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Effect of anionic size of PMMA Based Polymer Gel Electrolytes for Redox Capacitor

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Abstract

Different types of polypyrrole based electrochemical redox supercapacitors have been fabricated using the polymeric gel electrolytes comprising of polymethyl methacrylate (PMMA)-propylene carbonate (PC)-ethylene carbonate (EC)-sodium salts of different anions [I^-, $(ClO_4)^-$, $(SCN)^-$] with a view to using them as electrolytes in redox supercapacitors to see the effect of anionic size in the performance of electrochemical capacitor cells. These gel electrolytes exhibit high ionic conductivity of the order of nearly 10^{-3} S/cm at room temperature with good mechanical/dynamical stability suitable for the fabrication of capacitor cells. Comparative studies of all the above supercapacitor cells have been characterized using complex impedance spectroscopy, linear sweep cyclic voltammetry and constant current charge discharge tests. The capacitance values of the cells have been observed to be in the range of 31-75 mF cm^{-2} which is equivalent to single electrode specific capacitance of 207-501 F/gm. It corresponds to the energy density of 03-30 Wh/kg and power density of 02-04 kW/kg. Working voltage was kept at 1 V. Further it was observed that the capacitance of the capacitor cells is highly dependent on the anionic size of the salts used in the synthesis of gel electrolytes and it was in the order of NaI based gel > NaSCN > $NaClO_4$,showing smaller anion of the salts with higher capacitance values and vice versa.

Keywords: Supercapacitors, Polypyrrole, PMMA, EC, PC

I. Introduction

A global attention has been devoted, in recent years, to develop electrochemical supercapacitors in view of their potential use as an alternative power source in various electronic applications such as computer memory backup, electrical vehicles, spacecrafts etc. [1-4]. Depending on the types of electrode materials used and charge storage mechanism at the electrode electrolyte interfaces, supercapacitor may be divided into two different classes namely; electrical double layer capacitors (EDLCs) and redox supercapacitors [1-4]. In EDLCs different types of carbon and its various forms were used as an electrode material and its charge storage mechanism is electrostatic in origin[1, 3-5]. In redox supercapacitors either noble metal oxide like RuOx, CoOx, NiOx or conducting polymer such as polypyrrole, polyaniline, polythiophene etc were used as an electrode material. In this case at the interface of electrode-electrolyte, fast faradic charge transfer takes place which give rise to pseudocapacitance and is responsible for its capacitance behavior [1, 3-4]. Most of the redox supercapacitors reported in literature are based on liquid electrolytes [1-4, 6] but they have some similar disadvantageous as observed in liquid electrolyte based batteries, such as corrosion, leakage, bulky design etc. Solid state redox supercapacitor based upon polymer/gel electrolytes is the current area of research. Some of the studies have been performed on solid state redox capacitors based on different polymer/gel electrolytes, e.g. poly (methyl methacrylate) (PMMA)-EC-PC-$NaClO_4$, PVA-H_3PO_4, PEO-$LiCF_3SO_3$-PEG, Nafion etc [5,7].

Present paper describes the comparative studies of the polypyrrole based redox supercapacitor using PMMA based gel electrolytes having salts of different anions PMMA-EC-PC-salts (NaI, NaSCN, $NaClO_4$). The performance characteristics of the capacitor cell has been critically examined and compared on the basis of different nature and size of anions of the salts (with common cation) incorporated in the gel electrolytes.

II. Experimental

Materials preparation

The gel polymer electrolytes, PMMA-EC-PC-salts (NaI, NaSCN, $NaClO_4$) were prepared using standard solution-cast technique. PMMA (Average M.W. 120,000), EC, $NaClO_4$ were obtained from Aldrich. NaI was obtained from Merck whereas PC and NaSCN were obtained from Loba Chemie. All these chemicals were dried in vacuum oven prior to its use. The appropriate amount of salts were dissolved in a mixture containing EC-PC (1:1 v/v) and stirred thoroughly to get liquid electrolytes. The optimum composition of liquid electrolytes with different salts (i.e. 1.0 M salts in EC: PC mixture) were mixed with different amount of host polymer i.e. PMMA. The mixtures were then kept in oven at ~70 °C for about 12-14 hr for gelling. Finally the soft, semi transparent and lump type materials of different compositions were obtained after slow cooling upto room temperature.

