European Polymer Journal 92 (2017) 194–203

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Study on the specific capacitance of an activated carbon cloth modified with reduced graphene oxide and polyaniline by cyclic voltammetry

J. Fernández, J. Bonastre, J. Molina, A.I. del Río, F. Cases*

Departamento de Ingeniería Textil y Papelera, Escuela Politécnica Superior de Alcoy, Universitat Politècnica de València, Plaza Ferrándiz y Carbonell, s/n, 03801 Alcoy, Spain

ARTICLE INFO

Keywords:
Activated carbon cloth
Reduced graphene oxide
Polyaniline
Aniline adsorption
Capacitance

ABSTRACT

This work describes a two-step process for the electrochemical coating of reduced graphene oxide (RGO) and polyaniline (PANI) onto an activated carbon cloth (ACC) by cyclic voltammetry (CV). The fact that the two syntheses are carried out independently of each other, makes it possible to select the experimental conditions for each one and to study the electrochemical response of RGO, PANI, and PANI onto RGO (RGOPANI), separately. Thus, by modifying the potential limits of the aniline-polymerization reaction, it was possible to observe the influence of RGO and the maximum amount of PANI that the carbon cloth can receive in terms of proper electrochemical response. Electrochemical properties were characterized by CV, galvanostatic charge-discharge curves (using three or two-electrodes symmetric cell configurations) and electrochemical impedance spectroscopy (EIS). A maximum improvement of 25%, 56% and 61% over the initial specific capacitance of ACC (about 129 F g^{-1}) were obtained for RGO, PANI and RGOPANI coatings, respectively. Good cycling stability retaining 83% of the initial capacitance, after 1000 cycles stability test, was obtained for RGOPANI sample. Promising results of energy and power densities were also achieved. In the analyses by Fourier transform infrared spectroscopy (FTIR), the PANI-bands could be clearly identified which is indicative of a significant presence of PANI. Field emission scanning electron microscopy (FESEM) showed the morphology of RGO, PANI and RGOPANI onto the ACC fibers. These analyses helped to explain the electrochemical results.

1. Introduction

Activated carbons are of special interest due to the exceptional physical and chemical properties that they possess, such as porosity, high surface area, adsorption capacity, chemical stability, corrosion resistance, thermal resistance and electrical conductivity [1–4]. Activated woven carbon cloths are very promising materials because they provide continuous current paths that reduce the interparticle resistance [5]. In addition, the mechanical properties of textile materials, such as weigh and flexibility, add new possibilities to the design of energy storage devices [6]. Supercapacitators have attracted considerable attention in recent years because of their high power density, long life cycle, and potential applications [5]. However, the capacitance of carbon materials is low, and this is the reason why carbon materials are coated with pseudo-capacitive materials such as conductive polymers. Polyaniline (PANI) is good candidate for energy storage devices due to its ease of synthesis, environmental stability, fast redox activity and high specific capacitance [5–23]. Graphene has attracted much attention during recent years due to its unique

---

* Corresponding author.
E-mail address: fjcases@txp.upv.es (F. Cases).

http://dx.doi.org/10.1016/j.eurpolymj.2017.04.044
Received 16 January 2017; Received in revised form 26 April 2017; Accepted 28 April 2017

electronic and mechanical properties [24], high specific surface area, high electron mobility at room temperature and ability to sustain high electric currents densities [25,26]. Reduced graphene oxide (RGO) not only has good electrical properties and a large conjugated aromatic ring which can interact with porous carbon materials, but also many functional groups that can chemically interact with conducting polymers [5]. For the synthesis of RGO from graphene oxide (GO), several reducing agents such as *p*-phenylene diamine [5], glucose [11], aniline [14], hydrazine [9,17,18] and L-cysteine [16] have been tried. For the synthesis of PANI, persulfate salts were used to oxidize aniline [9,14,17,18]. The use of reducing agents for the GO reduction and oxidizing agents for the aniline oxidation makes these processes more expensive, arduous, and less environmentally friendly. Thus, electrochemical synthesis is seen as a good alternative to the use of chemicals. Different materials such as copper foil [10], glassy carbon [10,13,20], foamed nickel [10], Pt-plate [10] and indium tin oxide [20] were used as base of the graphene-PANI electroactive material for working electrodes. From a more practical point of view, the graphene-PANI material was anchored to different substrates. The flexibility of the substrate for electrodes has captured the attention of a number of researchers. Thus, flexible materials such as activated carbon cloth [5,16] or paper [6] have been cited as substrate for working electrodes. Flexible 3D-structures of graphene/polyaniline have also been reported [15,16,23] for supercapacitors.

