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Solid state electrochemical double layer capacitors with natural graphite and activated charcoal composite electrodes

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Abstract. Electrochemical double layer capacitors (EDLCs) which are fabricated using carbon based electrodes have been emerging at an alarming rate to fulfill the energy demand in the present day world. Activated charcoal has been accepted as a very suitable candidate for electrodes but its cost is higher than natural graphite. Present study is about fabrication of EDLCs using composite electrodes with activated charcoal and Sri Lankan natural graphite as well as a gel polymer electrolyte which is identified as a suitable substitute for liquid electrolytes. Electrochemical Impedance Spectroscopy, Cyclic Voltammetry and Galvanostatic Charge Discharge test were done to evaluate the performance of the fabricated EDLCs. Amount of activated charcoal and natural graphite plays a noticeable role on the capacity. 50 graphite : 40 AC : 10 PVdF showed the optimum single electrode specific capacity value of 15 F/g. Capacity is determined by the cycling rate as well as the potential window within which cycling is being done. Continuous cycling resulted an average single electrode specific capacity variation of 48 F/g – 16 F/g. Capacity fading was higher at the beginning. Later, it dropped noticeably. Initial discharge capacity drop under Galvanostatic Charge Discharge test was slightly fast but reached near stable upon continuous charge discharge process. It can be concluded that initially some agitation is required to reach the maturity. However, the results can be considered as encouraging to initiate studies on EDLCs using Sri Lankan natural graphite.

Keywords: electrochemical double layer capacitors; natural graphite; activated charcoal; gel polymer electrolytes; electrochemical impedance spectroscopy; cyclic voltammetry; galvanostatic charge discharge test

1. Introduction

Super capacitors have been identified as a category of energy storage devices of utmost importance to serve the current thirst for sustainable energy. They owe excellent performance including higher power densities, longer cycle lives and satisfactory environmental friendliness (Kotz and Carlen 2000, Simon and Gogotis 2008). Depending on the type of electrode and hence the charge storage mechanism, there are two types of super capacitors namely electrochemical

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double layer capacitors (EDLC) and redox capacitors (Pandey *et al*. 2013). EDLCs have carbon based electrodes and charge storage takes place via electrostatically. In redox capacitors, conducting polymers or transition metal oxides serve as electrodes and capacitance arises due to ion insertion / deinsertion with redox reactions (Snook *et al*. 2011). The soaring demand for energy in the modern technology based society has motivated incredible advances of super capacitors in terms of power, energy, cost, safety etc. Nowadays, a significant attention has been ignited towards raising capacitance. One line of interest has been to increase the surface area of the electrodes facilitating more charge storage. This has been identified as one crucial factor especially for EDLCs (Prabaharan *et al*. 2006). To address this issue, various carbon based materials such as graphene, carbon black and activated carbon have received a noticeable attention. Upon the rapid increase of global concern over clean and low cost, attempts have been launched to explore materials possessing those characteristics as well. Activated charcoal (AC) has been identified as a suitable candidate having a large surface area (Mishra *et al*. 2016, Kim *et al*. 2015). Also, it is low cost and available abundantly. Natural graphite (NG) is comparatively lower in price than AC and it is non toxic. Unfortunately, its surface area is not in a state to be employed for EDLCs alone. Several groups have adopted different methodologies to increase surface area of graphite (Li *et al*. 2008). However, employability of NG for super capacitors is not very common. There are many reports on rechargeable cells based on NG (Wang *et al*. 2017, Zhang *et al*. 2019). The present study was focused on blending AC with Sri Lankan NG to form electrodes with the prime objective of achieving many positive features including low cost, safety as well as a value addition to a Sri Lankan natural resource which has not been widely considered for energy and power applications. Graphite mines are available in many places in Sri Lanka. Hence, graphite is readily available at a cheap price. Purity is noticeably high. In addition to that, the electrolyte in the EDLCs was fabricated using a gel polymer electrolyte (GPE) in order to minimize the drawbacks associated with liquid electrolytes. At the moment, there is a huge concern over the issues from liquid electrolytes at the stages of designing, packaging, transporting and disposing. GPEs have obtained a considerable attention as a class of substitutes for liquid electrolytes (Rosdi *et al*. 2016). They show good conductivities comparable to liquid electrolytes and mechanical properties closer to solid electrolytes (Pandey *et al*. 2013).

In the present study, the composition of the electrode was varied to get the optimum performance. Characteristics of the EDLCs were monitored using Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and Galvanostatic charge discharge test (GCD). As per our literature survey, this is a very first kind of an EDLC having a composite electrode with AC and Sri Lankan NG with a GPE.

