

RESEARCH ARTICLE

A gel polymer electrolyte based on PVdF and ZnCl₂ for an electrochemical double layer capacitor

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Abstract: This paper is based on fabrication and characterization of a gel polymer electrolyte and evaluation its potential candidacy for electrochemical double layer capacitors. Gel polymer electrolyte samples consist of polyvinylidene fluoride (PVdF), zinc chloride (ZnCl₂), ethylene carbonate (EC) and propylene carbonate (PC) Salt and polymer concentrations were varied to obtain the best conductivity. The maximum room temperature conductivity of $8.6 \times 10^{-4} \text{ Scm}^{-1}$ was obtained with the composition, 6.875PVdF:1 ZnCl₂ : 12.5 EC : 12.5 PC (by weight). DC polarization test results proved that gel polymer electrolyte is predominantly an ionic conductor. The electrochemical double layer capacitor was assembled having two identical graphite electrodes with the gel polymer electrolyte. Cyclic voltammetry measurements were taken in different potential windows and at various scan rates using three electrode setups. The results proved the dependency of the potential window as well as the scan rate on the performance of the capacitor. Continuous charge discharge cycling for 50 cycles showed that the device is rather stable in spite of the decrement of specific capacity that occurred at the beginning. The initial specific capacity was about 8.68 Fg⁻¹. The present study showcases the value of Sri Lankan natural graphite in energy applications.

Keywords: gel polymer electrolytes; electrochemical double layer capacitors; graphite; specific capacity.

INTRODUCTION

Power is being deeply integrated into every aspect of present day life styles. So, the demand on power has exceptionally increased and it ignited various investigations towards fabricating clean, efficient and low cost energy storage devices throughout the globe. As a result, there has been a resurgence of the research activities in the area of batteries and super capacitors which are renowned as suitable energy storage devices (Kim *et al.*, 2015, Jayathilake *et al.*, 2014). With the rapid increase of global concerns towards clean and efficient energy storage sources, developing suitable materials for those devices has been greatly motivated. Super capacitors have become a major research focus with the emergence of hybrid/electric vehicles during the last couple of decades. These have higher power densities than batteries and higher energy densities than conventional capacitors (Xiong *et al.*, 2014). There are mainly two types of super capacitors depending on the

type of the electrode material and the respective charge storage mechanism namely electrochemical double layer capacitors (EDLCs) and redox capacitors. The former uses carbon based electrodes and the latter depends on transition metal oxides or conducting polymer electrodes (Perera *et al.*, 2017). Both have their own merits and demerits. As carbon based materials, different types of carbonaceous materials including graphite, activated carbon, carbon fiber cloth and carbon aerogels have been utilized. Several groups have initiated investigations on graphite to be used as electrodes during last couple of years. However, many of them have used commercially available graphite (Li *et al.*, 2008). In addition, many of the EDLCs designed in several years back had used liquid electrolytes. Due to the inherent drawbacks of those electrolytes with liquid nature, it is seen an eventual deployment of electrolytes in solid form. However, the solid electrolytes have poor conductivities and also possess some barriers on design flexibility. Among such electrolytes, gel polymer electrolytes (GPEs) have been able to surmount many of the drawbacks of solid electrolytes. Basically, GPEs are consisted of a polymer matrix within which a liquid electrolyte is trapped in. They exhibit acceptable conductivities while maintaining good mechanical stabilities. Therefore, they have been employed for a diverse range of electrochemical applications (Perera *et al.*, 2017, Tiong *et al.*, 2016).

The present study is based on preparation and characterization of a GPE with a rarely used salt and investigation its suitability for use in an EDLC based on Sri Lankan natural graphite. EDLC was characterized using Cyclic Voltammetry which assesses information on electrochemical phenomena both qualitatively and quantitatively.

