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SHORT COMMUNICATION

Acrylamide based proton conducting polymer gel electrolyte for electric double layer capacitors

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Abstract A new class of polymer gel electrolyte (PGE) was synthesized using acrylamide as host polymer and $LiClO_4$ as dopant. The polymer gel was subjected to electrochemical AC impedance analysis and thermal analysis. The polymer has conductivity in the order of 10^{-3} S cm^{-1} at ambient temperature. Thermogravimetric analysis (TGA) revealed the effect of dopant on host polymer matrix. A supercapacitor was fabricated using acrylamide based polymer gel electrolyte with activated carbon as electrode material and it was subjected to various electrochemical techniques like cyclic voltammetry, electrochemical AC impedance analysis and galvanostatic charge–discharge tests at various current densities. From cyclic voltammetry a specific capacitance of 28 F/g was obtained at a scan rate of 10 mV/s. The capacitor had good self-discharge behavior and good cycle life of more than 10,000 cycles. The coulombic efficiency was more than 95%. These results indicate that this acrylamide-based polymer gel electrolyte doped with $LiClO_4$ is a potential electrolyte for electric double-layer capacitors (EDLCs).

Keywords Polymer gel electrolyte · Polyacrylamide · $LiClO_4$ dopant · Supercapacitor · Specific capacitance

Introduction

The increasing attention being given to electric double layer capacitors (EDLCs) or supercapacitors is stimulated by the prospect of using such devices as secondary power devices in electric vehicle propulsion, uninterrupted power supply, and also for the memory backup system [1]. A supercapacitor is different from a conventional capacitor wherein the conventional capacitors have discharge time in microseconds while supercapacitors require seconds. They have high power density compared to that of the usual rechargeable batteries and they exhibit both high rate charge–discharge profile and long cycle life. Hence, the performances of supercapacitors are in the midst of conventional capacitors and batteries. The concept of supercapacitors is based on the accumulation of charges in electrical double layers [2].

Power density can be further increased by the use of solid electrolytes [3]. Polymer electrolytes may be defined as membranes that possess transport properties comparable to that of liquid ionic solutions. Recently much work has been carried out in the use of solid polymer gel as electrolyte for supercapacitors [4–6]. This results in the achievement of higher capacitance, good electrochemical stability, and better compatibility between the electrodes. The application of the polymer electrolytes is restricted due to low conductivity because of the presence of some impurity, poor contact, low mechanical strength and aqueous based gels, which limit the electrostatic potential window to 1 V only. In general, capacitors with polymer gel as electrolyte have shorter life time than those with aqueous electrolyte, as the ionic conductivity decreases with the number of cycles. Few works have been done so far using polyacrylamide based gel electrolytes for solar cells and other applications [7–8].

In the present work, we synthesized a new type of polymer gel from acrylamide along with plasticers like acrylamide-2-methyl propane sulfonic acid (AMPS) and lithium perchlorate as dopant. $LiClO_4$ was used because of its good dissociation property and thereby increasing the

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conductivity of the gel. Lithium perchlorate is a common dopant used for synthesizing polymer gel electrolytes for lithium battery applications [9]. For the first time, we used an acrylamide-based solid polymer gel using $LiClO_4$ as dopant for supercapacitor application.

Experimental

Acrylamide-based polymer gel electrolyte was prepared by solution casting method. Acrylamide and $LiClO_4$ (in the weight ratio of 1:1) were dissolved in 20-ml distilled water. Stoichiometric quantities of *N*,*N*′-methylene-*bis*-acrylamide and natural polymer (agar) with de-ionized water were mixed and the solution was stirred well to yield a homogeneous solution. This was followed by the addition of acrylamide 2-methyl propane sulfonic acid (AMPS). After about 6 h of mixing, six to seven drops of hydrogen peroxide were added as an initiator for the polymerization. The resulting viscous solution was cast on a glass plate onto a Petri dish to form a thin layer of gel by keeping it in an oven at 60 °C for 20 min. The final product was cooled in air and the gel electrolyte was cut into squares of the size of 1 cm^2. Supercapacitors were fabricated using this gel as electrolyte and activated carbon as electrode material and characterized by AC impedance, cyclic voltammetry, and galvanostatic charge–discharge methods.

