Sri Lankan Journal of Physics, Vol. 16 (2015) 19-27

INSTITUTE OF PHYSICS – SRI LANKA

Research Article

A Cyclic Voltammetry study of a gel polymer electrolyte based redox-capacitor.

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Abstract

This work describes the performance of a gel polymer electrolyte (GPE) based redox capacitor using the cyclic voltammetry technique.GPE was prepared with 22.5 wt% polyacrylonitrile (PAN), (1:1weight ratio) ethylene carbonate (EC) and propylene carbonate (PC) having a salt concentration of 1.0 M sodium iodide (NaI). Dependence of ionic conductivity of GPE on temperature was investigated using ac impedance spectroscopy. Two polypyrrole (PPy) electrodes were used as the electrodes of the redox capacitor. The performance of the device was evaluated by cyclic voltammetry. The redox-capacitors were cycled at different scan rates to determine the scan rate at which the maximum capacitance is obtained. After tracking that scan rate, continuous cycling was carried out at that scan rate to investigate the deterioration of capacitance upon cycling. The room temperature conductivity (σ) of the GPE was 4.29×10^{-3} S cm^{-1}. The conductivity variation with temperature followed the Arrhenius behavior. From the scan rates selected for the study, the maximum capacity could be obtained at the scan rate of 30 mV s^{-1}. The average specific capacity of the redox capacitor was 26.70 Fg^{-1}.

Keywords: gel polymer electrolyte, redox capacitor, conducting polymers

DOI: http://dx.doi.org/10.4038/sljp.v%vi%i.8026

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1. INTRODUCTION

There has been a rapid growth in research and development in the area of gel polymer electrolytes (GPEs) all over the globe[1,2,3]. GPEs are expected to have high ionic conductivity as well as good dimensional stability. They are prepared by incorporating a liquid electrolyte in to a host polymer matrix that is capable of forming a stable film[4]. Compared to liquid electrolytes, GPEs are having good mechanical properties, no leakage problems and no evaporation. Because of these properties, many potential applications of GPEs in electrochemical devices such as super-capacitors, batteries and solar cellscan be found.

Super-capacitors are energy and power storage devices that have technical and economic advantages in a diverse range of consumer and industrial applications[5,6]. They have high power capability than batteries and high energy capability than conventional capacitors. Depending on the types of electrode material as well as charge storage mechanism at the electrode electrolyte interface, super-capacitors are classified in to two categories as, electrical double layer capacitors (EDLCs) and redox-capacitors[7]. In EDLCs, different types of carbon and its various forms are used as electrode materials and its charge storage mechanism is electrostatic. In redox-capacitors either noble metal oxide like RuO, CoO or conducting polymers such as polypyrrole, polyaniline, polythiophene etc. are employed as electrode materials[8,9]. The reactions take place in redox-capacitors are faradic. Most of the redox-capacitors reported in the literature are based on liquid electrolytes[5,10]. They are associated with well-known disadvantages of corrosion, self- discharge and low energy density etc.

In this research work, redox-capacitors were fabricated using electrochemically deposited polypyrrole as the electrodes with a gel polymer electrolyte based on polyacrylonitrile (PAN), ethylene carbonate (EC), propylene carbonate (PC) and sodium iodide (NaI).Their performance has been studied using cyclic voltammetry.

2. METHODS AND MATERIALS

2.1 Preparation of gel polymer electrolyte

PAN (Aldrich), EC (Aldrich,98%), PC (Aldrich,99%) and NaI (Aldrich,99%) were used as received. GPE films were prepared using the hot pressed method[11]. The composition that was selected was 22.5 wt% PAN and 1.0 M NaI. EC and PC weight ratio was fixed as 1:1. First, the required amount of NaI to prepare a 1.0 M solution with 1:1 weight ratio of EC and PC was weighed by a chemical balance and dissolved in a EC / PC mixture by magnetic stirring. When NaI dissolved completely, 22.5 % of PAN was added to the mixture. After stirring for some time, the resultant mixture was heated at 130 ^{0}C for 1 ½ hours. Then, the hot mixture was pressed in between two well cleaned glass plates and left overnight in a vacuum desiccator. On the following day, the glass plates could be separated and a thin, bubble free film could be obtained.

