

Reduced Graphene Oxide – Conducting Polymer Nanocomposites for Supercapacitor Applications and Swift Heavy Ion Irradiation Effects

Abstract

The increasing world-wide demand for a novel, eco-friendly and sustainable energy storage device is one of the major challenges facing humanity in the 21st century. This need can likely be met through the development of electrochemical energy storage devices that can reduce the threat of global warming and climate change. Electrochemical capacitors also referred to as supercapacitors are under serious consideration as alternative energy sources due to their high power density and long cycle life than that of secondary batteries. These supercapacitors are attractive for a variety of applications like memory back-up, hybrid electric vehicle, renewable energy sources and portable electronics. Supercapacitors store charge by two different mechanisms, (i) by electrostatic charge accumulation known as electric double layer capacitance (EDLC) and (ii) by faradaic charge transfer reactions at the electrode-electrolyte interface, termed as pseudocapacitance. EDLCs exhibit high power density and long cycle life upto 10^6 cycles and are exhibited by carbon based electrode materials like carbon nanotubes, graphene, activated carbons etc. However, their low specific capacitance and energy density pose a challenge in their applications. On the other hand, conducting polymers and transition metal oxides based electrodes store charge by pseudocapacitive mechanism and possess high specific capacitance and energy density but they suffer from low power density and limited cycle life due to the repeated volume changes at the electrode-electrolyte interface caused by faradaic redox reactions. In order to develop an advanced supercapacitor device, enormous research has been focused to combine the two charge storage mechanisms to develop hybrid supercapacitors. In hybrid supercapacitors, both electrostatic and faradaic charge storage processes are utilized in a single electrode to achieve high specific capacitance and energy density without sacrificing the power density and cycle life.

Conducting polymer nanostructures of polypyrrole (PPy), polyaniline (PAni), poly(3,4-ethylene dioxythiophene (PEDOT) etc. are promising electrode materials

owing to their tunable electrical conductivity, controllable morphology, low cost, redox reversibility and high pseudocapacitance. In addition, the nanotubular structure of conducting polymers is better suited for electrochemical applications because of availability of both of its interior and exterior surfaces for charge storage as well as its effective charge transport along one controllable direction. Synthesizing nanocomposites of conducting polymers with carbon based materials is an effective approach to combine both EDL and faradaic charge storage mechanisms to achieve improved electrochemical performance. Graphene and its derivatives such as graphene oxide (GO), reduced graphene oxide (RGO) etc. are the most preferred carbonaceous materials due to their large specific surface areas, low density, high electrical conductivity and thermal stability. Incorporating graphene and its derivatives within conducting polymers to form nanocomposite electrodes can overcome the shortcomings of both the individual constituents and can boost the electrochemical performance of the electrode. In such hybrid nanocomposite electrodes, conducting polymers can provide high specific capacitance and energy density, while graphene can serve as an underlying conductive network that can enhance the charge transfer rate and cycle life. Moreover, the tendency of graphene sheets to re-aggregate due to their interlayer van der Waals interaction could be minimized by the presence of conducting polymer nanostructures as spacers between them. The electrochemical performance of a supercapacitor can be further improved by modifying the electrode surface. An electrode with a porous morphology can enhance electrode-electrolyte interfacial interaction and can provide short electrolyte ion diffusion pathways across a densely packed bulk electrode for charge storage. Swift heavy ion (SHI) irradiation is an effective technique to modify the electrode surface in a controlled manner. A wide range of SHI with different energies and fluences can be utilized to selectively tailor the morphology, structure, electrical and electrochemical properties of materials. The incident swift heavy ions transfer energy of about 1-10 keV/Å through electronic excitation and ionization of the target material, which makes it a unique tool over other methods for producing exotic and diverse effects in the target material like defect annealing, cluster of point defects, carbonization and formation of cylindrical ion tracks. The cylindrical ion tracks produced by energetic SHI along each ion impact site provide a way to produce randomly distributed pores on the electrode surface.

