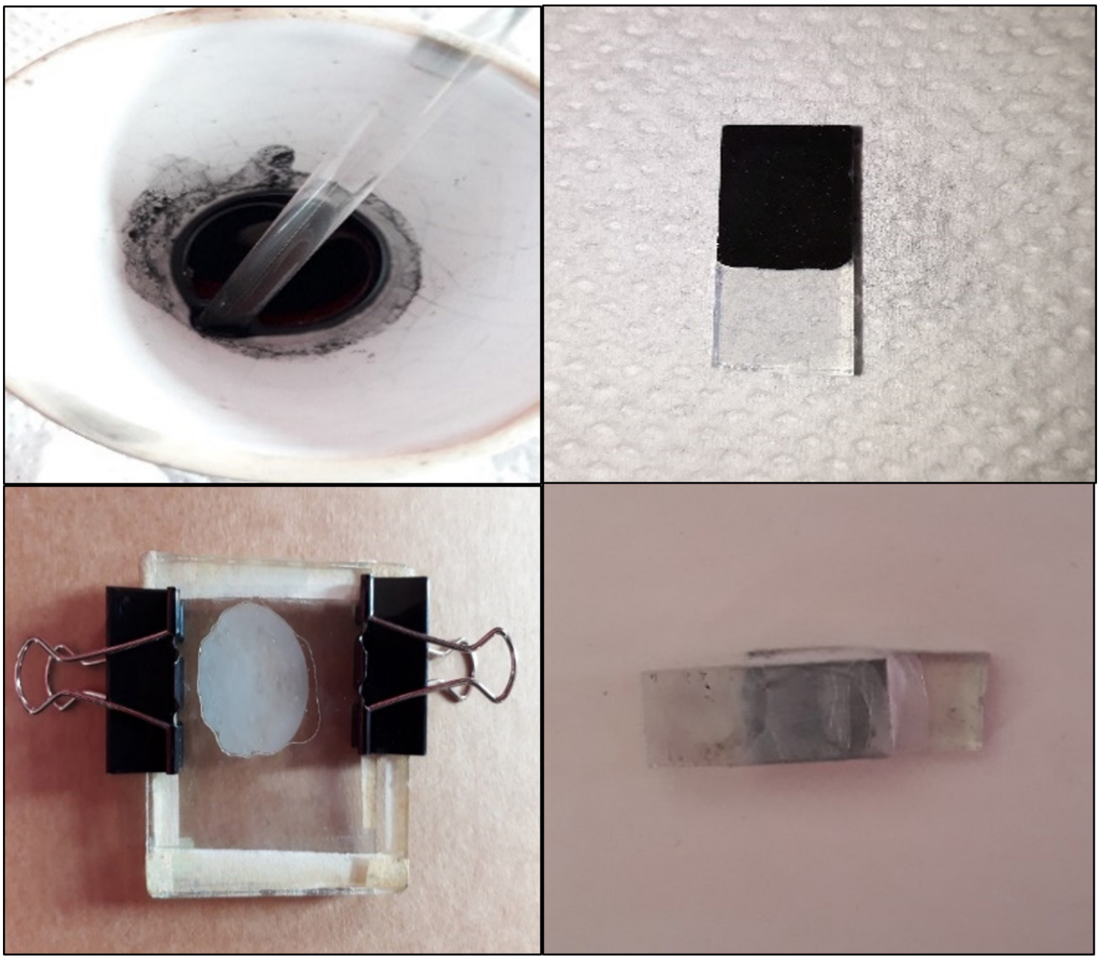
SHORT COMMUNICATION

Sri Lankan natural graphite/gel polymer electrolyte based electrochemical double layer capacitor

D.S.K. Rajaguru, K.P. Vidanapathirana* and K.S. Perera



Highlights

- EDLCs with graphite and gel polymer electrolyte were fabricated.
- Single electrode specific capacitance related to charge-discharge was 5.33 F g^{-1}.
- Capacity retention after 10000 charge discharge cycles was 91.3%.
- Single electrode specific discharge capacitance for discharge was 0.69 F g^{-1}.

