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Fabrication and Characterization of Electrochemical Double-Layer Capacitors using a Natural Rubber Based Polymer Electrolyte

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ABSTRACT

Electrochemical double-layer capacitors (EDLCs) based on solid polymer electrolytes (SPEs) have gained a significant attention due to their appeal in solid-state energy storage. However, the high cost and the toxicity of many polymers in those SPEs have been realized as central challenges for the wide popularization of such EDLCs. Therefore, world is looking for cheap and safe polymer hosts to be used for fabricating EDLCs. A substantial interest has been arose towards natural rubber (NR) based SPEs. This study is about preparing and characterizing EDLCs using a Sri Lankan NR based electrolyte with Sri Lankan natural graphite (NG) based electrodes. NR electrolyte was consisted with 49% methyl grafted natural rubber (MGNR) and zinc trifluoromethanesulfonate (ZnTf). NG electrodes were made using a slurry of NG and acetone. Electrochemical impedance spectroscopy (EIS) test, cyclic voltammetry (CV) test and galvanostatic charge discharge (GCD)test have been done to characterize the EDLC. Single electrode specific capacitance was about 2.87 F g^{-1} whereas the single electrode specific discharge capacitance was about 1.11 F g^{-1}. The EDLC with this novel ZnTf-natural rubber based SPE can be used for different energy applications with further enhancements.

Keywords: *natural rubber, graphite, single electrode specific capacitance*

1. INTRODUCTION

Today, use of electric energy grows dramatically very fast due to increasing demand in diverse applications. Nevertheless, the limited amounts of natural resources, the high cost of fossil fuel and environmental awareness have become the driving forces to find alternative solutions to fulfill the energy thirst. This has highlighted the need for covering energy requirements with limited use of fossil fuels and greater use of renewable energy [1].A noticeable attention has been focused on renewable sources such as solar,wind and tidal [2,3,4]. Energy from renewable sources needs to be stored and used when needed mainly due to its fluctuations with location, time etc. Hence, energy storage is the key part of renewable energy sources utilization. Use of batteries and conventional capacitors has been the practice for storing energy since long time ago. But, as per the present day demand, both of them have not been able to extend their service efficiently and effectively surpassing their demerits. Electrochemical double layer capacitors (EDLCs)have been identified as alternative to batteries and capacitors which are having high energy and power density [5]. They are composed of an electrolyte with two carbon based electrodes and possess very attractive features [6]. Early days, many of the EDLCs have been developed using liquid electrolytes. But, due to the associated problems of liquid electrolytes, many researchers have diverted their attention on solid polymer electrolytes (SPEs) to be used for EDLCs.

SPEs have received a great attention due to their outstanding performance in various potential applications [7]. High concern over the environmental friendliness and the cost has become a challenge for many SPEs which are based on toxic and expensive polymers. Now, there is a growing interest in the exploitation of suitable polymers and it has made natural rubber (NR) as one of the materials of choice [8,9]. As NR is an insulator, modification methodologies have been used to make it suitable for electrolytes. Those modified natural rubber (MNR) has a low glass transition temperature (Tg), soft elastomer characteristics at room temperature, good elasticity and possess adhesive properties. Several research groups are involved with NR based electrolyte research activities [10]. Many have used NR samples from Malaysia. In Sri Lanka, NR is one of the major export crops and it is grown in many areas supporting the family economy of a large number of people. But, it ahs not been given a proper attention to serve in energy and power sector other than exporting and consuming a small part for several local industries. Recently, we have paid our attention on this natural polymer with the prime objective of adding value in energy and power filed. At the moment, two polymer electrolyte systems incorporating magnesium trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$) and Lithium bistrifluromethanesulfonimide ($CF_3SO_2NLiSO_2CF_3Li$) have been prepared and characterized for their potential use in cells and EDLCs [11,12]. Modification methodologies are in progress.
In this study, fabrication of an EDLC using methyl grafted (MG) Sri Lankan NR based SPE and natural graphite (NG) electrodes is reported. SPE was prepared using zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$ as the salt. The performance characteristics of the fabricated EDLC have been investigated using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) test. The main novel feature of this EDLC is the combination of the electrolyte and the electrode using Sri Lankan natural NR and NG.

