# PERFORMANCE OF DEVELOPED SHINY-SLIPPERY-FIBROUS TYPE SRI LANKAN VEIN GRAPHITE ANODE IN THE LI-ION RECHARGEABLE BATTERY

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## ABSTRACT

Rechargeable Lithium-Ion Batteries (LIBs) are at present the most demanded rechargeable battery system due to its higher capacity, energy density and excellent cycleability. However, many investigations are presently proceeded on the development of the electrode materials in order to achieve higher efficiency in a more cost effective manner. Recently, natural graphite was identified as a potential low cost anode material for LIBs. Sri Lanka has its own established name for the high quality vein type natural graphite containing 95-98% of initial purity. Sri Lankan vein graphite (SLVG) has been categorized into four structurally distinct morphological varieties namely, shiny-slippery-fibrous graphite (SSF), needle-platy graphite (NPG), coarse striated-flaky graphite (CSF) and coarse flakes of radial graphite (CFR). Anisotropy of the surface and impurities present in trace levels cause profound alteration of chemical and electrochemical reactivity in natural graphite. Our recently introduced acid digestion method could result over 99.9 % of purity for all the four morphologies of SLVG, while simultaneously undertaking the surface modification. Further, studies have proved that this treatment method could enhance the performance of the NPG type SLVG anode. Therefore, this study aims to evaluate and compare the electrochemical performance of SSF type SLVG anode that was developed through acid digestion treatment.

The treated SSF type SLVG powder (<53 μm) developed by acid digestion was used for this study. Electrochemical half-cell studies were carried out using CR 2032 coin cells with treated SSF type SLVG as active material and 1 M $LiPF_6$ (EC: DMC; vol. 1:1) as the electrolyte. All the assembling steps were performed in an argon filled glove box under the controlled oxygen and moisture levels. Galvanostic charge-discharge studies were conducted at 0.2 current rate with "Landat" battery testing instrument. Treated anode shows high reversible discharge capacity of 440 mA h $g^{-1}$, which is higher than the theoretically expected capacity for a graphite anode. Initially, the first cycle discharge capacity was recorded as 517 mA h $g^{-1}$. In contrast to the NPG type SLVG anode treated with same method, the SSF type SLVG anode gradually faded form the 1st cycle to 5th cycle and achieved its stable reversible capacity. However, after the 5th cycle, the treated SSF anode could be able to maintain a high reversible capacity of 440 mA h $g^{-1}$ up to the 50th cycle. Further, charge-discharge curves didn't give evidences for any strong passivation reaction and a continuous formation of SEI layer could be observed up to 4th cycle. However, it may be absent or declined to a very low level after the 5th cycle. Hence, lithiation and delithiation occurred very smoothly without any degradation reaction and it achieved a high reversible capacity for the first 50 cycles while maintaining over 99% of Columbic efficiency. Altogether, this study reveals the promising performance of our developed shiny-slippery-fibrous type Sri Lankan vein graphite anode in the Li-ion rechargeable battery.

*Keywords* - vein graphite, anode, lithium-ion rechargeable battery, cell performance.

## 1. INTRODUCTION

Arrival with the novel technological aspects, the energy demand for the portable electronic devices and electrical vehicle increases rapidly. In order to cater this demand, several types of rechargeable batteries have been introduced. Due to their higher capacity, energy density and excellent cycleability, Rechargeable Lithium-Ion Batteries (LIBs) become the most prominent rechargeable battery type [1-2]. However, most of the current research studies are focusing on cost-effective electrode materials instead of synthetic electrode components, which are presently problematic with performance issues and high cost. Many of recent investigations have proved the favorable characteristics of natural graphite such as its high reversible capacity, appropriate potential profile and specially the low cost to be the anode material in LIBs [3]. Though such favorable conditions are there, still the large irreversible capacity loss during the first cycle, poor cycleability and poor rate capability are limiting its practical use [4-6].

There are three modes of naturally occurring graphite namely, flake, vein and amorphous graphite. Majority of studies, specially on the purification, have been reported of flake graphite [7]. In comparison, the vein graphite has very high purity and high crystallinity in raw form than flake graphite. It provides much favorable conditions for development of natural vein graphite for the intended anode application in LIBs.