The bulk conductivity of the PGE was determined from complex impedance spectra in the temperature range from 30°C to 100 °C by using an EG&G Princeton Applied Research Model 6310 electrochemical impedance analyzer. The high-frequency semicircle yields the bulk resistance and the low-frequency response carries information on the electrode/electrolyte interface. By sandwiching the polymer electrolyte between two blocking electrodes, the direct-current (DC) conductivity has been calculated. Thermal stability of the PGE was analyzed by using an SDT Q600 V8.2, (TA Instruments Model) USA, thermal analyzer and cyclic voltammetry was carried out by using a BAS 100B analytical system (Bioanalytical Systems, Inc, USA) over the electrostatic potential window of 0–1.5 V at various scan rates. Charge–discharge behavior of the PGE-based supercapacitor cell was galvanostatically investigated by using a WBCS 3000 battery cycler (Won-A-Tech, Korea) at various current densities for several cycles.

Results and discussions

Conductivity measurement

A semicircle was obtained in the Nyquist plot, indicating that the resistance is solely due to bulk transport (Fig. 1).

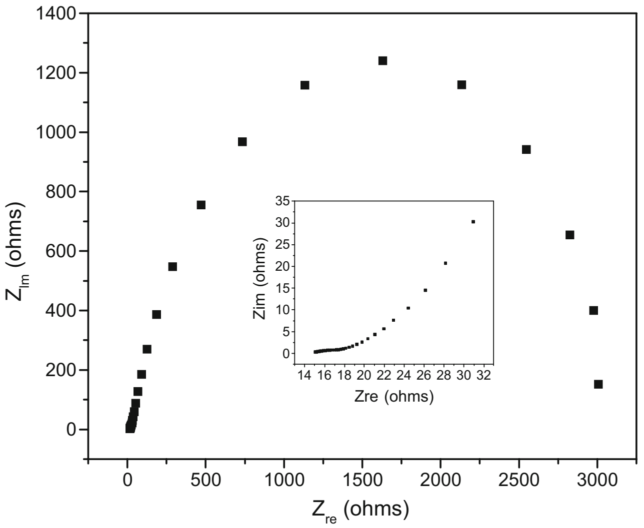


Fig. 1 Conductivity of the acrylamide-based polymer electrolyte. *Inset* shows Nyquist plot of PGE-based supercapacitor cell

The resistance (R_s), as inferred from the high-frequency intercept on real axis, was found to be 14 Ω. The conductivity of the PGE was calculated by the following equation:

$$\sigma = L/R_sA,$$

Where,

σ	Electrical conductivity (S cm^{-1})
L	Thickness of the gel (cm)
R_s	Solution Resistance (Ω)
A	Area of the gel (cm^2)

The conductivity was found to be in the order of 10^{-3} Scm^{-1} at ambient temperature. The temperature dependence of the conductivity is shown in Fig. 2, which shows an

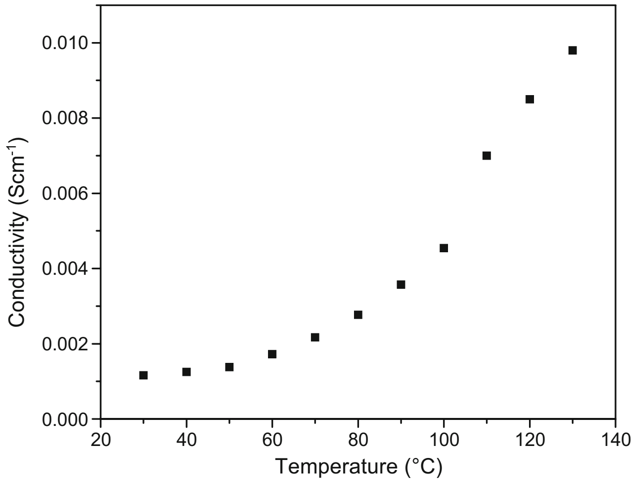


Fig. 2 Temperature dependence of conductivity of the polymer gel electrolyte

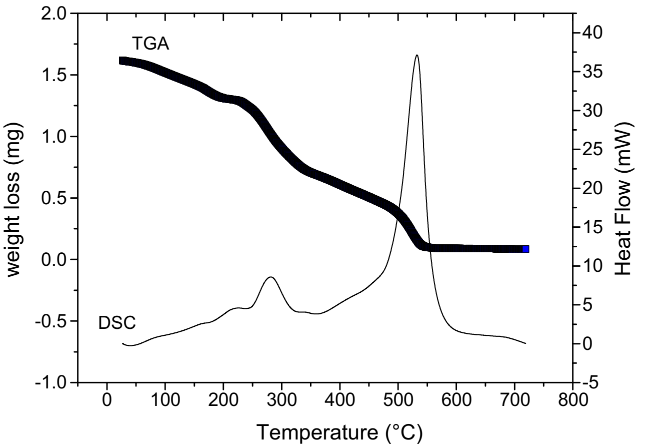


Fig. 3 Thermal analysis of the polymer electrolyte

activated process with activation energy of 0.11 eV and a conductivity of about 10^{-2} Scm^{-1} at 120 °C.

