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Electrochemical double layer capacitors with PEO and Sri Lankan natural graphite

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Abstract. Electrochemical double layer capacitors (EDLCs) have received a tremendous interest due to their suitability for diverse applications. They have been fabricated using different carbon based electrodes including activated carbons, single walled/multi walled carbon nano tubes. But, graphite which is one of the natural resources in Sri Lanka has not been given a considerable attention towards using for EDLCs though it is a famous carbon material. On the other hand, EDLCs are well reported with various liquid electrolytes which are associated with numerous drawbacks. Gel polymer electrolytes (GPE) are well known alternative for liquid electrolytes. In this paper, it is reported about an EDLC fabricated with a nano composite polyethylene oxide based GPE and two Sri Lankan graphite based electrodes. The composition of the GPE was [{(10PEO: $NaClO_4$) molar ratio}: 75wt.% PC] : 5 wt.% TiO_2. GPE was prepared using the solvent casting method. Two graphite electrodes were prepared by mixing 85% graphite and 15% polyvinylidenefluoride (PVdF) in acetone and casting n fluorine doped tin oxide glass plates. GPE film was sandwiched in between the two graphite electrodes. A non faradaic charge discharge mechanism was observed from the Cyclic Voltammetry study. GPE was stable in the potential windows from (-0.8 V-0.8 V) to (-1.5 V-1.5 V). By increasing the width of the potential window, single electrode specific capacity increased. Impedance plots confirmed the capacitive behavior at low frequency region. Galvanostatic charge discharge test yielded an average discharge capacity of 0.60 Fg^{-1}.

Keywords: gel polymer electrolyte; graphite; electrochemical double layer capacitors; cyclic voltammetry; electrochemical impedance spectroscopy; galvanostatic charge discharge; nyquist plots; super capacitors

1. Introduction

Super capacitors, a kind of promising, uninterruptable power sources, have received an enormous attention during the last few years in a wide range of applications. They combine the high energy storage capability of batteries and high power delivery capability of conventional capacitors (Hashmi 2004). They are projected as power sources for high power applications such as hybrid/electric automobiles, military devices, utility load maintenance and medical applications.

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In addition, they have been immensely used for low power applications including cameras, flash equipments and memory back up systems. In principle, super capacitors are divided in to two main categories as electrochemical double layer capacitors (EDLCs) and redox capacitors. In EDLCs, electrodes are based on carbon materials whereas redox capacitors employ transition metal oxides and conjugated polymer electrodes. Both types have their own merits and demerits. Many of the EDLCs investigated up to now, have used activated carbon, carbon nano tubes in preparing electrodes (Gamby *et al.* 2010, Hashmi *et al.* 2014). But, many have faced the challenges of acquiring high capacitance as well as reducing the cost with simple production processes. In addition, they suffer greatly from restricted rate capability and low energy storage capacity (Zhang *et al.* 2010). As an alternative approach, nowadays attention has been diverted towards utilizing graphite for EDLCs (Wang 2012). In principle, graphite is an excellent electric conductor. Hence, it is very suitable to be used as electrodes for EDLCs.

Unfortunately, scarcity and high price of graphite has set up a barrier for many researchers to use graphite for EDLC applications. Sri Lanka, being a country rich in various natural resources, has several graphite mines which have not been considered in the energy and power field at a satisfactory level. Sri Lankan natural graphite is not expensive as synthetic graphite. And also, it has a high purity which is comparable to synthetic graphite. Under those factors, Sri Lankan natural graphite are very appealing candidates for EDLCs.

