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Supercapacitors based on graphene–polyaniline derivative nanocomposite electrode materials

Punya A. Basnayaka[a,b], Manoj K. Ram[b,c,*], Elias K. Stefanakos[b,d], Ashok Kumar[a,b]

[a] Department of Mechanical Engineering, University of South Florida, 4202 E Fowler Avenue, ENB 118, Tampa, FL 33620, United States
[b] Clean Energy Research Center, University of South Florida, 4202 E Fowler Avenue, ENB 118, Tampa, FL 33620, United States
[c] Nanotechnology Research and Education Center, University of South Florida, 4202 E Fowler Avenue, ENB 118, Tampa, FL 33620, United States
[d] Department of Electrical Engineering, University of South Florida, 4202 E Fowler Avenue, ENB 118, Tampa, FL 33620, United States

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ABSTRACT

This manuscript discusses a comparative study of nanocomposite materials based on graphene and derivatives of PANI, i.e. 'methoxy' (—OCH_3) aniline and 'methyl' (—CH_3) aniline with graphene (G) for supercapacitor applications. The G-polyaniline (PANI), G-poly (o-methoxy aniline) [poly (o-anisidine) (POA)] and G-poly (o-methyl aniline) [poly (o-toluidine) (POT)] were synthesized by a chemical oxidative polymerization method and characterized to understand the nanocomposite formation of the materials. The electrochemical properties of G-PANI, G-POA, and G-POT nanocomposites based supercapacitors were investigated using cyclic voltammetry (CV), galvanostatic charge–discharge, and electrochemical impedance spectroscopy (EIS) techniques in 2 M H_2SO_4 electrolyte. The specific capacitances (Cp) of supercapacitors based on G-PANI, G-POA, and G-POT in 2 M H_2SO_4 electrolyte were estimated to be 400, 380, and 425 F/g, respectively. However, POT nanocomposite with graphene exhibited better capacitance (425 F/g) than the G-polyaniline or the G-POA based electrode materials. The relaxation time constants of 0.6, 2.5, and 5 s for the G-POT, G-PANI, and G-POA nanocomposite-based supercapacitors were calculated from the EIS analysis and such time constants revealed a quicker delivery of the stored energy than the carbon–carbon based supercapacitors. The high specific capacitance and small relaxation time constants of the G-substituted polyaniline paved the way for the fabrication of safe and stable supercapacitors.

1. Introduction

Supercapacitors are used for energy storage in uninterrupted power supplies (UPS), mobile/portable electronic devices, micro-autonomous robots, hybrid vehicles, and distributed sensor applications [1–3]. Transition metal oxides (RuO_2, MnO_2, V_2O_5), carbon-based materials (activated carbon, porous carbon, graphene, carbon nanotubes), and conducting polymers (polyaniline (PANI), polypyrrole (PPy), polythiophene (PTH), and polyethylenedioxythiophene (PEDOT)) have extensively been studied as supercapacitor electrode materials [4–8]. Besides pristine electrode materials, recent emphasis has been placed on the synthesis of hybrid and nanocomposite materials by combining a metal oxide with a conducting polymer (CP), a metal oxide with carbon nanotubes, and a copolymerizing monomer in the presence of metal oxide or carbon based nanomaterials [9–14]. Recently, the transition metal oxides with graphene, carbon nanotubes-CPs, metal oxides-CPs, etc. were synthesized in order to enhance the power density, specific capacitance and stability [4,9–19] of supercapacitor cells. The different morphological structures of G-PANI such as G-PANI nanofiber, G-PANI nanocomposite, and graphene-PANI papers are widely studied materials for supercapacitor application [9,13,18,19]. The presence of the electron-donating methyl group in poly (o-toluidine) is more effective than polyaniline in enhancing the capacitance of carbon fabric electrodes [20]. Our previous work has shown an increase in stability and energy density in supercapacitors based on graphene–CP materials that use an ionic liquid as the electrolytic medium [10,11,18]. In addition, studies have shown that G-PANI and G-PEDOT based nanocomposites could be better suited electrode materials than the pristine PEDOT, PANI, and polypyrrole based materials for supercapacitor applications [10,11,18–22].

The G-PANI, G-POT, and G-POA nanocomposite were synthesized, characterized, and analyzed as supercapacitor electrode materials under this manuscript. The G-POT and G-POA were found to be processable materials in common organic solvents for the fabrication of supercapacitor electrodes. The electrochemical behavior, specific capacitance, power density, energy density,

* Corresponding author at: Nanotechnology Research and Education Center, University of South Florida, 4202 E Fowler Avenue, ENB 118, Tampa, FL 33620, United States. Tel.: +1 813 396 9353; fax: +1 813 974 3610.
E-mail address: mkram@usf.edu (M.K. Ram).

