

Investigations on electrochemical supercapacitors using polypyrrole redox electrodes and PMMA based gel electrolytes

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Abstract

Polypyrrole based solid state electrochemical redox supercapacitors have been fabricated using the polymeric gel electrolytes comprising of poly methyl methacrylate (PMMA)-propylene carbonate (PC)-ethylene carbonate (EC)-perchlorate salts of different cations [Li^+ , Na^+ and $(\text{C}_2\text{H}_5)_4\text{N}^+$ (TEA $^+$)]. A comparative study has been carried out using linear sweep reversal voltammetry, complex impedance spectroscopy and constant current charge–discharge tests. The capacitance values of the cells have been observed to be in the range of 15.3–22.5 mF cm $^{-2}$ (equivalent to single electrode specific capacitance of 120–178 F g $^{-1}$ of polypyrrole). This corresponds to the values of energy density 16.7–24.7 Wh kg $^{-1}$ and power density 1.6–2.8 kW kg $^{-1}$ calculated for the working voltage of 1.0 V limited for polypyrrole based redox capacitors. Substantial improvements in the coulombic efficiency of the cells have been observed (close to 100%) due to the application of gel electrolytes showing flexible and liquid like behaviour. Further, the types and sizes of the cations in the gel electrolytes do not play any dominant role in the capacitive behaviour of the redox cells.

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1. Introduction

A world-wide 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, e.g. computer power

backup, medical equipment, etc. in addition to the high power applications including load leveling, electrical vehicles, space crafts, etc. [1–4]. It acts as intermediate power source between rechargeable batteries and conventional electrolytic capacitors, offering power density higher than batteries and energy density higher than conventional capacitors. On the basis of electrochemical behaviour and charge/energy storage mechanisms, the supercapacitors are categorized in two groups: namely electrical double layer capacitors (EDLCs) and redox supercapacitors. Various forms of carbonaceous materials

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are used as electrodes in EDLCs in which charge storage is of electrostatic in nature, whereas electroactive electrode materials like hydrous RuO_2 , MnO_2 , CoO_x , etc. or most importantly conducting polymers are used which leads to the pseudo-capacitive behaviour [1–4].

Out of several electrochemically active conducting polymers, the polypyrrole has aroused considerable interest in the electrochemical applications as rechargeable batteries and capacitors electrodes [5–7]. It possesses the difficulty in polymerization in n-doped state due to its chemical/electrochemical instability, hence its utilization is concentrated to p-dopable polymer to act as positive electrodes in batteries and capacitors. Particularly in redox supercapacitors, it is widely reported as identical and symmetrical electrodes in type-I capacitors or one of the electrode (p-doped) in the asymmetrical type-II and type-III capacitors in which the other electrode is either p-doped different conducting polymer or n-doped polymer, respectively [6,7].

Most of the reports on redox supercapacitors are based on liquid electrolytes [1–4,6–8], but these are associated with the similar disadvantageous problems as observed in the liquid electrolytes based batteries, such as corrosion, leakage, bulky design, etc. The development of all-solid state redox capacitors using polymer/gel electrolytes is the current area of research, which has not been widely reported. A few recent reports include the solid state redox capacitors based on different polymer/gel electrolytes, e.g. PVA- H_3PO_4 , PEO- LiCF_3SO_3 -PEG, PMMA-EC-PC- NaClO_4 , PMMA-EC-PC- LiClO_4 , Nafion, etc. [9–13].

The aim of this paper is to present a comparative studies of the polypyrrole based all solid state redox supercapacitors fabricated using PMMA based gel electrolytes having the common perchlorate salts of different cations (PMMA-EC-PC-salts: LiClO_4 , NaClO_4 and TEAClO_4). The performance characteristics of the capacitors have been evaluated by complex impedance spectroscopy, linear sweep voltammetry with prolonged cyclic tests and constant current charge–discharge techniques.

