Sprayed polyaniline layer onto chemically reduced graphene oxide as electrode for high performance supercapacitor

Mazhar B. Tayel[a], Moataz M. Soliman[b], Shaker Ebrahim[b], Mohamed E. Harb[a,*]

[a] Department of Electrical Engineering, Faculty of Engineering, Alexandria University, P.O. Box 21544, Egypt
[b] Department of Materials Science, Institute of Graduate Studies and Research, Alexandria University, P.O. Box 832, Egypt

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ABSTRACT

In this work supercapacitors were fabricated from reduced graphene oxide (RGO), polyaniline (PANI) and graphene/PANI (G/PANI) electrodes. The fabricated electrodes were characterized using scanning electron microscope (SEM) and UV–vis spectroscopy. The electrochemical activities of supercapacitors were assessed using cyclic voltammetry (CV), electrical impedance spectroscopy (EIS), and charge-discharge measurements. Graphene electrodes were prepared by exposure the graphene oxide (GO) sheets to hydrazine to reduce and restore the conducting carbon network. A maximum specific capacitance of 292 F/g with energy density of 40.5 Wh/kg in an aqueous electrolyte solution had been obtained for this graphene supercapacitor. Supercapacitor of sprayed PANI electrodes produced specific capacitance of 595 F/g and energy density of 82.63 Wh/kg. Finally, a hybrid supercapacitor had been developed by spraying PANI layer onto the reduced graphene oxide sheet (G/PANI). It was found that G/PANI supercapacitor displayed a specific capacitance of 916 F/g and energy density of 127.19 Wh/kg, which is much higher than that of pristine graphene and PANI electrodes supercapacitor.

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1. Introduction

An increasing demand and growing regards the energy requirement and climate change have stimulated intense research on the development of advanced energy storage and management devices [1–6]. Supercapacitors, a class of electrical energy storage devices with ultrahigh power density(10^3–10^4 W kg^{-1}), fast charging (seconds), and long cycling life (>100,000 cycle), have attracted attention due to their widespread different applications, such as hybrid electric vehicles, power tools and portable electronic equipment [7,8]. Graphene, a two-dimensional carbon material, is a good electrode candidate for supercapacitors owing to its interesting and unique properties, such as high surface area, high electrical conductivity, and electrochemical stability [9,10].

Conducting polymers are an important class of electrode material for supercapacitors [11]. Conducting polymers store and release charge through redox processes, resulting in the so-called pseudocapacitance. Charging in a conducting polymer takes place throughout the bulk volume of the polymer, not just on the surface, as is the case with carbon, so that the specific capacitance of polymers is high. The fast charge/discharge processes associated with conducting polymers give rise to high specific power. It was demonstrated that the cycle-life of conducting polymer based supercapacitors could be as high as several thousand cycles. Among the conducting polymers, polyaniline (PANI) has attracted much attention because of their low cost, chemical and thermal stability, controllable electrical conductivity, good solubility, and easy process ability [12].

Composite of PANI and various robust carbon materials such as graphite oxide, graphene, carbon nanotubes (CNTs), carbon fiber and mesoporous carbon, shows promising materials for the enhanced electrochemical properties [13–15]. In addition, the stability, electrical conductivity, and redox properties of PANI a great improvement when incorporated with conductive carbon materials can be obtained. Meng et al. have prepared paper-like flexible CNT/PANI composite which exhibited a maximum specific capacitance of 424 F/g [12]. Zhao and co-workers have developed and characterized high performance supercapacitor electrodes of hollow carbon spheres/PANI synthesized via in situ polymerization process and the electrode displayed a maximum specific capacitance of 525 F/g [14]. The incorporation of graphene within PANI matrix not only enhances the stability and conductivity of PANI but also significantly improves its electrochemical properties.

The main objective of this work is to fabricate different supercapacitors based on graphene, PANI and graphene/PANI electrodes. The supercapacitor performance was carried out using

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* Corresponding author.
  E-mail address: moh.harb@yahoo.com (M.E. Harb).

cyclic voltammetry (CV), electrical impedance spectroscopy (EIS), and charge-discharge measurements. Graphene/PANI supercapacitor introduces high specific capacitance and electrochemical activity compared with graphene or PANI supercapacitors due to a synergistic effect between graphene and ployaniline.

2. Experimental work

2.1. Materials

Graphite powder was purchased from Fischer Scientific. Sulphuric acid (98 wt.%), nitric acid (70 wt.%), hydrazine hydrate (65 wt.%), potassium permanganate and sodium nitrite were purchased from Sigma-Aldrich Ltd. Barium chloride (99%) was purchased from ALEC. Potassium hydroxide, silver chloride, sodium hydroxide and hydrogen peroxide (30 wt.%) were obtained from local chemical companies. Aniline (99%) was purchased from CDH. Ammonium persulphate (98.5%) was purchased from WINLAB. Hydrochloric acid (37%) and camphor sulfonic acid were purchased from Mereck.

