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

S.A. Hashmi [a,*], Ashok Kumar [b], S.K. Tripathi [a]

[a] *Department of Physics, North Eastern Regional Institute of Science and Technology, Nirjuli (Itanagar) 791 109, Arunachal Pradesh, India*

[b] *Department of Physics, Tezpur University, Tezpur, Napaam 784 028, Assam, India*

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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 $(C_2H_5)_4N^+$ (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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Keywords: Redox supercapacitors; Polypyrrole; Gel electrolytes; Poly methyl methacrylate (PMMA)

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 carboneous materials

* Corresponding author. Tel.: +91 360 225 7734; fax: +91 360 224 4307.
E-mail address: hashmisa2002@yahoo.co.in (S.A. Hashmi).

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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 cm^2). 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:

$$C = -\frac{1}{\omega Z''} \tag{1}$$

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:

$$C = \frac{i}{s} \tag{2}$$

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:

$$C_d = \frac{i\Delta t}{\Delta V} \tag{3}$$