2. Experimental details

2.1. Preparation of the materials

The polymeric gel electrolytes, comprising of PMMA-EC-PC-salts (LiClO_4 , NaClO_4 and TEAClO_4), were prepared using “solution-cast” technique. The PMMA (Average M.W. 120,000), EC, PC and salts, LiClO_4 , NaClO_4 and TEAClO_4 were obtained from Aldrich and used as received. The appropriate amount of salts were dissolved in EC:PC mixture (1:1 V/V) by stirring thoroughly to get liquid electrolytes. The optimum compositions of liquid electrolytes with different salts

(i.e. 1.0 M salts in EC:PC mixture) were mixed with different appropriate amount of PMMA. The mixtures were then kept in oven at 70 °C for about 10–12 h for gelling. Finally, the soft, semi-transparent and flexible lump materials of different compositions were obtained.

Polypyrrole films were electrochemically polymerized on indium tin oxide (ITO) coated conducting glass substrates (Balzers, sheet resistance 80 ohm cm²). The monomer, pyrrole (Merck) was distilled in vacuum before use. A single compartment three electrodes cell was used for the electro-polymerization with the platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. The electro-deposition of pPy was carried out in the cell containing 0.1 M pyrrole and 0.2 M LiClO_4 solution in acetonitrile at the constant current of 2 mA for 10 min. The solutions were purged with the dry nitrogen during electro-syntheses to eliminate the oxygen contents.

2.2. Electrochemical measurements

The bulk electrical conductivity of different compositions of gel electrolytes was evaluated using complex-impedance spectroscopy at room temperature (22 °C). The performance of the different capacitor cells was characterized using impedance analysis, linear sweep voltammetry and charge–discharge at constant current. The impedance measurements were carried out using computer controlled LCR HI TESTER (Model 3522–50, Hioki, Japan) in the frequency range from 10 mHz to 100 kHz. The signal level was kept at 10 mV. The overall capacitances ‘C’ of the capacitor cells were evaluated using the relation:

$$C = -\frac{1}{\omega Z''} \quad (1)$$

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

The linear sweep voltammetry was carried out with the help of Analytical Electrochemical Workstation (Model: AEW-2, Sycopel, UK). The capacitance values from this technique were evaluated using the relation:

$$C = \frac{i}{s} \quad (2)$$

where ‘i’ is the current and ‘s’ is scan rate.

The charge–discharge characteristics of the capacitor cells were evaluated at constant current. The discharge capacitance ‘ C_d ’ was evaluated from the linear part of the discharge curves using the relation:

$$C_d = \frac{i\Delta t}{\Delta V} \quad (3)$$

where ' i ' is the constant current and ' Δt ' is the time interval for the voltage change of ΔV . The coulombic efficiency ' η ' was calculated using the following Eq. (4) when the same current is used for charging and discharging.

$$\eta = \frac{t_D}{t_C} \times 100\% \quad (4)$$

where t_D and t_C are the times for galvanostatic discharging and charging, respectively.

3. Results and discussion

The composition of the polymeric gel electrolytes, PMMA-PC-EC-salts (LiClO_4 , NaClO_4 and TEAClO_4) were first optimized in order to get both substantially conducting and mechanically stable and flexible materials. The optimum compositions of the gel electrolytes, PMMA (20 wt%)-EC:PC (1:1 V/V)-1.0 M LiClO_4 / NaClO_4 / TEAClO_4 salts, were chosen for the construction of redox capacitors. All these gel electrolytes possess the conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ at room temperature with good mechanical strength, flexible enough to mould in the desirable area and thickness. The order of conductivity is acceptable for use in capacitor applications as they offer low resistance when these gel electrolytes are used in the film form of thickness 200–300 $\mu\text{m cm}^{-2}$. Being the flexible materials, these are able to form proper interfacial contacts for the maximum accessibility of the active electrode materials.

