Applicability of natural rubber based polymer electrolyte for electrochemical double layer capacitors

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Abstract
Natural rubber has received a great interest to be used for electrochemical applications recently. But, Sri Lankan natural rubber has not yet been considered for such activity other than exporting and using for some manufacturing processes. Main objective of the present study is investigating the candidacy of Sri Lankan natural rubber in electrochemical double layer capacitors. Methyl grafted natural rubber was dissolved in tetrahydrofuran and it was later mixed with a Li salt. Using the solvent casting method, it was possible to prepare a thin, bubble free film. It was sandwiched in between two identical Sri Lankan natural graphite electrodes. Performance evaluation was accomplished with cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge discharge test. Single electrode specific capacitance was depending on the potential window and the scan rate of cycling. Nyquist plots confirmed the capacitive behavior at low frequency region.

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average specific discharge capacity was 0.31 F g⁻¹. Obtained results show that natural rubber electrolytes are suitable candidates for electrochemical double layer capacitors and they are also encouraging to proceed towards improving the performance further.

Keywords: Natural rubber, Graphite, Electrochemical double layer capacitors, Solvent casting, Cyclic voltammetry, Electrochemical impedance spectroscopy

1. INTRODUCTION

Natural rubber (NR) is one of the three main export crops in Sri Lanka since long ago. In addition to export, a small quantity has been used for few manufacturing industries. NR is grown in large, medium and small scales in districts like Kalutara, Kegalle, Gampaha and Ratnapura. Life earning of many families has been the income from rubber tapping but due to several socio economic problems, rubber cultivation is facing a disaster at present. Many of the rubber estates have been converted to other activities and as a result, some local rubber product manufactures have been forced to import rubber to carry forward their processes without any disturbance. This has raised many drawbacks including a price hike. In global research arena, several research groups have identified the suitability of NR to be employed as electrolytes in various electrochemical devices¹,². Much attention has been centered on rechargeable cells. They have obtained NR mainly from Malaysia. But, up to date, no such considerable attention has been aimed at using Sri Lankan NR for those applications in the field of energy and power.

According to the pursue for green and cost effective devices, use of NR is an appealing solution. In general, to prepare many electrolytes, a large number of commercial polymers have been deployed. They all are expensive. Nonetheless, many are exceptionally toxic. NR on the other hand is notable for its elasticity as well as low glass transition temperature³. If Sri Lankan NR is used for advancement and innovative inventions in electrochemical applications, it may be possible to provide a value addition to this crop as well.

NR which is known as Hevea Brasiliensis is a polymer having a monomer called isoprene. In natural form, NR cannot be used for the purpose of an electrolyte as it is an insulator. Two approaches have been adopted namely methyl grafted NR (MG NR) and epoxidized NR (E NR)⁴,⁵. MG NR is the most widely used type because E NR samples are sometimes difficult to peel off from substrates.
In this present study, MG NR was complexed with a Li salt to prepare the electrolyte. Electrochemical double layer capacitors were fabricated with two identical Sri Lankan natural graphite electrodes. As per our literature survey, no report is available on fabricating an electrical double layer capacitor (EDLC) based on NR electrolyte and natural graphite electrodes. If this approach can be developed, fabricating low cost, safe EDLCs as well as giving a value to two Sri Lankan raw materials will be successful.

2. METHODS AND MATERIALS

2.1 Preparation of the electrolyte

MG NR received from Associated Specialty Rubber (Pvt) Ltd, Sri Lanka was minced into small pieces and mixed with tetrahydrofuran (THF, Aldrich). Lithium bistrifluoromethanesulfonimide (CF$_3$SO$_2$NLiSO$_2$CF$_3$ – LITFSI, Aldrich) was served as the salt. It was mixed with THF separately. After perfect dissolution, both were mixed together on a magnetic stirrer. Upon continuous stirring for 24 hours, the resulting mixture was poured on a glass petry dish and allowed for solvent evaporation. Thereby, it was possible to obtain a free standing, thin film. The composition of the electrolyte was 1 NR : 0.4 LITFSI (by weight).