In the present thesis, two different systems of reduced graphene oxide–polypyrrole nanotubes (RGO-PPyNTs) and reduced graphene oxide–polyaniline nanotubes (RGO-PAniNTs) nanocomposites have been synthesized, and their physico-chemical and electrochemical properties have been investigated for supercapacitor electrodes application. In each system, the nanocomposite sample exhibiting the highest electrochemical performance has been irradiated with 85 MeV C^{6+} swift heavy ions with a view to modify the electrochemical performance. In the first system, nanocomposites of RGO-PPyNTs have been synthesized by *in situ* reduction of graphene oxide (GO) in presence of PPyNTs as spacers to prevent the re-stacking of RGO nanosheets. Four nanocomposites have been synthesized by varying the concentration of GO as 5, 10, 20 and 40 wt. % with respect to PPyNTs. The variations in the morphology, structure, thermal stability, electrical conductivity and electrochemical performance of the nanocomposites with different RGO concentration have been studied. In the second system, the RGO-PPyNTs nanocomposite with 40 wt. % of RGO exhibiting the highest electrochemical performance parameters has been irradiated with 85 MeV C^{6+} ions at four different fluences of 6×10^{10} , 3.6×10^{11} , 2.2×10^{12} and 1.3×10^{13} ions cm^{-2} . The fluence dependent modifications in the physico-chemical and electrochemical properties of the nanocomposite have been investigated. In the third system, nanocomposites of RGO-PAniNTs have been synthesized by *in situ* reduction of GO in presence of PAniNTs as spacers between RGO nanosheets. The amount of GO has been varied as 5, 10, 20 and 40 wt. % with respect to PAniNTs and the morphological, structural, thermal, electrical and electrochemical properties of the nanocomposites have been investigated. In the fourth system, the RGO-PAniNTs nanocomposite showing the best electrochemical performance have been irradiated with 85 MeV C^{6+} ions at four different fluences of 6×10^{10} , 3.6×10^{11} , 2.2×10^{12} and 1.3×10^{13} ions cm^{-2} . The SHI induced modifications in the specific surface area, porosity, surface wettability, thermal, electrical and electrochemical properties of the nanocomposite at different fluences have been studied and compared with that of the pristine (unirradiated) nanocomposite.

The present thesis comprises eight chapters. **Chapter 1** begins with the overview of different types of electrochemical energy storage devices such as batteries, fuel cells, electrolytic capacitors and electrochemical supercapacitors. The importance of supercapacitors, their historical background, classification, charge

storage mechanisms and applications in diverse fields have been described. Different types of electrode and electrolyte materials that have been investigated for supercapacitor applications with an emphasis on conducting polymer and graphene electrodes have been discussed. This is followed by a brief description of swift heavy ion irradiation, their different processes of energy loss during passage through materials and their effects on conducting polymers. The chapter ends with the scope of the thesis and statement of the thesis problem.

The different theoretical models and mechanisms that describe the charge storage processes across the interface have been reviewed in **Chapter 2**. In this chapter, the factors that determine the charge storage efficiency of a supercapacitor and the theories of cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) have been discussed. Theories and methods employed to calculate the specific surface area, porosity and surface energy have also been included. Finally, the models used to describe the interaction of swift heavy ions with solid target material have been presented.

The materials and methods used for the synthesis of PPyNTs, PAniNTs, RGO and their nanocomposites have been discussed in **Chapter 3**. The synthesis procedure and formation mechanism of RGO-PPyNTs and RGO-PAniNTs nanocomposites have been described. The principles of different characterization techniques used in the present thesis work viz., HRTEM, SEM, XRD, FTIR, micro-Raman spectroscopy, TGA, I-V characteristics, contact angle and N₂ adsorption-desorption measurements have been discussed. Electrochemical characterization techniques used to calculate different electrochemical parameters viz., specific capacitance, coulombic efficiency, energy density, power density and cycle life of the pristine components and the nanocomposites have been highlighted.