Thermal analysis of the gel polymer electrolyte

The thermal stability of the gel polymer electrolyte was investigated by thermogravimetric analysis/differential scanning calorimetry (TGA/DSC). Figure 3 shows that the polymer degradation proceeds in three stages. The first stage is due to the dehydration of the moisture present in the sample; this continues up to 100°C, where the weight loss is around 13%. The second stage from 100 °C to 469 °C is due to the volatilization of the co-polymer and a weight loss of 72% was observed. During the next stage, the weight loss is further increased and reached a stable value of 6% at 552 °C. After that, no major weight loss was observed up to 700 °C. Differential scanning calorimetric analysis shows two peaks indicating exothermic reactions; the first one is due to the glass transition phenomenon and the other one to decomposition of the melt, which takes place at 550 °C.

Electrochemical characterizations

Cyclic voltammetry

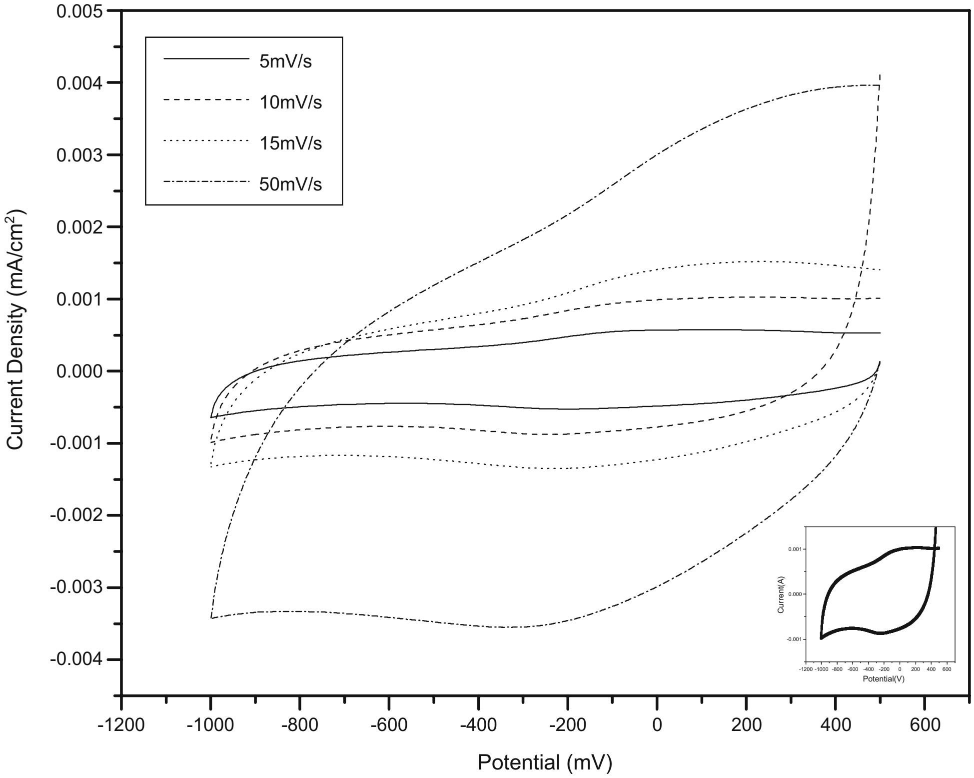
Cyclic voltammetry of the fabricated supercapacitor cell showed an electrostatic potential window from −500 to 1,000 mV. Voltammograms at various scan rates were measured and are presented in Fig. 4. All curves are of rectangular-like shape and reveal the capacitive behavior of the cell. The specific capacitance was calculated by using the following equation

$$\text{Specific capacitance} = \Delta I/(2 \times \mathrm{m} \times \mathrm{v})(\mathrm{F/g}),$$

where:

ΔI width of cyclic voltammogram (10^{-3} A),
m mass of electrode material (g),
v scan rate (mV/s).