2. Experimental

2.1 Preparation of the composite electrodes

Natural graphite (NR) received from Bogala Graphite Lanka Ltd, Bogala, Sri Lanka and activated charcoal (AC) purchased from Aldrich were used without further treatment. They were first mixed in at a selected weight ratio. Polyvinylidene fluoride (PVdF) (Aldrich) which was used as a binder was magnetically stirred with acetone for about 1 hour until mix thoroughly. Then, graphite and AC were added to the mixture and further stirring was done for about 3 hours. The resulting slurry was coated on fluorine doped tin oxide (FTO) glass pieces of 1 cm^2 area. Preparation of the electrodes was done under normal atmospheric conditions.

2.2 Preparation of gel polymer electrolyte (*GPE*)

The gel polymer electrolyte was prepared using solvent casting technique. First, the selected amount of zinc trifluromethanesulfonate ($Zn(CF_3SO_3)_2$ – ZnTF) (Aldrich) was dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) received from Aldrich by magnetic stirring. Polyvinylidene fluoride co hexafluoropropylene (PVdF-HFP) (Aldrich) was also dissolved in acetone by magnetic stirring for about 3 hours. Both solutions were then mixed together followed by further stirring for about 3 hours under normal atmospheric conditions. The final homogeneous mixture was poured in petri dishes and kept at room temperature to evaporate solvents slowly overnight. The composition of the electrolyte was 0.5 PVdF: 0.7 ZnTF: 1.0 EC: 1.0 DEC (by weight). In one of our previous studies, its conductivity has been found as 3.45×10^{-3} Scm^{-1}.

2.3 Fabrication of electrochemical double layer capacitors (*EDLC*)

Two identical composite electrodes were assembled together having a GPE film in between them. This assembling procedure was carried out at normal atmosphere.

2.4 Characterization of EDLCs

Capacitance of EDLCs can be evaluated mainly using electrochemical impedance spectroscopy (EIS) from the frequency domain as well as using cyclic voltammetry and galvanostatic charge discharge tests in time domain.

By varying the weight ratio between NR and AC, different electrodes were prepared and EDLCs were fabricated with them.

Impedance data for EIS technique were gathered for each EDLC at room temperature using a Metrohm impedance analyser. Single electrode specific capacitance (C_s) was calculated using the Eq. (1) and the Nyquist plot drawn between Z'' and Z'.

$$C_s = 1/2\pi f Z'' m \tag{1}$$

Here, f is the lowest frequency corresponding for the imaginary impedance, Z'' and m is the single electrode mass (Nadiah *et al*. 2016).

Capacitance is a depending variable of frequency. The relationship can be represented using the complex capacitance equation as follows (Tey *et al*. 2016)

$$C(\omega) = C'(\omega) - jC''(\omega) \tag{2}$$

where C'(ω) is the real part and C"(ω) is the imaginary part of the complex capacitance. Using the real part of the impedance (Z') and imaginary part (Z") of the complex impedance, C' as well as C" can be calculated.

$$C'(\omega') = -Z'' / \omega \left| Z^2 \right| \tag{3}$$

$$C''(\omega'') = Z' / \omega \left| Z^2 \right| \tag{4}$$

Here, Z is the complex impedance.

Variation of C' and C" with frequency or the so called Bode plots are ideal for showcasing numerous features in EDLC. From the graph of C" vs frequency, the relaxation time, τ_0 can be calculated as follows.

$$\tau_0 = 1/2\pi f_0 \tag{5}$$

F_0 is the frequency where maximum C" occurs.

The EDLC with the highest C_s was further tested with cyclic voltammetry (CV) test and galvanostatic charge discharge (GCD) test. Cyclic voltammetry measurements are taken by imposing an electric potential between the working and reference electrodes recording resulted current between counter and reference electrodes (Compton and Banks 2007). Under CV test, potential window as well as the scan rate was varied to trace the optimum performance and then, a continuous cycling was done to monitor the ability of EDLC to withstand for continuous operation. C_s values were calculated using Eq. (2).

$$C_s = 2\int (I\mathrm{d}t)/m.S.\Delta V \tag{6}$$

Here, $\int I\mathrm{d}t$ is the area of the cyclic voltammogramme, m is the single electrode mass, S is the scan rate and ΔV is the width of the potential window (Wang *et al*. 2013).

Galvanostatic Charge Discharge (GCD) test was performed at the constant current of 2×10^{-4} A between the potentials 0.09 V and 1.00 V. Single electrode specific discharge capacity (C_d) was calculated as follows.

$$C_d = I/(\mathrm{d}V/\mathrm{d}t)m \tag{7}$$

where I is the constant current, dv/dt is the rate of potential drop during discharge excluding IR drop.