Sri Lanka is the one of leading graphite supplier with a dominant worldwide reputation for unique vein graphite because of the high purity (about 95-99% of pure carbon), extensive mineralization, high crystallinity and mode of occurrence [8]. Sri Lankan vein graphite (SLVG) has been categorized into four structurally distinct morphological varieties namely, Shiny-Slippery-Fibrous (SSF), Coarse Striated-Flaky (CSF), Coarse Flakes of Radial (CFR) and Needle-Platy Graphite (NPG) [9]. Recent studies have identified Sri Lankan vein graphite as promising anode material for the LIBs. Further, the investigations on physical and chemical treatments could enhance the electrochemical performance of Sri Lankan vein graphite [10-12]. Our recently introduced acid digestion method could result over 99.9 % of purity for all the four morphologies of SLVG while simultaneously undertaking the surface modification. Apart from that, further studies on investigating electrochemical performances of NPG type SLVG anode revealed its suitable as a low-cost alternative anode material for the Li-ion rechargeable batteries [10]. Further to that, this study aims to investigate the electrochemical performance of SSF type SLVG anode that was developed through the same acid digestion treatment.

## 2. EXPERIMENTAL

The treated SSF type SLVG powder (<53 μm) developed by acid digestion was used for this study. To prepare the casting slurry of anode, 80% of the treated SSF graphite powder, 15% of polyvinylidene difluoride binder (PVDF ≥99.5%, MTI Corporation) and 5% of acetylene carbon black conductive additive (MTI Corporation #1333-86-4) were added to the N-Methyl-2-pyrrolidone (NMP/ 99.5% Sigma Aldrich #328634) solvent and mixed thoroughly to obtain a homogenous mixture. This homogenous mixture was cast on a copper current collector (thickness of 25 μm / Gelone) by using a specially designed stainless steel casting blade by employing the doctor blade tape casting method. The casted anode tapes were dried at 120 $^0$C for 24 hours in a vacuum oven. The dried electrode sheets were transferred into argon filled glove box and kept under controlled conditions for 24 hours.

The coin cells were assembled in an argon-filled glove box (MBRAUN) under controlled environment with moisture and oxygen contents kept below 0.1 ppm. CR 2032 size stainless steel coin cell components (Gelone) were used for the cell assembling. Circular electrode discs from cast SSF anodes, reference electrode discs of Li metal foil and circular discs of glass fiber separator film were cut by hand held steel cutters. Commercially available battery grade electrolyte, 1 M LiPF6 in ethylene carbonate and dimethyl carbonate (EC: DMC vol. 1:1 / Sigma Aldrich) was used as the electrolyte. The Galvanostic charge-discharge studies were conducted at 0.2 current rate with in the cutoff voltage window of 0.002-1.50 V vs. Li/Li+ at room temperature (25 $^0$C) by "Landat" battery testing instrument.

## 3. RESULTS AND DISCUSSION

*Cycling profile of treated SSF half cell*

Fig. 1 shows the cycling profile obtained at 0.2 C rate of the treated SSF type SLVG graphite by acid digestion method. Notably, as recorded for the treated NPG type [10], the treated SSF graphite anode also shows high reversible discharge capacity of 440 mA h $g^{-1}$ for the first 50 cycles, that is significantly higher than the expected theoretical capacity of graphite anode (372 mA h $g^{-1}$ for $LiC_6$).

Initially, the first cycle discharge capacity was recorded as 517 mA h $g^{-1}$. In contrast to the NPG type SLVG anode treated by the same method, the SSF type SLVG anode gradually faded form the 1st cycle to 5th cycle and thereafter achieved its stable reversible capacity. However, after the 5th cycle, the treated SSF anode could be able to maintain a high reversible capacity of 440 mA h $g^{-1}$ up to the 50th cycle without any considerable capacity fading. Hence, this SSF type SLVG anode was able to maintain over 99% of Columbic efficiency.