2.2 Fabrication of electrochemical double layer capacitors (EDLCs)

Natural graphite samples obtained from Bogala Graphite Lanka Ltd was used as received without any purification. Electrodes were prepared as reported by us earlier. The electrolyte sample was sandwiched in between the two graphite electrodes. The cross sectional area of the EDLC was 1 cm$^2$.

2.3 Characterization of EDLCs

First, cyclic voltammetry studies were carried out using a three electrode setup with Metrohm M101 potentiostat. One electrode was taken as the working electrode 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 250 cycles. Single electrode specific capacitance ($C_s$) was calculated at each characterization techniques using the following equation.
\[ C_s = 2\int I dv / S.m. \Delta V \]  \hfill [1]

Here, \( \int I dv \) is the area of cyclic voltammogramme (CV), S is the scan rate, m is the single electrode mass and \( \Delta V \) is the width of the potential window.

Impedance data were gathered in the frequency range, 0.01 Hz to 1 MHz at room temperature with the aid of an impedance analyser (Metrohm M101). Nyquist plots were drawn using real and imaginary values of impedance.

Galvanostatic Charge Discharge (GCD) test was carried out under a constant current of 6 \( \mu \)A for 800 cycles using a Metrohm M101 potetniostat / galvanostat. Specific discharge capacitance (\( C_d \)) was calculated using the equation given below:\(^7\).

\[ C_d = I dt / m dV \]  \hfill [2]

Here I is the constant current, \( dV/dt \) is the rate of discharge excluding the IR drop that occurs at the beginning of discharge and m is the single electrode mass.

3. **RESULTS AND DISCUSSION**

Figure 1 shows the CVs obtained by varying the potential window of cycling. Selecting the potential window from 0.1 V to 0.5 V, window was widened up to 1.1 V.

**Figure 1:** Cyclic voltammograms obtained within different potential windows while cycling the EDLC at 10 mVs\(^{-1}\)
CV of an ideal EDLC takes the shape of a parallelogram. It was noticed that many of the CVs after 0.5 V showed that shape. A possible reason might be the absence of activation of actual storage mechanism up to that potential window. For storage, charges should get accumulated on either side of the electrode / electrolyte interface. If the required potential for charge mobility is not available, they do not move and hence, there will not be charge accumulation. When the window was widened, $C_s$ increased. But, after exceeding the potential window of 0.8 V, a sharp increase in current could be seen destroying the usual shape of the CV significantly. This might be due to occurrence of some irreversible reaction inside the EDLC. Also, it can be attributed to a substantial value of equivalent series resistance. Hence, the window from 0.1 V to 0.8 V was selected for further investigations.

Figure 2 illustrates the CVs for different scan rates. When the scan rate was increased, a reduction of $C_s$ was observed. In general, charge storage takes place according to the ion rearrangements at the electrode electrolyte interface.

![Cyclic voltammogrammes obtained by cycling the EDLC at different scan rates](image)

**Figure 2:** Cyclic voltammogrammes obtained by cycling the EDLC at different scan rates

At higher scan rates, rate of potential change is high. That cannot be followed by the rate of ion rearrangement. As a result, $C_s$ goes down. When the scan rate is low, ion rearrangements have plenty of time and hence, $C_s$ increases. As before, the usual shape of
the parallelogram exists at all scan rates. And also, in both instances (varying potential window and scan rate), there are no peaks in CVs. It is a well known fact that peaks in CVs resemble involving redox reactions. The absence of such peaks clearly prove that in the EDLCs studied under the investigation are based on capacitance arises with double layer effect.