2.2 Preparation of electrodes

Pyrrole (Aldrich,99%) was distilled and stored in dark in a refrigerator prior to use. A 0.1 M pyrrole solution was electrochemically polymerized on to Fluorine doped Tin Oxide (FTO) conducting glass plates using a three electrode setup. A Ag/Agcl electrode and a Pt electrode were used as reference and counter electrodes respectively. An aqueous electrolyte with 0.05 M sodium dodecylbenzenesulfonate (SDBS) (Aldrich) as the salt was used for polymerization. The electrode film thickness was controlled to be of 1μm.

2.3 Characterization of GPE

A circular shape sample of 14 mm diameter was cut from the thin electrolyte film and it was sandwiched between two well cleaned stainless steel (SS) electrodes in a spring loaded cell holder. The impedance measurements were taken in the frequency range 0.01 Hz to 0.4 MHz from room temperature to 55 ^{0}C using Metrohm M101 frequency response analyzer. The conductivity of the GPE (σ) was calculated from the equation,

$$\sigma = t / (RA) \quad (1)$$

where t and A are the thickness and area of the GPE respectively. R is the bulk electrolyte resistance.

2.4 Fabrication of redox-capacitors

A GPE sample was sandwiched in between two FTO glass plates on which pyrrole was polymerized. The area of the redox capacitor was 1 cm^2.

2.5 Cyclic voltammetry study on redox capacitors

Cyclic voltammetry measurements were carried out within the potential range of -0.25 to +0.25 V. Cycling was done at different scan rates of 10 mVs^{-1}, 20 mVs^{-1} 30 mVs^{-1}, 40 mVs^{-1} and 50 mVs^{-1}. Specific capacity, C_s was calculated using the following equation[12].

$$C_s = (2\int Idv)/s.\Delta V.m \quad (2)$$

Here, $\int Idv$ is the area of the CV, s is the scan rate, ΔV is the potential window and m is the weight of a single electrode.

After finding the scan rate that corresponds to the optimum specific capacity, cycling was done many times to investigate the ability to withstand for continuous cycling.

3. RESULTS AND DISCUSSION

GPE prepared with 22.5 % PAN and 1.0 M NaI in 1:1 EC:PC solution was mechanically stable to handle for applications. Its room temperature conductivity was

4.29×10^{-3} Scm^{-1}.The conductivity (σ) variation of GPE with temperature is shown in Figure 1.

The graph shows a linear pattern suggesting that conductivity behavior of GPE with temperature follows Arrhenius behavior[13]. It is illustrated with the equation,

$$\sigma = A_0 \exp(-E_a/k_BT) \quad (3)$$

Here, A_0 is the pre-exponential factor, E_a is the activation energy, T is the absolute temperature and k_B is the Boltzmann constant.

The activation energy of the GPE was found to be 0.075 eV. As per the Fig.1, the conductivity seemed to increase with temperature. Possibly, it may be due to reducing of viscosity of the medium which improves ionic motion substantially. And also, upon increasing temperature, ions may gain sufficient energy to speed up the ionic motion and thereby, conductivity can increase.

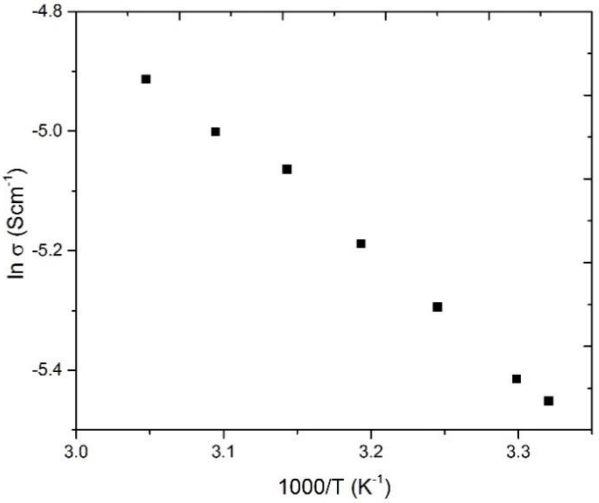

Figure 1: Conductivity as a function of temperature for GPE consisting with 22.5% PAN, 1M NaI and a 1:1 EC / PC mixture

