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RESEARCH ARTICLE

Fabrication and evaluation of an all solid redox capacitor with an iodine based gel polymer electrolyte

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Abstract: Gel polymer electrolytes (GPEs) have demonstrated a greater potential to be used as electrolytes for various applications such as batteries, super capacitors, electrochromic devices and dye sensitised solar cells. They consist of a salt and a mixture of solvents trapped in a polymer matrix. In this study, optimisation and characterisation of a GPE consisting of polyvinylidene fluoride, ethylene carbonate, propylene carbonate and sodium iodide and its application in a redox capacitor with two polypyrrole electrodes was studied. GPE shows a conductivity of 9.69×10^{-3} Scm^{-1} at room temperature (28 °C) with good mechanical stability. The corresponding composition is 1.13 PVdF : 2.5 EC : 2.5 PC : 0.4 NaI (by weight). The variation of conductivity with temperature follows Arhenius behaviour suggesting that the conductivity mechanism takes place *via* hopping of ions. Conductivity is purely ionic in nature. Properties of the redox capacitors were studied by the cyclic voltammetry (CV) technique, electrochemical impedance spectroscopy (EIS) technique and galvanostatic charge-discharge (GCD) test. The CV results showed the dependency of specific capacitance on the scan rate. The EIS results showed that capacitive behaviour becomes dominant only at low frequency range. The resulting specific capacitance was 3.19 Fg^{-1}. It was found that the redox capacitor exhibits an average discharge specific capacitance of 5.93 Fg^{-1} while having a specific energy density of 0.03 $Whkg^{-1}$ and a specific power density of 0.42 Wkg^{-1}.

Keywords: Bode plot, cyclic voltammetry technique, gel polymer electrolyte, redox capacitor.

INTRODUCTION

There has been a rapid growth in research and development in the area of energy storage devices all over the globe. Supercapacitor, a new type of reversible electrochemical energy storage device, also known as an ultra capacitor has been identified as a very attractive device for energy storage. It has aroused an enormous research interest due to its fast energy delivery, short charging time, high power capability, long durability and environment-friendly features (Yu *et al*., 2012). Supercapacitors possess higher capacitance than those achievable with conventional capacitors and can operate at substantially higher specific power than batteries (Tripathi *et al*., 2013). These have various consumer and industrial applications such as cellular communication devices, memory protection of computer electronics, hybrid automobiles and uninterruptible power supplies (Wang *et al*., 2013; Jayathilake *et al*., 2014a).

There are two types of supercapacitors which differ in the energy storage mechanism involved, namely, electric double-layer capacitor (EDLC) and redox capacitor (Singu *et al*., 2014). The EDLCs use carbon based electrodes. In redox capacitors, either metal oxide or conducting polymers such as polypyrrole, polyaniline, polythiophene etc., are used as the electrode material. Earlier, liquid electrolytes have been used commonly for redox capacitors but at present, attention has been diverted towards gel polymer electrolytes (GPEs) due to their attractive characteristics such as being free of internal shorting, no leakage and higher ionic conductivity (Jayathilaka *et al*., 2014b). GPEs which consist of a salt and solvent mixtures trapped in a polymer matrix possess high ionic conductivity and appreciable mechanical properties at ambient temperatures. For many of the

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redox capacitors investigated so far, polymers such as polymethylmethacrylate (PMMA), polyacrylonitrile (PAN) and polyvinylidene-co-hexafluoropropylene (PVdF-HFP) have been used extensively to prepare GPEs (Pandey *et al*., 2010; Gupta & Tripathi, 2013; Bandaranayake *et al*., 2016).

This paper describes a redox capacitor based on a GPE prepared using polyvinylidene fluoride (PVdF), ethylene carbonate (EC), propylene carbonate (PC) and sodium iodide (NaI). PVdF is a less studied polymer for redox capacitors. There are two reasons for selecting NaI as the salt. Firstly, it is highly considered for dye sensitised solar cells (Khanmirzaei *et al*., 2015); secondly, it has been reported that smaller anions in the electrolyte give rise to higher capacities (Gupta & Tripathi, 2013). For the characterisation of redox capacitors, cyclic voltammetry (CV) technique, electrochemical impedance spectroscopy (EIS) and galvanostatic charge discharge test (GCD) were used.

