Short communication

Enhanced electrochemical stability of all-polymer redox supercapacitors with modified polypyrrole electrodes

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Abstract

Redox supercapacitors are attracting increasing attention as high power electrochemical sources and can either be coupled with batteries to provide peak power or replace batteries for memory back-up. In the present work, all-polymer solid-state supercapacitors with $LiClO_4$ and $LiCF_3SO_3$ doped polypyrrole electrodes and P(VDF-HFP)-PMMA based polymer gel electrolyte are fabricated. The polypyrrole electrodes are irradiated with 160 MeV Ni^{12+} ions at 5×10^{10}, 5×10^{11} and 5×10^{12} ions cm^{-2}. A comparative study is made between unirradiated and irradiated supercapacitors with polypyrrole-based electrodes. An average capacitance of about 200 F gm^{-1} is obtained. On successive charging and discharging, the capacitance decreases for supercapacitors with unirradiated electrodes but remains stable when irradiated electrodes are used. In addition, the capacitance is slightly decreased compared with that for unirradiated electrodes. Charge–discharge studies show a decrease in total charge–discharge time for supercapacitors with irradiated electrodes. The capacitance values calculated from cyclic voltammograms are higher than those determined from charge–discharge plots due to the added contribution of a leakage current. The coulombic efficiency of all the supercapacitors is about 90%.
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1. Introduction

There is increasing interest in the application of electrochemical systems under conditions in which the electrical power demand is highly time-dependent, often in the form of short-term pulses. Because of the general observation that capacitors can be used to provide short electrical pulses, attention has focused on the use of electrochemical systems that exhibit capacitor-like characteristics. The concept of providing large quantities of electrical power, comparable in magnitude with that attainable in batteries, in reasonably small capacitors was proposed about five decades ago [1,2]. Only in the past 15 years or so, however, has the electrochemical charge-storage device variously called a 'supercapacitor' or an 'ultra capacitor' [3] become the subject of practical and commercial development for use in a hybrid mode

with batteries for electric vehicle power systems for the starting, lighting and ignition of internal combustion engine vehicles, and for small-scale consumer electronics [3].

Electrochemical supercapacitors bridge the gap between conventional capacitors and batteries. Supercapacitors have two unique characteristics, namely, large capacitance and high storage and delivery of power. Conducting polymers are very promising electrode materials for redox capacitors as they are less expensive than other electrode materials, e.g., noble metal oxides, may be easily synthesized in the form of extended surface thin films, and can store charge throughout their entire volume [4]. Swift heavy ion (SHI) irradiation of polymers has been found to produce useful modifications in their physical and chemical properties. Increases in hardness, strength and wear resistance [5–7], electrical conductivity [8–10], density [9], chain length [6–8], crystallinity [7–9] and solubility [5–9], as well as improvements in optical transmission [7–10] properties of the polymers have been reported. Many studies of ion irradiation with low energy (<1 MeV) on intrinsically