MATERIALS AND METHODS

Preparation of gel polymer electrolytes

GPE consisting with polyvinylidene fluoride (PVdF), zinc chloride (ZnCl₂), ethylene carbonate (EC) and propylene carbonate (PC) was prepared using the hot pressing method. The starting materials were used as received from Aldrich. Required amounts were magnetically stirred well and the resultant homogeneous mixture was heated at 115 °C for

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30 minutes. The hot viscous mixture was then pressed in between two well cleaned glass plates and left in a vacuum desiccator for some time. A thin, bubble free film could be obtained after separating the glass plates. Several samples were prepared varying the salt concentration as well as the polymer concentration.

AC conductivity measurements of the GPE samples

A circular shape sample was cut from the GPE film. It was sandwiched in between two stainless steel electrodes and housed in-side a sample holder which is sealed by means of an O-ring. Complex impedance measurements were gathered using a Metrohm M101 frequency response analyser within the frequency range, 0.01 Hz to 0.4 MHz. For each sample having different salt and polymer concentrations, complex impedance measurements were taken at the room temperature. Thicknesses of the samples were measured using a micrometer screw gauge.

DC polarization test

A circular shape sample was loaded inside a sample holder as explained before. By applying a DC potential of 1 V, the current variation with time through the sample was monitored.

Preparation of the electrodes

Natural graphite obtained from one of the mines in Sri Lanka was used as received. It was mixed with PVdF and activated carbon (AcC) at the weight ratio 80:10:10 using acetone (Aldrich) as the solvent. AcC received from Aldrich was used without any pre-treatment. The resulting slurry was applied on fluorine based tin oxide (FTO) glass plates of square shape. The effective area of the electrode was 1 cm².

Assembling the EDLC and analyzing with Cyclic Voltammetry technique

Two identical graphite electrodes were combined with a similar size GPE in between them. Cyclic Voltammetry

test was performed using one electrode as the working electrode and the other one as reference and counter electrodes. Initially, measurements were taken varying the potential window. After tracing the suitable potential window, cycling was done varying the scan rate within that potential window. Finally, continuous cycling was done to evaluate the stability of the EDLC considering the selected potential window and the scan rate.

RESULTS AND DISCUSSION

Complex impedance data were analyzed using the Electrochemical Impedance Spectroscopy technique. Using the Nyquist plots drawn between the imaginary and the real values of impedance, bulk electrolyte resistance (R_b) was determined. Conductivity (σ) was calculated using the equation,

$$\sigma = (1/R_b)(t/A) \quad (1)$$

where t is the thickness and A is the area of cross section of the electrolyte sample.

Figure 1 illustrates the variation of conductivity with the salt concentration.

It is a well-known fact that ionic conductivity is mainly governed by two factors as per the expression,

$$\sigma = ne\mu \quad (2)$$

where n is the charge concentration, e is the charge and μ is the mobility of charge carriers. These two factors, n and μ are found to play a major role in administering the conductivity of a system. Upon increasing the salt concentration, room temperature conductivity is increased initially. But, further increase has resulted low conductivities. At the first instance, conductivity increase may be due to the increase of charge carrier concentration associated with the salt concentration. Subsequent decrease of conductivity can result with the lowering of charge carrier mobility. When there is large number of charge carriers, their mobility is disturbed owing to the increase of viscosity of the medium (Harankahawa *et al.*, 2017). On

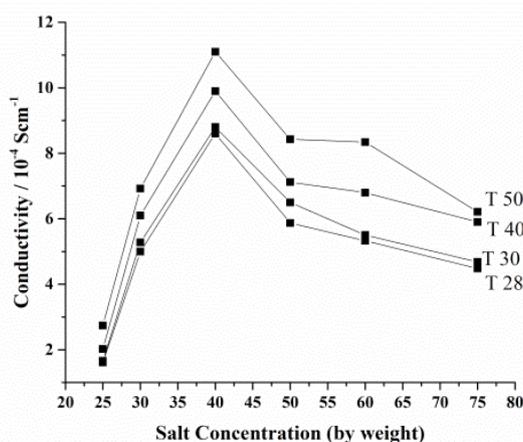


Figure 1: Conductivity variation with the salt concentration of the GPE, PVdF : ZnCl₂ : EC : PC at different temperatures.

the other hand, with high salt concentrations, build up of charge carriers can be offset when the retarding effect of ion clusters becomes dominant. Hence, the conductivity of GPE can go down. Another feature that can be observed is that conductivity variation is not steady. This is reported as due to transport mechanism associated with polymer segmental motion and free volume behavior (Jeong *et al.*, 2016).