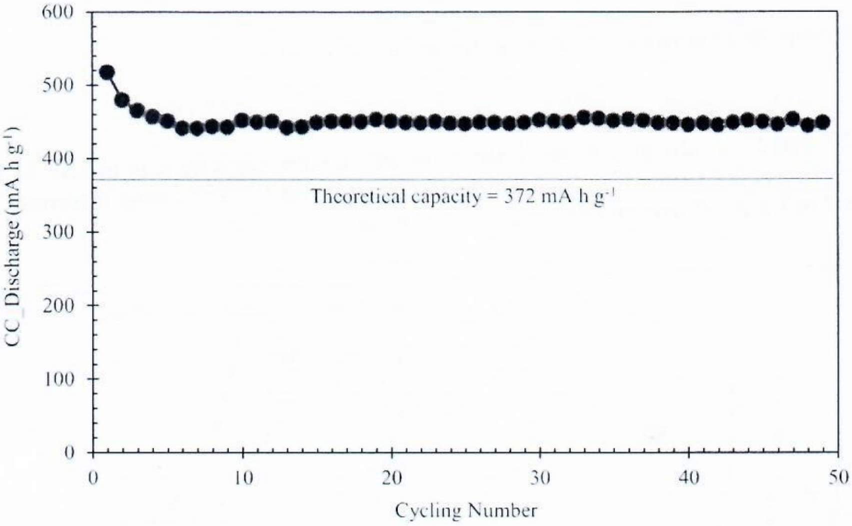

Fig. 1. Cycling profile of the purified and surface modified SSF graphite SLVG half-cell at 0.2 C rate.

*Charge-discharge profiles of treated SSF half cell*

Fig. 2 illustrates the initial discharge-charge profiles for the assembled SSF/$LiFP_6$/Li half-cell at the current rate of 0.2 C. The discharge curves drops down smoothly from OCV (1.68 V) without any strong passivation reaction up to 0.2 V, where the first lithium intercalation initiates. A slight plateau, "a" indicates the formation of SEI layer at 0.74 V (see Fig. 2).

The other plateaus, b, c and d, indicate the different stages of the phase transition occur in the graphite electrode where Li-ion intercalation is in progress. Moreover, five continuous phase transitions stages can be identified, such as OCV to plateau b, plateau b to c, c to d, d to e and e to 0 V and they can be attributed to $LiC_{72}$, $LiC_{36}$, $LiC_{27}$, $LiC_{18}$, $LiC_{12}$, and $LiC_6$, respectively [13].

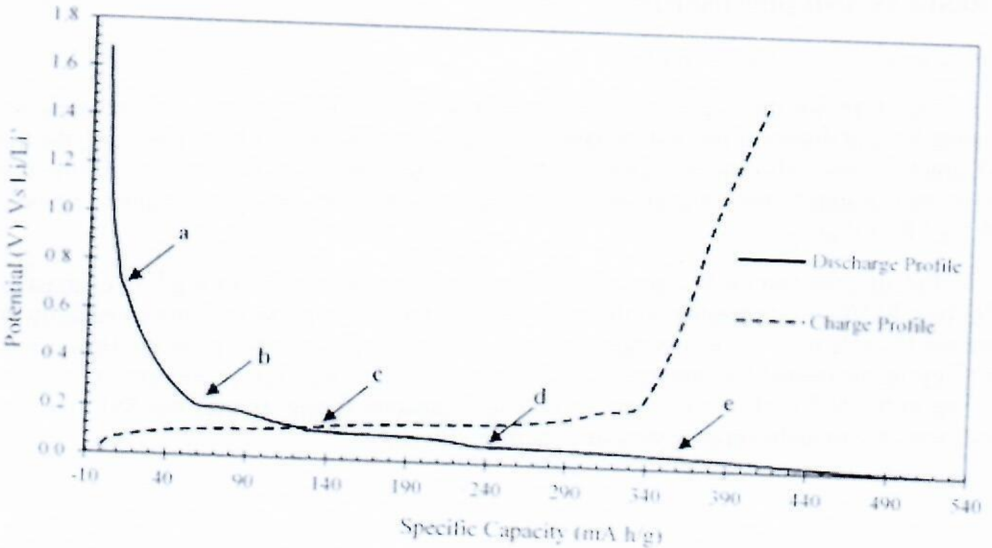

Fig.2. First cycle charge-discharge profile at 0.2 C rate for treated SSF SLVG half-cell.