Figure 3 illustrates the drop of $C_s$ with the cycle number resulted from the continuous cyclic voltammetry test within the potential window of 0.1 V – 0.8 V and at the scan rate of 10 mVs$^{-1}$. As there is a chance for different unwanted reactions to taking place at low scan rates and also due to some practical constraints, the scan rate of 10 mVs$^{-1}$ was chosen for the investigation even-though scan rates lower than 10 mVs$^{-1}$ exhibited higher $C_s$ values. $C_s$ decreased with continuous cycling as observed by several researchers$^{9,10}$. Rate of decrease is about 20%. At one instance, a slight increase of $C_s$ had taken place but, within a short period of time, it had returned to the normal state. The increase may be due to some problem in the interfaces or due to some internal reaction. Settling back to the normal state implies the presence of self-healing ability of the electrolyte which exists with some polymer electrolytes.

**Figure 3:** Variation of single electrode specific capacity with the continuous cycling done in the potential window from 0.1 V to 0.8 V and at the scan rate of 10 mVs$^{-1}$
Figure 4 shows the impedance plot drawn using the impedance data. Electrochemical impedance spectroscopy technique that is related with impedance data is one of the key characterization techniques use to study electrochemical devices. In general, capacitive properties become dominant at very low frequencies. Capacitive behavior is present in an Nyquist plot as a spike at low frequency region\textsuperscript{11}. Moreover, it is parallel to the imaginary ($Z''$) axis means device has more capacitive features. In addition, diffusion reactions are also noticeable in Nyquist plots at mid lower frequencies again as a tilted spike. In the present system, both spikes could be seen in addition to the part of a semi circular arc at higher frequency region. The latter features resistive behavior of the system\textsuperscript{12}. 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. The spike having a smaller slope stands for the diffusion controlled reactions. The resulting Nyquist plot is a very suitable pictorial representation for illustrating the frequency dependent characteristics.

![Resulting Nyquist plot obtained for the EDLC within the frequency range 0.01 Hz to 1 MHz at room temperature](image)

**Figure 4:** Resulting Nyquist plot obtained for the EDLC within the frequency range 0.01 Hz to 1 MHz at room temperature
Initial constant charge discharge cycles taken under constant current are shown in Figure 5. The average specific discharge capacitance ($C_d$) was 0.31 Fg$^{-1}$. The potential drop that takes place normally due to some reversible reactions during the transition from charging to discharging is rather low exhibiting the satisfactory performance of the EDLC$^{13}$. If there were adverse additional reactions took place, the pattern of charge discharge curves would vary.

![Figure 5: Initial galvanostatic charge discharge cycles obtained for the EDLC between the potential window between 0.1 V and 0.8 V under a constant current of 6 µA](image)

Figure 6 presents the variation of $C_d$ with prolonged cycle numbers. A fast drop of $C_d$ can be observed initially but, after about 200 cycles, the rate of decay has decreased noticeably. Initial decay can be due to filling of pores of the electrodes which disturbs charge storage mechanism. The rate of reduction after 200 cycles is about 0.03 % which is acceptable for this type of initial investigation. However, the decrease of $C_d$ after 200$^{th}$ cycle can be attributed to depletion of the electrolyte, immobilization of charges after prolonged charge discharge processes as well as loss of interfacial contacts.
4. CONCLUSION

Natural rubber based polymer electrolyte prepared with a Li salt is showing its ability to serve in an EDLC. The composition of the electrolyte was 1 NR : 0.4 LITFSI (by weight). Single electrode specific capacitance is a dependent on the width of the potential window as well as the scan rate. Impedance measurements prove the capacitive behavior of the device at low frequencies. An initial specific capacitance of about 0.28 Fg$^{-1}$ dropped by 20% during 250 cycles. GCD test done under a constant current of 6 μA showed a fast decay of $C_d$ initially. However, after about 200 cycles, the rate of decay was slow. The results obtained from the present study are encouraging to focus on improving the EDLC. Further investigations are being carried out to further fine tune the compositions of the electrolyte as well as the electrodes.

REFERENCES