In the present study, it is reported about fabrication and characterization of EDLCs employing Sri Lankan natural graphite. Most of the EDLCs fabricated with graphite has used different techniques to modify the structure of graphite (Wang 2012, Nandhini *et al.* 2012, Li *et al.* 2008). For the study, graphite samples were used as received from the mines. In addition to use of natural graphite, this study carries two more innovative features. They are employing a gel polymer electrolyte (GPE) as the electrolyte and using polyethylene oxide (PEO) as the polymer net work for GPE. Many of the EDLCs investigated so far, are based on liquid electrolytes with high performance. But, they have undergone various drawbacks such as corrosion, leakage and bulky design (Prabaharan *et al.* 2006, Basnayake *et al.* 2013). This has promoted the consideration of polymer electrolytes in place of liquid electrolytes. GPEs have a received a considerable interest due to their fascinating properties in terms of electrochemical and mechanical aspects. They possess appreciable ambient temperature ionic conductivities while retaining good mechanical properties. Also, their preparation methods are rather simple and easy. GPEs have been widely considered for a large number of applications such as batteries, dye sensitized solar cells and electrochromic devices. Recently, an intense interest has aroused to employ GPEs for super capacitors. GPEs are consisting with a polymer network within which a suitable liquid electrolyte formed using a salt and a solvent/s mixture is entrapped. Some of the common polymers that are being used by many researchers are polyacrylonitrile (PAN), polymethyl methacrylate (PMMA) and polyvinylidenefluoride (PVdF) (Jayathilake *et al.* 2015, Perera *et al.* 2011). PEO has been used for preparation of conventional polymer electrolytes and they have not exhibited satisfactory conductivities at normal temperatures mainly due to crystalline nature of PEO. Various attempts have been launched to disturb the crystalline phase of PEO and thereby to increase the conductivity of PEO based systems. Among them, introducing nano fillers has become very attractive and popular (Agrawal *et al.* 2013, Dey *et al.* 2013). PEO based polymer electrolytes have been intensively used for numerous applications. But, use of PEO for EDLCs is very rare to the best of our knowledge. Hence, this study done on an EDLC with the combination of natural graphite electrodes together with nano composite PEO based GPE may be a very fresh and innovative research approach in the field of super capacitors. With the results obtained, it was possible to prove the candidacy of such EDLCs to be considered for energy storage application.

2. Materials and methods

2.1 Preparation of graphite electrodes

Graphite sample kindly provided by Bogala Graphite Lanka (Pvt) Ltd, Bogala, Sri Lanka was used without further purification. 85% (weight basis) graphite was mixed well with 15% polyvinylidene fluoride (PVdF-ALDRICH) using Acetone in a mortar and pestel. When an uniform slurry was obtained, it was coated on fluorine tin oxide (FTO) glass slides of an area 1 cm^2. The prepared electrodes were dried over night before using them to fabricate EDLCs. Single electrode mass was 1.2 mg.

2.2 Preparation of GPE

Polyethylene oxide (PEO) (Mw~400,000, Aldrich), sodium perchlorate ($NaClO_4$) (>99%, Aldrich) and propylene carbonate (PC) (99%, Aldrich) were vacuum dried at 50°C for 24 hrs prior to use. Required amounts of PEO and $NaClO_4$ were added to acetonitrile (BDH) and stirring was done overnight using a magnetic stirrer to obtain a homogenous mixture. Then, titanium dioxide (TiO_2) (P-25 Degussa) were added and magnetic stirring was continued further. The final mixture was poured into a teflon petri dish and the solvent was allowed to evaporate. The selected composition was [{(10PEO: $NaClO_4$) molar ratio}: 75wt.% PC] : 5 wt.% TiO_2 which showed a room temperature conductivity of 5.42 x 10^{-3} Scm^{-1} (Perera *et al.* 2017). It was possible to obtain a very thin, mechanically stable film.

2.3 Assembling and evaluating the EDLC

Two graphite electrodes of the area 1 cm^2 were assembled having a GPE of the identical size in between them. Cyclic Voltammetry (CV) study was carried out using a three electrode cell having one graphite electrode as the working electrode and the other graphite electrode as reference and counter electrode. Scanning was done at the rate of 10 mV/s within different potential windows. From CV study, single electrode specific capacitance of the EDLC (C_s) was calculated using the Eq. (1).

$$C_s = (2\int Idv) / s.\Delta V.m \tag{1}$$

Here $\int Idv$ is the area of the cyclic voltammogramme, s is the scan rate, ΔV is the potential window and m is the mass of a single electrode. Impedance data were gathered from 0.4 MHz to 0.01 Hz using a Metrohm 110 impedance analyser. Theoretically, an impedance plot of a pure capacitor is a straight line parallel to the imaginary axis. In practical capacitors, a steep rising behavior is seen in the low frequency region accompanied with high frequency and mid frequency characteristics owing to the bulk and interfacial properties (Pandey *et al.* 2010). As such a typical impedance plot of a practical capacitor consists with two semi circles at high and mid frequencies and a tilted spike at low frequencies. The capacitance impedance data can be expressed using the complex capacitance equation given as Eq. (2) (Tey 2016).