Different model capacitor cells of the following configuration have been constructed with polypyrrole (pPy) electrodes and three different gel electrolytes:

Cell A: pPy |PMMA-EC-PC- LiClO_4 |pPy
 Cell B: pPy |PMMA-EC-PC- NaClO_4 |pPy
 Cell C: pPy |PMMA-EC-PC- TEAClO_4 |pPy

3.1. Cyclic voltammetric tests

Fig. 1(a)–(c) shows the linear sweep voltammograms for all the capacitor cells (A–C) at different scan rates. In such sweep-reversal (cyclic) voltammetry at constant scan rates, the profile of current response is ideally a rectangle when capacitance is constant (i.e. potential independent). On the other hand, a peaked structured voltammogram is observed in the case of potential dependent capacitance showing a differential profile. In the present studies, the sweep-reversal voltammograms for all the capacitor cells (A–C) are almost close to an ideal shape of rectangle even for higher scan rates (100 mV s^{-1}), as shown in Fig. 1(a)–(c). This is characteristic of capacitive behaviour and the indicative of fast switching rate of ions at the sites of electrode-electrolyte

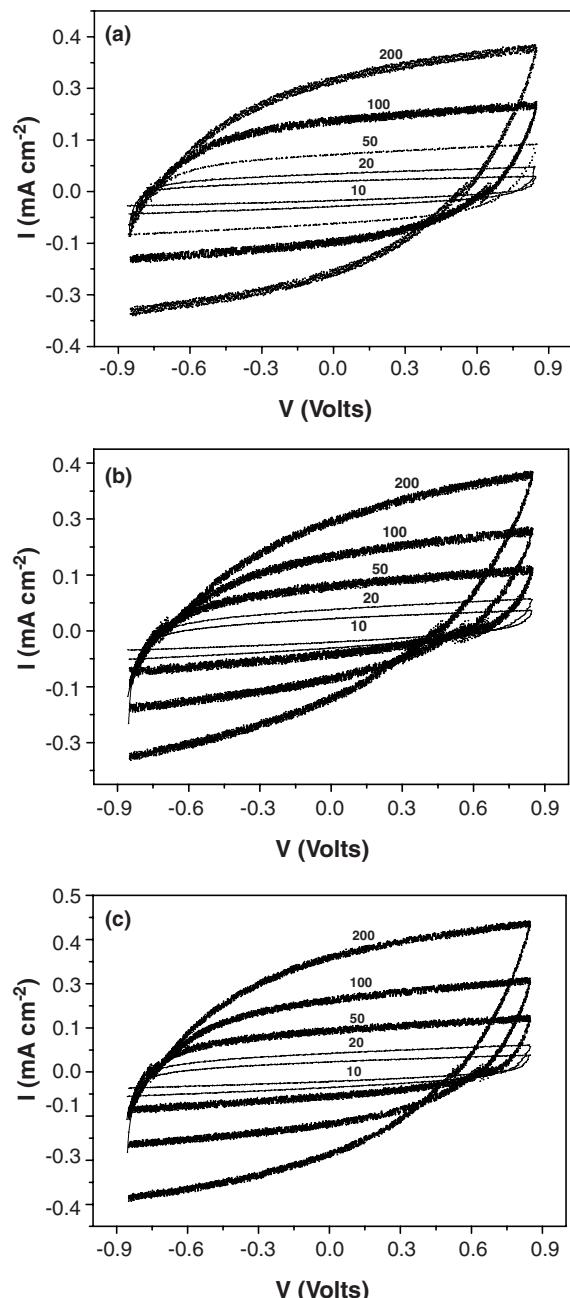


Fig. 1. Cyclic voltammograms of different capacitor cells, (a) Cell A: pPy | LiClO_4 -gel |pPy, (b) Cell B: pPy | NaClO_4 -gel |pPy and (c) Cell C: pPy | TEAClO_4 -gel |pPy at different scan rates. Scan rates (in mV s^{-1}) are marked on the figures.

interfaces. At higher scan rates (more than 100 mV s^{-1}) a slight deviation from the rectangular shapes has been observed for each cell, which is attributed to a substantial value of equivalent series resistance (ESR), present in real capacitors. The response of each capacitor cell

