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Exfoliated Graphite Based All Solid State Electrochemical Double Layer Capacitor

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ABSTRACT

Graphene is considered as an ideal electrode material for supercapacitors. However the conversion cost of graphite in to graphene is expensive. As an alternative low cost few layer graphite can be obtained through exfoliation. In this study, use of exfoliated graphite (EG) as electrodes in Electrochemical Double Layer Capacitor (EDLC) fabricated with a gel polymer electrolyte is reported. Exfoliated Graphite (EG) was synthesized by surfactant mediated exfoliation. EDLCs were characterized using Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD) tests. This inexpensive, eco-friendly EG supercapacitor showed specific discharge capacitance of 0.86 F g^{-1}. CV tests confirmed retention of 88.2 % of capacity from its initial value after 500 cycles, indicating excellent cycling stability.

Keywords: *Exfoliated Graphite, Electrochemical Double Layer Capacitor, Specific Capacitance*

1. INTRODUCTION

Supercapacitors are attractive alternative energy storage devices for batteries which will cater to world-wide energy demand. Based upon current trends, supercapacitors can be divided into two main categories: electrochemical doublelayer capacitors (EDLCs) and pseudo capacitors or redox capacitors [1]. Carbon is the most frequently used electrode material in EDLCs due to its advantageous factors like low cost, high surface area, availability and established electrode production technologies [2]. Graphite, which is the most inexpensive and easily obtained carbonaceous material, is composed of individual graphene sheets. Graphene sheet is an arrangement of sp^2 hybridized carbon in a hexagonal lattice. These sheets are stacked and bound together by van der Waals forces to form graphite [3]. Molecules can be readily introduced between the graphene sheets and allowed to break into monolayer and/or multilayer sheets. Separation into layers is known as 'exfoliation', and it can be done using several methods [4]. They are: mechanical exfoliation, thermal exfoliation, microwave irradiation and electrochemical exfoliation[5].Exfoliated graphite (EG) is a low dense graphitic carbon with a high temperature resistance[6].In addition to that, EG flakes are substantially interconnected to form a porous, conductive graphitic network comprising pores, which acts as an active material in supercapacitors. It has recently found that, EG can be easily synthesized in larger quantities using graphite exfoliation with certain solvents or surfactants. N-methyl-pyrrolidone (NMP), whose surface energy is almost same to that of graphene is such a solvent that exfoliation occurs freely giving defect-free EG. However, using NMP has some drawbacks. NMP is expensive and require special care when handling. And also, their high boiling points making it difficult to deposit EG onto surfaces[7].Considering all these factors, surfactants can be considered as the most suitable candidate as it avoids the use of toxic and expensive solvents [8]. This method will give an additional advantage to the other ions, preventing EG sheets from re-

stacking in the solution which yields a stable EG suspension[9].In this study, we were able to use non-oxidative, safe, user friendly method for the preparation of EG and demonstrate its application as an EDLC electrode. To investigate the electrochemical properties of fabricated supercapacitor, Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and Galvanostatic Charge Discharge (GCD) tests were carried out.

2. EXPERIMENTAL

2.1. Materials

Sri Lankan natural graphite was obtained from Bogala Graphite Lanka Ltd., Sri Lanka. Sodium dodecyl benzene sulfonate (SDBS), polyvinilidine fluoride (PVDF), zinc trifluoromethanesulfonate (ZnTF), 1-methyl-2-pyrrolidinone (NMP), ethylene carbonate (EC) and propylene carbonate (PC) were purchased from Sigma Aldrich and used without further purification.

2.2. Preparation of EG Electrodes

SDBS (Sodiumdodecylbenzenesulfonate) was dissolved in deionized water and graphite was added into that surfactant solution. The mixture was sonicated using ultrasonic homogenizer (ATP 150) for 45 minutes and was allowed to stand for 24 hours. After large particles being deposited to the bottom of the flask, top layers (20ml each) were decanted into 50 ml vials and it was centrifuged using the universal centrifuge (Model: PLC-036H) at 1500 rpm for 90 minutes. EG was filtered under vacuum and allowed to dry in vacuum oven for 24 hours. A small amount of 1-methyl-2-pyrrolidinone was added into the EG in order to make a slurry for coated on to two fluorine doped tin oxide (FTO) glass plates and allowed to dry at 100 ^{0}C for several minutes until the solvent get evaporated. Area of the electrode was of 1 cm^2 each.