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

Here, C’(ω) is the real part of the complex capacitance and C’’(ω) is the imaginary part of the complex capacitance. Low frequency C’(ω) corresponds to capacitance of EDLC and C’’(ω) refers to energy dissipation by an irreversible process that may lead to movement of molecules (Natalia, Sudhakar, Selvakumar, 2013). They can be evaluated using the Eqs. (3) and (4)

$$C'(\omega) = -Z''/[\omega Z(\omega)^2] \tag{3}$$

$$C''(\omega) = Z'/[\omega\, Z(\omega)^2] \tag{4}$$

based on real (Z’(ω)), imaginary (Z’’(ω)) parts of complex impedance (Z(ω)).The single electrode specific capacitance, C_s can also be found using the graph that is drawn between the real capacitance and frequency. The maximum real capacitance value refers to $C_{s.}$ In addition, the relaxation time (τ) can be calculated as

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

f_0 represents the frequency at which maximum imaginary capacitive behavior is observed.

Using the Nyquist plots, the behavior of the EDLC was observed.

The galvanostatic charge discharge of the EDLC was carried out in between the potentials 0.1 V and 1.5 V under a constant current of 50 µA for 230 cycles. Galvanostatic charge discharge test results can be used to calculate the discharge capacity of an EDLC using the Eq. (6)

$$C_d = I\,\Delta t / m\Delta v \tag{6}$$

where I is the constant current, m is the single electrode mass, (Δv/Δt) is the rate of potential drop excluding IR drop during discharging.

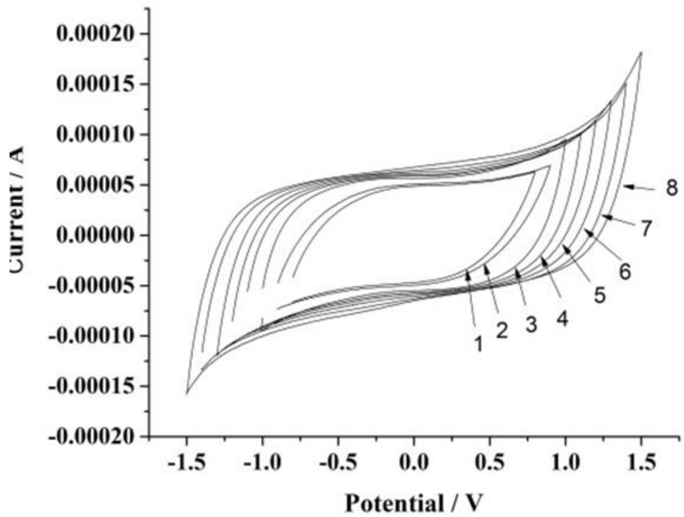


Fig. 1 Cyclic voltammograms obtained for different potential windows

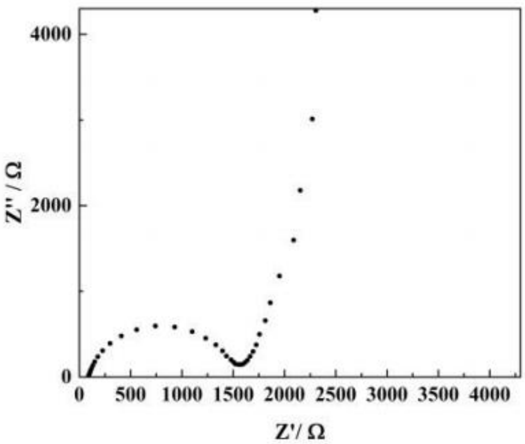


Fig. 2 Nyquist plot of the EDLC taken at the room temperature

3. Results and discussion

3.1 Cyclic Voltammetry analysis

Fig. 1 shows the cyclic voltammograms obtained with varying the potential window.