Chapter 4 presents the synthesis and characterization of RGO-PPyNTs nanocomposites with different RGO concentration synthesized by *in situ* reduction of GO in presence of PPyNTs as spacers. Four nanocomposites have been synthesized by varying the concentration of GO as 5, 10, 20 and 40 wt. % with respect to PPyNTs. A homogeneous distribution of PPyNTs onto the RGO nanosheets with an increase in RGO concentration is observed from SEM images. HRTEM micrographs confirm paper-like morphology of RGO and tubular structure of PPyNTs with an average outer diameter of 132 nm. The crystallinity of the nanocomposites increases with increase in RGO concentration as revealed by XRD

patterns. FTIR spectra depict the shifting of characteristic bands of PPyNTs in the nanocomposites towards higher wave numbers, which indicates π - π interactions between RGO and PPyNTs. Thermal degradation of the nanocomposites has been examined in the temperature range of 50-700 °C, which shows an increase in thermal stability of the nanocomposites with increase in RGO concentration. The current-voltage characteristics of the nanocomposites display decreased non-linear behavior with increase in RGO loading. The nanocomposites exhibit increased conductivity with increasing RGO concentration attaining the maximum value of 4.47 S cm⁻¹ for 40 wt. % of RGO loading. The CV curves of the nanocomposites display improved rectangular shape upon incorporation of RGO indicating increasing contribution of EDLC in the nanocomposites with increase in RGO concentration. The discharge duration of the nanocomposites increases in presence of RGO as recorded from the GCD measurements, which signifies enhanced specific capacitance of the nanocomposites. The specific capacitance increases from 128 F g⁻¹ for pristine PPyNTs to 299 F g⁻¹ for the nanocomposite with a RGO loading of 40 wt. %. A maximum coulombic efficiency of 96%, energy density of 24 W h kg⁻¹ and power density of 192 W kg⁻¹ have been obtained for RGO-PPyNTs nanocomposite with 40 wt. % of RGO. EIS studies indicate a lower equivalent series resistance of 6.95 Ω and charge transfer resistance of 4.6 Ω for RGO-PPyNTs nanocomposite as compared to 12.51 Ω and 37.45 Ω for pristine PPyNTs, respectively. The cyclic stability increases from 59% for pristine PPyNTs to 77% for the nanocomposite electrode with 40 wt. % of RGO after 1000 cycles.

Chapter 5 deals with the swift heavy ion irradiation effects of 40 wt. % RGO-PPyNTs nanocomposite, which exhibited the highest electrochemical performance as discussed in Chapter 4. The nanocomposite has been irradiated with 85 MeV C⁶⁺ swift heavy ions at four different fluences and the fluence dependent properties of the nanocomposite have been investigated. Widening of pores on the surface of the nanocomposite electrode with increase in irradiation fluence is observed from FESEM images. HRTEM micrographs reveal decrease in diameter of PPyNTs from 132 nm for pristine nanocomposite to 117 nm for the nanocomposite irradiated at a fluence of 2.2×10^{12} ions cm⁻². High fragmentation and decomposed morphology of PPyNTs is observed at the highest fluence of 1.3×10^{13} ions cm⁻² used in the present work. XRD results indicate that the crystallinity of the nanocomposite is not affected upto a SHI fluence of 2.2×10^{12} ions cm⁻², beyond