2.3 Preparation of Gel Polymer Electrolyte (GPE)

Required amounts of PVDF, EC, PC and ZnTf were weighed and the mixture was stirred well using magnetic stirrer while heating. The hot mixture was pressed between two glass plates to get a bubble-free thin film and was allowed to dry.

2.4 Fabrication and Characterization of EDLC

Laboratory scale EDLCs were assembled using the EG electrodes and with GPE of same size. They were characterized with Electrochemical Impedance Spectroscopy (EIS) technique in several frequency ranges at room temperature with the aid of an impedance analyser (Metrohm M101). Nyquist plots were drawn using real and imaginary values of impedance.

Cyclic voltammetry studies were carried out using a three electrode setup with Metrohm M101 potentiostat. One electrode was taken as the working electrodes while the other as reference and counter electrodes. Current variation with voltage was monitored varying the scan rate. Next, potential window within which the cycling was done was changed. Finally, continuous scanning was done for 500 cycles. Single electrode specific capacitance (C_s) was calculated using the following equation [10].

$$C_s = \frac{2\int IdV}{mS\Delta V} \qquad (1)$$

Where IdV is the area under the cyclic voltammogram, m is the electrode mass, S is the scan rate and ΔV is the potential window.

Galvanostatic Charge Discharge test was carried out within the optimum potential window at a constant current I using a Metrohm M101 potetniostat/galvanostat. Specific discharged capacitance C_d was calculated using the equation given below [10].

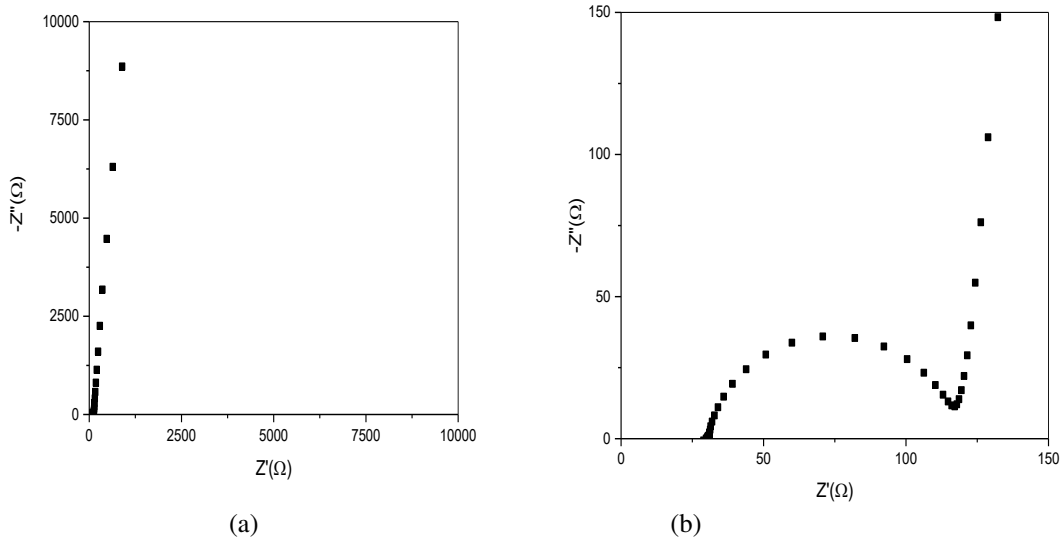
$$C_d = \frac{I}{m\frac{dV}{dt}} \tag{2}$$

Where, m is the mass of an electrode and dV/dt is the rate of potential drop excluding the IR drop that occurs at the beginning of discharge.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Impedance Spectroscopy Test

An impedance spectrum in the complex plane (Nyquist plot) of the EG is shown in Figure 1(a). The frequency was varied from 400 kHz to 0.01 Hz. In a typical Nyquist plot of an EDLC, semi-circle occurred at high frequencies represents the internal resistance which is shown by the Figure 1(b).



(a) (b)

Figure 1: Nyquist Plot for the EDLC in the frequency range from 400 kHz to 0.01 Hz. (a) - Full frequency plot, (b) - High frequency plot

Capacitive properties become dominant at very low frequencies. This behavior is present in Nyquist plot as a spike at low frequency region, which is characteristic for porous electrodes [11]. The spike at very low frequency region is not exactly parallel to Z" axis. It may be due to some problems in the electrode surfaces.

