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# Preparation and characterization of a Polyacrylonitrile based gel polymer electrolyte for redox capacitors

C.M. Bandaranayake, W.A.D.S.S. Weerasinghe, K.P. Vidanapathirana and K.S. Perera[1]

*Department of Electronics, Wayamba University of Sri Lanka, Kuliyapitiya, Sri Lanka*

Correspondence: [1]kumudu31966@gmail.com

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**Abstract.** In this study, a gel polymer electrolyte (GPE) consisting with polyacrylonitrile (PAN), ethylene carbonate (EC), propylene carbonate (PC) and magnesium trifluromethane sulfonate ($Mg(CF_3SO_3)_2$) was prepared using the hot pressed method. The starting materials were heated at 130 °C for 2 hours and the resulting hot viscous mixture was pressed in between two well cleaned glass plates. The composition was fine-tuned by varying the salt and the polymer concentration in order to obtain a mechanically stable, thin and flexible film with a high ionic conductivity. It was found that the composition, 105 PAN : 150 MgTF : 400 EC : 400 PC gives the maximum conductivity of $1.06 \times 10^{-2}$ $Scm^{-1}$. DC polarization test done with blocking electrodes confirmed the ionic nature of the sample while the results obtained with non-blocking electrodes proved that the anionic contribution for the conductivity is dominant. The sample was used in redox capacitors having two identical polypyrrole electrodes doped with dodecylbenzesulfonate. Cyclic Voltammetry, Galvanostatic Charge Discharge and Electrochemical Impedance Spectroscopy techniques were used to evaluate the performance of the redox capacitors. The specific capacitance was high at low scan rates. The electrolyte was quite stable when use in the redox capacitors. Further, redox capacitor was having a good cycleability which is one of the important key issues to be considered for practical applications.

**Keywords.** Gel polymer electrolyte, Redox capacitor, Polyacrylonitrile, Polypyrrole, EIS.

## 1 Introduction

Basically, a gel polymer electrolyte (GPE) consists of a polymer network, a salt and solvent/s. So, they exhibit higher ambient temperature ionic conductivities comparable to liquid electrolytes and good mechanical properties similar to solid electrolytes. In addition, they possess some several unique properties like ease of preparation, wide range of composition with control properties, good adhesive properties and satisfactory thermal and electrical stability. The role of the polymer network is very important as it envelopes the liquid part containing the salt and the solvent/s and thereby prevents their escape. Due to that, GPEs do not undergo leakage problems suffer by liquid electrolytes. Hence, GPEs have been recognized as better alternatives for liquid electrolytes in a wide range of applications such as batteries, electrochromic devices, dye sensitized solar cells, artificial muscles and super capacitors (Liu *et al*. 2014; Perera *et al*. 2007; Wu *et al*. 2013).

Today, energy storage devices have received a global attention due to predicted power crisis that may come up in the next few decades. Super capacitors are thought as one class of potential energy storage devices to be employed in hybrid automobiles, digital telecommunication etc. There are two types of super capacitors namely electrochemical double layer capacitors (EDLCs) and redox capacitors (Wang *et al*. 2015). EDLCs use carbon based materials as electrodes. In redox capacitors, electro active materials such as conducting polymers and metal oxides are used as electrodes and they exhibit capacitive behaviour due to redox (faradaic) reactions when assembled with a suitable electrolyte. At the moment, many of the reports about redox capacitors are based on liquid electrolytes (Ingram *et al*. 2004; Hashmi 2004). But, they have undergone different disadvantages such as leakage, corrosion and bulky design. Hence, use of gel polymer electrolytes in place of liquid electrolytes has emerged as a novel concept in the field of energy storage devices.

In this study, a GPE consisted with polyacrylonitrile (PAN), ethylene carbonate (EC), propylene carbonate (PC) and magnesium trifluromethane sulfonate ($Mg(CF_3SO_3)_2$) was prepared by fine tuning the composition to optimize the ionic conductivity. The properties of the sample having the highest room temperature conductivity and good mechanical stability were investigated and then, its potential candidacy in conducting polymer based redox capacitors was evaluated.

## 2 Materials and Methods

### 2.1 Preparation of gel polymer electrolytes

Starting materials polyacrylonitrile (PAN) (ALDRICH,MW 150000), ethylene carbonate (EC)(ALDRICH, 98%), propylene carbonate (PC)(ALDRICH, 99%) and magnesium trifluromethane sulfonate ($Mg(CF_3SO_3)_2$, MgTF)(ALDRICH, 99%) were used as received. To prepare the samples, hot-pressed method was used. First, the required amount of PAN was dissolved in a mixture of EC/PC. The weight ratio of EC and PC was kept at 1:1. After performing magnetic stirring for about 2 hours, appropriate amount of MgTF was mixed in. Heating was done at 130 °C for about 2 hours. The resulting hot viscous mixture was pressed in between two well cleaned glass plates and vacuum dried at room temperature overnight. This procedure was repeated by varying salt concentration as well as polymer concentration. Preparation steps were carried out in side an Argon filled glove box.