Cyclic voltammograms obtained between -0.25 V and 0.25 V potential range at the scan rates, 10 mVs^{-1}, 30 mVs^{-1} and 50 $mVs^{-1}$are shown in Figure 2. When the capacitance is potential independent, the cyclic voltammogram has a rectangle shape[14]. But, if the capacitance is depending on potential, the shape of cyclic voltammogram shows a different profile. The resultant cyclic voltammograms are almost close to rectangle shape at all scan rates suggesting the potential independent capacitive behavior. Also, this shape is an indication for the fast switching of ions at the electrode electrolyte interfaces as well the good capacitive behavior of electrodes[15]. All CV patterns exhibit a nearly mirror image

symmetry of current response about zero current line. This demonstrates the reversibility of the redox-capacitor.

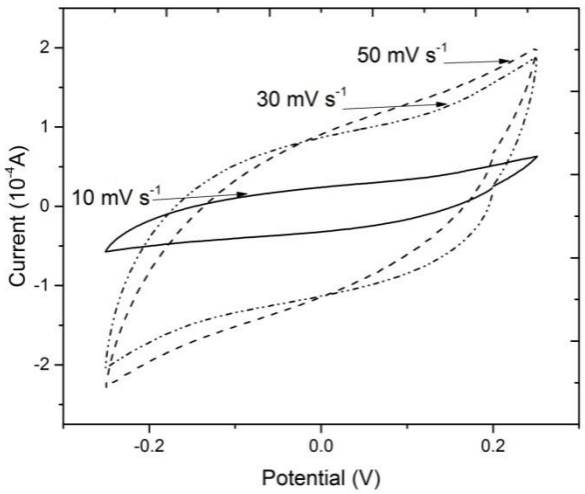

Figure 2: Cycle voltammograms of redox capacitor obtained at different scan rates

The response of redox-capacitors is seemed to be dependent on scan rate. Due to that, cyclic voltammograms are not having the same area. This elucidates the fact that specific capacitance values at different scan rates are different. Specific capacitance at different scan rates was calculated and they are tabulated in Table 1.

Table 1: Specific capacitance values of the redox capacitors at different scan rates.

Scan Rate ($mV\ s^{-1}$)	Specific capacitance Value ($F\ g^{-1}$)
10	21.90
20	24.44
30	27.00
40	23.20
50	15.68

It is seen from the table that, at the scan rate of 30 mV s^{-1}, the redox-capacitors show the highest specific capacitance. The specific capacitance is a parameter that depends on several factors such as resistance for ion transport, speed of ion diffusion/migration and diffusion length. With low scan rates, the resistance for ion transport may be dominant and hence reactions corresponding for charge storage may decrease so that, the specific capacitance may be low.

But, increasing scan rate would eliminate the resistive effect thereby increasing capacitance. Reduction of capacitance with increasing scan rate further (after 30 mVs^{-1}) would be due to relatively long diffusion length and also inability to complete respective reactions. Reversibility for a larger number of charge discharge cycles is one of the major characteristics of all super-capacitors over rechargeable cells. Figure 3 shows cyclic voltammograms obtained under continuous cycling at the scan rate of 30 mV s^{-1}.

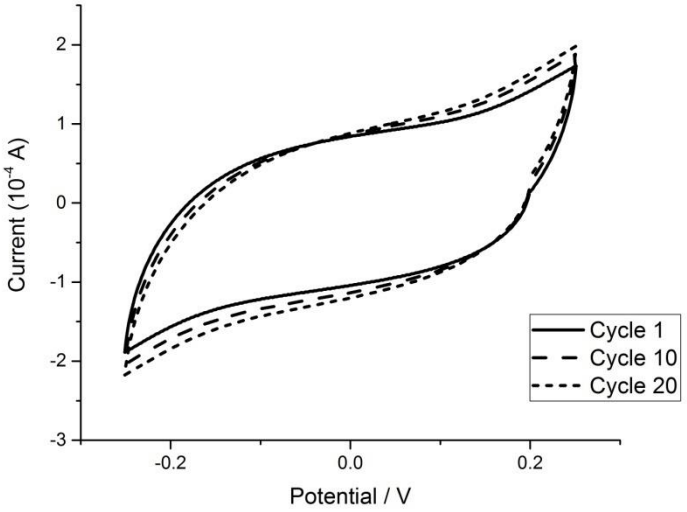

Figure 3: Cyclic voltammograms obtained under continuous cycling at the scan rate of 30 mV s^{-1}