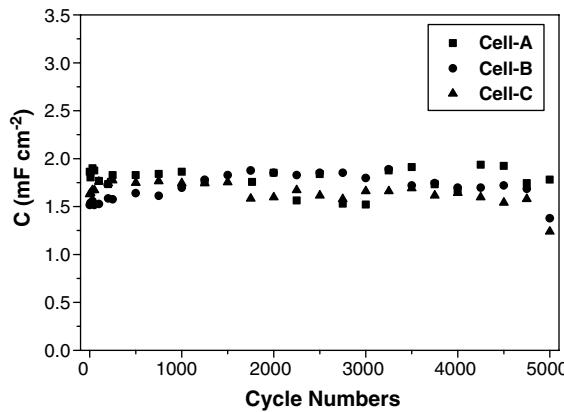


Fig. 2. Variation of the capacitance of different capacitor cells, (a) Cell A: pPy |LiClO₄-gel |pPy, (b) Cell B: pPy |NaClO₄-gel |pPy and (c) Cell C: pPy |TEAClO₄-gel |pPy as a function of voltammetric cycles at the scan rate 100 mV s⁻¹.

has been found to be dependent on scan rates, which is a characteristic of capacitor cells [1,4].

One of the most important and attractive aspect of supercapacitors over rechargeable batteries is their reversibility for large number of charge–discharge cycles. Fig. 2 refers the variation of capacitance values as a function of voltammetric cycles between −850 mV and 850 mV recorded for all the cells (A–C) at scan rate 100 mV s⁻¹. Reasonably stable and almost constant values of capacitance have been observed for each capacitors cells upto 5000 cycles. A slight decrease (fluctuation) in capacitance for initial few cycles has been observed, which is attributed to the charge consumption due to some possible faradic reaction(s) with loosely bound surface groups at the electrode electrolyte interfaces.

3.2. Impedance analysis

The complex impedance plots of different capacitor cells (A–C) are illustrated in Fig. 3(a)–(c). The polypyrrole shows the capacitive behaviour (i.e. steep rising response of Z'' asymptotically for approximately constant value of Z' , i.e. almost parallel to the Z'' -axis) in the lower frequency range up to 10 mHz with each gel electrolyte employed to fabricate redox capacitors in the present studies. The expanded portion of the higher frequency response is shown as inset in each impedance plot [Fig. 3(a)–(c)], which is the characteristic of bulk electrolyte and electrode-electrolyte interfacial properties. It can be noted that instead of the distinct semicircular spur, almost linear impedance (Z'' vs. Z') response has been observed in the higher frequency region [Fig. 3(a)–(c) insets]. This indicates the interfacial characteristics having specific porous structure of the electrodes in contact