Fig. 4 Cyclic voltammogram of supercapacitor at various scan rates. *Inset* shows the voltammogram at 10 mV/s



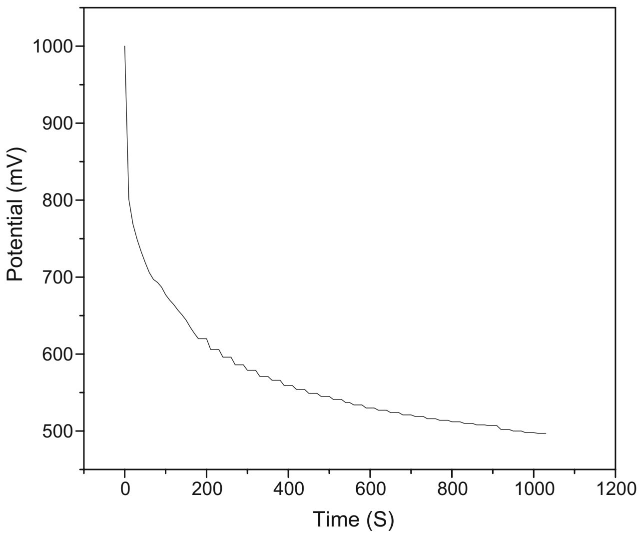


Fig. 5 Self-discharge behavior of acrylamide gel-based supercapacitor cell

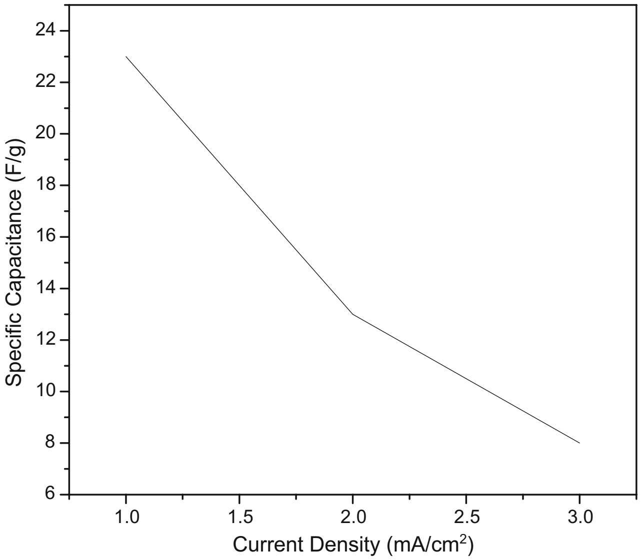


Fig. 7 Plot of current density vs specific capacitance

The specific capacitance was found to be 28 F/g at a scan rate of 10 mV/s. The oxygen evolution which should take place at 1.23 V was shifted to 1.5 V due to the overvoltage with the activated carbon electrodes. The widening of the graph with increase in the scan rate reveals that the current also increases. In the rectangular shape of the voltammograms, the current quickly reaches the plateau region after the reversal of the voltage sweep. This is due to the formation of a homogeneous and ideally polarizable double layer formed at the interface. The time taken to reach plateau region is more at higher sweep rates compared to the time taken at lower sweep rate. This is because charges are trapped at the pores and not able to cope up with the sweep rate (which is called distributed capacitance effects).

AC impedance studies

The presence of the Warburg impedance (Fig. 1) indicates that the matrix of microscopic pores within the electrode structure offers a complex series/parallel equivalent circuit of a distribution of ohmic (resistive) and capacitive elements. This concludes that the electrodes have a non-uniform effective resistance and capacitance, dependent on frequency or on the time-scale of pulsed or non-constant rates of charging.

The good performance of the polyacrylamide membrane in terms of the conductivity is due to the lower viscosity of