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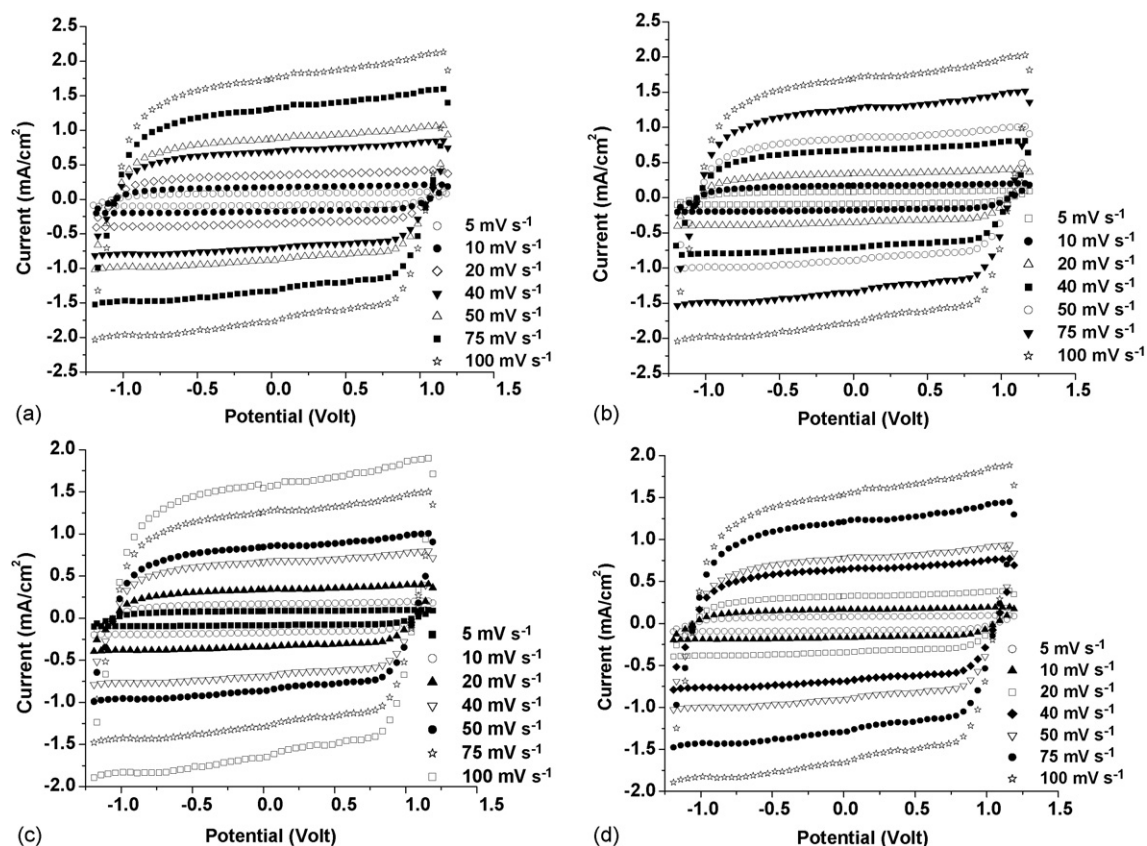 *E-mail address:* abu@tezu.ernet.in (A.M.P. Hussain).

Fig. 1. Cyclic voltammograms of supercapacitors with $LiClO_4$ doped polypyrrole electrodes: (a) before irradiation; after irradiation at (b) 5×10^{10}, (c) 5×10^{11} and (d) 3×10^{12} ions cm^{-2}.

electron-conducting polymers have been undertaken [11–19], but it would appear that our studies [20–22] were the first to show that SHI irradiation with high energy (>80 MeV) enhances the electrochemical stability of polypyrrole and polyaniline electrodes. In the present investigation, all-polymer redox supercapacitors are fabricated with $LiClO_4$- and $LiCF_3SO_3$-doped polypyrrole electrodes that are either unirradiated or 160 MeV Ni^{12+} ion irradiated. The electrolyte was a PVDF-HFP (20 wt.%)–PMMA (10 wt.%)–$LiCF_3SO_3$ (10 wt.%)–PC + DEC (57 wt.%)–SiO_2 (3 wt.%) polymer gel. Cyclic voltammetry, charge–discharge cycling and cycle-life stability tests are performed to evaluate supercapacitor performance.

2. Experimental

The polypyrrole films were electrochemically synthesized on glass substrates coated with indium tin oxide (ITO) from a solution of pyrrole monomer (Aldrich, USA) and dopant $LiClO_4$ and $LiCF_3SO_3$ (Aldrich, USA) in acetonitrile (LOBA, India). A potentiodynamic method was used. The monomer was distilled under reduced pressure and stored in the dark prior to use and other chemicals are employed as-received. The PVDF-HFP (20 wt.%)–PMMA (10 wt.%)–$LiCF_3SO_3$ (10 wt.%)–PC + DEC (57 wt.%)–SiO_2 (3 wt.%) gel polymer electrolyte was prepared by a solution casting technique. All-polymer, solid-state, redox supercapacitors were fabricated with either unirradiated or irradiated polypyrrole electrodes and had the following

configuration:

ITO|polypyrrole|polymer gel electrolyte|polypyrrole|ITO

The ITO-coated glass acts as current-collector on both sides of the capacitor. Cyclic voltammograms of the supercapacitors were recorded using a potentiostat (Sycopel Scientific, UK) and galvanostatic charge–discharge measurements were carried out with a battery testing unit (Maccor 2300) connected to a personal computer.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammograms of supercapacitors with $LiClO_4$ and $LiCF_3SO_3$ doped unirradiated or irradiated polypyrrole electrodes and recorded at different scan rates are shown in Figs. 1 and 2, respectively. The capacitances of the supercapacitors are calculated from these data by means of the relation [23]:

$$C = \frac{I}{s} \tag{1}$$

where I is the current and s is the sweep rate in V s^{-1}.