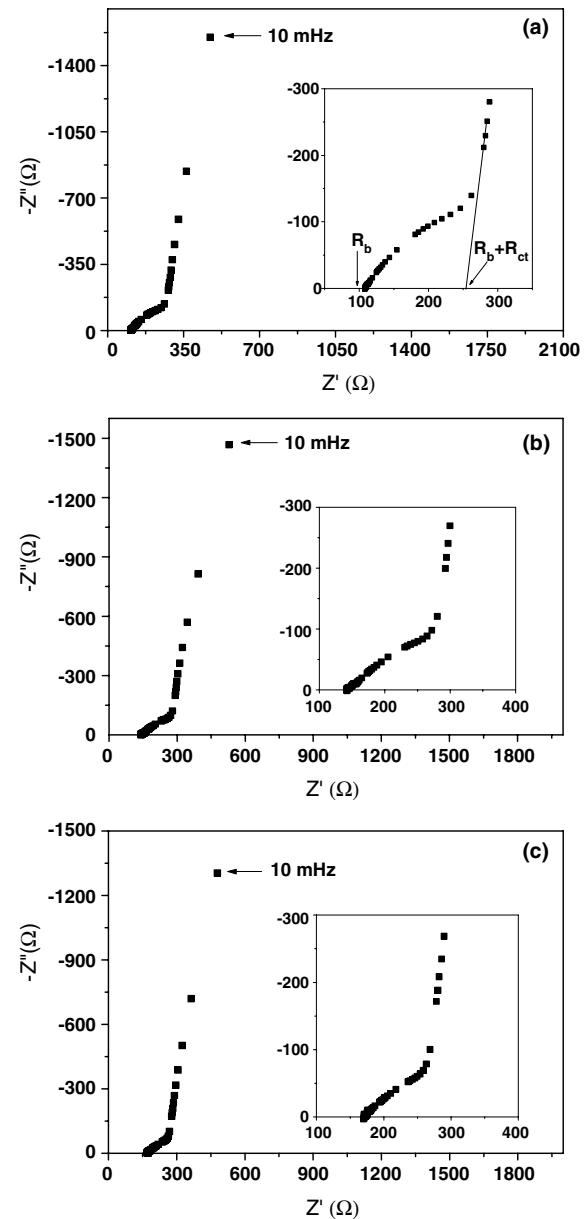


Fig. 3. Typical impedance plots of different capacitor cells, (a) Cell A: pPy |LiClO₄-gel |pPy, (b) Cell B: pPy |NaClO₄-gel |pPy and (c) Cell C: pPy |TEAClO₄-gel |pPy recorded at room temperature in the frequency range 100 kHz to 10 mHz.

with highly flexible gel electrolytes. Few workers [1,14] described the theoretical approach of the impedance response considering different possible geometries of pore structure of the electrodes. A comparison with the present experimental observations indicates that the electro-chemically deposited polypyrrole on ITO conducting glass substrates possesses almost rectangular geometry of the pores accessible to the gel electrolytes. This

Table 1
Electrical parameters of different capacitor cells from impedance analysis

Cells	R_{ct} ($\Omega \text{ cm}^2$)	R_b ($\Omega \text{ cm}^2$)	100 mHz			10 mHz		
			R ($\Omega \text{ cm}^2$)	C		R ($\Omega \text{ cm}^2$)	C	
				(mF cm^{-2}) ^a	(F g^{-1}) ^b		(mF cm^{-2}) ^a	(F g^{-1}) ^b
A	102–200	85–130	220–410	7.0–10.0	55–78	370–550	12.0–13.0	94–102
B	86–92	110–145	230–280	9.0–10.0	70–86	415–560	13.0–16.0	102–125
C	55–130	100–135	200–265	9.0–12.0	70–94	375–500	12.0–16.0	94–125

^a Overall capacitance of the cells.

^b Single electrode capacitance.

corresponds to the transmission line type RC equivalent circuit for such electrode-electrolyte interfaces.

The values of bulk electrolyte resistance, R_b and interfacial charge transfer resistance, R_{ct} have been evaluated from the intercepts of the impedance response on real (Z')-axis, as illustrated in Fig. 3(a), inset. The values of capacitance at lower frequencies 100 mHz and 10 mHz have been calculated from Eq. (1). The values of R_b , R_{ct} , overall resistances R and capacitance C for different capacitor cells have been summarised in Table 1. The values of capacitance for each capacitor cell have been observed to be in the range of 12–16 mF cm^{-2} (equivalent to the single electrode specific capacitance of 94–125 F g^{-1} mass of polypyrrole). The capacitance values are comparatively lower than the liquid electrolyte based capacitors with the same electrodes [6–8], but reasonably higher than that of the capacitors using solid conventional PEO or PVA based polymer electrolytes [9–11]. This difference is associated with the accessibility limit of the electrolytes to form interfacial contact with the active electrodes like polypyrrole. This has further been confirmed from a comparison of charge transfer and overall resistances (Table 1) with the liquid electrolytes and solid conventional polymer electrolytes based capacitors [6–11]. The application of gel electrolytes in the capacitors leads to a substantial improvement in the capacitance and resistance values over the solid conventional polymer electrolytes based capacitors due to their highly flexible nature and the higher conductivity. Further, the capacitance and resistance values have been observed to be almost in the same range for all the cells employing different gel electrolytes in the present studies (Table 1). This indicates that the types and size of the cations (Li^+ , Na^+ and TEA^+) in the gel systems do not play any effective role in the capacitive behaviour of the redox supercapacitors.