### 2.2 AC conductivity measurements

Electrochemical Impedance Spectroscopy (EIS) is a powerful analytical technique to gather information about the resistive and capacitive properties of materials. In this method, properties of materials are analysed using the impedance data gathered by varying the frequency.

A circular shape electrolyte sample having a diameter of 14 mm was sandwiched in between two stainless steel (SS) electrodes inside a spring loaded brass sample holder which is sealed by means of an O ring. AC impedance data collection was accomplished in the frequency range 0.01 Hz to 0.4 MHz at room temperature using Metrohm M101 impedance analyser. This was repeated for each GPE sample having different salt and polymer concentrations. The room temperature conductivity, $\sigma$ was calculated using the equation, $\sigma = (1/R_b)(t/A)$ where $R_b$ is the bulk resistance, t is the thickness and A is the area of cross section of the GPE. $R_b$ was determined by analysing the impedance data. t and diameter of the sample were measured using a micrometer screw gauge. For the composition having the maximum conductivity at room temperature, impedance measurements were taken from room temperature up to 55 °C in the frequency range 0.01 Hz to 0.4 MHz. Conductivity at each temperature was calculated using the above equation The same composition was used for further investigations.

### 2.3 Transference number measurements

First, a circular shape electrolyte sample was loaded inside a brass sample holder in between two SS electrodes. A DC bias voltage of 1 V was applied and the current variation with time was monitored. Ionic transference number, $t_i$ was calculated using the equation, $t_i = (I_i - I_s) / I_i$ where $I_i$ is the initial current and $I_s$ is the steady state current. Same procedure was repeated using two magnesium electrodes. The cationic transference number was evaluated using the equation, $t_+ = I_s / I_i$. Here, $I_i$ is the initial current and $I_s$ is the steady state current.

### 2.4 Preparation of conducting polymer electrodes

Pyrrole (ALDRICH) which has been stored in the dark in a refrigerator was electrochemically polymerized in the presence of sodium dodecylbenzenesulfonate (NaDBS)( ALDRICH, 98%) on fluorine tin oxide (FTO) glass plates by electrochemical polymerization using a computer controlled potentiostat (Metrohm Autolab 101). The concentration of the monomer, NaDBS was 0.1 M. The three electrode electrochemical cell used for electrochemical polymerization was consisted of a working electrode (FTO), a Ag/Agcl reference electrode and a Pt counter electrode. Polypyrrole (PPy) films of the thickness of $1 \times 10^{-6}$ m were prepared by applying a current density of 1 mA $cm^{-2}$.

### 2.5 Fabrication and characterization of redox capacitors

Symmetrical redox capacitors of the configuration, PPy:DBS / GPE / PPy:DBS was assembled inside a glove box purged with Ar. Cross sectional area of the assembly was 1 $cm^2$. Cyclic Voltammetry technique was used to study the withstanding of the redox capacitor for continuous cycling at a constant scan rate of 5 $mVs^{-1}$. In the three electrode setup, one PPy : DBS electrode was taken as working electrode whilst the other electrode was the (reference + counter) electrodes. The redox capacitor was cycled in the potential window -2.4 V to 2.4 V. The specific capacitance was calculated using the equation, $C_s = 2(\int IdV) / m(\Delta V)S$ (Bandaranayake *et al.* 2015). Here $\int IdV$ is the area of integral under the cyclic volatmmogram, m is the single electrode mass, $\Delta V$ is the potential window and S is the scan rate. Redox capacitor was subjected to galvanostatic charging and discharging in the potential window 0.0 V – 1.5 V. The constant current was set to $2 \times 10^{-4}$ A. The discharge capacitance was calculated using the equation, $C_d = (2I) / m(dV/dt)$ [Wang *et al.* 2013]. Here, I is the constant current, m is the single electrode mass, dV is the discharge potential and dt is the discharge time. Impedance data were collected in the frequency range from 0.01 Hz to 0.4 MHz at the room temperature for the redox capacitor to investigate the resistive and capacitive properties as well as the specific capacitance. For the low frequency region, there exists a relationship between specific capacitance, $C_s$, Z" at low frequency region and f as $Z" = 1/ (2\pi f C_s)$ [Pandey *et al.* 2013] which was used to calculate $C_s$.