2.2. Graphene oxide preparation

Graphene oxide was prepared by a modified Hummers method [16–22]. Typically, 4.0 g of natural graphite powder and 2 g of sodium nitrate were mixed with 92 mL concentrated sulfuric acid in a conical flask place in an ice bath. The obtained solution was stirred with a slowly addition of 12 g potassium permanganate with continuous stirring for 2 h. This mixture was transferred to water bath at 35 °C with stirring for 30 min. After that, 184 mL of deionized water was slowly added into the mixture and the temperature was controlled at about 98 °C for 30 min. Then, 560 mL deionized water and 40 mL of hydrogen peroxide was added sequentially to the mixture to terminate the reaction. The observed color of mixture was dark yellow. The resulting product was filtered and rinsed with 5% HCl to remove sulfate groups that was checked by barium chloride. This step was repeated till the white precipitate appears and followed by washing with distilled water to remove HCl and was checked with silver chloride for several times till no white color appears in the solution. The graphite oxide powder was obtained after drying in vacuum at 60 °C overnight. The powder was then dispersed in distilled water to make concentration of 0.5 mg/mL, and exfoliated by ultrasonication for 1 h to obtain graphene oxide (GO). Finally, the stable suspension of brown graphene oxide was obtained. Graphene oxide was filtered and dried in an oven at 60 °C for 12 h.

2.3. Polyaniline preparation

Ammonium persulfate (13.5 g) was dissolved in 225 mL of 1.2 mol/L HCl previously cooled to 0 °C. Aniline (20 mL) was also dissolved in 250 mL of precooled 1.2 mol/L HCl. Ammonium persulfate as an oxidizer was then slowly added to aniline solution for 1.5 h to inhibit the temperature from exceeding 5 °C. The reaction was conducted by the in situ polymerization method in ice bath for 1 h then left at rest to polymerize for 24 h at room temperature. The prepared mixture was filtered and washed with distilled water and methanol [23–25]. PANI was simultaneously dedoped by 25 mL 8 M sodium hydroxide at 95 °C for 20 h. The emeraldine base was dried in air and then at 60 °C for 24 h. PANI was doped with camphor sulfonic acid (CSA) with 1:3 wt%, respectively and dissolved in chloroform.

2.4. Characterization

UV–visible spectra were obtained using a Thermo (Evolution 600) instrument in the range of wavelength from 200 to 900 nm.

The spectra were obtained for GO and graphene suspended in water and PANI doped with CSA dissolved in chloroform. Scanning electron microscope images were obtained by JEOL JSM 6360LA for the samples coated with a thin layer of gold.

2.5. Supercapacitor fabrication

Graphene oxide was deposited on the stainless steel 304 current collector and was reduced using filter paper soaked in hydrazine hydrate to obtain graphene electrodes. PANI electrodes were fabricated by direct spray coating method onto current collector. Hybrid G/PANI electrodes were fabricated by spray coating of PANI layer onto reduced graphene oxide layer. The separator used was a filter paper soaked in aqueous potassium hydroxide (6 M). Supercapacitor was assembled by stacking two fabricated electrodes with a separator. The fabricated supercapacitor was sealed by lamination with plastic foil and was fixed by two clamps.

2.6. Electrochemical measurements

The electrochemical performance was analyzed for supercapacitor electrodes in a two-electrode system by CV and EIS using potentiostat (Gamry G750) instrument and the galvanostatic charge-discharge characteristics were carried out with a Gamry 3000. The CV response of the electrodes was measured at different scan rates varying from 1 mV/s to 100 mV/s. Galvanostatic EIS measurements were carried out with sinusoidal signal of 5 mA over the frequency range from 0.05 Hz to 300 kHz. Performance of supercapacitor as a function of temperature was studied from in the range 25 °C–75° C. The specific capacitance of the electrode was calculated from the CV curves according to the following equation [26]:

$$C = \frac{\int \mathbf{i} \mathbf{dV}}{(\Delta \mathbf{V} \times \upsilon \times \mathbf{m})} \tag{1}$$

where C is the specific capacitance (F/g), i is the positive/negative scan current (A), V is the corresponding voltage (V), υ is the scan rate (V/s), ΔV is the potential differences (V) and m is the weight of the active material (g). In addition, the specific capacitance was also calculated from the charge-discharge measurement according to the following equation:

$$c = \mathbf{i} \frac{\Delta t}{\mathbf{m} \times \Delta V} \tag{2}$$

where C is the specific capacitance (F/g), i is the discharge current (A), Δt is discharged time (s) and ΔV in the potential window (V).

The energy and power densities of the supercapacitor were calculated according to the following equations [26]:

$$E = \frac{1}{2} \times C \times V^2 \times \frac{1000}{3600} \tag{3}$$

$$P = \frac{E}{t} \tag{4}$$

where E is the energy density (Wh/Kg), C is the specific capacitance (F/g), V is the cell voltage (V), P is the average power density (W/Kg) and t is the discharge time (h).

3. Results and discussion

3.1. Structural characterizations

Fig. 1 shows the UV–vis spectra of GO, graphene and PANI doped with CSA. Spectrum of GO has a typical absorption peak at 233 nm