2. EXPERIMENTAL

2.1 Materials

MG Sri Lankan NR was received from Associated Speciality Rubber (PVT) Ltd in Kegalle, Sri Lanka and zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$ - ZnTf, 98%) was purchased from Sigma-Aldrich. Well-cleaned fluorine-doped tin oxide (FTO) glasses were used for the fabrication of EDLC.

2.2 Preparation of Solid Polymer Electrolytes

49% MGNR (MG49) was minced into smaller pieces and mixed intetrahydrofuran (THF). It was kept for 24 hours without stirring and then magnetic stirring was done for 24 hours. ZnTF solution was prepared separately in THF and stirred well. MG49-ZnTF were then mixed together and stirred further to form a homogenous electrolyte solution. The final solution was then poured into a petri dish and left to slowly evaporatethe solvent. Thereby, a thin electrolyte film could be obtained. The selected composition was 1 NR : 0.6 ZnTf (weight basis).

2.3 Preparation of Graphite Electrode

The electrode was consisting of Sri Lankan natural graphite which was obtained from Bogala Graphite Lanka Ltd., Bogala, Sri Lanka. At room temperature, acetone and graphite were mixed in the ultrasonic homogenizer (Athena-Technology) to form a graphite paste. This paste was applied on the surfaces of two FTO glass plates. Before

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use, FTO glass plates were cleaned and dried well. Surface area of the graphite electrode was 1 cm^2.

2.4 Fabrication and Characterization of EDLC

EDLCs were of the configuration, graphite/ ZnTf based SPE / graphite.EIS test for EDLC was performed with the use of Metrohm Autolab Impedance Analyzer M101 at ambient temperature. Impedance data were gathered in the frequency range from 0.01Hz -400KHz. CV tests were done with the aid of a three electrode setup where one graphite electrode was used as the working electrode and the other electrode was used as counter and reference electrode. For GCD test, continuous charging and discharging was done under a constant current of 15 μA.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Impedance Spectroscopy (EIS)

AC impedance measurements were taken to investigate the capacitive properties of the EDLC. Figure 1 illustrates the resulted Nyquist plot.

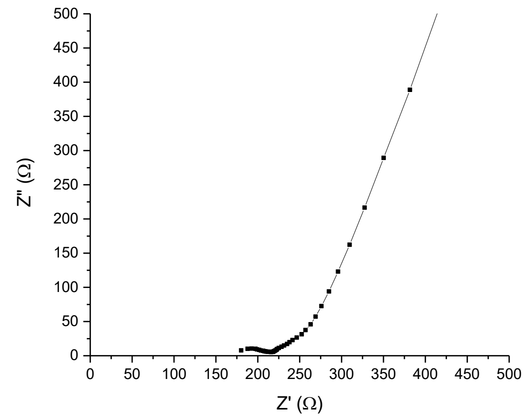

Figure 1: Resulted Nyquist plot of the EDLC with ZnTf-Natural rubber based

In the high frequency region, there are no features but in the mid frequency region, there is a semi circle. There are two spikes in the low frequency region having two inclinations.

According to the literature reviews, Nyquist plot of an EDLC has a semi-circle at high frequency ranges and it denotes the bulk electrolyte resistance [13]. In the resulted Nyquist plot, high frequency semi- circle is absent which might be due to the availability of required high frequency values. Mid frequency region represents the electrode/electrolyte resistance as well as resistive features of the electrode and it is represented by a semi circle. Mid frequency semi circle is present in the Nyquist plot showcasing resistive properties dominating in the electrodes. A vertical line exists in the low frequency region as a result of the frequency dependence of ion diffusion at the electrolyte/electrode interface leading to capacitive features. For ideal cases, this vertical line should be nearly parallel to the imaginary axis [14, 15]. From the results, the one at the most lowest region stands for the capacitive behavior while the other is due to Warburg diffusion [13]. The spike at the lowest frequency region is not perfectly vertical to Y-axis and that can be due to the surface roughness as well as non-uniform active layer thickness [16].