3. Results and discussion

3.1 Electrochemical Impedance Spectroscopy technique

Fig.1 illustrates one of the resulting nyquist plots obtained from impedance data.

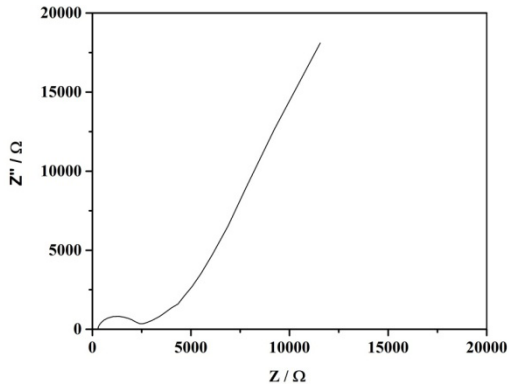

Fig. 1 One of the resulted nyquist plots of an EDLC at room temperature

Theoretically, nyquist plot of an EDLC consist with two semi circles at high and medium frequencies whereas spikes of two inclinations appear at low frequency regions. The semi-circle at high frequency region represents bulk electrolyte properties. The second semi-circle is due to the properties at the electrolyte electrode interfaces. The spike that appears after the second semi-circle represents capacitive effects arises due to reactions at same rate whereas the spike at the very low frequency region presents the capacitive features. In the resulting nyquist plot, the high frequency semi-circle is not present probably due to the absence of the required frequency range. All other characteristic features are available showcasing the properties of an EDLC. The spike at the lowest frequency region should be parallel to the imaginary axis for an ideal capacitor. However, in the resulting nyquist plot, it is having an inclination. This might be due the electrode surface irregularities.

Figs. 2(a) and (b) illustrate the bode plots of one the EDLCs fabricated.

In Fig. 2(a), at low frequency region, *C*' represents the capacitance of electrode material. When the frequency increases, a considerable drop of *C*' occurs. This proves the fact that the capacitive properties become dominant at low frequency region. Beyond 0.1 Hz, it acts as a pure resistor

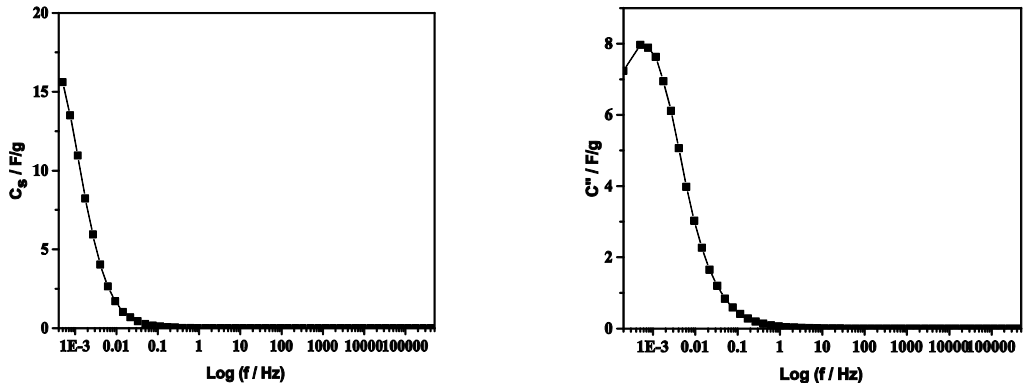

Fig. 2 (a) Variation of real part of capacitance with the frequency for an EDLC at room temperature; (b) variation of imaginary part of capacitance with the frequency for an EDLC at room temperature

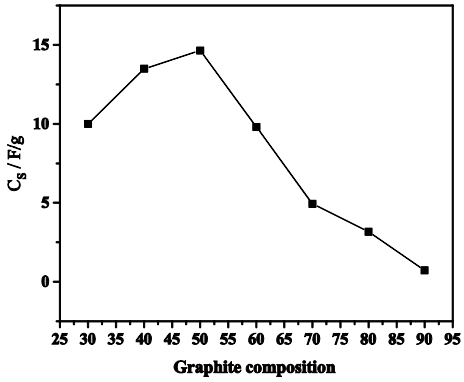

Fig. 3 Variation of single electrode specific capacity (C_s) with the amount of graphite in the electrode at room temperature

having no capacitive effect. Bode plot shows the transition from capacitive characteristics to resistive characteristics. The maximum *C*' is considered as the transition point (Wang *et al*. 2011). The calculated relaxation time is about 159 s. This is a quite higher value which hints the slow ion transfer. This might be due to the presence of graphite which is not very porous.