METHODOLOGY

Preparation of the gel polymer electrolyte

Polyvinylidene fluoride (PVdF) (Aldrich, Mw-534 000), ethylene carbonate (EC) (Aldrich, 98 %), propylene carbonate (PC) (Aldrich, 99 %) and sodium iodide (NaI) (Aldrich, 99 %) were used to prepare the GPE film with the hot press method (Jayathilake *et al*., 2015). The EC and PC weight ratio was fixed as 1:1. First, PVdF and NaI were dissolved in the EC:PC mixture and magnetic stirring was done for 1 h until a homogenous mixture was formed. The mixture was heated at 120 ºC for 45 mins. The hot mixture was pressed in between two well-cleaned glass plates. After separating the glass plates, it was possible to obtain a thin, free standing film. Several samples were prepared with different PVdF and NaI concentrations to optimise the composition to get the highest room temperature conductivity and mechanical stability.

AC conductivity measurements

A circular shape sample of diameter 14 mm was cut from the thin electrolyte film and it was sandwiched in between two well cleaned stainless steel (SS) electrodes in a spring loaded sample holder. The impedance measurements were taken in the frequency range of 0.01 Hz to 0.4 MHz from 28 ºC to 55 ºC using Metrohm M101 impedance analyser. Thickness of the circular shape films was measured using a micrometer screw gauge. Conductivity of the GPE, σ, was calculated from the equation,

$$\sigma = (1/R_b)\, l/A \qquad ...(1)$$

where, l is the thickness of the GPE film and A is the area of the GPE film. The bulk electrolyte resistance, R_b was calculated using the resultant impedance plot and non linear least square fitting method.

DC polarisation test

DC polarisation test was done to find the ionic transference number (t_i) of the GPE sample. In this characterisation method, SS electrodes were used as blocking electrodes. A circular shape GPE sample was loaded in between two SS electrodes in a sample holder. Under a fixed 1 V DC voltage, the current was monitored as a function of time. t_i of the GPE was calculated according to the relationship,

$$t_i = (I_t - I_s)/I_t \qquad ...(2)$$

where I_t is the maximum current and I_s is the steady state current.

Fabrication of redox capacitors

Using a 3 electrode setup, the monomer pyrrole (Aldrich, 98 %) was electrochemically polymerised on to FTO (fluorine doped tin oxide) conducting glass plates in the presence of sodiumdodecylbenzenesulfonate (SDBS) (Aldrich, 99 %). Ag/AgCl and Pt were used as reference electrodes and counter electrodes, respectively. The pyrrole concentration was 0.1 M and the SDBS concentration was 0.05 M. The polypyrrole (PPy) film thickness was controlled to be 1 μm using a current density of 1 mA during a period of 240 s (Vidanapathirana & Careem, 2006). Single electrode mass was about 0.5 mg. The redox capacitors were fabricated by sandwiching a GPE film between two PPy / DBS electrodes.

Characterisation of redox capacitors

Cyclic voltammetry technique

Cycling was done by varying the cycling scan rate using a computer controlled potentiostat (Metrohm Autolab M101). The specific capacitance (C_s) values from this technique were evaluated using the expression,

$$C_s = (2\int I\,dv)/m\Delta V s \qquad ...(3)$$

where, $\int I dv$ is the integrated area of the cyclic voltammograms, m is the mass of a single electrode, ΔV is the potential window and s is the scan rate (Wang *et al*., 2013).