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Abstract: Supercapacitors are a promising elucidation among the energy storage devices to cater to the ever-increasing energy demand. Graphite takes a prominent place as a carbonaceous electrode material in electrochemical double layer capacitors (EDLCs) to fulfill the requirement. The present study is based on the performance evaluation of an EDLC fabricated with Sri Lankan natural graphite electrodes incorporating a gel polymer electrolyte. Electrochemical properties of the laboratory scale device were examined using cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) techniques. EDLC displayed a single electrode specific capacitance (C_{sc}) of 5.33 F g^{-1} with CV which retained 84.8% capacity from its initial value after 500 cycles. GCD results revealed initial single electrode discharge capacitance (C_{sd}) of 0.69 F g^{-1} with 91.3% retention from its initial value after 10,000 charging and discharging cycles.

***Keywords*:** Cyclic voltammetry; electrochemical double layer capacitor; galvanostatic charge discharge; gel polymer electrolyte; graphite; specific capacity.

INTRODUCTION

Supercapacitors are attractive alternative energy storage devices since they were built to replace the gap of energy/power between the high-power conventional capacitors and high energy fuel cells/batter. Based upon contemporary developments, supercapacitors can be divided into two main categories: electrochemical double layer capacitors (EDLCs) and pseudo capacitors or redox capacitors (Libich *et al*., 2018). Carbonaceous materials are used as the electrode material in EDLCs due to their expedient features, such as low-cost, high surface area, availability, and established electrode production technologies (Chen *et al*., 2017). Graphite is one of the commonly used carbonaceous electrode material which can be obtained in purest form. It is composed of individual graphene sheets in a hexagonal lattice with an arrangement of sp^2 hybridized carbon atoms. Therefore, it is a good electrical conductor within the graphene layers enabling them to be used as electrode materials (Chung, 2002). Despite graphite bears no initial charge, it can be readily intercalated to host various atoms and molecules, and reversibly accumulate/release ions at very high and low potentials (Sengupta *et al*., 2011).

Most research work reported on supercapacitors is based on liquid electrolytes owing to their high conductivity and good physical contact with electrodes. However, the use of liquid electrolytes has several drawbacks, such as safety issues, due to the leakage problems, need of separators, unstable performances under continuous mechanical deformation and different operating temperatures. Consequently, gel polymer electrolytes (GPEs) which possess both cohesive properties of solids and diffusive properties of liquids are identified as suitable candidates to be used in supercapacitors since it prevents leakage and internal short circuiting which ultimately strengthens the shelf life (Ngai *et al*., 2016).

This study aims to give a value addition to Sri Lankan natural graphite by using it as an electrode in electrochemical double layer capacitor (EDLC) with a GPE. To investigate the electrochemical properties of fabricated EDLC, cyclic voltammetry (CV), and galvanostatic charge discharge (GCD) tests were carried out.

MATERIALS AND METHODS

Sri Lankan natural graphite was obtained from Bogala Graphite Lanka Ltd., Bogala, Sri Lanka. Polyvynilidene fluoride (PVdF), zinc trifluoromethanesulfonate [$Zn(CF_3SO_3)_2$-ZnTf], ethylene carbonate (EC), propylene carbonate (PC) and acetone were purchased from Sigma Aldrich and used without further purification.

Graphite was combined with a small amount of acetone to make a slurry and coated onto fluorine doped tin oxide (FTO) glass plates using the doctor blade method and allowed to air dry. The area and the thickness of the electrode were maintained as 1 cm^2 and 20 µm, respectively. For the gel polymer electrolyte (GPE), required amounts of PVdF, EC, PC and ZnTf were stirred well and heated at 130 °C (Jiang *et al*., 1997). The hot mixture was pressed between two glass plates to obtain a bubble-free thin film. Laboratory scale EDLCs were fabricated using the graphite electrodes prepared and the GPE. They were characterized using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests.

