



# Polyvinyl alcohol–polystyrene sulphonic acid blend electrolyte for supercapacitor application

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## ABSTRACT

A new polymer blend electrolyte based on poly vinyl alcohol and poly styrene sulphonic acid has been studied as an electrolyte for supercapacitors. A carbon–carbon supercapacitor has been fabricated using this electrolyte and its electrochemical characteristics and performance have been studied. The conductivity has been calculated using the bulk impedance obtained through impedance spectroscopy. The real and imaginary parts of the electrical modulus of samples show a long tail feature, which can be attributed to high capacitance of the material. The super capacitor showed a fairly good specific capacitance of  $40 \text{ F g}^{-1}$  and a time constant of 5 s.

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## 1. Introduction

Electrochemical capacitors (ECs) often called as supercapacitors are currently widely investigated due to their interesting characteristics in terms of power and energy densities. ECs are electrical devices with highly reversible charge storage and delivery capabilities. ECs have properties complementary to secondary batteries and find usage in hybrid power systems for electric vehicles, diesel locomotives, military, and medical applications [1]. ECs employ both aqueous and non-aqueous electrolytes in either liquid or solid state. Solid electrolytes provide the advantages of compactness and reliability without leakage of liquid components. Depending on the charge-storage mechanism, an EC is classified as an electrical double layer capacitor (EDLC) or a pseudocapacitor. Double-layer capacitors have several advantages over secondary batteries, such as faster charge–discharge, longer cycle-life ( $> 10^5$  cycles) and higher power density. Pseudocapacitors are also called redox capacitors because of the involvement of redox reactions in the charge-storage and delivery processes. Energy storage mechanisms in pseudocapacitors involve fast faradic reactions such as under potential deposition, intercalation or redox processes occurring at or near a solid electrode surface at an appropriate potential. Redox processes often occur in conducting polymers and metal oxides making them attractive materials for pseudocapacitors [1–3]. Polymer electrolytes, such as polyethylene oxide-salt complexes, [4–7] which are prepared by doping of ionic salt to polymers, are the most common solid electrolytes employed in electrochemical devices. Solid polymer electrolytes have ionic conductivity between  $10^{-8}$  and  $10^{-7} \text{ S cm}^{-1}$ , which are too low to

be of use in practical devices. Considerable efforts have been put to enhance the ionic conductivity of polymer electrolytes by different techniques [4]. However, little attention has been paid to the polymer electrolytes that in large amounts are also hazardous to the environment. Intensive work is being done on developing and use of environmental friendly materials during manufacturing which can help to reduce the environmental impact of many products throughout all phases of the product life cycle [8–10]. The use of biodegradable polymers has contributed to a reduction in environmental problems. As a result there has been a trend towards the production of degradable natural and synthetic polymers and natural/synthetic polymer blends [11,12]. Among biodegradable synthetic polymers, polyvinylalcohol (PVA) is one of the most attractive ones due to its availability and good mechanical properties. A review of literature suggested that there are very few reports on biodegradable polymer electrolytes for use in electronic devices [10,13]. Hence, in view of the aforesaid discussion and as a part of our ongoing research program on biodegradable polymers and polymer devices [11,12,14,15], we provide the first report of a biodegradable polymer blend electrolyte based on polystyrenesulphonic acid (PSA) and PVA for use in supercapacitors. These polyvinyl alcohol films showed good strength and ionic conductivity of the polymer electrolytes increased with increase in polystyrenesulphonic acid content in the blend.

## 2. Experimental procedures

### 2.1. Materials

All the chemicals used are of analytical reagent grade. Poly vinyl alcohol (PVA) (number average molecular weight: 1,50,000)

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polystyrene sulfonic acid (PSA) (number average molecular weight 70,000) from Alfa Aesar, India, activated carbon surface area 400 m<sup>2</sup>/g from Aldrich, USA were used as received. Double distilled water was used for the preparation of polymer solutions.