Electrochemical impedance spectroscopy

The impedance data were gathered by using Metrohm autolab impedance analyser in the frequency range of 0.01 Hz – 0.4 MHz. The specific capacitance value was determined using bode plot of real part of the complex capacitance $C'(\omega)$ *vs* frequency. The real capacitance was calculated using the equation,

$$C'(\omega) = -Z''(\omega) / [\ \omega\ |\ Z(\omega)|^2] \qquad ...(4)$$

where Z'' is the imaginary part of the complex impedance, ω is the angular frequency and Z is the complex impedance (Tey *et al*., 2016). The maximum value of $C'(\omega)$ was used to find the specific capacitance.

Galvanostatic charge discharge test

The charge-discharge test of the redox capacitor was carried out galvanostatically at 85 µA and within the potential window + 0.1 V and + 0.4 V for 725 cycles.

Specific energy density (E_s) and specific power density (P_s) were calculated using the following equations,

$$E_s = C_s V^2 / 2 \qquad ...(5)$$

and

$$P_s = E_s / t \qquad ...(6)$$

respectively. Here C_s is the discharge capacitance, V is the charging potential and t is the discharging time.

RESULTS AND DISCUSSION

AC conductivity measurements of GPE

The composition of GPE was initially optimised in order to get a highly conducting, mechanically stable and flexible film for employing as an electrolyte in redox capacitors. Figure 1 shows the variation of conductivity of GPE with NaI concentration at seven different temperatures. It is observed that the conductivity increases with increasing NaI concentration and the maximum conductivity was obtained at a salt concentration of 0.4 mg. The conductivity of a material is governed by several factors, mainly by the concentration as well as the mobility of charge carriers. The initial increase of conductivity with salt concentration is noticeable due to the increase of charge carrier concentration. The subsequent decrease of conductivity after reaching the maximum value is very likely due to the formation of ion pairs in the GPE, which do not facilitate conductivity (Bandaranayake *et al*., 2016). Also upon increasing the salt concentration, viscosity of the medium may increase. This reduces the mobility greatly. In order to optimise the composition of GPE further, the PVdF concentration was also varied.

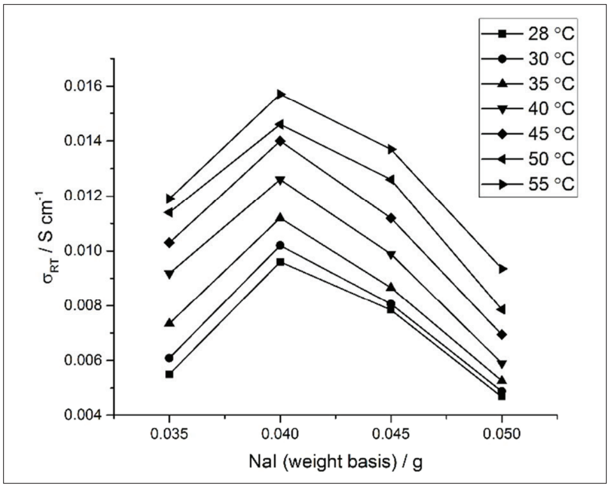

Figure 1: Isothermal graphs for the conductivities of GPEs of four different NaI concentrations at different temperatures

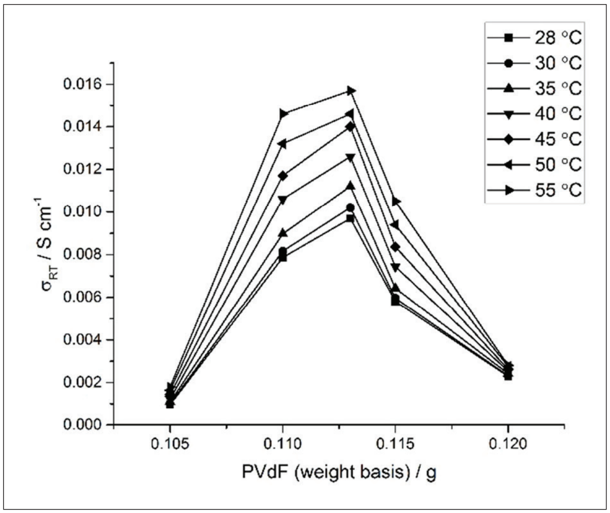

Figure 2: Isothermal graphs for the conductivities of GPEs of five different PVdF concentrations at different temperatures at the optimum NaI concentration