Fig. 3 shows the variation of C_s with the graphite composition. The material composition in the electrode was selected as *x* graphite : (90-*x*) AC : 10 PVdF.

According to the graph, when the amount of graphite is increased, C_s increased initially. But, after the value of 50, a descending trend of C_s could be observed. Initial increase might be due to the assistance from graphite to store more charges in the electrode. The subsequent decrease of C_s may be due to the high amount of graphite in the electrode. The amount of graphite may be too large which disrupts the charge storage process. So, even the presence of AC is available, it is not dominant with the high amount of graphite. Hence, the EDLC with the composition, 50 graphite : 40 AC : 10 PVdF was chosen for further studies which showed a value of 15 F/g for C_s. This value is rather low compared to the value observed by Pandey *et al*. (2010). Their electrode composition was 75 AC : 15 NG : 10 PVdF. Higher C_s may be due to the larger amount of AC in the composition.

3.2 Cyclic Voltammetry (CV) Test

Fig. 4 illustrates the cyclic voltammograms obtained with varying the potential window of cycling.

Potential was varied having the starting potential as 0.1 V. No peaks were observed in all cyclic voltammograms indicating the fact that redox reactions are absent within all potential windows. In other words, this evidences that capacitive nature is purely non faradaic. Shapes were of near rectangular shape which is a characteristic feature of EDLCs (Natalia *et al*. 2013). When widening the window, it was observed that current increased towards anodic side. As a result, higher C_s values were obtained. But, this is not favorable as increase of current might be due to some irreversible reactions. Hence, the potential window of 0.1 to 1.6 V was selected for further investigations.

Fig. 5 shows the cyclic voltammograms corresponding to different scan rates.

All were close mirror images around the zero current axis. This evidences the reversibility of

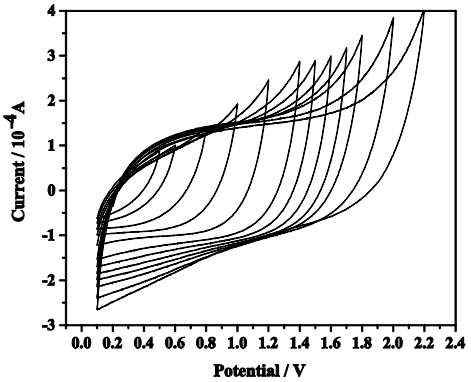

Fig. 4 Cyclic voltammograms obtained by varying the potential window of cycling at the scan rate of 10 mV/s at room temperature

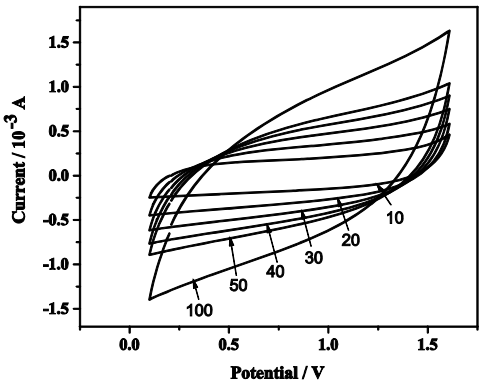

Fig. 5 Cyclic voltammograms obtained by varying the scan rate of cycling within the potential window 0.1 V – 1.6 V at room temperature

reactions. Low scan rate cyclic voltammograms show conventional parallelogram shape indicating that charge discharge takes place in the synchronous region where the rate of reactions are equal. Due to the inability of the slow fraction of capacitive states to keep up with the applied voltage perturbation, shape of cyclic voltammograms becomes biconvex (Fletcher *et al*. 2014). Further, Hashmi *et al* have reported that some shape deviations could be observed with higher scan rates probably due to higher ESR values (Hashmi *et al*. 2007). Amount of deviation would have been controlled by high conducting GPE.

When the scan rates were increased, C_s values showed a decreasing trend as reported in literature (Wang *et al*. 2013). For proper and complete charge storage, there should be ample time for the respective mechanism to take place. At slow scan rates, charges can go deeper into the electrodes. This contributes for higher C_s. In addition, at high scan rates, energy loss increases and as a result, charge storage becomes weak. This leads to decrease in specific capacity. But, very slow scan rates on the other hand can give rise to unwanted reactions which might disturb the proper operation of EDLCs. The scan rate of 10 mV/s was selected to be used for continuous cycling.