At lower scan rates, all of the supercapacitors give cyclic voltammograms of nearly ideal rectangular shape. At higher scan rates ($\sim$100 mV S^{-1}), however, the shapes deviate from
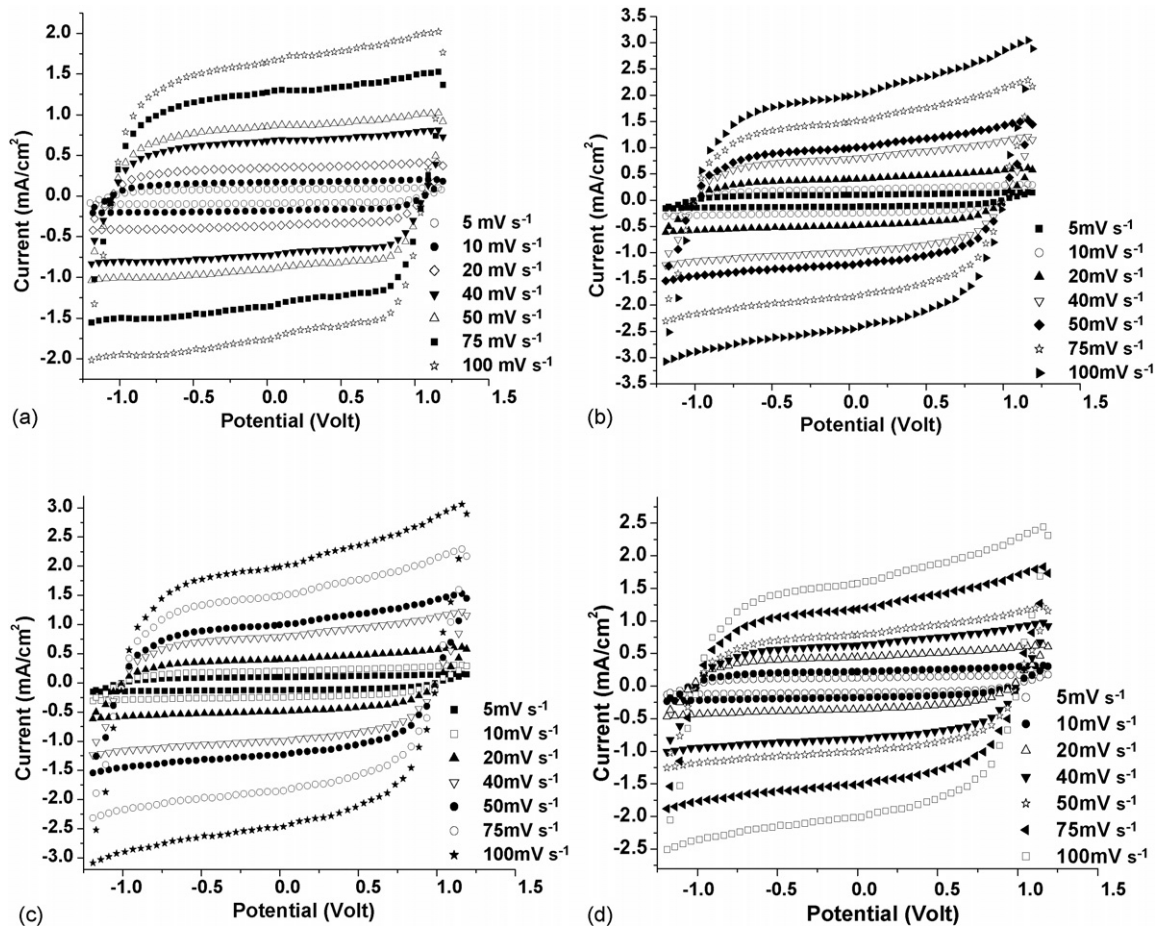
Fig. 2. Cyclic voltammograms of supercapacitors with LiCF$_3$SO$_3$ doped polypyrrole electrodes: (a) before irradiation; after irradiation at (b) 5×10^{10}, (c) 5×10^{11} and (d) 3×10^{12} ions cm^{-2}.

the rectangular shape and an increase in current is observed at high potentials. This can be attributed to the redox property of the conducting polymer electrodes which become oxidized. This feature becomes more pronounced with increase in the scan rate.