Figure 2 shows the variation of conductivity with the polymer concentration.

When the polymer concentration is increased, the conductivity increases initially followed by a decrease upon further increase of polymer. This hints that there should be a noticeable effect on conductivity by the polymer. There should be some factors giving rise to an inter play between two concentration regions. The paths for ion movement within the polymer may increase with increase of polymer concentration and as a result, ionic motion may be improved leading to high conductivity. After the polymer concentration of 275 which shows the highest room temperature conductivity, the tortuosity of the GPE may increase disturbing the ionic motion. This will

lower the ionic conductivity greatly.

The optimized composition is 6.875 PVdF : 1 ZnCl₂ : 12.5 EC : 12.5 PC (by weight) which gives the highest room temperature conductivity of $8.6 \times 10^{-4} \text{ Scm}^{-1}$.

Figure 3 depicts the DC polarization graph showing the variation of current with time when the GPE was assembled in between two stainless steel electrodes. These electrodes are acting as blocking electrodes for ions. At the beginning of application of a DC potential, ions tend to polarize and a large current can be seen initially. With time, ionic motion is blocked and as a result, current decreases rapidly. Ultimately, only electron movement exists in the assembly. The constant current is mainly due to those electrons. The ionic transference number (t_{ion}) was calculated using the equation,

$$t_{\text{ion}} = (I_{\text{total}} - I_s) / I_{\text{total}} \quad (3)$$

Here, I_{total} is the initial total current and I_s is the saturated current. In this case, the estimated value of t_{ion} is 0.99. This well confirms the predominant ionic nature of the sample (Bandaranayake *et al.*, 2016).

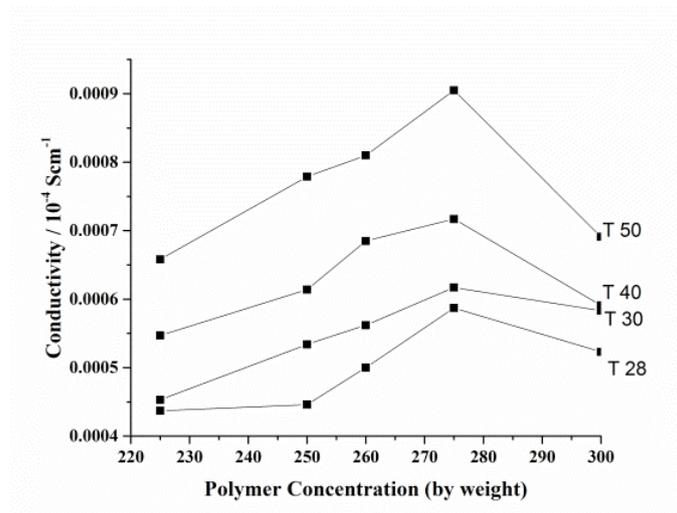


Figure 2: Conductivity variation with the polymer concentration of the GPE, PVdF : ZnCl₂ : EC : PC at different temperatures.