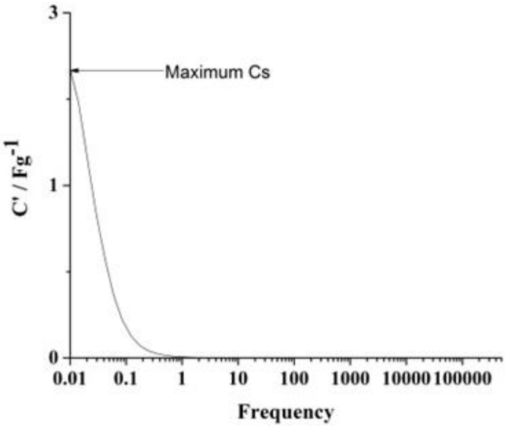
When the potential window is widened starting from the range (-0.8 V -+0.8 V) to (-1.5 V - +1.5 V), cyclic voltammograms retain at rectangular shape. This shape evidences the typical capacitor like behavior (Prabaharan *et al.* 2006). Another observation that be seen is the stability of GPE in the wider electrochemical window (Tey *et al.* 2016). The absence of peaks in the cyclic voltammograms well confirms the fact that faradaic reactions that lead to pseudo capacitive behavior are not taking place inside the EDLC. Hence, the charge storage mechanism may be based on the electrostatic mechanism. Upon increasing the width of the potential window, the single electrode specific capacitance increased from 1.28 Fg^{-1} to 2.06 Fg^{-1}. This may be due to the occurrence of complete charge discharge processes. Anodic and cathodic currents had increased proportionally with the voltage. This suggests good reversibility of the charge discharge processes (Wang *et al.*, 2012). All cyclic voltammogrammes show mirror image symmetry of the current responses around zero current line suggesting the capacitive behavior with double layer formation. Further widening may end up with higher anodic and cathodic currents. This shows the exceeding of the electrochemical stability window which may end up in unwanted reactions. However, this type of widening has been possible with the use of gel polymer electrolyte in non aqueous state. If it were an aqueous form, presence of water limits the potential window.

3.2 Electrochemical impedance spectroscopy studies

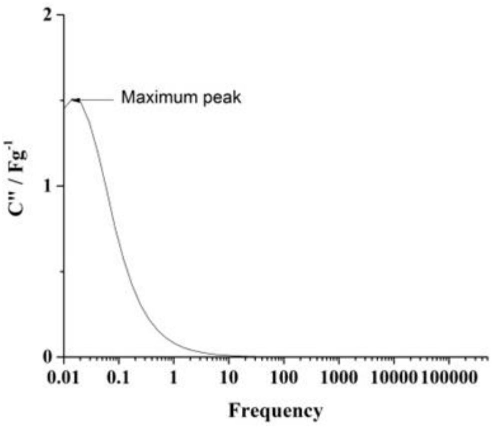
Fig. 2 illustrates the Nyquist plot obtained for an EDLC.

It does not contain the high frequency semicircle. But, at mid frequency region, a semicircle appears followed by a tilted spike at low frequency region. The absence of the high frequency semicircle may be due to the unavailability of required high frequency values. The mid frequency semicircle features the interfacial properties including charge transfer resistance and double layer capacitance. The straight line becomes more parallel to the imaginary impedance axis at low frequencies. This implies the attaining pure capacitive behavior at low frequencies. When the frequency is lowered, ion movement becomes higher and as a result, resistive nature vanishes allowing capacitive features to become dominant (Natalia *et al.* 2013). For ideal capacitors, this spike is perfectly parallel to the imaginary axis. In this study, it was not possible to obtain such a parallel line due to some surface roughness problems in the electrodes .