## 3 Results and Discussion

Figure 1 shows the variation of room temperature conductivity with the salt concentration for the GPE. The conductivity first increases until it reaches the maximum when the concentration is 150 mg and then decreases with the increase of salt concentration further.

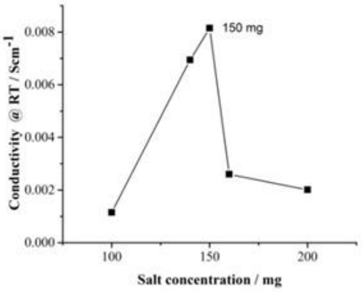

**Fig. 1. Variation of room temperature conductivity with salt concentration**

The initial increment can be attributed essentially to an increase of free ions which are contributed for conductivity (Jayathilake *et al*. 2015)**.** When the salt concentration increases further (after the maximum), there is a tendency towards formation of ion aggregates. This reduces the availability of free mobile ions which subsequently reduces conductivity (Ravindran *et al*. 2012).

Room temperature conductivity was measured by varying the polymer concentration and it is given in Fig.2

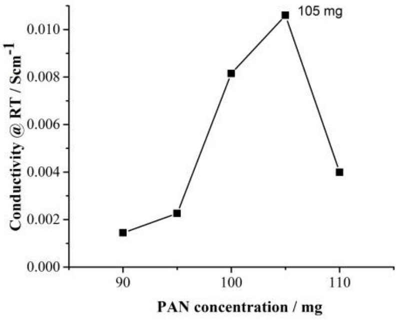

**Fig. 2. Variation of room temperature conductivity with polymer concentration.**

In Figure 2, it is seen an increment of conductivity initially with increasing PAN concentration followed by a decrement of conductivity with further increment of PAN concentration. This is an indication of a simultaneous occurrence of two competing processes. They are free ion concentration at low PAN concentration and low mobility of ions at high PAN concentration (Sharma *et al*. 2006; Perera *et al*. 2011). It was found out that the composition that exhibits the maximum conductivity at room temperature was 105 PAN : 150 MgTF : 400 EC : 400 PC (by weight basis). The value of the conductivity at the maximum is 1.06 x $10^{-2}$ Scm$^{-1}$.

Fig. 3 shows one of the resulting Nyquist plots of the optimized composition at the room temperature. For a cell assembly with the configuration, SS / GPE / SS, the Nyquist plot should contain two semicircles at high and intermediate frequencies while a spike appears at low frequency region. The semicircle at high frequency region corresponds to the bulk electrolyte and the other semi-circle represents the charge transfer process at the electrode/electrolyte interface (ayathilake *et al*. 2014). The spike appears due to the capacitive behaviour of electrodes. In the resulting plot (Fig.3), the high frequency semicircle is absent. This may be due to the unavailability of the required high frequency range in the study (>0.4 MHz) (Ramesh *et al*. 2012). The first intercept on the real axis was used to calculate the conductivity, σ.

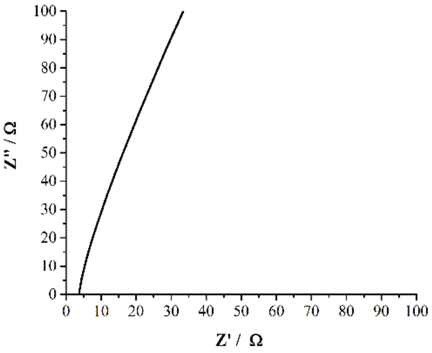

**Fig. 3. The resulting Nyquist plot obtained at the room temperature for the GPE of the composition**. 105 PAN : 150 MgTF : 400 EC : 400 PC

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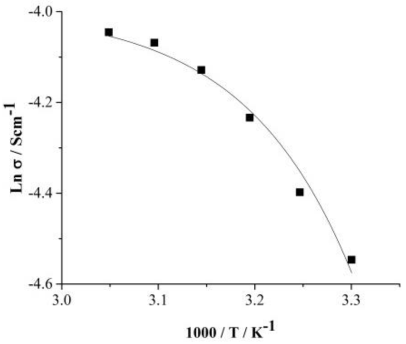

**Fig. 4. Variation of conductivity with reciprocal temperature for the GPE of the composition,** 105 PAN : 150 MgTF : 400 EC : 400 PC

Figure 4 shows the ln σ variation with reciprocal temperature. The data could be fitted with Vogel-Tamman-Fulcher (VTF) equation, $\sigma = AT^{-1/2}$ exp($-E_a$ / ($T-T_0$) where A is a pre-exponential factor, T is the absolute temperature and To is related to the glass transition temperature. This clues that conductivity behaviour of the system with the temperature takes places via the free volume formed inside the polymer network (Jayathilake *et al*. 2014).