3.3. Charge–discharge tests

The capacitor cells have also been tested with the constant current charge–discharge methods. The typical charge–discharge characteristics of all the capacitor cells are shown in Fig. 4. All the cells were charged up to

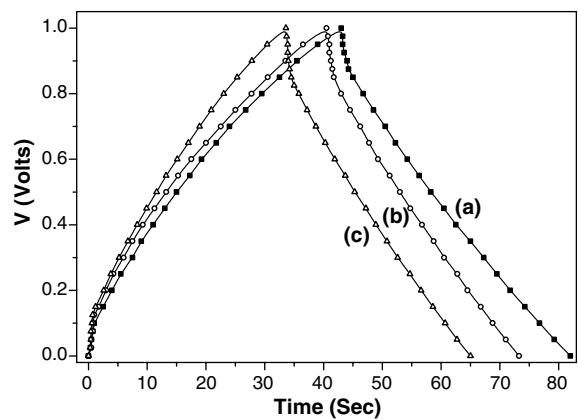


Fig. 4. Typical charge–discharge curves of different capacitor cells, (a) Cell A: pPy | LiClO_4 -gel | pPy, (b) Cell B: pPy | NaClO_4 -gel | pPy and (c) Cell C: pPy | TEAClO_4 -gel | pPy at constant current density 0.38 mA cm^{-2} .

1.0 V, which is the voltage limit of doping–dedoping of polypyrrole [6,7,9–11]. The voltage limit of the electrochemical stability of the gel electrolytes is wide enough (more than 4.0 V) for such devices. The linear portions of the discharge characteristics confirm the capacitive behaviour of all the cells. In general, a real capacitor is represented by an equivalent circuit comprising of an ideal capacitor in series with the internal resistance (R_i). The initial sudden change in voltage response with respect to time while charging and discharging has been found due to ohmic loss across the internal resistance of the cells. The internal resistances of the cells have been estimated from this voltage loss. The values of discharge capacitances have been evaluated from the linear part of the discharge characteristics using Eq. (3). The values of discharge capacitance, C_d , internal resistance, R_i and coulombic efficiency, η (evaluated using Eq. (4)) are listed in Table 2. The capacitance and internal resistance values are almost consistent with the values obtained from impedance analysis (Table 1). Fig. 5(a)–(c) represents variation of discharge capacitance, C_d and internal resistance, R_i with respect to the varying current density for the capacitor cells. Almost stable values of C_d and R_i

Table 2

Typical charge-discharge characteristics of different capacitor cells at current density of 0.38 mA cm^{-2}

Cells	$R(\Omega \text{ cm}^2)$	Discharge capacitance, C_d	Working voltage(V)	Energy density (Wh kg^{-1})	Power density (kW kg^{-1})
		(mF cm^{-2}) ^a	(F g^{-1}) ^b		
A	320–458	15.8–18.5	124–145	1.00	17.2–20.2
B	420–445	15.5–18.7	122–147	1.00	17.0–20.5
C	280–430	15.3–22.5	120–178	1.00	16.7–24.7

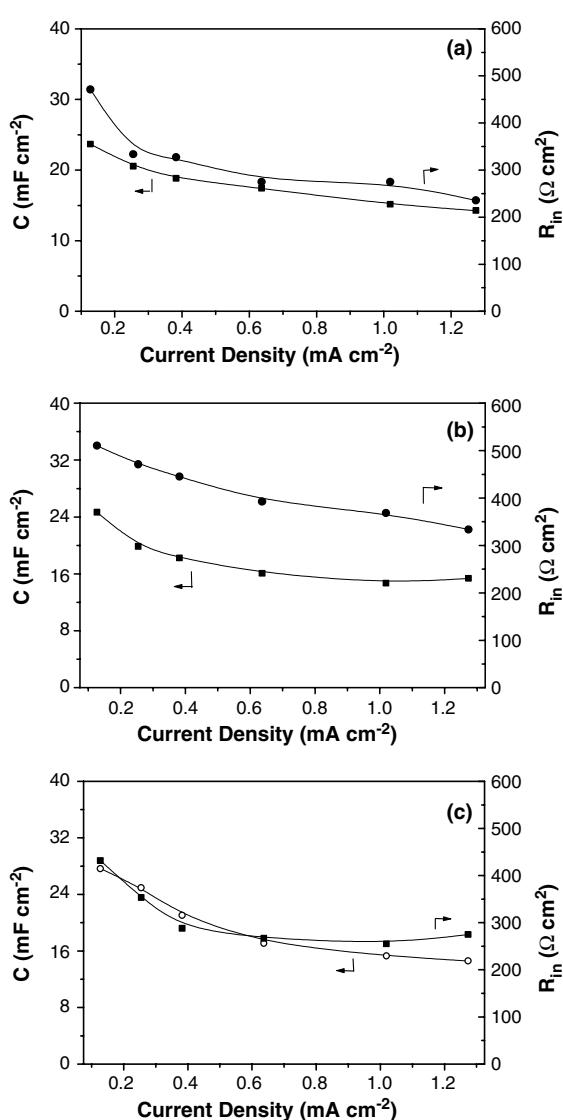
^a Overall capacitance of the cells.^b Single electrode capacitance.