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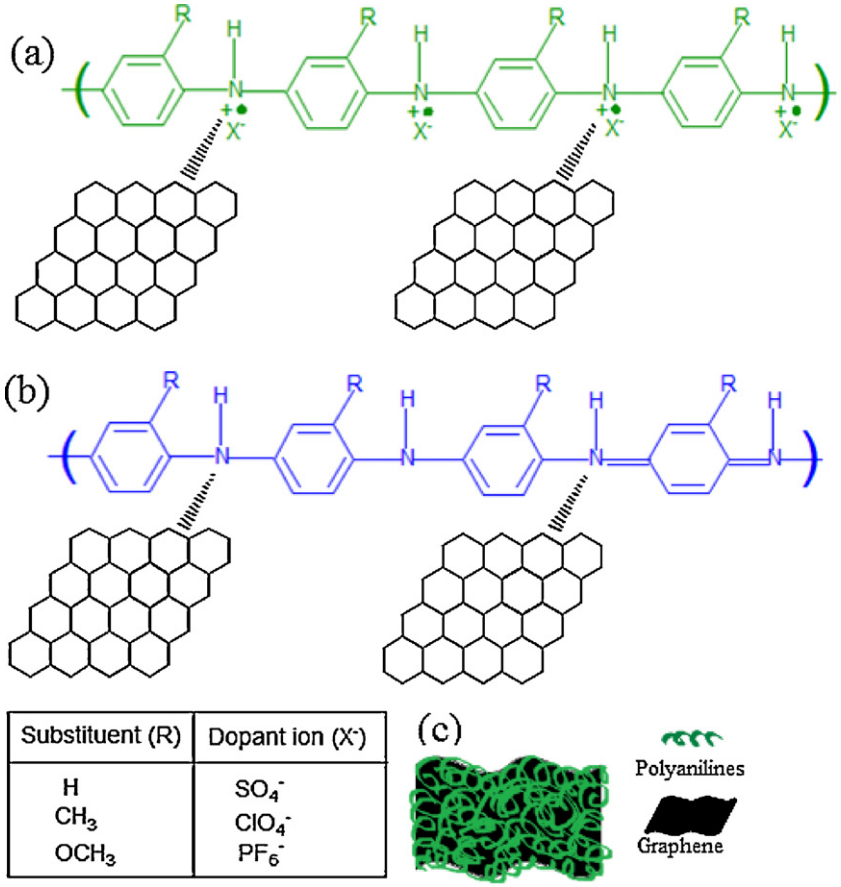

Fig. 1. (a) Emeraldine salt form of graphene–polyanilines nanocomposite, (b) emeraldine base form of graphene–polyaniline nanocomposites, (c) formation of CPs wrapping around graphene.

and frequency dependent properties of G-PANI, G-POT and G-POA as electrode materials in 2 M H_2SO_4 electrolyte were investigated at length. The G-POT nanocomposite exhibits excellent capacitive properties and quicker discharge of energy (two to four times) than the other two G-PANI derivative based nanocomposite electrodes. Therefore, the electrochemical behavior of the G-POT nanocomposite as a possible electrode for supercapacitor in different electrolytes (1 M BMIM-PF6 and 0.2 M $LiClO_4$ electrolytes) has been discussed extensively in our manuscript.

2. Experimental

2.1. Material synthesis

The materials used in this study were employed as ACS grade. Aniline, o-anisidine o-toluidine, ammonium peroxydisulfate (APS), H_2SO_4, and solvents were purchased from Sigma–Aldrich. The graphene platelets were purchased from Angstrom Materials, USA.

The G-PANI, G-POA, and G-POT were synthesized by chemical oxidative polymerization of a monomer using the oxidizing agent $(NH_4)_2S_2O_8$ (APS) in 1 M HCl under controlled conditions [18]. The monomer to graphene weight ratio was kept 1:1 for all nanocomposites synthesis precesses. The monomer (aniline, o-anisidine or o-toluidine) was added in 200 ml of 1 M HCl solution at 4 °C in an ice bath. 0.2 M APS was dissolved in 200 ml of 1 M HCl solution at 4 °C. Later, the APS in 1 M HCl was slowly added to aniline and dissolved in 1 M HCl with the reaction continued for 24 h under constant stirring. The precipitate of G-PANI, G-POA, and G-POT obtained in each reaction was filtered and washed using deionized water and methanol. The precipitate was dried at 100 °C for 6 h to obtain the nanocomposite materials.

2.2. Characterization

The morphologies of G-PANI, G-POA, and G-POT were investigated using the Scanning Electron Microscope (SEM). In addition, SEM images of PANI derivatives are provided in Fig. 2 to compare the morphology difference with nanocomposites. The G-PANI was dissolved in N-methyl-2-pyrrolidinone (NMP), whereas, G-POA and G-POT were dissolved in chloroform ($CHCl_3$) for the fabrication of supercapacitor electrodes. The electrodes were fabricated by drop casting on substrates (graphite, ITO coated glass plate, etc.) and heated at 100 °C for 2 h. Each PANI nanocomposite electrodes dipped in a 2 M HCl for a few seconds in emeraldine salt form was used to fabricate supercapacitor cells. The redox properties of the nanocomposites were investigated by measuring Cyclic Voltammetry (CV) at different scan rates (200, 100, 50, 25, 10 and 5 mV/s). The galvanostatic charging–discharging at constant current density of 1 mA/g and impedance measurements in the range of 100 mHz–100 kHz frequency were also performed to understand the EIS properties of supercapacitors.

3. Results and discussion

Fig. 1 shows the structures of graphene–polyaniline derivatives in emeraldine base (Fig. 1a) and emeraldine salt forms (Fig. 1b). Fig. 2 observes the SEM images of conducting polymers (PANI, POA, and POT) and conducting nanocomposites (G-PANI, G-POA, and G-POT) materials. G-PANI derivatives depict larger surface area