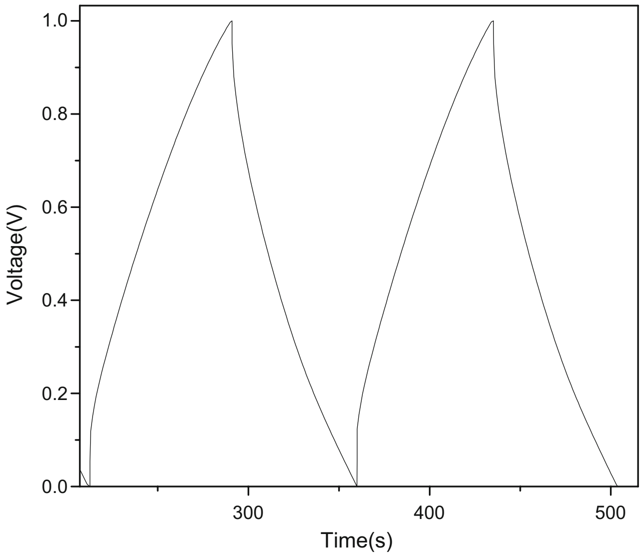


Fig. 6 Typical charge–discharge profile of PGE-based supercapacitor at a current density of 1 mA/cm^2

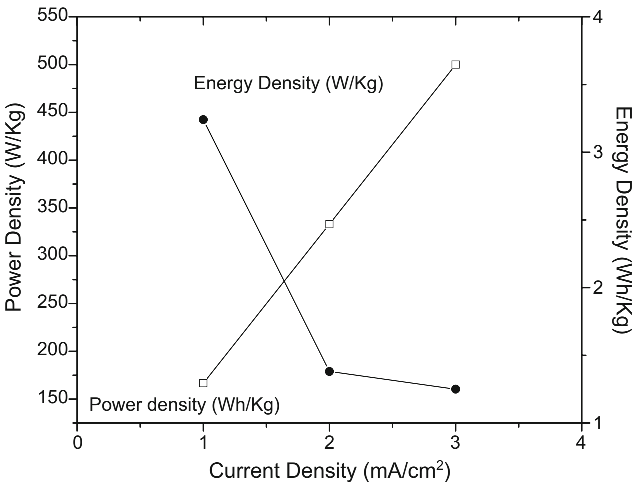


Fig. 8 Plot of power density vs energy density for PGE-based supercapacitor cell

the components in the polymer film. The R_{Ct} value was obtained from the diameter of the circle on the real axis, which was found to be 4.35 Ω.

Galvanostatic charge–discharge studies

The self-discharge of the supercapacitor cell using acrylamide-based gel electrolyte was measured by leaving the cell fully charged by a current density of 1 mA/cm^2 and recording voltage decay up to its full discharge. As activated carbon of high surface area favors oxidation of the electrolyte, the observed leakage current was very high. From the plot (Fig. 5) it is confirmed that the capacitor has appreciable self-discharge behavior.

The supercapacitor cycle life was studied by galvanostatic charge–discharge cycle tests. Typical charge–discharge behavior of the supercapacitor cell at 1 mA/cm^2 current density is shown in Fig. 6. The curves are sharp, linear, and symmetrical. Even though the polymer gel electrolyte was stable up to 1.5 V, which was inferred from cyclic voltammetry studies, the voltage was restricted to 1 V for charge–discharge tests. Initially the specific capacitance was found to be 23 *F*/*g* for current density of 1 mA/cm^2. Variation of the current density shows that the specific capacitance decreases with increasing current density.

The cycle life was more than 10,000 cycles. At a higher current density of 3 mA/cm^2, a small IR drop was observed. After 10,000 cycles, the specific capacitance was found to be 3 F/g at a current density of 2 mA/cm^2. The specific capacitance was calculated for various current densities using the following equation,

$$\text{Specific capacitance} = I \times t/(V \times m)(\mathrm{F/g}),$$

where

I current density (A/cm^2),
t discharge time (s),
V voltage (V),
m mass of electrode material (g),

The variation of specific capacitance with current density is plotted in Fig. 7. The coulombic efficiency was calculated using the following formula,

$$\eta = (t_d/t_c) \times 100,$$

where

t_d discharge time (s)
t_c charging time (s)

The coulombic efficiency was still around 90% after 10,000 cycles. Both energy density and power density were calculated for various current densities and are given in Fig. 8. These data were calculated using the formulas

$$\text{Power density} = \Delta E \times I/m(\mathrm{W/kg}),$$

where

ΔE $(E_{max}+E_{min})/2(\mathrm{V})$,
I current density (A/cm^2),
m mass of electrode material (Kg),

Energy density = Power density × Discharge time (Wh/kg).

Accordingly, the supercapacitor had a peak energy density of 3.24 Wh/kg and a power density of 500 W/kg.

Conclusion

The results suggest that the presently investigated acrylamide-based polymer gel can be used as a potential polymer gel electrolyte for activated carbon-based supercapacitors.

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