## 2.2. Preparation of polymer solutions and blend films

Dilute solutions of 10% (w/v) PVA and 5% (w/v) PSA in H<sub>2</sub>O were prepared separately in different stoppered conical flasks. Solutions of lower concentrations were then prepared by appropriately diluting these stock solutions with H<sub>2</sub>O. Similarly films of different blend compositions were prepared by mixing appropriate quantities of stock solutions of PVA and PSA. The so prepared blend solutions were cast on clean Teflon dish. Films were dried initially at room temperature and were then kept in a vacuum oven at 60°C for 48 h to complete dryness.

## 2.3. Electrochemical studies

The bulk ionic conductivities ( $\sigma$ ) of the blends were determined from the impedance spectra in the frequency range between 0.1 Hz and 10 kHz with a perturbation of 5 mV rms in the temperature range of 298–343 K. Samples were mounted on the conductivity holder with stainless steel electrodes of diameter 1 cm under spring pressure. Complex impedance data,  $Z^*$  can be represented by its real,  $Z_R$  and imaginary,  $Z_I$  parts by the relation

$$Z^* = Z_R + jZ_I \quad (1)$$

The relationships between complex impedance, admittance, permittivity and electrical modulus can be found elsewhere [16,17].

The equations for the dielectric constant,  $\epsilon_R$ , the dielectric loss,  $\epsilon_I$ , the real electrical modulus  $M_R$  and the imaginary electrical modulus  $M_I$  can be shown as

$$\epsilon_R = \frac{Z_I}{\omega C_0(Z_R^2 + Z_I^2)} \quad (2)$$

$$\epsilon_I = \frac{Z_R}{\omega C_0(Z_R^2 + Z_I^2)} \quad (3)$$

$$M_R = \frac{\epsilon_R}{(\epsilon_R^2 + \epsilon_I^2)} \quad (4)$$

$$M_I = \frac{\epsilon_I}{(\epsilon_I^2 + \epsilon_R^2)} \quad (5)$$

Here  $C_0 = \epsilon_0 A/t$  and  $\epsilon_0$  is the permittivity of the free space,  $A$  is the electrolyte–electrode contact area and  $t$  is the thickness of the sample and  $\omega = 2\pi f$ ,  $f$  being the frequency in Hz.

Electrochemical characterization of the carbon–carbon supercapacitor was carried out by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge studies. All the electrochemical studies were carried out using an Autolab Electrochemical System (Eco Chemie BV, The Netherlands).

## 3. Results and discussion

### 3.1. Ionic conductivity studies

The bulk ionic conductivities ( $\sigma$ ) of the solid polymer electrolytes were determined from the complex impedance spectra using the equation,  $\sigma = L/RA$ , where  $L$ ,  $A$  and  $R$ , are respectively, the thickness, area and bulk resistance of the solid polymer electrolyte. The bulk resistance was calculated from the

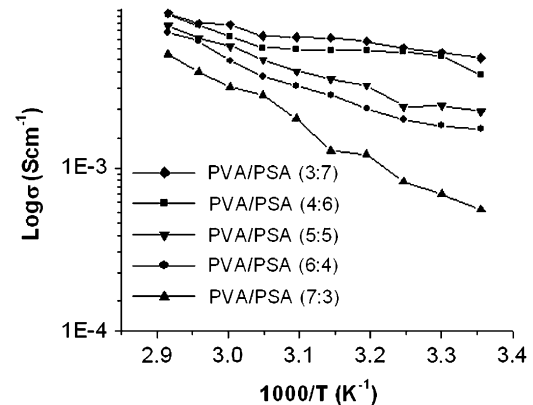


Fig. 1.