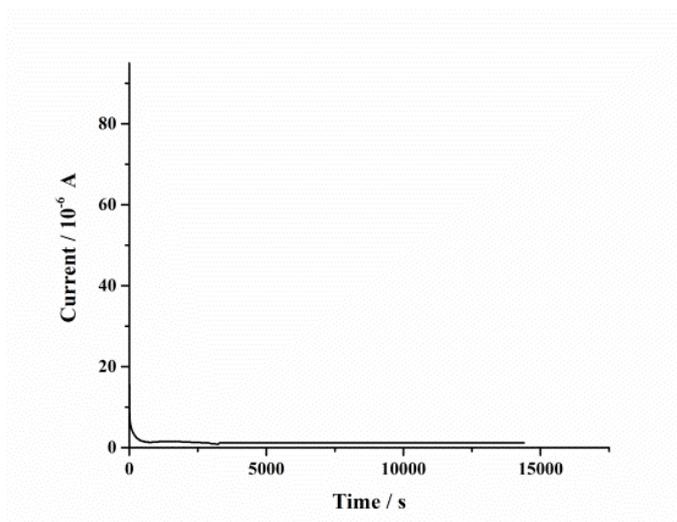


Figure 3: DC polarization graph of the GPE with stainless steel electrodes at room temperature.

Figure 4 shows the cyclic voltammograms obtained by varying the potential window.

All graphs in Figure 4 show rectangular shape which is expected for EDLCs [6]. The absence of peaks in the cyclic voltammograms suggests that no pseudo capacitive contribution exists in the present device and hence charge storage procedure can be considered as purely electrostatic [Tey *et al.*, 2016]. Single electrode specific capacity (C_{sp}) was calculated using the relationship,

$$C_{sp} = 2 \int IdV / m \Delta V S \quad (4)$$

where $\int IdV$ is the area of a cyclic voltammogram, m is the mass of a single electrode, ΔV is the potential window and S is the scan rate. With widening the potential window, C_{sp} value increases. This may be due to the involvement of higher amount of charges for the charge-discharge process. The widening of potential window has been possible because of the non aqueous electrolyte. With aqueous electrolytes, this cannot be happened due to the

presence of water. In each cyclic voltammogram, anodic and cathodic currents increases proportionally suggesting good reversibility of the charge storage process (Wang *et al.*, 2012). However, it can be observed that when the potential window is widened, the current is increased abruptly. It may be due to some distortion in the system. Hence, the potential window -1.7 V to 1.7 V was chosen as the optimum window.

Figure 5 is the resulting cyclic voltammograms obtained by varying the scan rate.

It was found out that upon increasing scan rate, specific capacity decreases as reported by many groups (Nathalia *et al.*, 2013). A possible reason may be the mismatch between the scan rate and the rate of reactions that lead to charge storage. Except at the scan rate of 50 mV/s, cyclic voltammograms obtained at lower scan rates show near equal rectangular shapes which is the characteristic shape of EDLCs. Disappearance of the rectangular shape at high

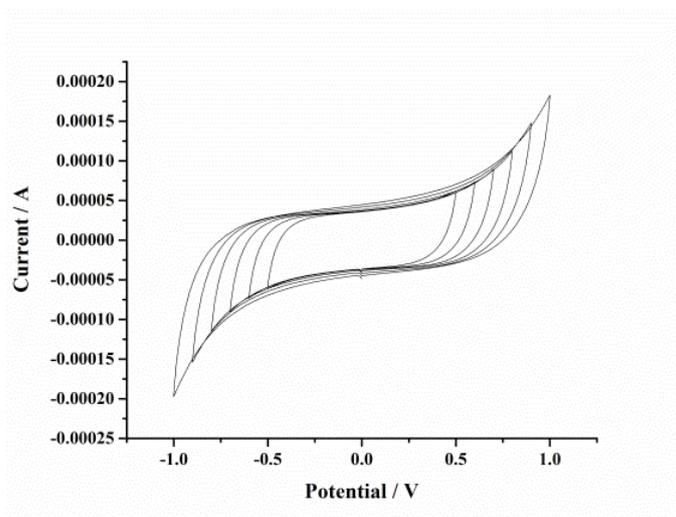


Figure 4: Cyclic Voltammograms obtained for the EDLC for different potential windows.