Figure 5 exhibits the current variation with time recorded with SS electrodes that are acting as blocking electrodes for mobile ions.

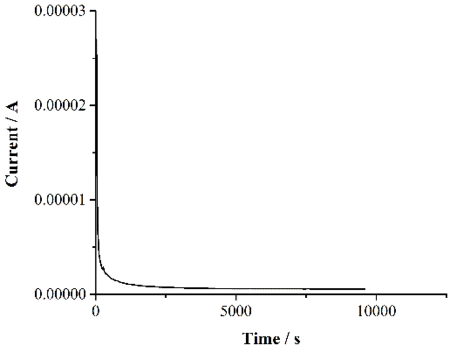

**Fig. 5. Variation of current with time for the configuration SS / 105 PAN : 150 MgTF : 400 EC : 400 PC / SS at room temperature**

An abrupt current decrement could be observed initially followed by a steady state current (Fig. 5). That initial sudden drop is due to polarization of ionic species at the electrolyte/electrode interface. The steady state current arises due to electrons. The calculated value of ti = 0.96 ascertains the dominance of ionic charge transport over electron transport in the electrolyte (Kumar et al. 2010). This is highly essential to use the GPE as an electrolyte.

The results of the DC polarization test done with two Mg electrodes are shown in Fig. 6.

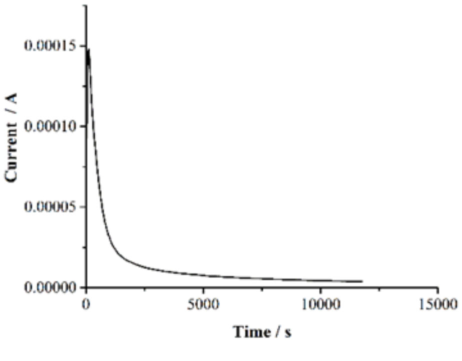

**Fig. 6. Variation of current with time for the configuration Mg / 105 PAN : 150 MgTF : 400 EC : 400 PC / Mg at room temperature**

The cationic and anionic contribution for the conductivity was evaluated using the resultant polarization graph shown in Fig.6. The initial current drop is not very steep. Due to Mg ions for which the electrodes are non-blocking, current has reached the steady state soon. The value of $t_+$, which is 0.30, implies the fact that anion contribution is dominant than cation contribution for the conductivity.

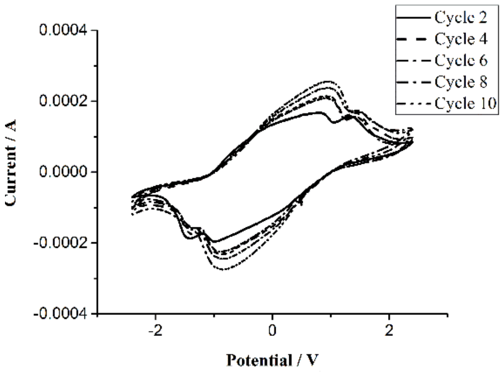

**Fig. 7. Cyclic Voltammogram of the redox capacitor in the configuration,** PPy : DBS / 105 PAN : 150 MgTF : 400 EC : 400 PC / PPy : DBS at room temperature

In Fig.7, the resulting peaks are corresponding for reduction/oxidation redox reactions. The cyclic volatmmogram with such peaks also reflects the potential dependence of capacitance (Hashmi *et al*. 2005). The mirror image around 0 V potential is a characteristic of better reversibility. The average specific capacitance calculated from the CVs is 151.67 $Fg^{-1}$. CVs obtained for each cycle shows similar shape as well as equal area. This is an indication for the presence of a stable specific capacitance over continuous cycling. In other words, results prove the distinctive cycleability of the redox capacitor. Current values in a wide potential window demonstrate the behaviour of the GPE/PPy as charge-storing electrodes in the GPE medium for capacitor application.