It is seen from the cyclic voltammogram that the capacity fade upon cycling is very low. Also, they are of rectangle shape proving the fact that the capacity remains independent of potential. The specifc capacity variation with the cycle number is shown in Figure 4. It can be seen that the specific capacity remains almost stable with cycling. This is a good evidence to show the potential capability of redox capacitors to sustain with continuos cycling or in other words, long life time with consistent performance. The average spacific capacitance obtained is 26.70 Fg^{-1}. This is a small value compared to the results reported with double layer capacitors where carbon based electrodes and liquid electrolytes are employed[16,17]. It is a well accepted fact that carbon based electrodes are inherantly having better electrode performace than conducting polymers. But, due to some features like ease of fabrication and low cost, conducting polymers are receiving an attention to be used as electrodes.

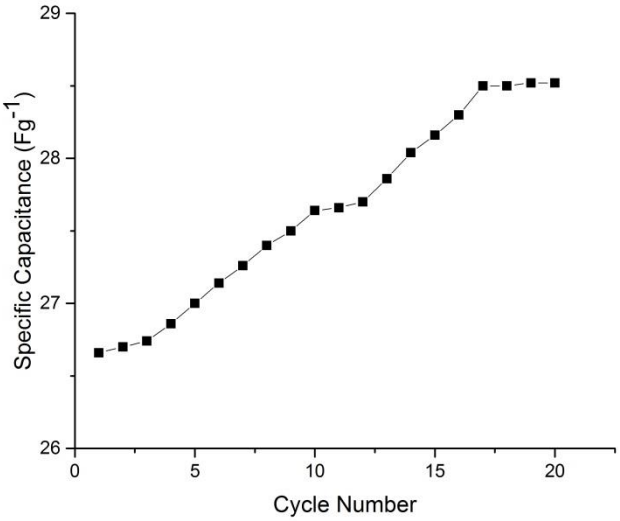

Figure 4: Variation of specific capacitance with cycle number at the scan rate of 30 mVs^{-1}

With regard to liquid electrolytes, they are having high ionic conductivity values than gel polyemr electrolytes. But, it is compensated with advantages of gel polymer electrolytes over the liquid electrolytes.

Further investigations are being carried forward to improve the perfomance of redox-capacitors based on conducting polymer electrodes and gel polymer electrolytes.

4. CONCLUSIONS

GPE used to fabricate the redox capacitor consisted of polyacrylonitrile, ethylene carbonate, propylene carbonate and sodium iodide. The composition, 22.5 wt % polyacrylonitrile, 1:1 wt ratio of ethylene carbonate, propylene carbonate and 1.0 M sodium iodide resulted in a mechanically stable, free standing film. It had an ionic conductivity of 4.29×10^{-3} Scm^{-1} at room temperature. The conductivity variation with temperature follows the Arrhenius behavior with an activation energy of 0.075 eV. The configuration of the redox capacitor was, PPy:DBS / GPE / PPy : DBS. As per the cyclic voltammetry study, specific capacitance values of all redox-capacitors were potential independent. But, they were depending on the scan rate. At the scan rate of 30 mVs^{-1}, an optimum capacitance could be obtained. The redox capacitor has a good potential to retain the capacitance upon continuous cycling. The average specific capacity resulted was 26.70 Fg^{-1}. One major importance of this study is that it could be realized that iodide based gel polymer electrolytes which are commonly used for dye sensitized solar cells can be used for redox-capacitors too.

ACKNOWLEDGEMENT

Assistance from University Grants Commission (UGC/VC/DRIC/IRG-2014/WUSL) and National Science Foundation (RG/2014/BS/01) are greatly acknowledged.

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