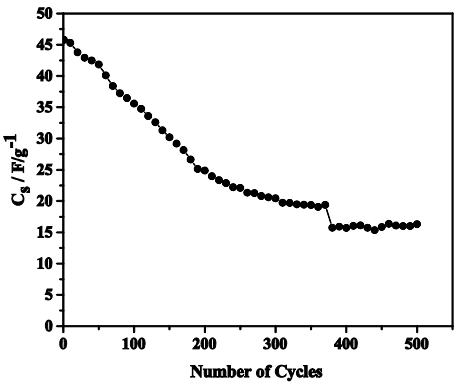

Fig. 6 Variation of single electrode specific capacity (C_s) with cycle number at the scan rate of 10 mV/s within the potential window 0.1 V – 1.6 V at room temperature

Fig 6 shows the variation of C_s with cycle number. C_s variation from about 48 F/g to 16 F/g occurred while cycling for 500 cycles.

The rate of decrease is fast during first 300 cycles. After that, it had reached a nearly steady state. At the beginning, the interfacial contacts may not be mature enough to take part in the charge storage process. Upon continuous cycling, the setup may reach maturity resulting somewhat stable performance. It is a well-accepted fact that, from the total capacity of an EDLCS, 10-20% is due o redox capacitance. It is a faradaic process involving electron transfer. If redox capacitance was present, peaks should appear in voltammograms (Liew and Ramesh 2014). But, in none of the case, that behavior could not be observed. This indicates that the charge storage mechanism of the present EDLCs are purely electrostatic giving rise to pure capacitive behavior.

3.3 Galvanostatic Charge Discharge (GCD) Test

Fig. 7 shows several initial GCD curves and Fig. 8 represents the variation of single electrode discharge capacity (C_d) with cycle number.

As per Fig. 7, it is seen the presence of ohmic loss across the internal resistance which is called as equivalent series resistance (ESR) with the initial sudden jump/drop of potential in charge/

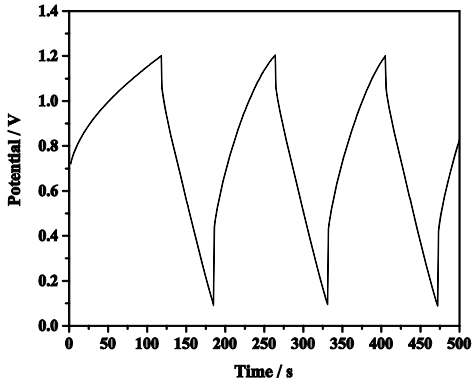

Fig. 7 Initial charge discharge profile obtained under a constant current of 2×10^{-4} A at room temperature

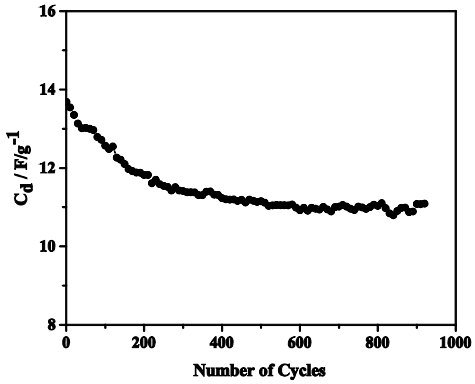

Fig. 8 Variation of single electrode specific discharge e capacity (C_d) with cycle number

discharge stages (Pandey *et al*. 2013). For 900 cycles, C_d has changed from 13.68 F/g to 11.01 F/g which is not a fast decrease. Only up to about 200 cycles, the decrease rate is quite faster. Then, C_d becomes more or less stable. During initial cycles, the fast capacity fade may result due to two reasons as suggested by Pandey *et al*. namely i. consumtion of some charges for irreversible reactions ii. possibility of permanent filling of some micro pores of AC (Pandey *et al*. 2010).

However, capacitance values obtained by different techniques are not comparable to each other due to mismatch of time scales of measurements. As an example, if the time durations taken for charge and discharge processes in CV and GCD tests are not equal, the results may be different. Anyway, different methodologies should be used to evaluate the performance under numerous conditions such as scan arte, potential window of cycling and frequency range.

4. Conclusions

All solid state EDLCs were prepared using a composite electrode having NG, AC and PVdF with a GPE. NG blends well with AC and results the optimum C_s of 14.65 F/g for the composition of 50 NG and 40 AC. Above and below 50, C_s is somewhat lower showcasing the fact that NG plays a role on determining C_s. Continuous cycling at the potential window of 0.1 to 1.6 V and the scan rate of 10 mV/s evidenced the ability of the EDLC to withstand for continuous operation. But, further work is needed to improve the performance. Higher value of relaxation time is an evidence for the slow charge transfer in the device. This should be expedited. C_d did not change very fast which is a satisfactory feature for using the EDLC for applications. The most appealing feature of this study is exploring the suitability of Sri Lankan NG for super capacitor applications.

Acknowledgments

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