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CV studies were carried out using a three electrode setup with Metrohm M101 potentiostat. One electrode of the EDLC was connected to the working electrode lead while the other was connected to reference and counter leads of the potentiostat. Potential window within which the device could operate without disruptions was determined by cycling in different potential windows. In the selected potential window, current variation with voltage was monitored varying the scan rate. Continuous scanning was done for 500 cycles for the chosen potential window and scan rate. From the area of the cyclic voltammogram obtained, single electrode specific capacitance (C_{sc}) was calculated using Equation 1 (Tey *et al*., 2016).

$$C_{sc} = \frac{2\int I\,\mathrm{d}V}{mS\Delta V} \qquad (1)$$

where $I\mathrm{d}V$ 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. Single electrode specific discharged capacitance (C_{sd}) was calculated using the equation given below (Tey *et al*., 2016).

$$C_{sd} = \frac{I}{m\frac{\mathrm{d}V}{\mathrm{d}t}} \qquad (2)$$

where m is the mass of an electrode and $\mathrm{d}V/\mathrm{d}t$ is the rate of potential drop excluding the internal resistance (IR) drop that occurs at the beginning of discharge.

RESULTS AND DISCUSSION

Cyclic voltammograms obtained for different potential windows are demonstrated in Figure 1.

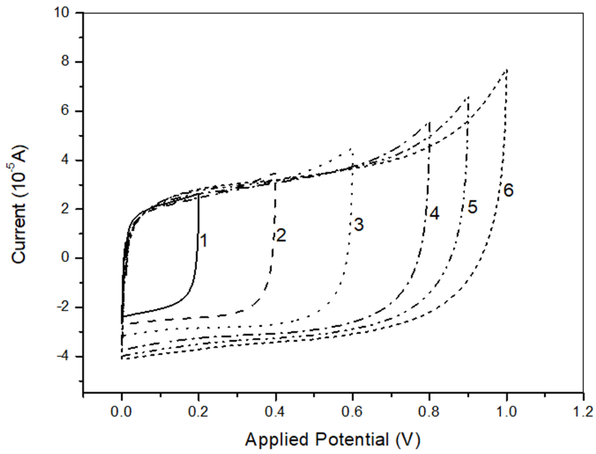

Figure 1: Cyclic voltammograms of EDLC [(1) 0.001-0.2 V, (2) 0.001-0.4 V, (3) 0.00 -0.6 V, (4) 0.001-0.8 V, (5) 0.001-0.9 V, (6) 0.001-1.0 V] at a scan rate of 10 mV s^{-1}.

All voltammograms obtained were parallelograms with almost symmetrical curves around zero current line (vertex line) displaying the typical capacitive features of an EDLC. All the voltammograms show a rapid current response on voltage reversal at each end potential. Absence of redox peaks ensures the double layer formation between the electrode-electrolyte due the electrostatic charge storage. When the window is widened, area covered by cyclic voltammograms gets increased. After surpassing the potential value from +0.8 V, a sharp increase in current could be observed destroying the usual shape of cyclic voltammograms. Thus, the +0.001 V to +0.8 V potential window was chosen for further studies.

Scan rate variation was carried out between 5 mV s^{-1} and 100 mV s^{-1}, and the cyclic voltammograms obtained are shown in Figure 2.

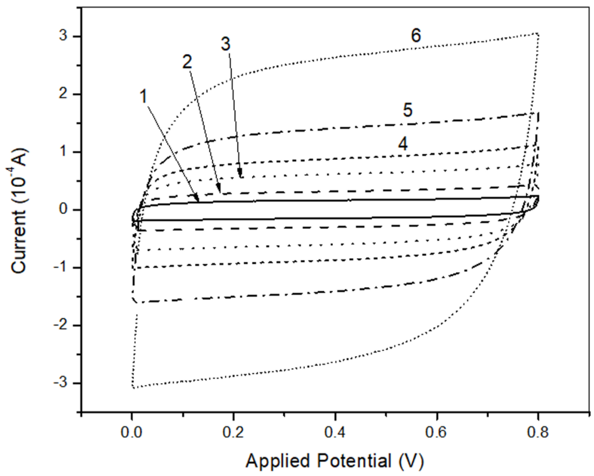

Figure 2: Cyclic voltammograms of EDLC obtained with the scan rate variation from 5 to 100 mV s^{-1}. [(1) 5 mV s^{-1}, (2) 10 mV s^{-1}, (3) 20 mV s^{-1}, (4) 30 mV s^{-1}, (5) 50 mV s^{-1}, (6) 100 mV s^{-1}].