The p-doped polypyrrole films were electrochemically deposited on indium-tin oxide (ITO) coated conducting glasses (Balzers, sheet resistance about 80 Ω cm^2). The monomer pyrrole (Aldrich) and acetonitrile (Merck) were distilled before use. A single compartment three electrodes cell was used for the electro-polymerization with platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. The electro-deposition of pPy was carried out in a cell which contains 0.1 M pyrrole and 0.2 M $LiClO_4$ solution in acetonitrile at constant current of 2mA for 3 min in the presence of dry nitrogen purging.

Electrochemical measurements

The bulk electrical conductivity of the polymeric gel electrolytes was determined by a.c. impedance spectroscopy at room temperature (25°C) by sandwiching them between two stainless steel blocking electrodes. The performance characteristics of the capacitor cells were performed by using impedance spectroscopy, linear sweep voltammetry and galvanostatic charge-discharge techniques. The impedance measurements were carried out by using computer controlled LCR HI TESTER (Model 3522-50, Hioki, Japan) in the frequency range from 1 mHz to 100 kHz. The overall capacitance of the capacitor cells were evaluated using relation:

$$C = -1/\omega Z'' \quad (1)$$

Where ω (= 2πf) represents the angular frequency and Z" represents imaginary part of the total complex impedance. The single electrode specific capacitance values were evaluated by multiplying the value of overall capacitance by the factor of two and divided by the mass of a single electrode material.

The linear sweep cyclic voltammetry was carried out by using computer controlled CHI 608C, CH Instruments, USA. The capacitance values from this technique were evaluated by using the relation

$$C = i/s \quad (2)$$

where 'i' represents the current and 's' is the scan rate.

The galvanostatic charge-discharge characteristics of the capacitor cells were also carried out by using computer controlled CHI 608C, CH Instruments, USA. The discharge capacitance 'C_d' was evaluated from linear part of the discharge curves using the relation:

$$C_d = i\Delta t/\Delta V \quad (3)$$

where 'i' represents the constant current and 'Δt' is the time interval for the voltage change ΔV.

III. Results and Discussions

The composition of the polymeric gel electrolytes, PMMA-EC-PC-salts (NaI, NaSCN, $NaClO_4$) were first optimized in order to get substantially conducting and mechanically stable materials. The optimum composition of gel electrolyte is PMMA (20 wt %)-EC:PC(1:1 v/v)-1.0 M salts (NaI, NaSCN, $NaClO_4$) were chosen for the fabrication of redox supercapacitors. The room temperature conductivity of all the gel electrolytes is of the order of 10^{-3} S/cm with good mechanical strength and flexibility in order to mould it into desirable shapes. This order of conductivity is acceptable from device fabrication point of view.

Different solid state redox supercapacitor cells have been fabricated using electrochemically deposited pPy on ITO electrodes and the optimized polymeric gel electrolytes.

Cell A: pPy| PMMA (20 wt%)-EC: PC (1:1 v/v)-1.0 M NaI| pPy

Cell B: pPy| PMMA (20 wt%)-EC: PC (1:1 v/v)-1.0 M $NaClO_4$| pPy

Cell C: pPy| PMMA (20 wt%)-EC: PC (1:1 v/v)-1.0 M NaSCN| pPy

In order to characterize these capacitor cells various techniques like linear sweep cyclic voltammetry, ac impedance spectroscopy and galvanostatic charge discharge tests have been applied.

3.1 Cyclic Voltammetry tests

Fig. 1 shows the linear sweep voltammograms for the cells (A-C) at different scan rates. In the present

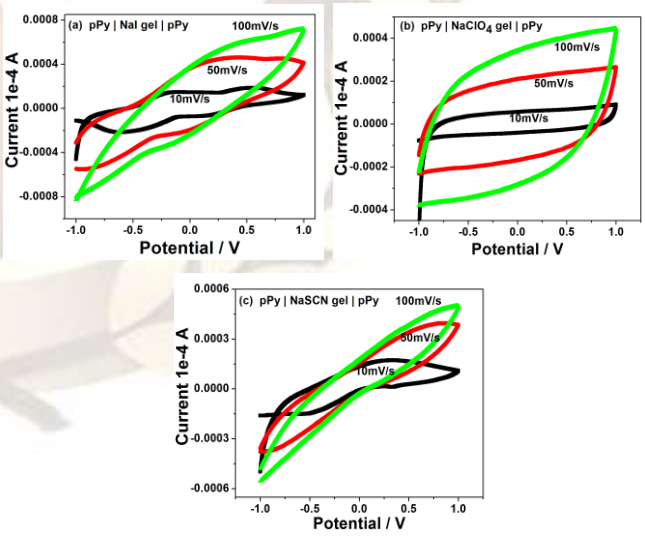

Figure 1: Cyclic voltammograms of different capacitor cells, (a) Cell A: pPy| NaI gel|pPy, (b) Cell B: pPy| $NaClO_4$ gel| pPy, (c) Cell C: pPy| NaSCN gel| pPy at different scan rates. Scan rates (in mV/sec) are marked on the figures studies, the sweep reversal voltammograms for all capacitor cells (A-C) are almost close to an ideal shape of rectangle even for higher scan rates. This is characteristic of capacitive