3.2 Cyclic Voltammetry Test

Figure 2 illustrates the cyclic voltammograms obtained for the EDLC at different potential windows. The voltammograms demonstrate almost symmetrical images when zero current line was considered as the vertex line, indicating capacitive behavior of the EG supercapacitor with the double layer formation of the electrode-electrolyte interface

showing EDLC characteristic features. Charges are stored electrostatically, therefore no peaks as in redox capacitors.

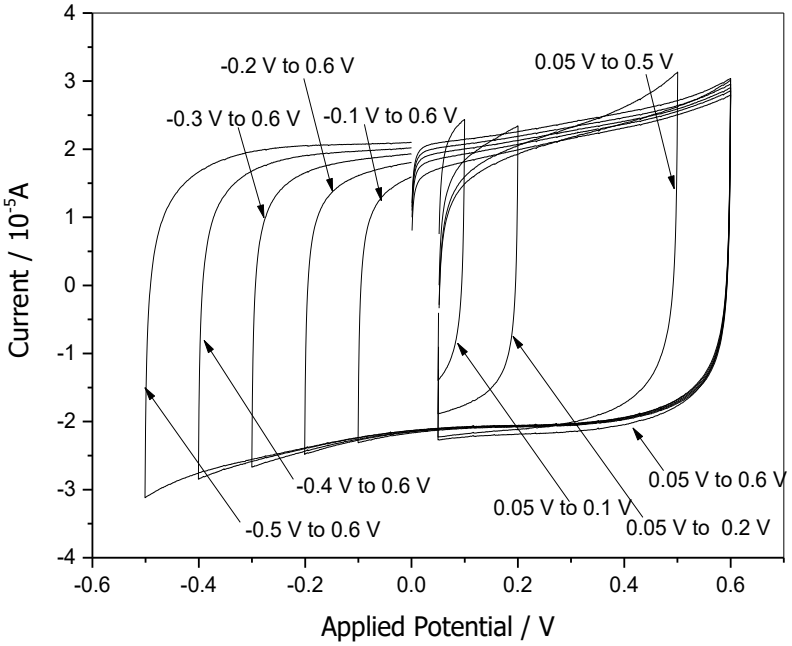


Figure 2: Cyclic voltammograms of the EDLC in the configuration EG/GPE/EGat Different potential windows.Scan rate 10 mVs^{-1}

Cyclic voltammograms shows the shape of parallelograms, which is typical for EDLCs.When the window was widened, area of the cyclic voltammogram get increased. But, after exceeding the potential window of -0.5 - 0.6 V, a sharp increase in current could be seen destroying the usual shape significantly. This might be due to occurrence of some irreversible reaction inside the EDLC [12]. It can be attributed to a substantial value of equivalent series resistance. Hence, the window from -0.5 V to 0.6V was selected for further investigations

Figure 3, illustrates the cyclic voltammograms obtained at different scan rates. Charged ions have to move through the pores of EG electrode, therefore, completeness of reactions in the supercapacitor depends on the scan rate. At low scan rates, there is ambient time for the occurrence of reaction, but at very low scan rates, the push given for the charges may not enough for the full coverage of the electrode surface. At higher scan rates, rate of potential change is high. That cannot be followed by the rate of ion rearrangement. As a result, specific capacitance (C_s) goes down. The optimal scan rate obtained was 20 mV s^{-1}, giving the highest C_s of 2.55 F g^{-1}. The results show that the shape of cyclic voltammograms remain as parallelograms even at higher scan rates indicating the features of EDLC.

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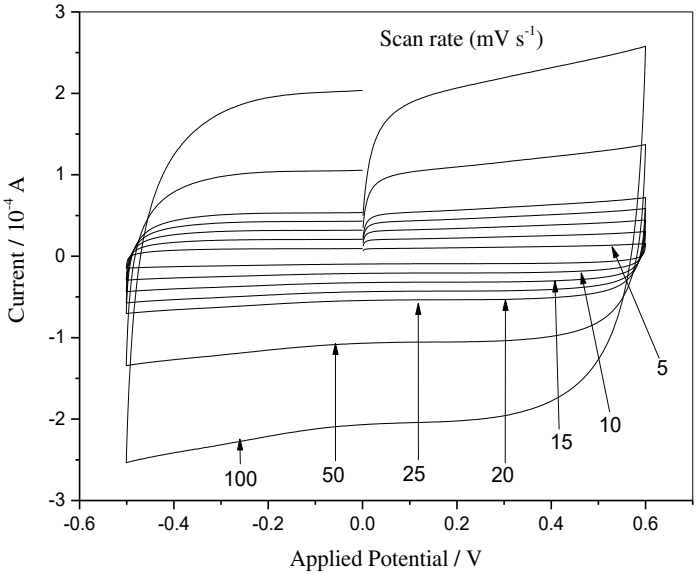