Fig. 5. Variation of discharge capacitance, C_d and internal resistance R_i of different capacitor cells, (a) Cell A: pPy | LiClO_4 -gel | pPy, (b) Cell B: pPy | NaClO_4 -gel | pPy and (c) Cell C: pPy | TEAClO_4 -gel | pPy as a function of current density.

for different current densities have been observed after an initial slight decrease in the values. This decrease in the capacitance values is associated with the possible charge loss during the charge-discharge at the initial stage due to irreversible faradic reaction(s) with the foreign surface groups (most possibly hydroxyl groups) present at the interfaces. The initial decrease in the internal resistances indicates the slight improvement in the electrode-electrolyte contacts during the initial charge-discharge.

The energy density of each capacitor cell has been estimated from their corresponding values of the capacitance and the working voltage (1.0 V in the present case of polypyrrole). The power density values have been evaluated by dividing the energy density values by the discharge time of the cells [12]. The energy and power density values are also listed in Table 2. Although the energy density values are comparatively lower than the rechargeable batteries, but the power density values make such supercapacitor devices attractive from the application point of view as power sources for the peak requirements [1–4].

The coulombic efficiency of each capacitor cell (cells A–C) has been found to be in the range of 95–100%. In general the polypyrrole shows the coulombic efficiency close to 100% for the liquid electrolytes based batteries and capacitors [5]. The values observed for the polypyrrole and solid polymer electrolytes capacitors have been reported to be limited to 60–80% [9,10]. The present studies indicate that the improvement in the coulombic efficiency is owing to the possible improvement in interfacial properties of the solid-state capacitor cells due to the application of highly flexible gel electrolytes, which offer the liquid like properties.

4. Conclusions

In this paper, a comparative studies have been carried out for electrochemically deposited polypyrrole based redox supercapacitors with gel electrolytes PMMA-EC-PC-salts of different cations (Li^+ , Na^+ and TEA^+) and common anion (ClO_4^-) using various techniques such

as CV tests, a.c. impedance analysis and charge–discharge studies. The gel electrolytes, showing conductivity of the order of 10^{-3} S cm $^{-1}$ at room temperature have been found to be suitable electrolytes for their use in redox supercapacitors. All the cells show the capacitive behaviour with the larger value of capacitance of 15.3–22.5 mF cm $^{-2}$ (equivalent to single electrode specific capacitance of 120–178 F g $^{-1}$) of polypyrrole and comparatively lower values of internal resistances of the order of few hundreds ohm cm 2 owing to the flexible nature of the gel electrolytes. A comparison indicates that the types and sizes of the cations of the salts used in the gel electrolytes do not play any effective role in the capacitive behaviour of the redox capacitor cells. The energy and power density of the cells have been found to be in the range of 16.7–24.7 Wh kg $^{-1}$ and 1.6–2.8 kW kg $^{-1}$, respectively. The substantial improvements in the coulombic efficiency of the polypyrrole based capacitor cells have been observed (close to 100%) due to the application of highly flexible gel electrolytes showing liquid like properties.

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