which the crystallinity decreases due to the loss of local ordering and breaking of polymer chains upon irradiation. FTIR spectra indicate weakening of the characteristic bands of PPyNTs at the highest fluence of irradiation indicating chain scissioning of PPyNTs. Micro-Raman spectra reveal defect annealing of the nanocomposite upto a fluence of 6×10^{10} ions cm^{-2} , beyond which defects are induced in the nanocomposite, which increases with increase in ion fluence. A slight decrease in thermal stability of the nanocomposite is observed upto a fluence of 2.2×10^{12} ions cm^{-2} followed by complete degradation of the sample at the highest fluence. The conductivity of the nanocomposite increases upon irradiation from 4.47 S cm^{-1} for pristine nanocomposite to 7.18 S cm^{-1} for 2.2×10^{12} ions cm^{-2} irradiated nanocomposite. At the highest fluence of 1.3×10^{13} ions cm^{-2} , increased defect density of RGO and chain scissioning of PPyNTs disrupt the π -electron delocalization decreasing the conductivity to 4.21 S cm^{-1} . An increase in BET specific surface area of the nanocomposite is obtained from $208 \text{ m}^2 \text{ g}^{-1}$ to $263 \text{ m}^2 \text{ g}^{-1}$ with increase in irradiation fluence upto 1.3×10^{13} ions cm^{-2} . The pore size distribution range of the nanocomposite increases upon irradiation from 4-30 nm to 6-50 nm. Contact angle measurements reveal an improved surface wettability of the nanocomposite electrode with increasing ion fluence of irradiation, which is confirmed by surface energy calculations using Owens, Wendt, Rabel and Kaelble (OWRK) method. CV curves display improved current response and enhanced overall CV area of the nanocomposite upon irradiation. Moreover, a transition in the CV curves from quasi-rectangular shape to non-rectangular 'leaf-like' shape is observed with increase in ion fluence upto 2.2×10^{12} ions cm^{-2} , which indicates increased pseudocapacitance of the nanocomposite electrode upon irradiation. At the highest fluence of 1.3×10^{13} ions cm^{-2} , the non-rectangular 'leaf-like' CV shape changes back to the quasi-rectangular shape implying the decline in pseudocapacitance due to increased fragmentation of PPyNTs. GCD curves reveal prolonged discharge duration of the nanocomposite upto a fluence of 2.2×10^{12} ions cm^{-2} , which indicates increase in specific capacitance of the nanocomposite. The specific capacitance increases from 299 F g^{-1} for pristine nanocomposite to 346 F g^{-1} for 2.2×10^{12} ions cm^{-2} irradiated nanocomposite. EIS studies depict lower equivalent series and charge transfer resistances of the nanocomposite upon irradiation. A maximum capacitive retention of 89% after 1000 cycles is obtained for

the 2.2×10^{12} ions cm^{-2} irradiated nanocomposite as compared to 77% for the pristine nanocomposite.

Synthesis of RGO-PAniNTs nanocomposites and characterization of their physico-chemical and electrochemical properties have been described in **Chapter 6**. The nanocomposites have been synthesized by *in situ* reduction method by varying the concentration of GO as 5, 10, 20 and 40 wt. % with respect to PAniNTs. HRTEM micrographs confirm the formation of the nanocomposites displaying a sheet-like morphology of RGO and an average outer diameter around 134 nm of PAniNTs. The increasing amount of crystalline component RGO increases the crystallinity of the nanocomposites as revealed by XRD patterns. Thermogravimetric analysis indicates increase in onset and rapidest decomposition temperatures of the nanocomposites from 200 °C and 282 °C to 392 °C and 586 °C, respectively with increase in RGO concentration. A transition in the I-V characteristics from non-linear to linear behavior is observed upon incorporation of RGO. The conductivity of the nanocomposites is enhanced with increase in RGO loading from 0.61 S cm^{-1} for pristine PAniNTs to 8.04 S cm^{-1} for 40 wt. % RGO-PAniNTs nanocomposite. The CV curves of the nanocomposites display two redox peaks of PAniNTs that arise due to the leucoemeraldine-emeraldine and emeraldine-bernigraniline faradaic transitions of PAni and signify pseudocapacitive charge storage. With increase in RGO concentration, the CV curves exhibit enhanced current response with larger enclosed area indicating the increasing EDL contribution in the nanocomposites from RGO. GCD curves of the nanocomposites with higher RGO loadings show linear and faster discharge in the potential range of 0.8-0.4 V followed by a slower discharge in the potential range of 0.4-0 V that deviates from the initial linear behavior. The initial linear discharge curve corresponds to EDL characteristics of the electrode due to RGO, while the latter longer discharge arises from the synergistic effect of EDLC and pseudocapacitance in the nanocomposites. An increase in specific capacitance is obtained with increase in RGO concentration from 194 F g^{-1} for pristine PAniNTs to 448 F g^{-1} for 40 wt. % RGO-PAniNTs nanocomposite. The energy density and power density increase from 11 to 30 W h kg^{-1} and 163 to 174 W kg^{-1} , respectively upon incorporation of RGO. Nyquist plots depict lower x-intercept and smaller diameter of semi-circle for the nanocomposites, which imply lower equivalent series resistance and charge transfer resistance. The nanocomposite with 40 wt. % of RGO exhibits a maximum cyclic stability of 89% after 1000 cycles as compared to 62%

for PANiNTs, which is due to the flexible multilayered RGO nanosheets that accommodate the volume change experienced by PANi during the faradaic reactions resulting in a stable capacitance.