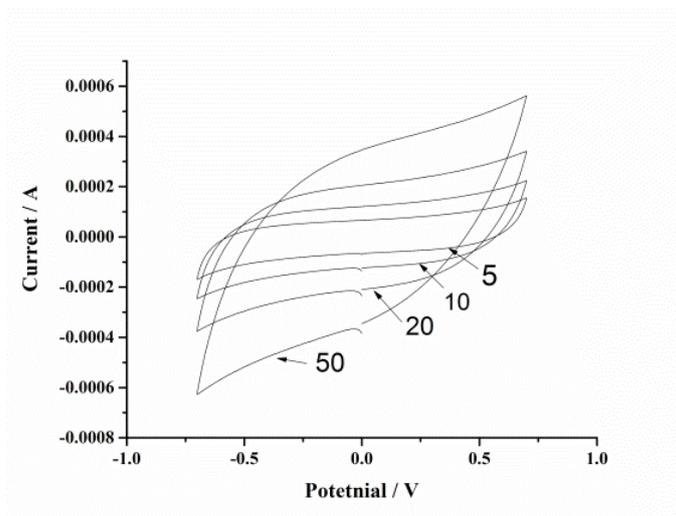


Figure 5: Cyclic Voltammograms obtained for the EDLC at different scan rates in mV/s.

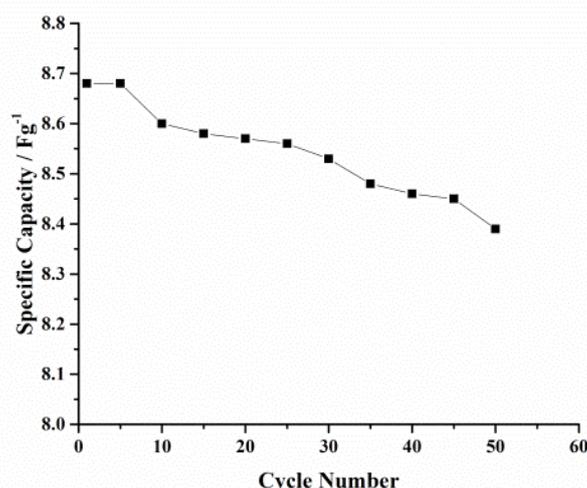


Figure 6: Variation of specific capacity with cycle number.

scan rates is mainly attributed to the larger time constant. Then, more time is needed to charge the capacitor and as a result, the rectangular shape of the current profiles is collapsed. In addition, all voltammograms exhibit mirror image current response on voltage reversal. This evidences the good reversibility.

In general, stability of a device is a crucial factor to be competitive in the market. For that, performance evaluation upon continuous operation should be monitored. In the cyclic voltammograms, even upto 50th cycle, the near rectangular shape prevails without much deviation from the first cycle. This is a solid verification for the existence of the stability of the EDLC as well as the continuation of the charge discharge process without any interference.

The specific capacity variation with cycle number is illustrated in Figure 6. The initial specific capacity is about 8.68 Fg⁻¹. At 50th cycle, it had reached to a value 8.33 Fg⁻¹. The drop of the specific capacity was about 4% which is quite small.

CONCLUSION

Gel polymer electrolytes were prepared using PVdF, ZnCl₂, EC, PC by following the hot pressing method. The highest room temperature conductivity obtained from the composition, 6.875 PVdF : 1 ZnCl₂ : 12.5 EC : 12.5 PC (by weight) was $8.6 \times 10^{-4} \text{Scm}^{-1}$. DC polarization test done with stainless steel electrodes confirmed that the above sample is purely an ionic conductor having an ionic transference number 0.99. Electrodes were prepared using natural graphite, PVdF and Activated carbon (AcC). Electrochemical double layer capacitor in the configuration, Graphite :PVdF : AcC / GPE / Graphite :PVdF : AcC was tested under cyclic voltammetry technique. With increasing the potential window, even the specific capacity increased, there was a limitation due to the electrochemical stability. When the scan rate was increasing, it was possible to notice a drop in the specific capacity. The variation of specific capacity from the first cycle to the 50th cycle upon continuous cycling is quite small. Further studies are being

carried out to improve the performance.

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