behavior and it also indicates the fast switching rate of ions at electrode-electrolyte interfaces. At higher scan rates (more than 100 mV/sec) a slight deviation from the rectangular shapes has been observed which is due to equivalent series resistance (ESR) that is practically present in the real capacitors. The response of each capacitor cells has been found to be dependent on scan rates, which is characteristic of capacitor cells [1,4]. The capacitance value of all the cells as calculated using equation (2) for different polymeric gel electrolytes in the present studies has been observed in the range of 06 mF/cm^2 to 32 mF/cm^2 and are almost showing the same behavior of smaller the size of anion, larger is its capacitance values as obtained from charge discharge analysis as well as impedance spectroscopy measurements (discussed in the following sections).

3.2 Charge-Discharge tests

The fabricated cells have also been tested with the constant current charge-discharge methods. The typical charge discharge plots of the capacitor cells (A-C) are shown in fig. 2. All the cells were charged

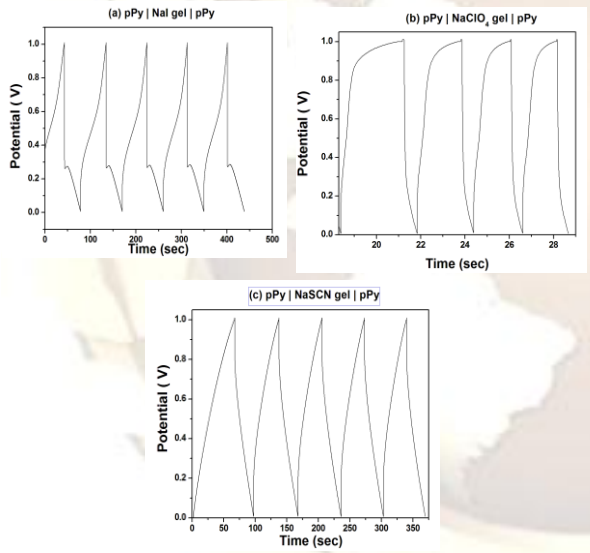

Figure 2: Typical charge discharge curves of capacitor cells, (a) Cell A: pPy| NaI gel|pPy, (b) Cell B: pPy| $NaClO_4$ gel| pPy, (c) Cell C: pPy| NaSCN gel| pPy at constant current density of 100 µA cm^{-2}.

upto 1.0 V, which is the voltage limit of doping-dedoping of polypyrrole [6-7]. The discharge characteristics of all the cells were found to be linear, which further confirms the capacitive behavior of all the cells. The initial sudden increase in voltage while charging and sudden drop while discharging of all the cells at constant current density is due to ohmic loss across the internal resistance R_i, which is also known as equivalent series resistance, ESR of the cells. The discharge capacitance values are calculated by using equation (3).

The energy density of all the cells has also been estimated from their corresponding values of the capacitance by keeping the working voltage, 1.0 V. The power density values of all the cells have been evaluated by dividing the energy density values by discharge time of the cells [5]. The value of specific energy observed is in the range of 03-30 Wh/kg, are relatively lower than that of rechargeable batteries, it is due to the limited voltage range. The power density obtained is about 02-04 kW/kg which is quite higher as compared to conventional batteries. All these values are in well agreement with the values obtained from impedance spectroscopy and cyclic voltammetry studies. Although, the energy density values are smaller as compared to rechargeable batteries but higher values of power density make the supercapacitors attractive from the application point of view as power sources.