On the basis of the above, the present work aims to modify the capacitance of an activated carbon cloth (ACC) by electrochemical coating of RGO and PANI on its surface. Both direct electrosyntheses were carried out by CV using a small piece of ACC as working electrode (WE). CV, EIS, and galvanostatic techniques were used for the electrochemical characterization of the different samples. A test-cell (Swagelok-type cell) dedicated to the characterization of aqueous battery and capacitor systems, wired up for three or two electrode testing, was used for this purpose. The surface morphologies and chemical structures were characterized by FESEM and FTIR, respectively. To assess the deliverable performance for real-life applications, the energy and power densities were calculated from the charge-discharge curves for the two-electrode symmetric cell.

2. Experimental

2.1. Reagents and chemicals

Monolayer graphene oxide (GO) powders were acquired from Nanoinnova Technologies S.L. (Spain). Lithium perchlorate ($LiClO_4{\cdot}3H_2O$), analytical grade sulphuric acid (H_2SO_4) and aniline were purchased from Merck. Aniline was purified by distillation before use. Distillation was performed at reduced pressure in order to avoid thermal degradation of the monomer. After distillation, aniline was stored in the dark at 5 °C. Ultrapure water was obtained from an Elix 3 Millipore-Milli-Q Advantage A10 system with a resistivity near to 18.2 mΩ cm. The solutions for the CV-syntheses were deoxygenated by bubbling nitrogen gas (N_2 premier X50S).

2.2. Electrodes

The surface (3 mm diameter disc) of a glassy carbon electrode (GCE) was polished with 0.05 μm alumina and then thoroughly rinsed with water. The voltammetric study, using the GCE as working electrode, was carried out in a conventional voltammetric cell of three electrodes. A 3 g L^{-1} GO and 0.1 M $LiClO_4{\cdot}3H_2O$ solution was used for the RGO synthesis. The characterization of GCE/RGO was performed in a 0.1 M $LiClO_4{\cdot}3H_2O$ solution.

The company Chemviron Carbon supplied the activated carbon woven cloth Zorflex® FM10, 0.5 mm thick with a surface density of 120 g m^{-2}. The textile electrodes (WEs) were prepared by cutting a 1 cm × 3 cm strip from the carbon fabric. A proper electric contact was obtained by gluing the textile samples to 2 mm diameter copper rods, with the tip flattened to improve the electric contact, using CircuitWorks® conductive epoxy resin by Chemtronics®. The resin was hardened in an oven at 90 °C and the joint was wrapped with Teflon tape and glued with epoxy resin to isolate it from the solution. WEs will be used as working electrodes for the RGO and PANI syntheses.

2.3. Electrochemical cells

The CV-coating onto WEs were carried out in a conventional cell for voltammetry equipped with a Pt cylindrical mesh (6 cm height and 3 cm diameter) for the RGO synthesis or a stainless steel cylindrical mesh (4 cm height and 3 cm diameter) for the aniline polymerization, as counter electrodes (CE). The reference electrode was an Ag/AgCl (3 M KCl). The WE was placed in the center of the cylinder and 3 cm^2 (geometrical area) was introduced into the solution. The solution 3 g L^{-1} GO and 0.1 M $LiClO_4{\cdot}3H_2O$ was sonicated with the aid of an ultrasound bath for 30 min for the dispersion of GO monolayer powders. During the CV-experiments, the GO-solution was gently stirred to avoid the precipitation of GO. The 0.2 M aniline solution was prepared by dissolving freshly distilled aniline in 1.0 M H_2SO_4 solution. The electrochemical characterization of the textile samples was carried out in a test-cell (Swagelok-type cell) ECC-Aqu from EL-CELL. The parts of the cell that come in contact with the electrolyte are made of fine gold and thermoplastic polymer PEEK. Two textile samples of 0.5 cm × 0.5 cm (cut from WE) were positioned in parallel on both sides of the separator and at the same time, between the two circular gold current collector (2 cm diameter). These samples were described as ACC/RGO_aPANI_b, where subscripts “a” and “b” are the number of cycles of synthesis.

The separator is a circular piece (2 cm diameter) of glass fiber filter, 0.3 cm thick, 1.2 μm nominal pore size, soaked with 1 M H_2SO_4 solution. The test-cell worked in three-electrode or two-electrode symmetric configurations. In the three-electrode configuration, a gold metal pin was the reference electrode (RE). The reference electrode potential was −0.3 V vs. Ag/AgCl under the experimental conditions. RE was positioned close to the separator edge in between the working and the counter electrode (current