Fig. 3(a) and 3(b) show the variations of real and imaginary capacitances with frequency respectively. At lower frequencies in Fig. 3(a), the capacitive behavior is dominant but with increasing frequency, capacitive behavior tends to vanish and resistive behavior becomes dominant. The calculated single electrode specific capacitance is 2.1 F/g. The value of the relaxation time is found to be 11 s which is slightly higher for an EDLCs. This may be due to low rate of movement of molecules.



(a)



(b)

Fig. 3 Variation of (a) real capacitance and (b) imaginary capacitance with the frequency

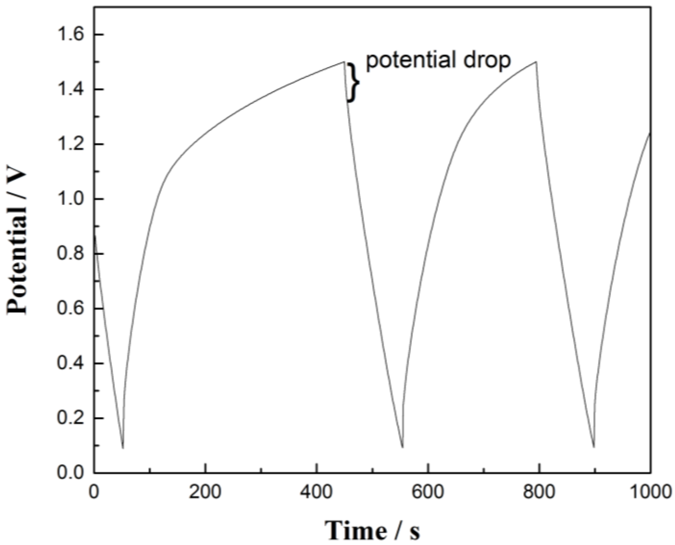


Fig. 4 The charge discharge profile of the EDLC

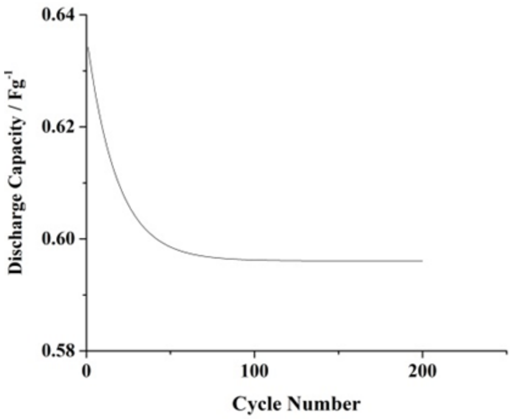


Fig. 5 Variation of C_d with time for EDLC

3.3 Galvanostatic charge discharge test

Fig. 4 illustrates the charge discharge profile of the EDLC.

Variation of C_d with time is shown in Fig. 5. Decrease in discharge capacity is observable initially but upon continuous cycling, it has attained a constant value of 0.60 Fg^{-1}.This proves the stable charge discharge processes in the EDLC (Li *et al*. 2008). C_s obtained from cyclic voltammetry test refers to the complete charge available for charge and discharge process whereas C_d refers only the charge available for discharge process. If the charge discharge processes are identical to each other, the amount of total charge should be twice the charge involved in each individual process. C_s and C_d values result from the present study prove the above fact very well.

4. Conclusions

An EDLC with a PEO based nano composite GPE and Sri Lankan natural graphite electrodes was fabricated successfully. The performance of EDLC was evaluated using Cyclic Voltammetry, Electrochemical Impedance Spectroscopy and Galvanostatic Charge Discharge Test. Single electrode specific capacity was in the range 1.28 Fg^{-1} to 2.06 $Fg^{-1}$when cycled in different potential windows. GPE was stable in a wider potential window like -1.8 V-1.8 V. The charge storage mechanism is of non-faradaic nature. Impedance data proves the dominant capacitive nature at low frequencies. Charge discharge profile obtained for 230 cycles gives an average discharge capacity of 0.6 Fg^{-1}. EDLC becomes stable and maintains a near equal discharge capacity after few initial charge discharge cycles. Further studies are being continued to improve the performance and thereby to provide a value to a Sri Lankan natural resource and also to initiate steps to fabricate low cost, environmental friendly EDLCs for future energy storage requirements.

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