3.2 Cyclic Voltammetry (CV) Test

Figure 2 illustrates the cyclic voltammograms obtained for the fabricated EDLC at different scan rates.

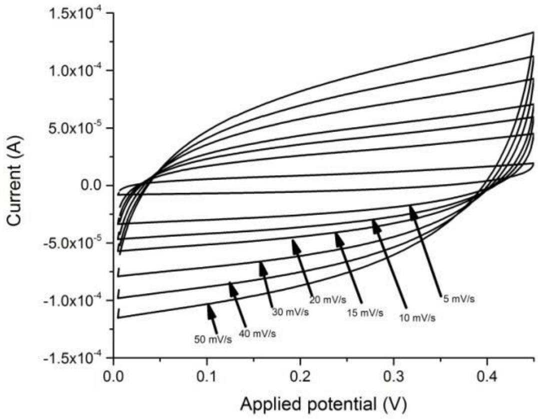

Figure 2: Resulted cyclic voltammograms for different scan rates

All cyclic voltammograms which have been obtained at different scan rates are having near mirror image symmetry for the current response about the zero current line. This indicates the capacitive behavior of the EDLC arises with the double layer formation of the interface [17]. Also, the symmetric behavior confirms the fact that the charge-discharge responses of the electric double layer are highly reversible [18]. Cyclic voltammograms of rectangular shape are one of the typical distinctive features for an EDLC. The resulting CV curves show that the characteristic with an almost rectangular shape. In none of the cyclic voltammograms, peaks are seen. These carbon-based electrodes are not involved with the redox reactions and there is a only a rapid accumulation of charges at the electrode-electrolyte interface and within the electrode. This is well evidenced with the absence of peaks in the voltammograms [19]. If redox reactions were present, peaks are appearing at potentials where such reactions occur.
Single electrode specific capacitance (C_s) can be calculated as follows,

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

Where ∫ Idv is the area under cyclic voltammograms, m is the mass of an electrode. S is the scan rate and ΔV is the width of the potential window [20].
Table 1 shows C_s values resulted at different scan rates.
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Table 1: Single electrode specific capacity variation with the scan rate

Scan Rate (mVs^{-1})	C_s ($F\ g^{-1}$)
2	2.05
5	1.72

10	1.49
15	0.99
20	0.74
30	0.64
40	0.42
50	0.35

From the table, it is seen that C_s reduces with increasing scan rate. From the eq. (1), it is clear that Cs of the EDLC is dependent on the scan rate [21]. As the scan rate increases, C_s may reduce. On the other hand, this can be explained in a theoretical point of view. With high scan rates, ions undergo sluggish transportation. And also, there is tendency for underutilization of many micro pores in the active material. At low scan rates, a higher amount of ions participate for accumulation using all pores [22]. Even C_s is higher at low scan rates, there is a possibility to occur deterioration of EDLC. And also practical issues arise with usage of longer time periods for completion of a full cycle. Therefore, the scan rate of 10mV/s was chosen as the suitable scan rate for further investigations.

The cyclic voltammograms obtained for the different potential windows and at the scan rate of 10 mV/s are illustrated in figure 3.

Peaks are not seen in all windows as before due to lack of redox reactions took place at the graphite electrodes in the EDLC. When the width of the potential window was increased, C_s values were in an increasing trend. But, attention should be paid on the exact charge storage mechanism followed by reversible charge discharge process which is evidenced by symmetric shapes of cyclic voltammograms. Nearly symmetric cyclic voltammograms were obtained while increasing potential window upto 0.3 V. In parallel to that, Cs also increased. But, after 0.3 V, symmetry disappeared and C_s increased further. Oxidation current has increased more than cathodic current. This justifies occurrence of some parasitic reactions destroying the device. Therefore,0.005-0.30 V was selected as the optimized potential window for further cycling.

Figure 4 illustrates the specific capacity variation with the cycle number for continuous 250 cycles.