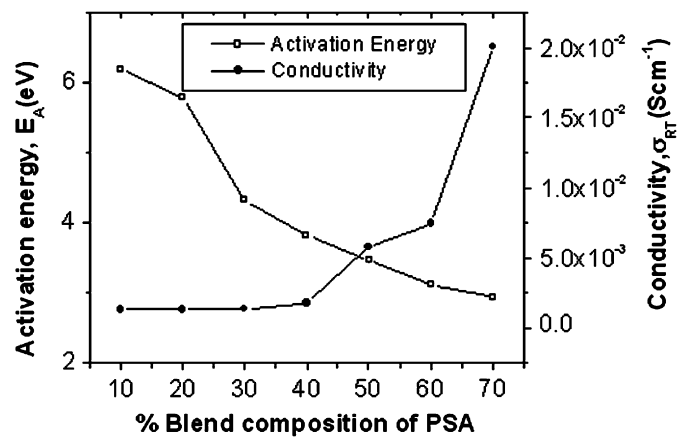


Fig. 2.

high frequency intercept on the real impedance axis of the Nyquist plot [18]. The temperature dependence of conductivity for the PVA–PSA blends have been shown in Fig. 1. The plot shows that as temperature increases, the conductivity increases. This trend is quite expected because increase in temperature increases the mobility of the ions and this in turn increases the conductivity. As there is no sudden change in the value of conductivity with temperature it may be inferred that these complexes do not undergo any phase transitions within the temperature range investigated. The activation energies have been calculated using Arrhenius equation given by  $\sigma = \sigma_0 \exp(-E_A/kT)$  where  $\sigma$  is specific conductivity of the film,  $\sigma_0$  is the pre-exponential factor,  $E_A$  is activation energy,  $K$  is Boltzmann constant and  $T$  is absolute temperature. Activation energy,  $E_A$  has been calculated from the slope of the  $\log \sigma$  vs.  $10^3/T$  graph. Fig. 2 shows how activation energy and room temperature conductivity varies as a function of polystyrene sulphonic acid concentration. The material with highest conductivity shows minimum activation energy as expected.

### 3.2. Dielectric studies

The conductivity behavior of polymer electrolyte can be understood from dielectric studies [19]. The dielectric constant is a measure of stored charge. The variations of dielectric constant and dielectric loss with frequency at different temperatures for

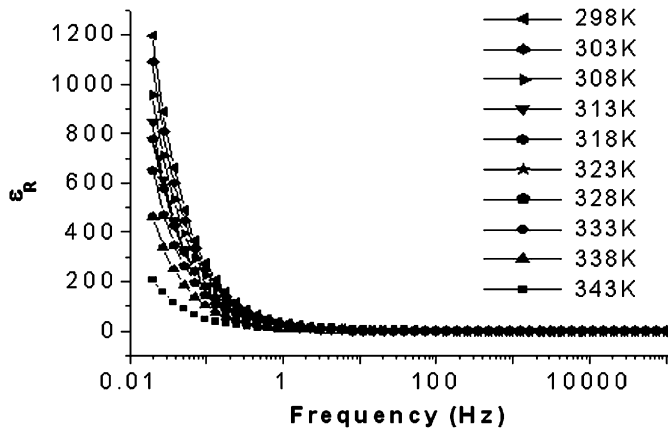


Fig. 3.

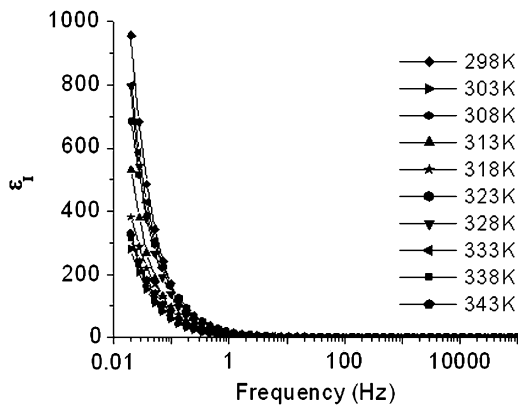


Fig. 4.

