Furthermore, the electrochemical performance of silver vein graphite composite shows the high reversible capacity and coulombic efficiency in the first cycle and cycling behavior.

5. ACKNOWLEDGMENT

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