In **Chapter 7**, the 40 wt. % RGO-PANiNTs nanocomposite that exhibits the best electrochemical performance as discussed in Chapter 6 has been irradiated with 85 MeV C⁶⁺ swift heavy ions at four different fluences with a view to modify its electrochemical properties. HRTEM micrographs depict fragmented and shortened PANiNTs at the fluence of 2.2×10^{12} ions cm⁻² with no significant distortion of the outer boundary and the inner hollow core, above which indistinguishable inner hollow core and outer surface of PANiNTs are observed due to increased fragmentation at the highest fluence of 1.3×10^{13} ions cm⁻² used in the present work. XRD patterns indicate decrease in crystallinity of the nanocomposite at the highest fluence. Micro-Raman spectra reveal decrease in disorder parameter (I_D/I_G) of the nanocomposite at a low fluence of 6×10^{10} ions cm⁻² followed by an increase with further increase in fluence. A slight increase in thermal degradation temperature of the nanocomposite is observed upon irradiation upto a fluence of 2.2×10^{12} ions cm⁻², beyond which a rapid degradation occurs at the highest fluence. The conductivity of the nanocomposite increases with increase in ion fluence upto 2.2×10^{12} ions cm⁻² from 8.04 S cm⁻¹ for pristine to 9.63 S cm⁻¹ followed by a decrease in conductivity at the fluence of 1.3×10^{13} ions cm⁻². SHI irradiation results in an increase in BET specific surface area of the nanocomposite from 196 m² g⁻¹ to 231 m² g⁻¹ and pore size distribution from 2-4 nm to 2-6 nm with increasing fluence upto 1.3×10^{13} ions cm⁻². The enhanced specific surface area and porosity of the nanocomposite upon irradiation significantly improve the surface wettability of the nanocomposite electrode as observed from contact angle measurements. CV curves reveal an increase in the intensity of PANi redox peaks with increase in SHI fluence upto 2.2×10^{12} ions cm⁻², beyond which complete disappearance of the redox peaks is observed. This is attributed to the increased pseudocapacitive charge storage upto a fluence of 2.2×10^{12} ions cm⁻² due to enhanced specific surface area of the nanocomposite electrode caused by fragmentation of PANiNTs upon irradiation. The charge-discharge curves of the nanocomposite exhibit a linear discharge with a slight curvature signifying the contribution of both EDL and pseudocapacitive mechanisms in the nanocomposite electrode. The specific capacitance as calculated from the GCD curves increases upon irradiation from 448 F g⁻¹ for pristine nanocomposite to

482 F g⁻¹ for 2.2×10^{12} ions cm⁻² irradiated nanocomposite. This is attributed to enhanced specific surface area and porosity of the nanocomposite upon irradiation, which contributes to the available electrochemically active sites in the electrode to be accessible by the electrolyte giving rise to the enhanced capacitance. The capacitance decreases to 394 F g⁻¹ at the highest fluence of 1.3×10^{13} ions cm⁻² due to increased defect density of RGO and decomposed PANiNTs at this fluence. EIS studies depict lower interfacial contact resistance and easier charge transport across the electrode-electrolyte interface with increasing ion fluence upto 2.2×10^{12} ions cm⁻². The cycle life of the nanocomposite increases upon irradiation to 92% after 1000 cycles as compared to 89% for the pristine nanocomposite.

The main conclusions drawn from the present thesis work have been summarized in **Chapter 8**. The future scope of research in the field of hybrid nanocomposites for improved supercapacitor electrodes application has also been briefly mentioned in the end of this chapter.