Initial C_s of the EDLC was about 2.87 F g^{-1}. This is 10 times higher than the value reported by us for a Li salt based EDLC [12]. The salt that was used for that study was Lithium bistrifluromethanesulfonimide ($CF_3SO_2NLiSO_2CF_3Li$). Ion dissociation of that salt may be rather weak than ZnTF. Due to that, charge storage may be lower. C_s decreased with the cycle number initially and then increased followed by another decrease. Up to 250 cycles, variation of C_s is not uniform. Average reduction of C_s was about 6.9 %.This can be occurred due to loss of interfacial contacts between the electrode and electrolyte and also due to degradation of electrolyte and or electrodes. After a decrement, an increase may had occurred due to self healing property of the electrolyte. Further modifications are needed to make the variation more stable.

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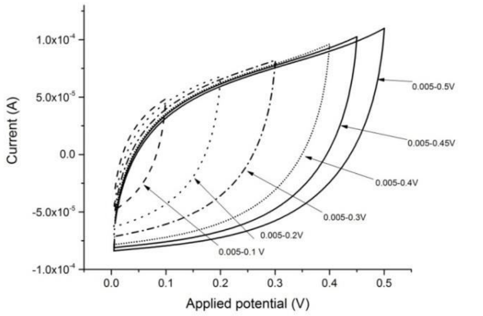

Figure 3: CV obtained in different Potential windows

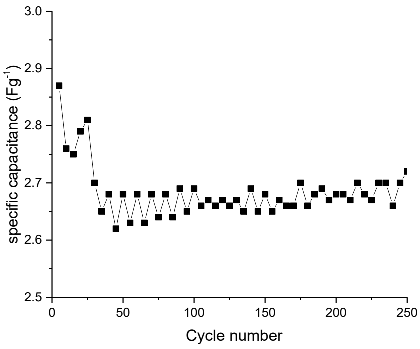

Figure 4: Variation of the single electrode specific capacitance of the EDLC as a function of cycle number at scan rate 10 mV/s

Galvanostatic Charge Discharge (GCD) Test

The single electrode specific discharge capacitance (C_d) was calculated using the following equation,

$$C_d = \frac{I(\Delta t)}{m(\Delta V)} \quad [2]$$

Where I is the constant current, m is the mass of the single electrode and $\Delta V/\Delta t$ is the rate of drop of potential excluding IR drop during discharge.
Figure 5presents the variation of C_d with 250 cycles.

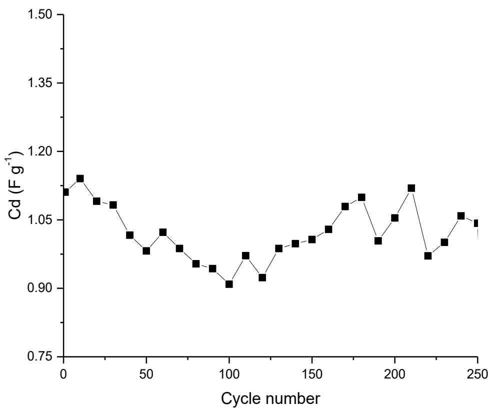

Figure 5: Single electrode discharge capacitance variation for 250 cycles

Initially, the drop of discharge capacitance was faster upto 100th cycle except the slight increase around 50th cycle. This may be due to consumption of some ions in irreversible reactions [23]. And also, soon after fabrication, the contacts are not properly formed and hence, decrease of C_d can be expected. For the first cycle, C_d was 1.11Fg^{-1}. After250 cycles, it was found to be 1.04 F g^{-1} and the average reduction was 6.3 % which is quite small. The unstable behavior might arise due to multivalence nature of Zn. With Li systems, this type of variation was not observed [12].

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4. CONCLUSION

The EDLC with configuration NG / NR - ZnTf based SPE/ NG was fabricated successfully at room temperature. Capacitive features are dominant at low frequency range. The continuous CV test was done between the optimized potentials of 0.005-0.45 V at a scan rate of 10 mV s^{-1}.The specific capacitance of the EDLC was about 2.87 F g^{-1}.The initial single electrode discharge capacity at the first cycle was found to be 1.11 F g^{-1}. After about 250 charge discharge cycles the value was 1.04 F g^{-1}. Further studies are progressing to enhance the performance of the EDLC making it suitable for practical applications.

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