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Effects of 160 MeV Ni^{12+} ion irradiation on polypyrrole conducting polymer electrode materials for all polymer redox supercapacitor

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Abstract

Electronically conducting polymers are suitable electrode materials for high performance supercapacitors, for their high specific capacitance and high dc conductivity in the charged state. Supercapacitors and batteries are energy storage and conversion systems which satisfies the requirements of high specific power and energy in a complementary way. Ion beam {energy > 1 MeV} irradiation on the polymer is a novel technique to enhance or alter the properties like conductivity, density, chain length and solubility.

Conducting polymer polypyrrole thin films doped with $LiClO_4$ are synthesized electrochemically on ITO coated glass substrate and are irradiated with 160 MeV Ni^{12+} ions at different fluence 5×10^{10}, 5×10^{11} and 3×10^{12} ions cm^{-2}. Dc conductivity measurement of the irradiated films showed 50–60% increase in conductivity which is may be due to increase of carrier concentration in the polymer film as observed in UV–Vis spectroscopy and other effects like cross-linking of polymer chain, bond breaking and creation of defects sites. X-ray diffractogram study shows that the degree of crystallinity of polypyrrole increases in SHI irradiation and is proportionate to ion fluence. The capacitance of the irradiated films is lowered but the capacitance of the supercapacitors with irradiated films showed enhanced stability compared to the devices with unirradiated films while characterized for cycle life up to 10,000 cycles.

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1. Introduction

Organic conducting polymers are getting much interest due to their high dc conductivity, high specific capacitance in doped state [1]. One of the most interesting conducting polymers, polypyrrole, has good environmental stability, good mechanical properties, high conductivity, and its synthesis is easy. These properties are promising for applications such as gas sensors [2,3], biosensors [4], molecular electronics, actuators [5], and light emitting diodes [6]. Organic materials provide the opportunity to fabricate potentially inexpensive, flexible, and lightweight, optoelectronic components [7]. Organic device has received great attention for high capacity, low power consumption, and low cost. Electronic and optoelectronic applications of semiconducting polymers often require high current densities that can be achieved by either heavy doping or high levels of charge injection.

Since polymers are low-mobility materials (typically less than 10^{-2}–10^{-1} $cm^2 V^{-1} s^{-1}$) high current densities imply high concentrations of charge carriers. Another notorious feature of disordered organic materials is strong localization of charge carriers in potential wells formed by single molecules or conjugated molecular segments [8]. Concomitantly, charge transport can only occur via carrier hopping within a positionally random and energetically disordered system of localized states.

The physical properties of polypyrrole films largely depend on both the sample preparation methods and the nature of the dopant. It has recently been shown [9] that a lower polymerization temperature of polypyrrole leads to higher electrical conductivity. This increase in conductivity is speculated as due to improved ordering and morphology even though a direct evidence of ordering has not yet been provided. Since conductivity change of a polypyrrole film is very sensitive to changes in the chemical environment, it has been considered to be a promising gas sensor for polar molecules, such as water and ammonia [10,11].

The concept of being able to store, in reasonably small capacitors, relatively large quantities of electrical energy, comparable in magnitude at least with storage energy-densities attainable in batteries, was proposed already 47 years ago [12]. However, only over the past 14 years or so have such devices [13] variously called 'supercapacitor' or 'ultra capacitor', became subject to practical commercial development for possibility of utilizing them in a hybrid configuration for electric vehicle power system and for starting, lighting and ignition in regular internal combustion engine powered vehicles, as well as for some other smaller scale applications. Two principal types of supercapacitor have been investigated, developed and tested: (i) the double-layer capacitor, and (ii) the redox or ad-species pseudo-capacitor, the later one first developed at University of Ottawa [14].

Enhancement of the electrical conductivity of both insulating and conducting polymers and generation of active sites for surface physical and surface chemical modification of polymers, ion beam irradiation is a very effective technique [15]. The primary phenomenon associated with ion beam and polymer interactions are cross-linking, chain scission and emission of atoms, molecules and molecular fragments [15,16].

Swift heavy ion (SHI) irradiation of conducting polymers is a new area of research. Many experiments of ion irradiation with low energy (energy < 1 MeV) on intrinsically electron conducting polymers were reported by some workers [17–25], but irradiation with high energy (energy > 80 MeV) is a new work. The low energy irradiation is in fact ion implantation and if electro-active ion is implanted that may be referred as doping by irradiation. In high energy ion irradiation, the electronic energy loss of the incident ion is released into (i) radiative decay and (ii) production of new reactive species (radicals, gases) and defects (instauration, scission, cross-link) and heat. In some cases, amorphous samples get modified into crystalline species after ion irradiation.

2. Experimental

Monomer pyrrole (Aldrich, USA) was distilled under reduced pressure and stored in darkness prior to use. Dopant salt $LiClO_4$ and solvent acetonitrile (Aldrich, USA) are used as received.