3.2. Electrochemical stability

The stability of the supercapacitors was evaluated for 10,000 cycles and the capacitance values were calculated at 1000-cycle intervals. Stability plots of the supercapacitors, in terms of capacitance versus cycle number, are presented in Fig. 3. The initial decrease in the capacitance is attributed to an irreversible faradic reaction occurring at the electrode surface due to the presence of volatile surface groups, e.g., OH$^-$, CN$^-$, CH$_3^+$, which cause loss of charge. This behaviour occurs to a lesser degree for those supercapacitors with irradiated electrodes and is considered to result from suppression of the reactive volatile surface groups, which are either stabilized or removed from the electrode surface it should be noted, however, that the initial capacities are slightly less than those given by unirradiated electrodes. Stabilization of the surface groups on the former electrodes may occur due to cross-linking that is induced by huge energy deposition via an electronic energy loss mechanism upon SHI irradiation [5–10]. The volatile surface groups may also evaporate due to

energy transfer upon SHI irradiation. The concentration of the volatile surface groups decreases with increase in the level of SHI irradiation and hence gives rise to a concomitant rise in electrochemical stability.

3.3. Charge–discharge characteristics

The galvanostatic charge–discharge characteristics at 100 μA of supercapacitors with either unirradiated or irradiated polypyrrole electrodes are presented in Fig. 4. The discharge capacitance of the capacitor cell can be evaluated from the linear region of the plots using the relation:

$$C = i \frac{\Delta t}{\Delta V} \qquad (2)$$

where ΔV is the change in potential for a time interval of Δt. The characteristic parameters of the supercapacitors with either unirradiated or irradiated LiClO$_4$ or LiCF$_3$SO$_3$ doped polypyrrole electrodes are shown in Figs. 5 and 6, respectively.

The discharge capacitances of the supercapacitors determined from charge–discharge plots are slightly less than those calculated from cyclic voltammograms. This may be because the current in a cyclic voltammogram is in part due to an electronic current through the electrolyte that results from the continuous
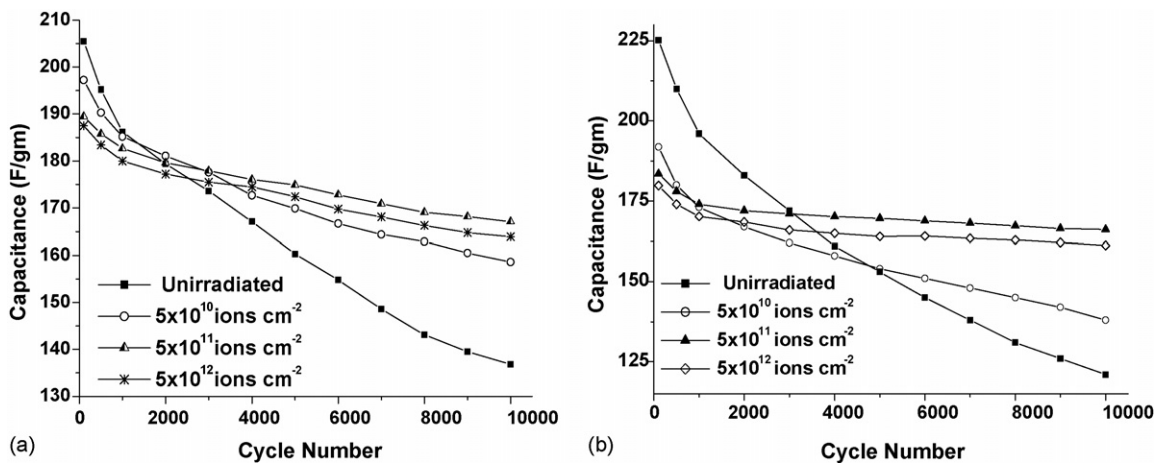
Fig. 3. Stability plot of supercapacitors with (a) LiClO$_4$ and (b) LiCF$_3$SO$_3$ doped polypyrrole electrodes.
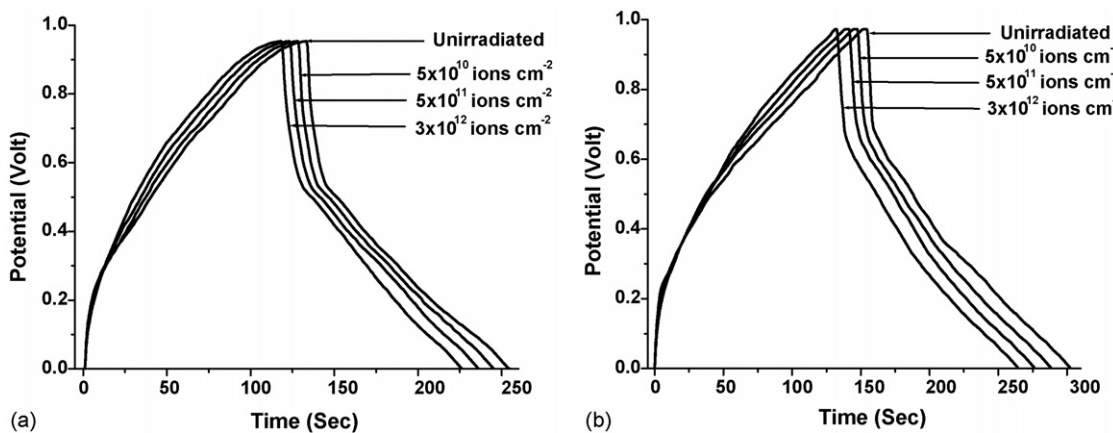