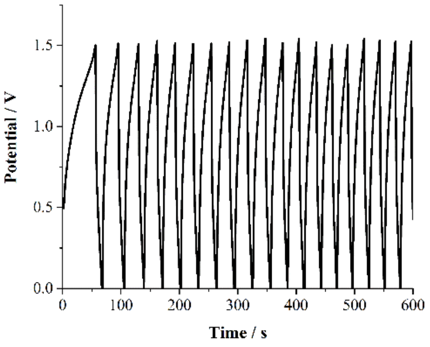

**Fig. 8. Galvanostatic charge-discharge curves of a redox capacitor,** PPy : DBS / 105 PAN : 150 MgTF : 400 EC : 400 PC / PPy : DBS at room temperature

The redox capacitors were subjected to charge and discharge under a constant current of 2 x $10^{-4}$ A. This value was extracted from the maximum value of current in the resulting CV. Figure 8 shows the continuous charge discharge behaviour for several cycles.

Though the investigation was carried out for 1000 cycles, only few cycles are shown in the figure. The charge-discharge curves are nearly linear. The average specific capacitance was 8 $Fg^{-1}$ which is lower than the value obtained from the cyclic voltammetry technique. This deviation may be due to the difference in scan rates used in the two techniques. The cyclic voltammetry technique was carried out at a scan rate of 5 $mVs^{-1}$. But, for charge discharge test, the calculated value of the scan rate is about 100 $mVs^{-1}$. When the scan rate increases, the specific capacitance reduces as the ions can only partially penetrate into the inner surface of electrodes (Sun *et al*. 2012 ; Uppugalla *et al*. 2014). With that explanation, the value obtained at 5 $mVs^{-1}$ should be nearly 20 times higher than the value obtained at 100 $mVs^{-1}$. Accordingly, the two capacitance values (151.67 $Fg^{-1}$ and 8 $Fg^{-1}$) are agreed subject to the difference of scan rate.

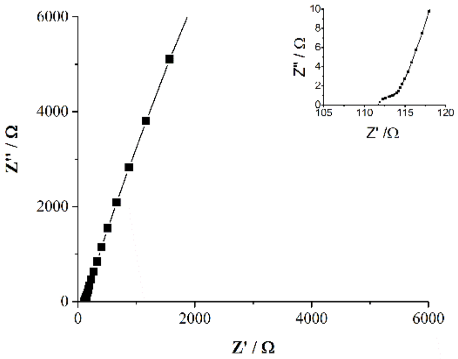

**Fig. 9. A resulting Nyqusit plot of a redox capacitor**

EIS is a good technique to learn about the characteristic frequency responses of redox capacitors. Figure 9 shows the Nyquist plot obtained for the redox capacitor investigated in the present study. In general, a Nyquist plot of a conventional capacitor should consist of a vertical line parallel to the imaginary impedance axis. But, this is not so under normal situations. Hence, it consists with numerous features at different frequency regions. At high frequency region, a semi-circle appears representing the bulk electrolyte. Another semicircle appears at intermediate frequency region due to the charge transfer resistance and associating double layer capacitance. At lower frequencies the capacitive behaviours become dominant. A tilted line can be seen due to the capacitance related to Warburg diffusion and it will be followed by another tilted line having a steep rise representing the capacitive behaviour of the electrodes. The line having the steep rising behaviour is not perfectly parallel to imaginary axis of impedance as for a typical capacitive behaviour. It may be due to the surface roughness as well as non-uniform active layer thickness (Prabhaharan *et al*. 2006). In the resulting Nyquist plot, the semi-circle corresponding to the bulk electrolyte is absent. It may be due to the unavailability of required high frequency values. The observed bulk electrolyte resistance from the Nyquist plot was used to calculate the bulk electrolyte conductivity and it was in the order of $10^{-2}$ $Scm^{-1}$ which is comparable with the value obtained with SS electrodes. This is an indication for the stable nature of GPE in redox capacitors. The depressed semicircle in the intermediate frequency range can be attributed for irregularities of electrode surfaces. The two tilted lines with different slopes are present and the calculated specific capacity value was about 2 $Fg^{-1}$ which is quite closer to the value obtained with continuous charge discharge test.

## 4 Conclusions

Polymer and salt concentration affects the conductivity and the mechanical properties of the GPE. The highest conductivity at room temperature, 1.06 x $10^{-2}$ $Scm^{-1}$, could be obtained with the composition, 105 PAN : 150 MgTF : 400 EC : 400 PC. Furthermore, it was possible to obtain a bubble free, thin and flexible film from that composition. The GPE is predominantly an anionic conductor. The results obtained for redox capacitors confirm the followings.

i. Conducting properties of the GPE remained unchanged when employed in redox capacitors
ii. GPE can withstand for continuous cycling maintaining a constant specific capacitance
iii. Specific capacity varies proportionally with the scan rate
iv. GPE considered in the present study is a suitable candidate to be used in redox capacitors.

Further studies are being carried out to improve the performance.

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