Figure 3: Cyclic voltammograms of EDLC at different scan rates for -0.5 V to 0.6 V potential window

The cycling life of a supercapacitor is the most important factor when practical and industrial applications are considered. Figure 4 shows the variation of C_s with continuous cycling within the potential window from -0.5 V to 0.6 V at 20 mV s^{-1}. Initial C_d value of 2.55 F g^{-1} was remained at 88.2 % after 500 cycles. This decrease may be due to the loss of interfacial contacts and degradation of electrode and/or electrolyte.

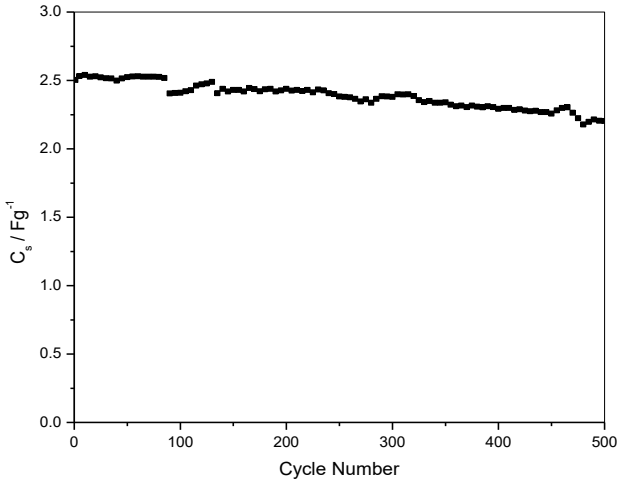

Figure 4: Variation of single electrode specific capacity with the continuous cycling in the potential window from -0.5 V to 0.6 V and at the scan rate of 20 mVs^{-1}.

3.3 Galvanostatic Charge Discharge (GCD) Test

Specific discharge capacitance C_d obtained from GCD test is shown in Figure 5. Initial C_d was 0.86 F g^{-1} and it was reduced to 0.83 F g^{-1} after 800 cycles. In between there were ups and downs in the C_d value which may be due to rearrangements between the electrode and electrolyte interface or may be due to some side reactions.

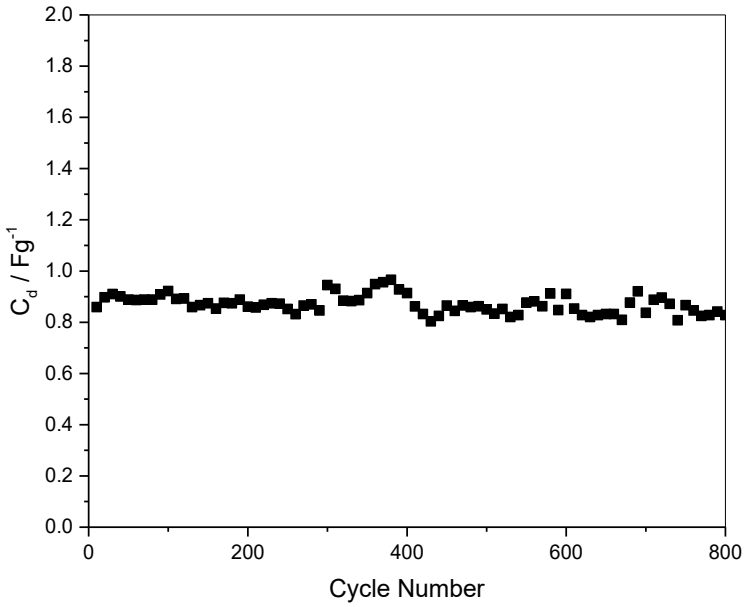

Figure 5: Variation of the specific discharge capacitance with cycle number

4. CONCLUSION

EDLCs in the form of EG/GPE/EG were fabricated successfully at room temperature. EIS tests confirmed the capacitive behavior of the EDLC. CV tests revealed that the EDLC can be operated in the potential window of -0.5 – 0.6V and continuous cycling resulted 88.2% capacity retention after 500 cycles. GCD results also proved that the EDLC is stable for long cycling. These findings point out that EG can be used as electrode material in EDLCs and further improvements may allow to use it as low-cost, eco-friendly electrode material. Further investigations are carried out to optimize the results.

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