1st, 2nd and 5th discharge curves illustrate the irreversible capacity loss in SSF SLVG half-cell while cycling at 0.2 C rate (fig. 3). From 1st to 2nd cycle and 1st to 5th cycle, it records 37.8 mA h g$^{-1}$ and 66.7 mA h g$^{-1}$ of irreversible capacity loss, respectively.

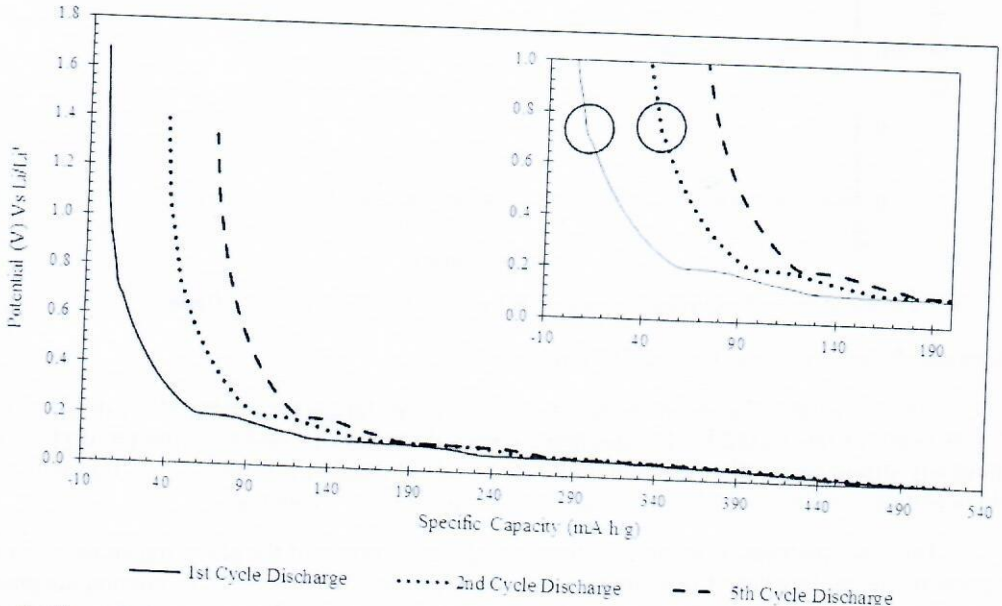

Fig.3. 1st, 2nd and 5th discharge profiles for treated SSF, SLVG half-cell at 0.2 C rate.

Moreover, the discharge curves are clearly indicated, a slight plateau that denote the formation of Solid Electrolyte Interface (SEI) layer only on 1st and 2nd cycle discharge curves. This indicates the electrolyte components are irreversibly reduced on the graphite surface during 1st to 4th cycle and continuously form a stable passivation film. The SEI layer formation seems to be absent or limited to very low deposition from the 5th cycle and onwards. Hence, the lithiation and delithiation occur very smoothly without any degradation reaction resulting a high reversible capacity till 50th cycle, where his measurements was ended.

## 4. CONCLUSION

The charge–discharge studies revealed a high stable reversible capacity of 440 mA h $g^{-1}$, which is significantly higher than the theoretical capacity (372 mA h $g^{-1}$of $LiC_6$). Further, the low irreversible capacity loss acquiesces to the high Columbic efficiency of over 99.9%. The formation of SEI layer does not leads to any strong passivation reaction and stabilized after few cycles. Hence, lithiation–delithiation process under goes smoothly without any further structural exfoliation. Altogether, this study reveals the promising performance of our developed shiny-slippery-fibrous type Sri Lankan vein graphite anode in the Li-ion rechargeable battery.

## 5. ACKNOWLEDGEMENT

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