Fig. 4. Charge–discharge plot of supercapacitors with (a) LiClO$_4$ and (b) LiCF$_3$SO$_3$ doped polypyrrole electrodes.

sweep of the polarity of the electrode potential. Decrease in the total charge–discharge time of the supercapacitors with irradiated electrodes is observed in the plots with a small increase in coulombic efficiency. This feature may be attributed to the increase in conductivity of the polymer electrodes after irradiation, which supports faster charge transport in the electrodes.

The coulombic efficiency η of the capacitor cell can be calculated from the galvanostatic charge–discharge experiments as
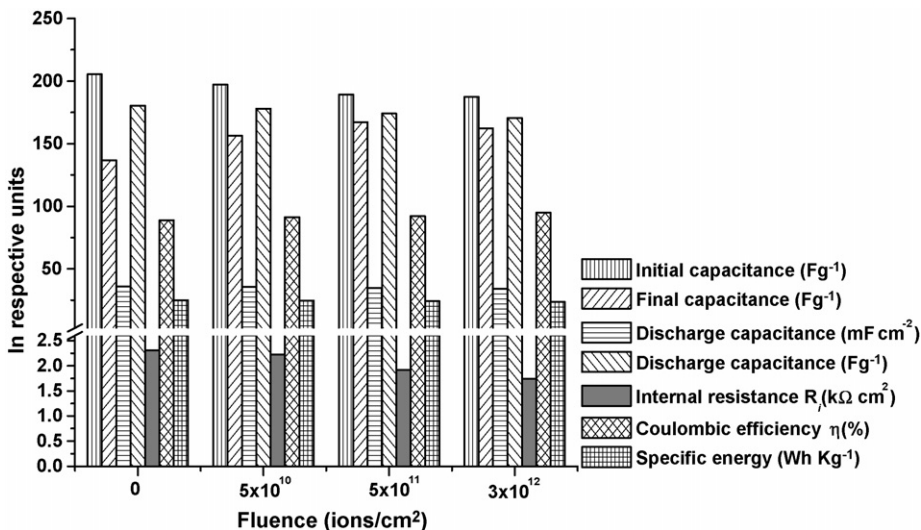