3.3 Impedance Analysis

Fig. 3 shows the typical impedance plots of all the capacitor cells (A-C). The impedance analysis is one of the important techniques for electrical characterization of supercapacitors, which helps in

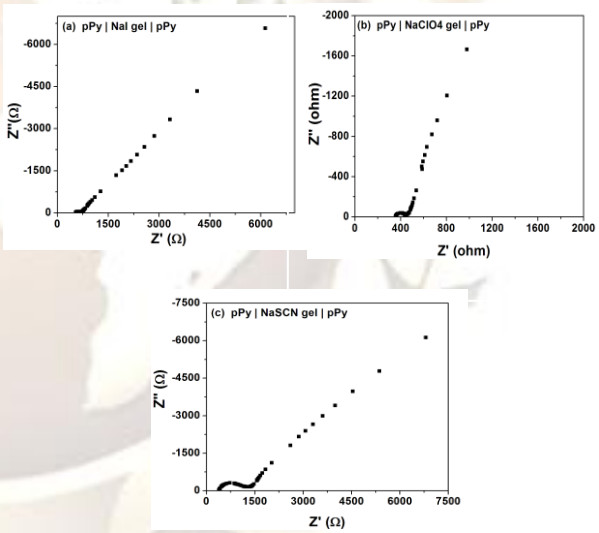

Figure 3: Typical impedance plot of different capacitor cells, (a) Cell A: pPy| NaI gel|pPy, (b) Cell B: pPy| $NaClO_4$ gel| pPy, (c) Cell C: pPy| NaSCN gel| pPy recorded at room temperature in the frequency range of 100 kHz to 1 mHz.

finding out the various parameters associated with bulk properties of electrolytes and electrode-electrolyte interfaces including equivalent series resistance (ESR) of the capacitor cells, low frequency capacitance and potential dependent faradic resistance etc. to be evaluated in different frequency regions. It should be noted that an ideal impedance response for a pure capacitor is a straight line parallel to the imaginary axis of the complex impedance

plots. But in real capacitors, the steep rising capacitive impedance response is observed in low frequency region accompanied with high frequency semicircular features owing to the bulk and interfacial properties. The impedance response of all the cells (A-C) in present studies shows a semicircular spur in the high frequency followed by steep rising portion in the lower frequency region upto 1 mHz. The values of bulk resistance R_b and interfacial charge transfer resistance R_{ct} of the different capacitor cells can be evaluated from the intercepts on the real axis of the complex impedance response. A comparison with the impedance response indicates that the polypyrrole, electrodeposited on ITO conducting glass, shows almost rectangular geometry of the pores accessible to the gel electrolytes.

Various electrical parameters such as bulk resistance R_b, interfacial charge transfer resistance R_{ct}, total resistance R and capacitance C at frequencies 10 mHz and 1 mHz are summarized in Table-1.

Table 1: Electrical parameters of supercapacitor cells (A-C) from impedance analysis.

Cells	R_{ct} (Ωcm^2)	R_b (Ωcm^2)	C (1 mHz) (mF/cm²)	(F/g)	C (10 mHz) (mF/cm²)	(F/g)
A	188	701	75	501	26	175
B	36	224	31	207	16	106
C	1927	741	74	495	25	1168

The capacitance values observed for each cell is found to be comparable within same range (31-75 mF/cm^2), equivalent to a single electrode specific capacitance of (207-501 F/g) for all the gel electrolytes. A comparison indicates that the electrochemically deposited polypyrrole electrode shows almost capacitive behavior with all the PMMA based polymeric gel electrolytes under the present studies. A further comparison reveals that polypyrrole electrode shows different capacitive characteristics with PMMA based gel electrolytes having sodium based different anionic (I^-, SCN^-, ClO_4^-) salts. It has been observed from the table that smaller the anionic size larger is its capacitive values and vice versa. The size of anions is in the order of ClO_4^-(2.4Å)>SCN^-(2.08Å)>I^-(2.06 Å).

IV. Conclusions

On summarizing the above experimental studies, following conclusions can be drawn:

1) The PMMA (20 wt%)-(EC-PC)-NaX (X = I^-, SCN^-, ClO_4^-) based polymeric gel electrolytes having room temperature conductivities of the order of 10^{-3} S/cm are suitable electrolytes for the fabrication of electrochemical redox supercapacitor using polypyrrole as conducting polymer electrode.

2) The anionic size of the salts used in polymeric gel electrolytes plays important role in the capacitive properties of the redox capacitors with polypyrrole electrodes. It has been observed from the present studies that smaller the anionic size larger is its capacitance values and vice versa. The size of anions is in the order of ClO_4^-(2.4Å)>SCN^-(2.08Å)>I^- (2.06 Å).

3) Overall capacitance is about (31-75 mF/cm^2), equivalent to a single electrode specific capacitance of (207-501 F/g) of polypyrrole, which corresponds to energy density of 03-30 Wh/kg and power density of 02-04 kW/kg.

4) The internal/overall resistance of each cell has been found to be of the order of few hundred ohm cm^2, which is comparatively lower than that of the solid state cells based on conventional solid polymer electrolytes.

V. Acknowledgement

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