the sample with 70% PSA composition have been shown in Figs. 3 and 4 respectively. There are no appreciable relaxation peaks observed in the frequency range employed in this study. Both dielectric constant and dielectric loss rise sharply at low frequencies indicating that electrode polarization and space charge effects have occurred confirming non-debye dependence [20,21]. On the other hand, at high frequencies, periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. Polarization due to charge accumulation decreases, leading to the observed decrease in dielectric constant and dielectric loss [19,22] the dielectric constant and dielectric loss increase at higher temperatures due to the higher charge carrier density. As temperature increases, the degree of salt dissociation and redissociation of ion aggregates increases resulting in the increase in number of free ions or charge carrier density. A further analysis of the dielectric behavior would be more successfully achieved using dielectric moduli, which suppresses the effects of electrode polarization [23]. The real and imaginary parts of electrical modulus are shown in Figs. 5 and 6, respectively. As can be seen from the plots, both  $M_R$  and  $M_I$  values tend to zero at low frequency regime. The appearance of this long tail at low frequencies is indicative of the large capacitance associated with the electrodes [24]. Fig. 7 shows the Nyquist impedance plots of the polyelectrolyte film at different temperatures. As can be seen from the figure, resistance of the films decrease with increase in temperature. The plots corresponding to lower conductivities show two well defined regions. An arc

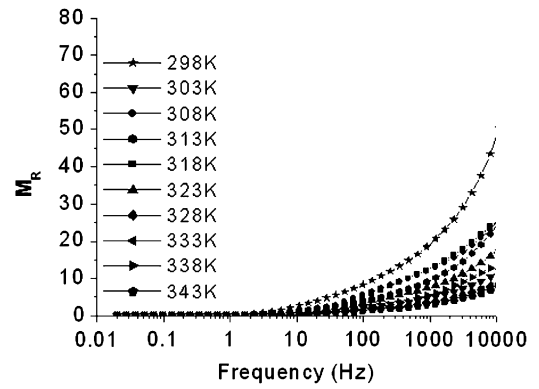


Fig. 5.

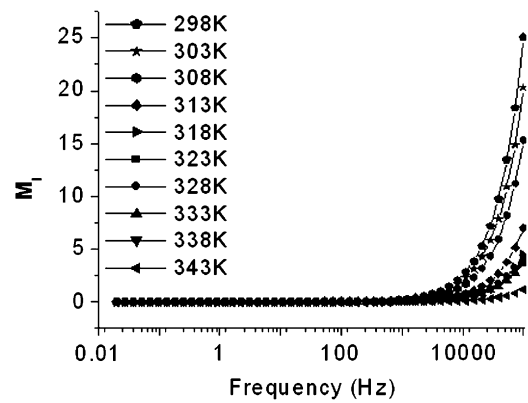


Fig. 6.

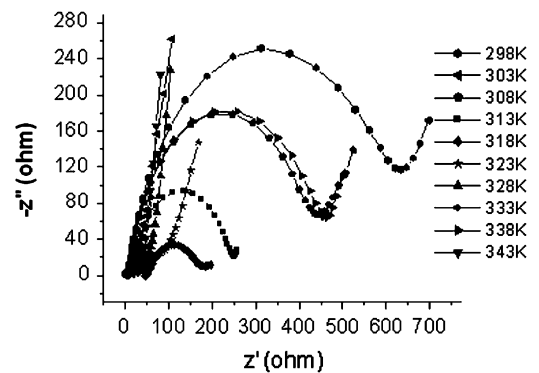


Fig. 7.

passing through the origin at high frequency limit is related to conduction process in the bulk of the material. A monotonically decreasing linear part with increasing frequency at low frequency limit is attributed to the electrode–solid electrolyte interface which is also known as Warburg impedance [1,25]. Since the acid dissociates as polystyrene sulfonate anion,  $\text{PSSO}_3^-$  and  $\text{H}^+$ , the resulting membranes are essentially proton conducting solid electrolytes. At low temperature the conductivity is Grotthuss-type in which a proton moves rapidly from  $\text{H}_3\text{O}^+$  to a hydrogen bonded water molecule and is transferred further along a series of hydrogen-bonded water molecules by a rearrangement of

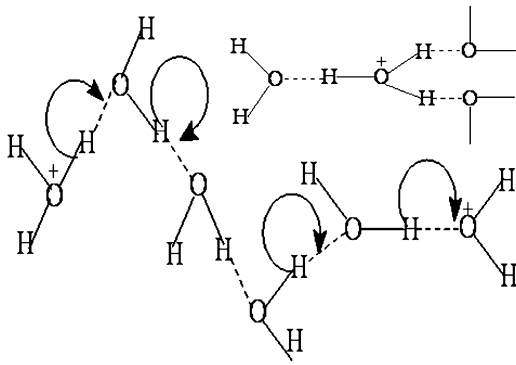


Fig. 8.