The conductivity variation of GPE with the PVdF concentration is shown in Figure 2. When increasing the polymer concentration, assistance for ion motion from the polymer network may increase. This might be the reason for initial conductivity enhancement. As the PVdF concentration increases further, viscosity of the system also increases so that there will be a resistance for ion mobility. Due to this, the conductivity may be reduced. The maximum room temperature conductivity is found to be 9.69 × 10^{-3} Scm^{-1}. The composition of GPE that results this conductivity is 1.13 PVdF : 2.5 EC : 2.5 PC : 0.4 NaI (by weight). The room temperature conductivity value is very suitable for applications. In addition, this composition results a very thin film.

The plot of ln σ *vs* 1000/T for optimised GPE is shown in Figure 3. It is observed that the plot is linear thus suggesting that σ variation with T of this GPE follows Arrhenius equation. The Arrhenius behaviour can be explained by the equation,

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \qquad ...(7)$$

where, σ_0 is the pre-exponential factor, E_a is the activation energy for conduction, K_B is the Boltzman constant and T is the absolute temperature. The Arrhenius equation describes ion motion *via* a hopping mechanism where ions jump into the neighbouring vacant sites and that gives rise to the conductivity.

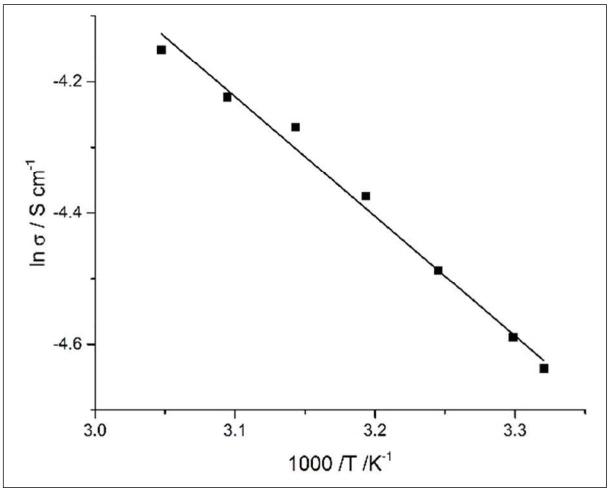

Figure 3: Temperature dependence of the conductivity of the GPE 1.13 PVdF : 2.5 EC : 2.5 PC : 0.4 NaI (weight basis)

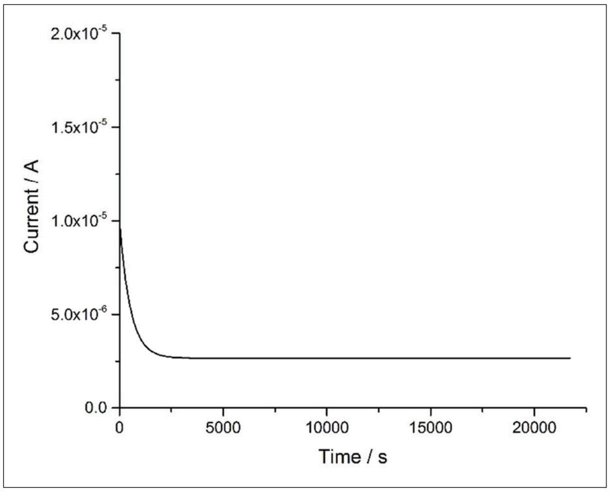

Figure 4: Variation of current through the symmetric cell with two SS electrodes under 1.0 V DC bias potential