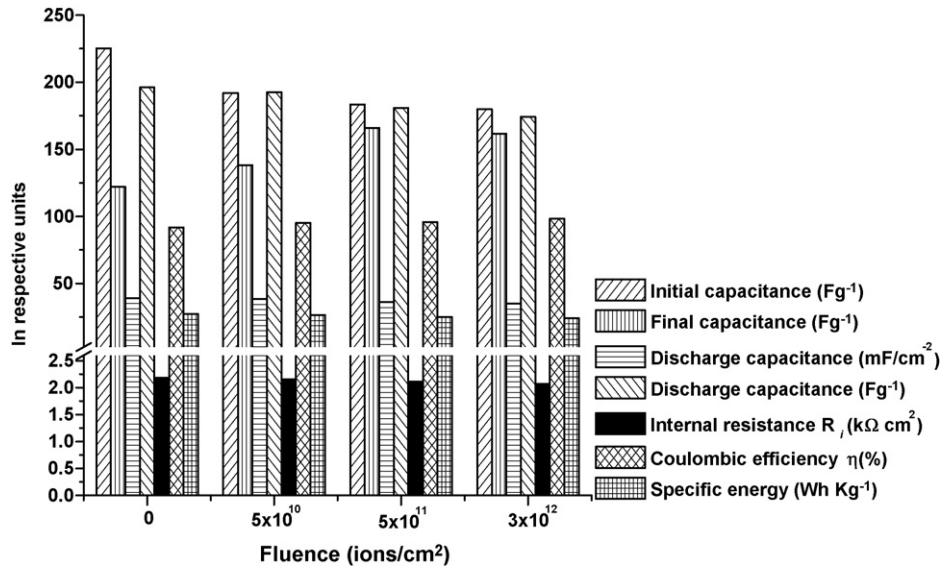Fig. 5. Characteristic properties of supercapacitors with irradiated, LiClO$_4$ doped, polypyrrole electrodes.

Fig. 6. Characteristic properties of supercapacitors with irradiated, $LiCF_3SO_3$ doped, polypyrrole electrodes.

follows.

$$\eta = \frac{\Delta t_D}{\Delta t_C} \times 100\% \qquad (3)$$

where Δt_D and Δt_C are the times of charging and discharging, respectively.

The internal resistance of the supercapacitors is determined from the steep rise in the potential of the charge–discharge plot using the relation:

$$R = \frac{V}{i} \qquad (4)$$

where i is the charging current and V is the magnitude of the vertical rise/fall of potential during charging/discharging. A very small decrease in internal resistance of the supercapacitors is found after irradiation (Figs. 5 and 6), which can be attributed to the increase of conductivity of the polymer electrodes upon irradiation. This decrease, however, is not as much as the increase obtained in conductivity [20,21]. Thus, it can be inferred that the internal resistance arises mostly from the interfacial resistance of the electrode|electrolyte contact, which depends on the surface morphologies of the electrodes and the electrolyte. Scanning electron micrographs of unirradiated and irradiated polypyrrole
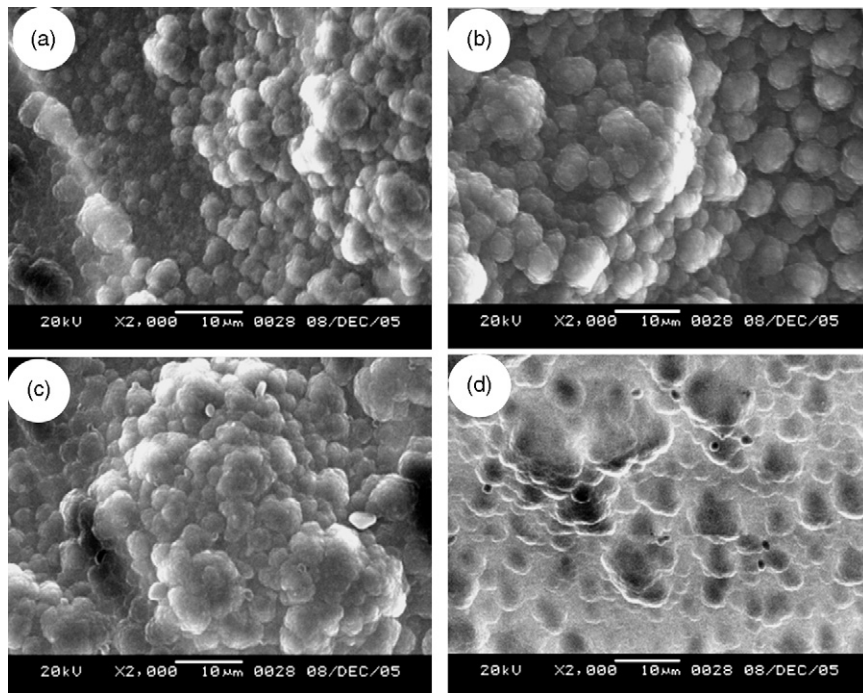