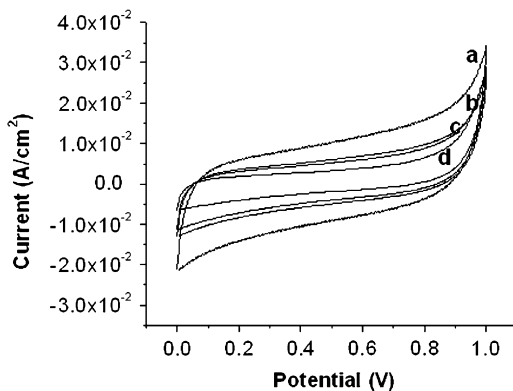


Fig. 9.

hydrogen bonds, as illustrated in Fig. 8. The translational modes are negligible here. With increasing temperature, the hydrogen bonds progressively elongate and break rendering the suppression of proton transfer and the stimulation of translational degrees of freedom [26].

### 3.3. Cyclic voltammetry studies

Cyclic voltammetry (CV) responses for the carbon-carbon symmetrical supercapacitor at various sweep rates are shown in Fig. 9. The behavior observed are characteristic of double layer capacitive features. The specific capacitance values of the electrode and the supercapacitor have been calculated from the respective cyclic voltammograms using the equation;  $C = i/s$ , where 's' is the potential sweep rate, 'i' the average current and C, the specific capacitance. The carbon-carbon supercapacitor fabricated using this solid polymer electrolyte showed a maximum specific capacitance of  $40 \text{ F g}^{-1}$  at a scan rate of  $5 \text{ mV s}^{-1}$ .

The AC impedance response (Nyquist plot) of the carbon-carbon supercapacitor is shown in Fig. 10. The plot shows a semicircle of large radius at high frequency range and a straight line in the low frequency region. The capacitance value increases at low frequencies because of a large number of ionic movements, which causes a decrease in the bulk resistance of the capacitor. The semicircle results from the parallel combination of resistance and capacitance and the linear region is because of warburg impedance. In the low frequency region, the straight line part leans more towards imaginary axis and this indicates good capacitive behavior [1].

Using Normalized reactive power  $Q/|S|$  and active power  $|P|/|S|$  versus frequency plot for the  $1 \text{ cm}^2$  cell, the time constant of the fabricated (p/p) supercapacitor has been calculated and is

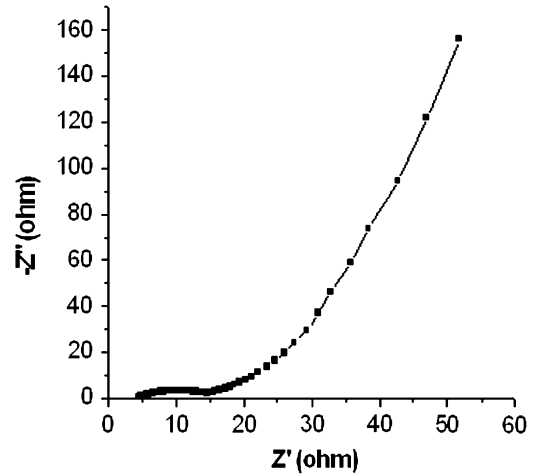


Fig. 10.

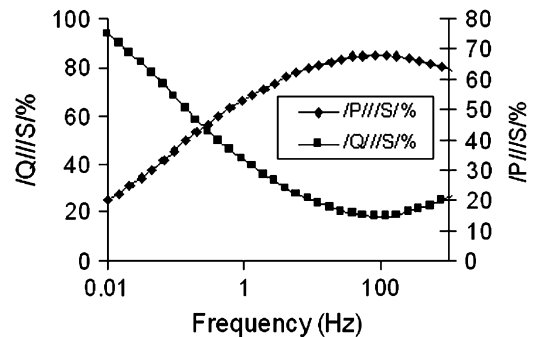


Fig. 11.