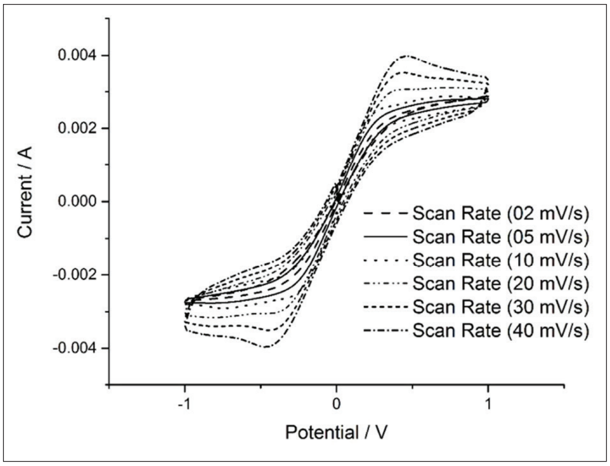

Figure 5: Cyclic voltammograms obtained by varying the scan rates of cycling of the redox capacitor (potential window + 1.0 V to - 1.0 V)

Transference number measurements

Figure 4 shows the graph of current variation through the symmetric cell with time obtained from the polarisation test with SS electrodes. The calculated t_i value is 0.84 and this clearly shows that the system under study is a pure ionic conductor.

This optimised composition was used to fabricate the redox capacitors as it was able to obtain a free standing, mechanically stable film with a good ionic conductivity.

Characterisation of redox capacitors

Cyclic voltammograms (CVs) of the redox capacitor obtained between - 1.0 V and + 1.0 V potential range at the scan rates of 2, 5, 10, 20, 30 and 40 mVs^{-1} are shown in Figure 5. All CV patterns exhibit a nearly mirror image symmetry of the current. The oxidation and reduction processes of ions during redox processes are symbolised by the peaks in the CVs. The peaks at 0.5 V are due to oxidation whereas those at - 0.5 V are due to reduction. During every scan rate, oxidation and reduction have taken place at the identical potential. This is a good indication for the systematic redox processes in the system. Apart from that, it is an evidence to prove that no irreversible or unwanted reactions are occurring in the system.

The specific capacitance of redox capacitors seem to be depending on the scan rate. Figure 6 shows the specific capacitance variation with the scan rate.

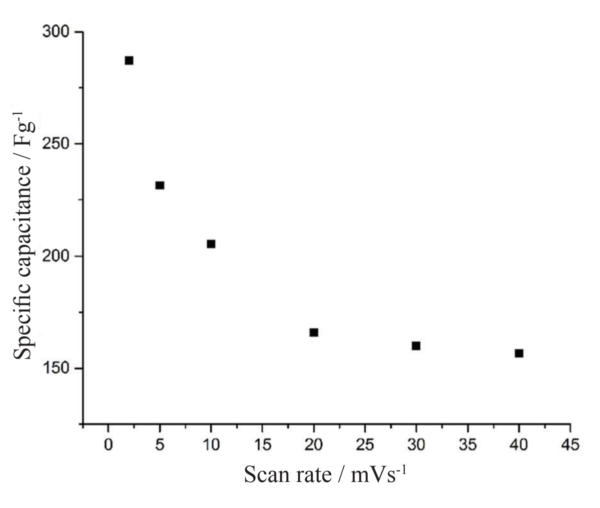

Figure 6: Variation of specific capacitance with the scan rate

When increasing the scan rate, specific capacitance decreased significantly down to 20 mVs^{-1}. After that it remained more or less constant. Upon increasing the scan rate, the time needed for the ions to diffuse into the inner surface of the electrode is not sufficient and at higher scan rates, ions may merely penetrate into the inner surface. The reason for the specific capacitance for not pronouncing after 20 mVs^{-1} may be the formation of parallel ionic and electronic conduction paths. Due to this, capacitive property might remain despite the increment of the scan rate.