From the area of the cyclic voltammogram, single electrode specific capacitance (C_{sc}) was calculated using Equation 1. It was determined that C_{sc} decreased with increasing scan rate. At low scan rates, there exists ambient time for the ion intercalation giving the maximum C_{sc}. However, when the scan rate is increased, compatibility of the rate of potential change and the rate of ion rearrangement is decreased. As a result, C_{sc} goes down. Considering above factors, the scan rate of 10 mV s^{1} was selected for the investigation of cycling ability.

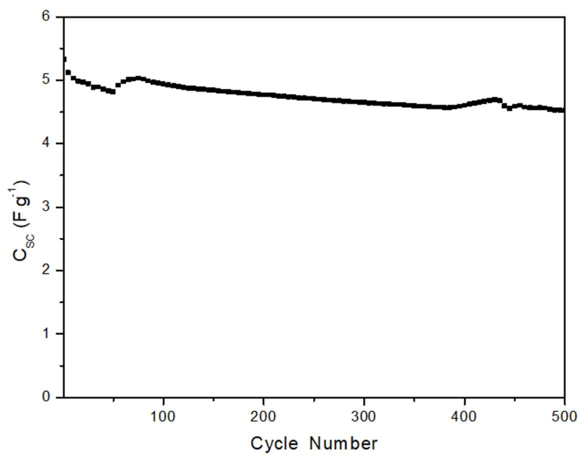

Figure 3: Single electrode specific capacitance (C_{sc}) variation for 500 cycles.

Cycling life of an EDLC is one of the important parameters for practical applications. This was tested with continuous cycling of the EDLC for 500 cycles. The variation of C_{sc} with the cycle number is displayed in Figure 3. Up to about the 75th cycle, there is a somewhat faster drop of C_{sc}. This may be possibly due to immature contacts at the initial stage. Upon continuous cycling, device gains maturity with the formation of proper contacts. Initial C_{sc} value of 5.33 F g^{-1} was decreased to 4.52 F g^{-1} after 500 cycles exhibiting 84.8% of C_{sc} retention from its initial value.

GCD test was carried out in the voltage range of +0.1 V to +0.8 V with a constant current of 0.034 mA. A rapid voltage drop was noticeable at the beginning of the discharging process. This happens due to the ohmic loss (IR drop) arising from internal resistance of the device. Further, EDLC showed an initial single electrode specific discharge capacitance (C_{sd}) of 0.69 F g^{-1} excluding the IR drop.

Figure 4 shows the variation of C_{sd} with respect to the cycle number. However, the variation of C_{sd} with the cycle number displayed slight fluctuations. Even under such variations, EDLC has been able to maintain a more or less constant C_{sd}. This might be due to the self-healing property of the GPE (Cheng *et al.*, 2018). Even after 10,000 cycles, C_{sd} of 0.63 F g^{-1} remained giving capacity retention of 91.3%. This indicates the outstanding rate capability.

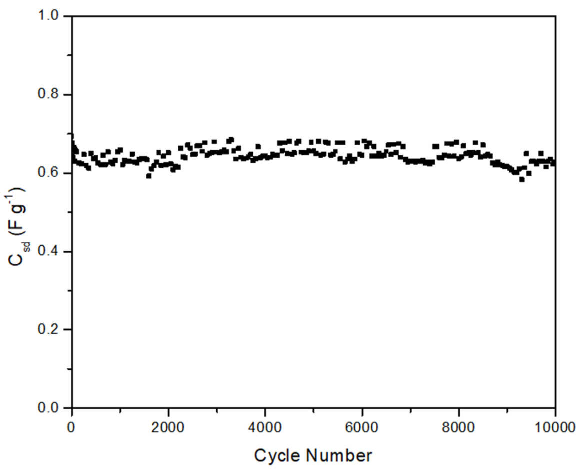

Figure 4: Single electrode specific discharge capacitance (C_{sd}) variation with the cycle number.

CONCLUSION

An EDLC based on Sri Lankan natural graphite and a GPE was successfully fabricated and evaluated. Results of both characterization tests revealed its excellent cycling stability. With CV, EDLC displayed a C_{sc} of 5.33 F g^{-1} which retained 84.8% from its initial value after 500 cycles. The GCD test indicated C_{sd} of 0.69 F g^{-1} with 91.3% capacity retention from its initial value after 10,000 charging and discharging cycles.

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DECLARATION OF CONFLICT OF INTEREST

Authors do not have any conflict of interest.

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