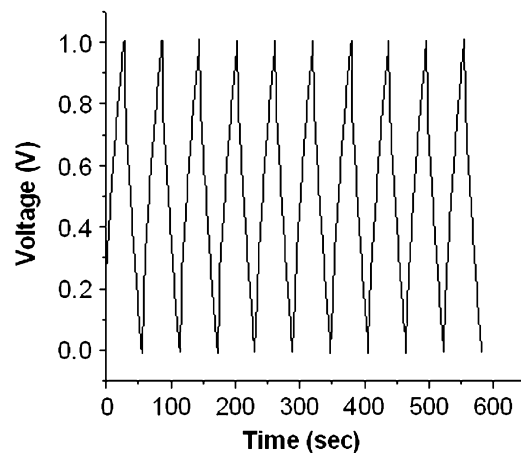


Fig. 12.

shown in Fig. 11. The theoretical details of this plotting technique can be found elsewhere [27,28]. The calculated time constant was found to be equal to 5 s. The time constant  $\tau_0$ , represents a transition for the supercapacitor between a resistive behavior for frequency higher than  $1/\tau_0$  and a capacitive behavior for frequencies lower than  $1/\tau_0$ . Hence, the observed time constant value of 5 s indicated that the present system can be efficiently used at low frequencies. Fig. 12 shows the charge-discharge profile of the supercapacitor as measured by galvanostatic method at a constant current density of  $2 \text{ mA cm}^{-2}$  between 0 and 1.0 V, for the first 10 cycles. From the figure, it can be seen that the

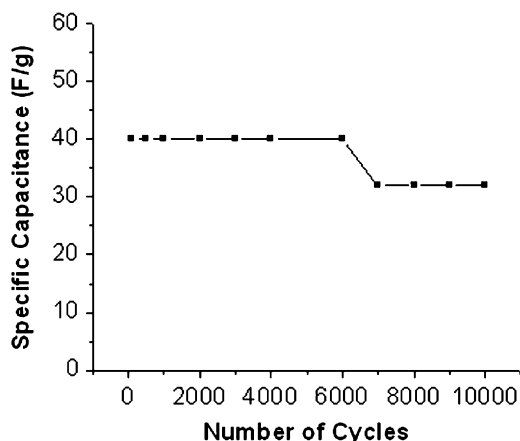


Fig. 13.

initial voltage drop during discharge is quite small and the voltage of the capacitor varies almost linearly with time during both charging and discharging processes for various cycles. It is evident from the figure that the charging time and also discharging time remained constant with increasing number of cycles. However, there may be a slightly higher voltage drop and decrease in the charging and discharging time with cycling's as well as with current density beyond 1000 cycles because of the degradation possibility of solid-polymer electrolyte in supercapacitor. The coulombic efficiency of the supercapacitor calculated from charge–discharge cyclings is also high in the range of 98–99%. Fig. 13 represents the variation of specific capacitance of the supercapacitor with cyclings. The data reflect that the device exhibited almost constant capacitance during the test. However, at higher cycle numbers the capacitance is expected to decrease slightly because of the decrease of double layer activity of the supercapacitor.

#### 4. Conclusions

The electrochemical properties of a newly prepared biodegradable electrolyte based on polyvinyl alcohol and polystyrene sulphonic acid and a carbon carbon supercapacitor fabricated using

this electrolyte have been studied. The conductivity of blend electrolyte films increased with temperature. The blend film with PVA:PSA composition of 3:7 showed maximum conductivity of  $2 \times 10^{-2} \text{ S cm}^{-1}$  and the material has been used for further studies. The dielectric studies indicated the high capacitive nature and absence of any relaxation process in the material. The carbon–carbon supercapacitor fabricated using this electrolyte showed good double layer capacitive features and gave a capacitance of  $40 \text{ F g}^{-1}$  at a scan rate of  $5 \text{ mV s}^{-1}$ . The supercapacitor was quite stable during charge–discharge cyclings and exhibited high coulombic efficiency.

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