Figure 7 shows the Bode plots of the real part, *C'*(*ω*) of the complex capacitance of the redox capacitor as a function of frequency. The maximum point of the curve associates with the specific capacitance and it is about 3.19 Fg^{-1}. This is quite smaller than the value range obtained with the CV technique. A possible reason may be that in the CV technique, charging and discharging are being done at different scan rates, which directly affect the specific capacitance. If the cycling were done at a faster scan rate, the two specific capacitance values may be comparable. The reduction of the real component of the capacitance with increasing frequency provides evidence for the transition where the redox capacitor changes from capacitive to resistive (Wang *et al*., 2011). In the low frequency region, a capacitive property of the electrode material is dominant (Tey *et al*., 2016). When frequency increases, capacitive behaviour vanishes and resistive behaviour becomes dominant.

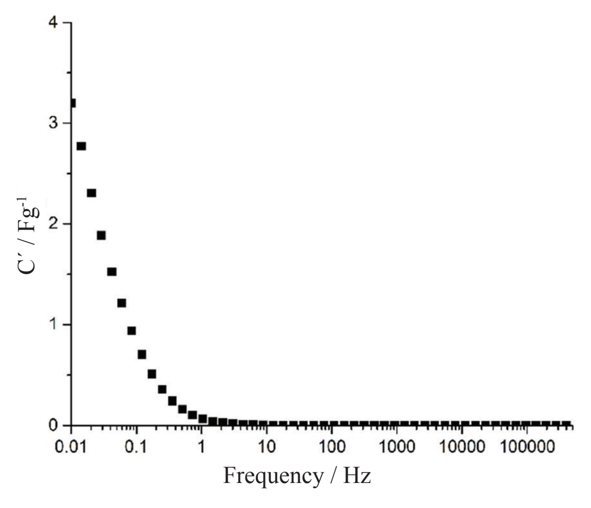

Figure 7: Bode plot for real part of capacitance as a function of frequency in logarithmic scale

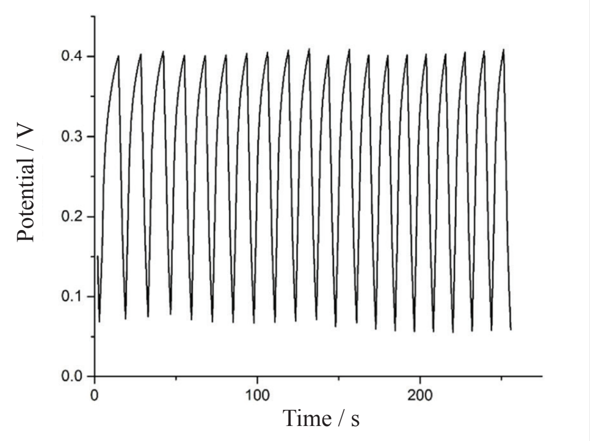

Figure 8: GCD curves obtained for the redox capacitor (charging and discharging current: 85 μA)

The redox capacitor has also been tested with the galvanostatic charge-discharge method. The typical charge-discharge characteristics of the redox capacitor are shown in Figure 8. The average discharge capacitance was 5.93 Fg^{-1}, and specific energy density and specific power density were 0.03 $Whkg^{-1}$ and 0.42 Wkg^{-1}, respectively. Somewhat lower energy and power density values may be due to the IR drop of interfacial contact between the electrode and electrolyte.

CONCLUSION

GPE having the composition 1.13 PVdF : 2.5 EC : 2.5 PC : 0.4 NaI (weight basis) shows the highest room temperature conductivity of 9.69×10^{-3} Scm^{-1} and it was possible to obtain a thin, stable film with the composition. The conduction mechanism is associated with the hopping mechanism. The sample is purely an ionic conductor as evidenced by transference number measurements with SS electrodes. The specific capacitance values obtained from CV are directly related to the cycling rate. Higher capacitance could be seen at smaller scan rates and when the scan rate increases, specific capacitance reduces down to a certain level and then remains somewhat constant. From EIS technique, the resultant specific capacitance was 3.19 Fg^{-1}. The average discharge capacitance of the redox capacitor fabricated from two PPy/DBS electrodes is 5.93 Fg^{-1} from the GCD test, and the corresponding specific energy density is 0.03 $Whkg^{-1}$ and the specific power density is 0.42 Wkg^{-1}.

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