Fig. 7. Scanning electron micrograph of $LiClO_4$ doped polypyrrole films: (a) before, irradiation; after irradiation at (b) 5×10^{10}, (c) 5×10^{11} and (d) 3×10^{12} ions cm^{-2}.
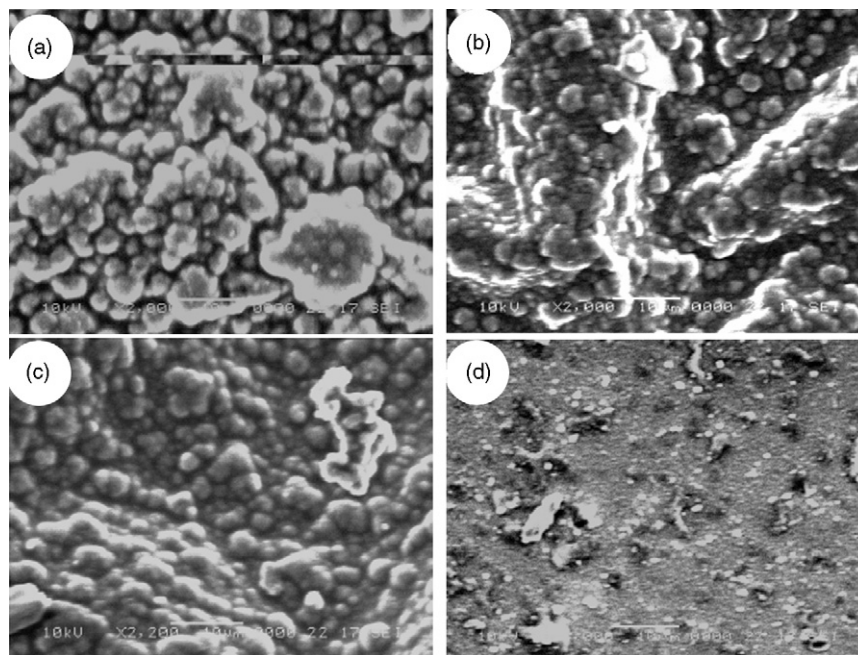
Fig. 8. Scanning electron micrograph of $LiCF_3SO_3$ doped polypyrrole films: (a) before, irradiation; after irradiation at (b) 5×10^{10}, (c) 5×10^{11} and (d) 3×10^{12} ions cm^{-2}.

electrode films doped with $LiClO_4$ or $LiCF_3SO_3$ are presented in Figs. 7 and 8. The polymer films become dense and smooth upon irradiation and the density increases with increase in the SHI level as a result of the huge electronic energy transfer of the irradiating ions. This improved morphology of the polymer films creates a larger electrode|electrolyte contact surface area and hence leads to a decrease in the resistance of the supercapacitors.

The specific energy of the supercapacitors with conducting polymer electrodes is calculated using the relation:

$$E_d = \tfrac{1}{2}CV^2 \qquad (5)$$

where C is the discharge capacitance of the electrode material (in F g^{-1}) and V is the working potential, i.e., the highest potential at which the supercapacitor exhibits capacitive behaviour. A slight decrease in the specific energy of the supercapacitors with irradiated electrodes is observed on account of a slight decrease in the capacitance with the working potential remaining almost the same as that for unirradiated electrodes.

4. Conclusions

Solid-state, all-polymer, redox supercapacitors fabricated using electrochemically deposited and SHI irradiated polypyrrole conducting polymer films as electrodes and a PVDF-HFP (20 wt.%)–PMMA (10 wt.%)–$LiCF_3SO_3$ (10 wt.%)–PC + DEC (57 wt.%)–SiO_2 (3 wt.%) polymer gel electrolyte show promising results. Though the capacitance and coulombic efficiency are slightly decreased, the cyclic electrochemical stability shows a remarkable improvement. The initial sharp decrease in capacitance observed with unirradiated electrodes is reduced on irradiation. This is attributed to the removal (or stabilization) of volatile surface groups such as OH^- CN^-, CH_3^+ from the elec-

trode surface due to the deposition of energy from the SHI ion beam. Slight decreases in the internal resistance of the supercapacitors are observed on SHI irradiation due to an accompanying increase in the conductivity of the polymer electrodes. Decreases in the total charge–discharge times for supercapacitors with SHI irradiated electrodes may be due to the increase in conductivity of the polymer electrodes, that gives rise to faster charging and discharging of the supercapacitors. Overall, it can be inferred that SHI irradiation is a useful technique for modification of the conducting polymer electrodes for application in supercapacitors that results in enhanced electrochemical stability, though at the cost of a slight lowering in capacitance.

Acknowledgements

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